UGPHS-06

BLOCK-1

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Utter Pradesh
Rajarshi Tandon Open University

UGPHS-06

THERMODYNAMICS AND STATISTICAL MECHANICS

Block

1

THE ZEROTH LAW AND THE FIRST LAW

UNIT 1

Basic Concepts of Thermodynamics 7

UNIT 2

Measurement of Temperature 25

UNIT 3

The First Law of Thermodynamics 42

UNIT 4

Applications of the First Law of Thermodynamics 60

THERMODYNAMICS AND STATISTICAL MECHANICS

Energy has reigned all facets of human activity ever since man lived in cave. In its manifestation as heat, energy is intimate to our existence. The energy that cooks food, lights our houses, operates machines and runs trains originates in heat released in burning of wood, coal, gas or oil. What is heat? How can we specify the direction of flow of heat? Our quest to answer these and other related questions is contained in the subject of thermodynamics. This subject developed on a postulatory basis long before we knew the nature of behaviour of elementary constituents of matter such as electrons, atoms or molecules.

There are two distinct approaches to learn this subject. The traditional or classical approach is based on some postulates derived from experience. In the statistical approach, on the other hand, the firm physical and statistical basis of thermodynamics is first demonstrated by relating the properties of bulk systems to the behaviour of their elementary constituents. One can argue for and against either alternative. But we think that a distance learner will find it easy to understand the subject following the formal postulatory approach, which is illustrated in first two blocks of this course. Among others, you will learn the contributions of Joule, Carnot, Clausius, Kelvin, Maxwell and Gibbs in the development of this subject.

Theromodynamics has some limitations, which can be overcome by making hypotheris regarding the nature of matter. It was postulated that matter is made up of molecules, which can exist in free state while possessing all basic properties of a substance. This gave birth to the **moluculár theory.** Starting with molecular theory we can obtain bulk properties of matter in two different ways. When we supplement molecular theory with the law of mechanics for individual molecules, we obtain the **Kinetic theory of matter.** In block 3 you will learn Kinetic theory 1 of gases under equilibrium as well as non equilibrium conditions. This subject owes its development largely to Bernoulli, Clausius, Maxwell, Joule, Vander waals and Jeams. You will realise than Kinetic theory has great austhetic elegance.

The classical statistical mechanics evolved out of the efforts of Boltzmann. He supplemented purely statistical methods (considerations of probability) by the laws of (classical) mechanics for a large number of particles making up the system. With the advent of quantum mechanics, this subject got a new shape at the hands of Bose, Einstein, Fermi, Dirac and Fowler. Many new phenomena, completely unknown to the domain of classical statistical physics, could be satisfactorily explained. You will learn it in Block 4 of this course

In its present state, thermodynamics and statistical mechanics is one of the most fascinating courses taught to undergraduate physics students. It finds use in material science, engineering, chemistry, quantum, atomic and molecular physics, spectroscopy and beyond. It provides ample opportunities to develop a sensibility towards nature; the essential part of physics education. Therefore, while a simplistic reading will enable you to understand the subject, more thoughtful study will bring extra rewards!

One last word about how to study the course material.

Study Guide

The best way to learn a subject is to solve problems. We have given many solved examples, self assessment questions, and terminal questions. Some of these are intended to check your progress while a few are quite challenging. Answers to SAQs and TQs are given at the end of each unit. But you are advised not to read through these answers. Do them yourself because only self-doing leads to creativity, enjoyment and appreciation of the subject.

This is a 4-credit course which means that you have to put in 120 hours of work. Of these, you should spend about 80 hours to study course material and solve SAQs and TQs. The remaining time is intended for assessment, counselling sessions, audio and video programmes. We hope that you will enjoy the subject.

We wish you success.

BLOCK 1 THE ZEROTH LAW AND THE FIRST LAW

The first block of this course deals with the basic concepts of thermodynamics, the Zeroth law, measurement of temperature, and the first law of thermodynamics. From your school physics course, you are familiar with some of these concepts. But to make the block self-contained, we have included them yet again. In Unit 1 we have explained all the terms and basic concepts to be used in this course. This is followed by the discussion of zeroth law of thermodynamics. You will also learn the basic mathematical tools employed in the study of thermodynamics.

In Unit 2 we have dealt with measurement of temperature over a wide range. You will learn details of constant volume gas thermometer, platinum resistance thermometer, thermocouples and pyrometers.

We have discussed the thermodynamic concepts of heat and work in Unit 3. (In this process you will learn about the concept of internal energy of a system.) Then we have established the first law of thermodynamics. The applications of this law to diverse physical systems including adiabatic lapse rate and propagation of sound are given in Unit 4.

The units are not of equal length. We are suggesting the following estimate for the study time required for each unit:

Unit 1	—	5 hours
Unit 2	—	6 hours
Unit 3	—	6 hours
Unit 4	—	5 hours

Your actual study time will, of course, depend on your sincerity as well as academic background. If you have passed class XII examination recently, you will find the mathematics used in these units quite simple. However, if you passed class XII or equivalent examination a few years back, you may have to brush up your knowledge of calculus. For this you may go through the class XII (NCERT) book on mathematics. It will be available at your Study Centre.

Some of the abbreviations used in the text are Fig. for Figure, Sec. for Section, Eq. for Equation, SAQ for self assessment questions and TQ for terminal questions. For example, Fig. X.Y refers to the Yth Figure of Unit X. That is, Fig. 1.4 is the fourth figure in Unit 1. Similarly Sec. 2.7 is the seventh section in Unit 2 and Eq. (3.6) is the sixth equation in Unit 3.

UNIT 1 BASIC CONCEPTS OF THERMODYNAMICS

Structure

1.1 Introduction
  Objectives
1.2 Thermodynamic Systems
  Classification of Systems
  Classification of Boundaries
1.3 Thermodynamic State of a System and Thermodynamic Variables
  Intensive and Extensive Variables
  Thermodynamic Equilibrium
1.4 Thermodynamic Processes
  Reversible and Irreversible Process
  Quasistatic Process
  Representation of a Process on an Indicator Diagram
1.5 The Zeroth Law of Thermodynamics
1.6 The Equation of State
  Deductions from the Equation of State
1.7 Summary
1.8 Terminal Questions
1.9 Solutions and Answers

1.1 INTRODUCTION

In your daily life you might have observed that when you use a bicycle pump to inflate the tyre, the pump gets hot. Similarly when you rub your hands together you get the feeling of warmth. In these examples, the heating is not caused in the conventional way by putting a flame or something hot underneath the pump or the hand. But it arises as a result of the mechanical work done in compressing the gas in the pump or forcing the hand to move against friction. These examples show that there is a relation between mechanical and thermal effects. The study of the relationships between mechanical and thermal energy is known as thermodynamics.

The study of thermodynamics is based on four empirical laws, that is, thermodynamics is a phenomenological science. This means that the laws are derived from experience and they need no proof. These laws find application in design of internal combustion engines, refrigeration and air conditioning systems, power stations etc. With the help of these laws one can determine the efficiency of all types of mechanical devices such as steam engines, electric power plants and automobiles. These laws are also used to analyse energy transformations in bio-chemical and geological systems.

In this unit we will discuss the basic concepts which will be used in the study of thermodynamics. We will also introduce the concept of temperature through the zeroth law of thermodynamics. Finally, you will learn to use the equation of state for deriving mathematical relations between quantities such as coefficient of volume expansion, compressibilities, elasticity, etc.

In the next unit you will read about the principles of measurement of temperature.

Objectives

After studying this unit, you should be able to

- identify several thermodynamic systems with its surroundings and boundaries
- explain what are thermodynamic variables and identify these variables for several systems
- explain thermal, mechanical and chemical equilibria
- distinguish between a reversible and an irreversible process
- understand the importance of a quasistatic process

- identify and represent different kinds of thermodynamic processes
- explain the concept of temperature using the zeroth law of thermodynamics
- apply the equation of state of a system to solve problems in thermodynamics.

1.2 THERMODYNAMIC SYSTEMS

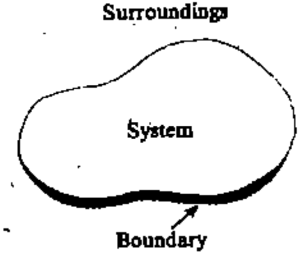


Fig. 1.1 : System, surroundings and boundary

Whenever we read a biography our attention gets drawn towards an individual. We get to know about his achievements, how he has interacted with other individuals and many such other things. To the reader's mind this individual assumes the role of someone who is distinct from others and around whom the biography develops almost like a story. Likewise, for any kind of study in thermodynamics we need to set aside a certain quantity of matter or a region of space which is considered distinct and separated from everything else, which can influence it. We refer to this as **thermodynamic system** or simply a **system.** Every such system is enclosed by an arbitrary surface which is called its **boundary.** The boundary may be real or imaginary, either in rest or in motion and may change its size or shape. The region of space that lies outside the boundary of a system is called its **surroundings.** Strictly speaking everything other than the system is its surroundings. But in thermodynamics we consider that portion as the effective surroundings of a system which can influence it. In Unit 3, you will read about the different manners in which the surroundings can influence a system. Any study in thermodynamics begins with the identification of the system, its boundary and its surroundings. These are schematically illustrated in Fig. 1.1. Let us now take up some specific examples of systems with different kinds of boundaries.

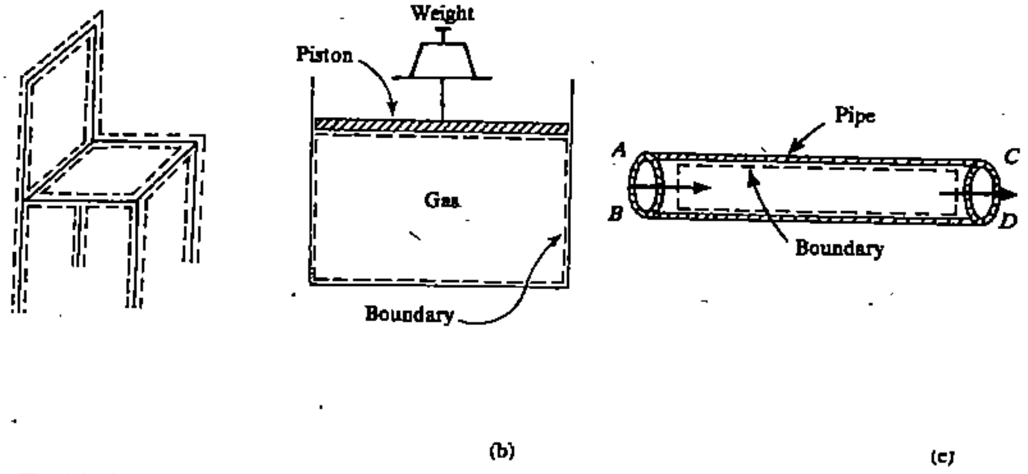


Fig. 1.2: Several thermodynamic systems and their boundaries. In each case the boundary is shown by means of a dotted line. (a) The chair system, (b) Compressed gas in a cylinder, (c) Flow of liquid through a pipe.

For the chair system (Fig. 1.2a) the boundary is real and fixed. Everything other than the chair constitutes the surroundings. For the system of a compressed gas in a cylinder (Fig. 1.2b) the boundary is real. It is movable as the inner surface of the piston, which is a part of the boundary, can be moved. Everything outside the gas, including the piston and the cylinder, is the surroundings. For the system of a certain mass of liquid flowing along a pipe as shown in Fig. 1.2c the boundary is imaginary. The inside surface of the pipe may form a part of the boundary as it presents an obstruction to the flow of liquid. But there is no real obstruction at the two ends *AB* and *CD*. So a real boundary does not exist. However, the dotted line is one possible choice of a boundary, fixed in space. Such type of boundary is imaginary. Everything lying outside this imaginary boundary is the surroundings.

A system may be simple, such as water in a vessel; or complex like a Daniel cell, which has Zn and Cu electrodes, dilute H_2SO_4 electrolyte and $CuSO_4$ depolariser. A system may be completely uniform with respect to its chemical composition and physical conditions (homogeneous) or otherwise (heterogeneous). For instance, air in a cylinder, air being a mixture of gases (N_2, O_2, CO_2, etc.) is a homogeneous system. This is because the constituent gases have the same composition throughout. Whereas ice and water in a beaker form a heterogeneous system of a solid and a liquid.

The classification of systems from the point of view of its interaction with its surroundings is of more importance in thermodynamics. We shall do that now.

1.2.1 Classification of Systems

Closed System : A closed system consists of a fixed amount of mass. It is also known as **control mass.** No mass can cross its boundary. But energy can cross the boundary and the volume of such a system need not be fixed (Fig. 1.3).

For example, let us again consider the case of the enclosed gas in a cylinder fitted with a piston (Fig. 1.2b). In this case the gas is a system. The inner surfaces of the piston and the surface of the cylinder form the boundary. As no mass can cross this boundary it is a closed system. You must note that energy may cross the boundary.

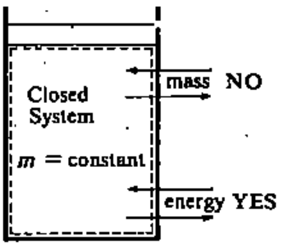


Fig. 1.3 : Characteristics of a closed system

Open System: An open system is a properly selected region in space which has a fixed volume. It is also known as **control volume.** Both mass and energy can cross its boundary (Fig. 1.4).

As an example of such a system let us consider the water heater shown in Fig. 1.5. Suppose the water in the tank is heated in order to get a steady supply of stream of hot water. Since hot water will leave the tank and will get replaced by cold water, it is not convenient to choose a fixed mass of water as our system. Instead we can direct our attention on the volume formed by the inner surfaces of the tank. Then we can consider the hot and cold water streams as mass leaving and entering the control volume or the open system.

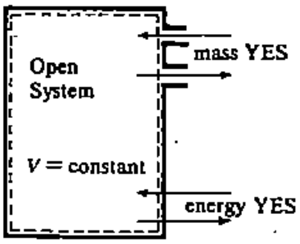


Fig. 1.4 : Characteristics of an open system

Isolated system : An isolated system is that for which there can be no interchange of energy with the surroundings. The contents of an ideally sealed thermos flask is an example of such a system.

While reading about the classification of systems did you realise that the characteristics of the boundary plays an important role in determining the nature of the system. So let us now study about the different kinds of boundary.

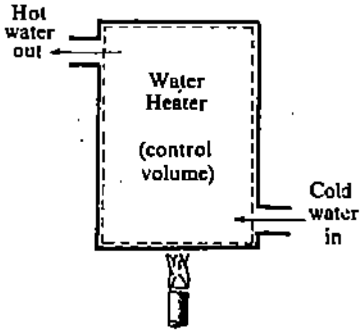


Fig. 1.5 : An open system with one inlet and one exit

1.2.2 Classification of Boundaries

(i) **Diathermal Boundary:** If the boundary is such that heat can flow between the system and its surroundings, then we say that it is diathermal or thermally conducting and the system is in thermal contact with the surroundings. A metallic tea pot provides a diathermal boundary to its contents.

(ii) **Adiabatic Boundary :** If the boundary is such that it does not allow any heat flow across it, then we refer to it as an adiabatic boundary and the system is said to be thermally isolated. The walls of an ideal thermos flask are adiabatic and a filled thermos is an example of a thermally isolated system.

(iii) **Rigid Boundary :** If the boundary is such that it cannot be moved, however great an external force acting on it might be, we call it rigid. A system having such a boundary can neither be compressed nor expanded. Strictly speaking, an ideal rigid boundary does not exist. The surface of a heavy spherical ball (used for "shot put") is a close approximation to a rigid boundary.

(iv) **Permeable Boundary :** If the boundary allows exchange of matter, we refer to it as permeable.

(v) **Semi-permeable Boundary :** The boundary which permits some components to pass through and stops others is known as semi-permeable. For example, hot quartz allows helium to pass but stops other gases.

Now you may like to work out an SAQ based on what you have learnt so far.

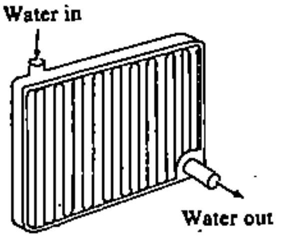


Fig. 1.6 : Car Engine Radiator

SAQ 1

a) Cite an example (different from what you have read just now) each for a system with (i) a real fixed boundary, (ii) a real movable boundary, and (iii) an imaginary boundary.

b) The schematic diagram of a car engine radiator is shown in Fig. 1.6. Should it be modelled as a closed or an open system?

c) A bottle of soft drink at room temperature is put into the refrigerator so that it can cool. Would you model the bottle of soft drink as a closed or an open system?

d) A rose plant in a garden is an example of an open system. Comment.

e) Mention the nature of the system (i.e. open, closed or isolated) that is enclosed by a (i) diathermal boundary, (ii) permeable boundary.

Now, you learnt what is meant by a system and its surroundings. For a particular problem these must be properly defined as per its requirement and the boundary must fulfil the conditions imposed by it.

As an illustration of the statement made above, suppose you want to assess the performance of a refrigerator kept in your dining room. Here the refrigerator along with its contents forms a system, its walls the boundary and the room in which it is placed constitutes its surroundings. However, if we consider the problem of air conditioning of the same dining room, then the room itself becomes the system while its walls, roof, doors, windows etc. constitute the boundary and its neighbouring rooms, verandah, etc. are its surroundings.

Thus you have learnt to identify a thermodynamic system, its surroundings and its boundary. Once we have selected a system for study, we must be able to describe it in terms of precise numerical quantities. For example in mechanics we need to define primarily the position and velocity of a particle in order to describe its motion. We say that the variables viz. position and velocity specify the mechanical state of the particle. Likewise we define the thermodynamic state of a system about which you will study now.

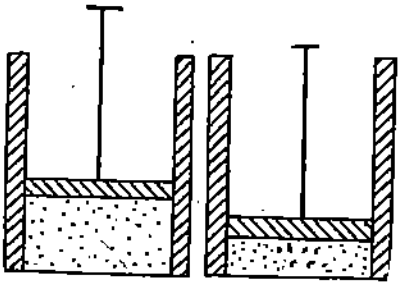


Fig. 1.7 : Different set of values of pressure and volume in (a) and (b) shows two different states of the same system

1.3 THERMODYNAMIC STATE OF A SYSTEM AND THERMODYNAMIC VARIABLES

In thermodynamics a system is described by specifying its physical properties such as pressure, volume, temperature, mass, density etc. For example, the state of a gas is characterised by the value of its temperature, pressure and volume. The state of a stretched wire is specified by its length and tension in it. These physical properties or parameters are called **thermodynamic variables**. The value of a property, which uniquely defines the state of a system, is always fixed. This value depends on the condition of the system at that particular instant at which the property is being measured. For example, the pressure and volume of a system of a gas kept in cylinder have fixed but different values in the two conditions shown in Fig. 1.7a and 1.7b. Therefore, the state of a system means specifying those properties of the system which ensure that it is uniquely defined.

You must note that the properties mentioned above can be measured directly using calibrated devices. In other words they can be perceived by our senses. These properties which represent the gross characteristics of the system are called **macroscopic properties.**

You know that the pressure of a gas can be related to the average rate of change of momentum due to the collision of the molecules made on a unit area of the wall of the container in which it is kept. Higher the rate of change of momentum, higher the pressure. Similarly, the temperature of a gas can be related to the average kinetic energy of translation of its molecules. This means that the system can also be described in terms of the properties of the atoms and molecules that constitute the system. These properties are not directly perceptible and are referred to as **microscopic properties.** You will be required to describe a system in the above manner while studying its **thermodynamic behaviour using statistical methods.** You will do that in Block 4 of this course.

There are two classes of thermodynamic variables – intensive and extensive. Let us study the difference between them.

1.3.1 Intensive and Extensive Variables

Let us consider a system A as shown in Fig. 1.8. Suppose it is divided into two parts A_1 and A_2 having equal masses. Now if you measure the temperature of system A and then of the systems A_1 and A_2 you will find that its value is the same. But the volume of the systems A_1 and A_2 is different from that of system A. Those variables which have the same values when the system is sub-divided or multiplied in size are called **intensive** and those variables for which values are altered are called **extensive.** Here, pressure and temperature are intensive whereas mass and volume are extensive. The intensive variables are independent of mass whereas the extensive variables are dependent on mass. We have given below a list of systems along with intensive and extensive variables describing them. Some places are kept vacant for you to fill up.

Table 1.1: Thermodynamic Variables

System	Intensive variable(s)	Extensive variable(s)
Gas in a cylinder	pressure (p) temperature (T) density (ρ)	mass (m) volume (V)
Paramagnetic solid	flux density (B)	intensity of magnetisation (M)
Stretched wire	tension (F)	——
Surface film	——	area (A)
Electric cell	——	——

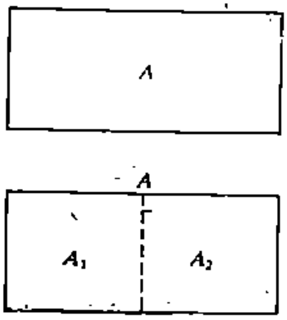


Fig. 1.8 : Illustrating the difference between intensive and extensive variables

SAQ 2

a) Fill in the gaps in Table 1.1.

b) "If f and g are two extensive variables, f/g is intensive." Justify this statement with the help of an example.

c) What are the thermodynamic variables required for specifying the following systems :
   (i) Air inside a bicycle pump
   (ii) A dielectric substance placed in an electric field.

At times the state of a system may be completely identified even from a knowledge of some of its properties. This is because the values of all remaining properties can be obtained using the known properties. For example, say, we know the values of pressure (p), volume (V) and the number of molecules (n) of an ideal gas. Then we can obtain its temperature (T) by using the ideal gas equation

$$pV = nRT \tag{1.1}$$

An equation of the type (1.1) is called an **equation of state.** It is a relation between the values of the variables p, V, n and T, when the system has attained equilibrium. In fact the properties of a system are truly defined only when it is in equilibrium. We refer to this as thermodynamic equilibrium. Let us learn about this in some detail

1.3.2 Thermodynamic Equilibrium

Suppose you have some water at 60°C in a container. If the container filled with water is left to itself it would finally attain the room temperature. This means that the water in the container interacts with the surroundings, and its temperature decreases with time. When it attains the room temperature, i.e. a temperature equal to that of the surroundings there occurs no further change in its temperature. We say tha the water in the container has attained **thermal equilibrium** with the surroundings.

If within the system, there are variations in pressure or elastic stress then parts of the system may move or expand or contract. Eventually when these expansions or contractions will cease, i.e. when there will be no unbalanced forces or torques acting on the system, it will be in **mechanical equilibrium.** For example, during the formation of the earth it was in a molten state. So the centrifugal force due to the axial rotation of the earth was greater than the cohesive force. Since the centrifugal force is maximum at the equator and decreases with latitude becoming minimum at the poles, the earth bulged out at the equator in the process of attaining mechanical equilibrium.

Finally, suppose that a system contains substances that can react chemically. After a sufficient time when all possible chemical reactions will have taken place, the system is then said to be in **chemical equilibrium.** In other words, a mixture of substances is in chemical equilibrium if there is no tendency for a chemical reaction to occur.

Strictly speaking, in addition to thermal, mechanical and chemical equilibria, one must include the aspect of phase equilibrium. However we shall not consider this now. You will get to know about this in Unit 9, Block 2.

A system which is in thermal, mechanical and chemical equilibrium is said to be in **thermodynamic equilibrium.** Under this condition the macroscopic properties of a system do not change with time. Thus, from now onward, by the phrase 'state of a system' we will mean an equilibrium state.

Now that you have learnt about an equilibrium state, we shall now discuss how a system goes from one equilibrium state to another.

1.4 THERMODYNAMIC PROCESS

When any of the thermodynamic variables associated with a system undergoes change in its value while going from one equilibrium state to another the system is said to execute a **thermodynamic process.** Thus, a process signifies change of a system from one equilibrium state, called the initial state, to another equilibrium state, called the final state. For example, the expansion of a gas in a cylinder at constant pressure due to heating is a thermodynamic process. Again suppose a wire is stretched taut between two rigid supports (Fig. 1.9a). It has a certain tension and length. Now, if this wire is allowed to cool it would shrink. Since the wire is not permitted to shrink, a tension is developed in the wire to stretch it (Fig. 1.9b). So it will have a different tension and length, and will be said to have executed a thermodynamic process.

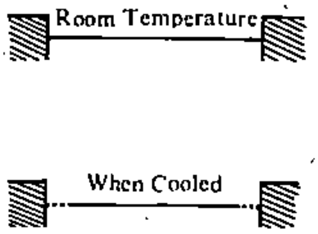


Fig. 1.9 : Tension is developed in the wire when it is allowed to cool. The wire is said to have executed a thermodynamic process.

In the subsequent units, as you will see, our aim will be to analyse thermodynamic processes. In order to do that, first we would like to represent a thermodynamic process graphically. Suppose two variables x and y specify a system. Refer to Fig. 1.10. Here A is the initial equilibrium state represented by the coordinates (x_A, y_A) and B is the final equilibrium state represented by the coordinates (x_B, y_B). The points A and B are joined. Such a graphical representation of the thermodynamic process is called a **path.** Notice that you can join the points in several ways as shown in Fig. 1.10. But in whichever way you draw a path, you would like that the intermediate points must also be defined by specific coordinates. What does this imply? It implies that all the intermediate stages between A and B must be equilibrium states. But is it possible in practice? To answer this question we shall first define two kinds of thermodynamic processes.

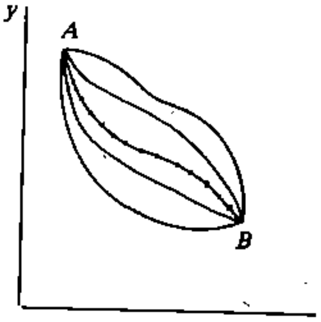


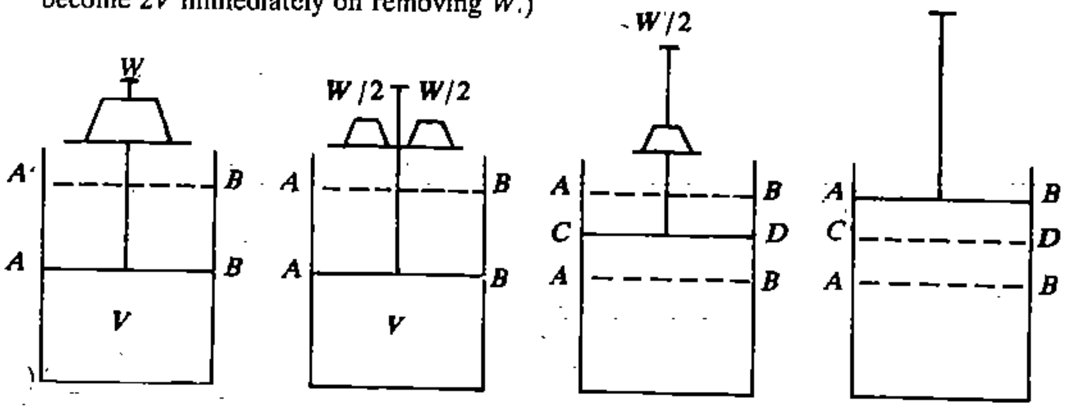
Fig. 1.10 : Graphical representation of several processes occurring between *A* and *B*

1.4.1 Reversible and Irreversible Processes

If a process is executed in a very slow and controlled manner so that all the intermediate states between the initial and final one are in equilibrium and if necessary the process may be executed back along the same equilibrium states from the final to the initial state then it is called **reversible.** If the above conditions are not satisfied then it is called **irreversible.**

Now let us take an example to see whether a reversible process can be executed in practice or not.

Suppose a cylinder containing gas is fitted with a piston (Fig. 1.11a). The volume occupied by the gas is V. The weight W placed on the piston is such that on its removal the piston takes up the position $A'B'$ and the volume of the gas becomes $2V$. Now suppose we want to increase the volume of the gas to $2V$. If we do it just by removing W, the process would be irreversible as it occurs quickly. (The volume of gas will become $2V$ immediately on removing W.)



(d)

Fig. 1.11: Demonstration showing that a reversible process cannot be achieved in practice; it can only be idealised

Now instead of having a single weight W, if we take two weights, each equal to $W/2$ (Fig. 1.11b), the situation is similar to that of Fig. 1.11a. Now, on removing one such weight the piston will take up a position CD midway between AB and $A'B'$ (Fig. 1.11c). Then on removing the next weight it goes to $A'B'$ (Fig. 1.11d). Thus we get one intermediate equilibrium state (denoted by CD) between the initial and final states.

Likewise by using three weights, each equal to $W/3$, we can generate two intermediate equilibrium states. By using n equal weights, each equal to W/n, we can generate $(n-1)$ intermediate equilibrium states. But for this expansion process to be reversible all the intermediate states must be in equilibrium. For this n has to be infinity, which is impossible. This indicates that a reversible process can only be idealised and cannot be achieved in practice.

You must note that a system can be restored to its initial state either by a reversible or an irreversible process. But, for a reversible process, this restoration is made without leaving any net change in the surroundings, whereas for an irreversible process, there occurs some change in the surroundings. For example suppose a pendulum bob (Fig. 1.12) is released from the position A. It goes upto B and then again comes to A, i.e. the initial state. In doing so the pendulum bob is restored to its original state but there occurs a slight change in the temperature of the surroundings because the bob has to overcome air resistance in course of its motion. So the process is irreversible. Had the pendulum been set up in perfect vacuum, air resistance would have been totally absent and hence there would have been no change in the temperature of the surroundings. Thus the process would have been reversible. But as you know perfect vacuum can never be created. This again shows that a reversible process can only be idealised and never be achieved in practice.

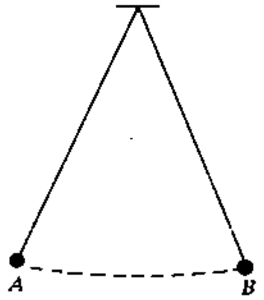


Fig. 1.12 : When the pendulum bob swings from the position A to B and then back to A, there is a slight change in the temperature of the surroundings due to air resistance showing that the process is irreversible.

Thus we understand that all natural processes are irreversible.

This means that for such processes, the intermediate stages are not in equilibrium and hence such processes cannot be represented by a path. If it cannot be represented by a path then its analysis from thermodynamic point of view is not possible. This raises a very vital question. Can we not at all analyse natural processes thermodynamically? The answer lies in the description of a quasistatic process which we shall study now.

1.4.2 Quasistatic Process

If a process is so executed that it passes through states which are not equilibrium states but deviates only infinitesimally from equilibrium, then it is called **quasistatic.** Thus a quasistatic (i.e., almost static) process closely approximates a succession of equilibrium states. If there are finite departures from equilibrium, the process is **non-quasistatic.**

Suppose we wish to increase the temperature of a system from an initial value T_1 to a final value T_2. The temperature could be increased by enclosing the system in a diathermal boundary and maintaining the surroundings of the system at the temperature T_2. But this process would not be quasistatic because the temperature of the system near its boundary would increase more rapidly than at the internal points. To increase the temperature quasistatically, the temperature of the surroundings be kept at the initial temperature T_1 and then this temperature should be increased sufficiently slowly so that at all times it is only infinitesimally greater than that of the system.

Now, all actual processes are non-quasistatic because during the process, there always exists a finite difference of pressure, temperature, etc. between several parts of a system. So for dealing with such a process we shall visualise it as being executed quasistatically. This will enable us to analyse the process. You will be able to appreciate the above statement when you solve actual problems.

You may now like to work out an SAQ on the concepts of reversible and irreversible processes.

SAQ 3

a) Classify the following processes as reversible or irreversible.
(i) A gas enclosed in a cylinder provided with a frictionless piston is quickly compressed (ii) Mixing of sugar in milk (iii) Oscillations of an ideal simple pendulum with a frictionless support.

b) Energy is dissipated during an irreversible process—illustrate this statement with the help of an example.

Before moving on to next sub-section try to do an activity which will enable you to understand quasistatic process more clearly.

Activity

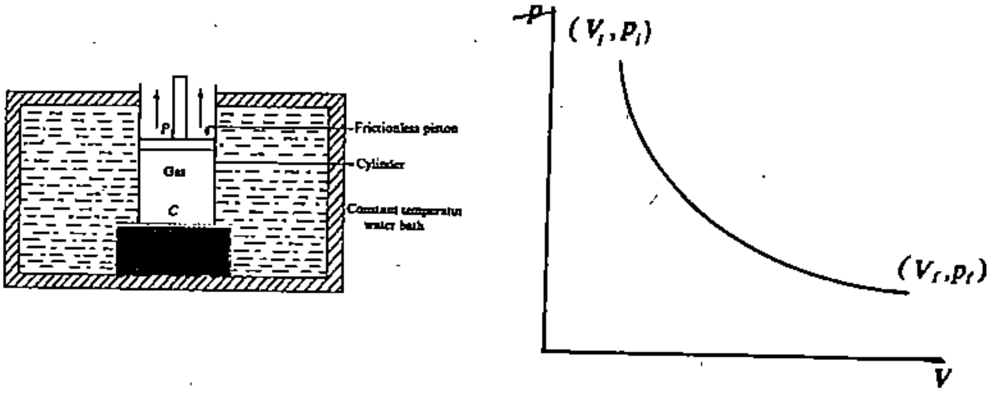
Take any clock which has all the three hands. Observe the movement of the second-hand. Compare its movement with the movement of minute and hour-hand. Comment.

Now that you have learnt about a quasistatic process, we can discuss about the representation of an actual process.

1.4.3 Representation of a Process on an Indicator Diagram

You must have realised that the stages of a quasistatic process are a series of approximately equilibrium states. As you have seen in Fig. 1.10, equilibrium states can be indicated by a series of points in the xy-plane where x and y are two thermodynamic variables. As you know, a curve through these points represents the path of the process. Such a representation is known as an **indicator diagram.** Let us now learn to represent an actual process on an indicator diagram.

Consider a gas contained in a cylinder C fitted with a frictionless piston P having diathermal walls and immersed in a constant temperature water bath as shown in Fig. 1.13a.



(a) (b)

Fig. 1.13(a) : Arrangement for expansion of a gas at constant temperature. (b) p vs. V diagram for a quasistatic isothermal expansion of a gas. It is also referred to as an indicator diagram.

Suppose that the initial state of the gas is defined by (p_i, V_i, T_i). Now, we pull out the piston very slowly so that the gas expands at constant temperature in such a way that at any instant the external pressure on the piston differs from the gas pressure by an infinitesimal amount dp. Let the final state of the gas be (p_f, V_f, T_i). While undergoing change from the initial state to the final state, the system is characterised by a series of values of p and V differing only infinitesimally from each other. The plot of these successive values with V along the abscissa and p along the ordinate gives us the required representation (Fig. 1.13b).

So far we have classified processes on the basis of the pace of their execution. We can also classify processes, on the basis of the fact that some property of the system remains constant during the process. That is, one of the variables of the system remains constant. We specify these processes by using the prefix 'iso' before that property. For example, in the abovesaid process, the gas has been expanded at constant temperature. Thus, the above process is **isothermal.** If a process takes place at constant pressure, we label it as **isobaric.** A process taking place at constant volume is called **isochoric** or **isovolumic** or **isovolumetric.** A change of state (i.e. water to steam or water to ice) takes place at constant temperature and pressure. This is an example of **isothermal-isobaric** process.

Furthermore, if the system has adiabatic boundaries and the process takes place without any exchange of heat between the system and the surroundings, we refer to it as an **adiabatic process.** For example, a single stroke of the piston or an internal combustion engine is very nearly adiabatic. The reason is that the duration of the process is extremely small and no heat can flow in or out of the system during this time.

If the transformation of the system is such that it returns to its original state covering any path, then we say that it has undergone a **cyclic process.** The working substances of all heat engines and refrigerators go through several cycles of operation.

We have represented some of the above-mentioned processes on the p-V diagrams (Fig. 1.14) below:

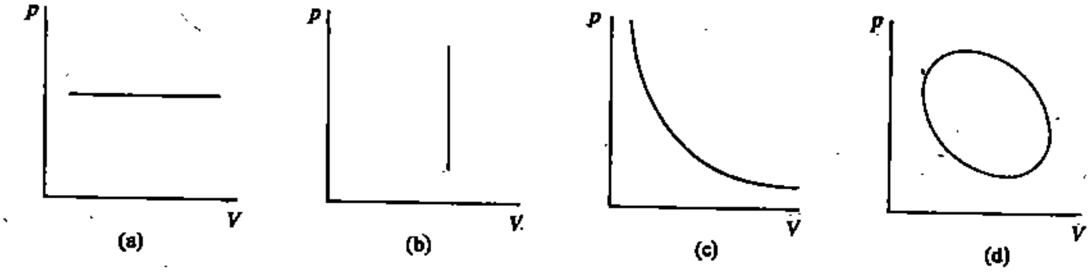


Fig. 1.14: (a) isobaric (b) isochoric (c) isothermal (d) cyclic

You may now like to work out an SAQ on the representation of processes.

SAQ 4

Draw V–T and p–T diagrams for a perfect gas undergoing following processes.
(i) Isobaric expansion (ii) Isochoric compression (iii) Isothermal compression.

Before proceeding further it would be worthwhile to know how the concept of temperature got introduced. Actually, we have been using the term temperature quite freely (since it is very familiar to you) but its basis lies in a law of thermodynamics. Let us study this law which is known as the zeroth law.

1.5 THE ZEROTH LAW OF THERMODYNAMICS

The zeroth law of thermodynamics states :

"If two systems A_1 and A_2 are in thermal equilibrium independently with a third system A_3, then A_1 and A_2 are also in thermal equilibrium with each other."

Let us discuss the meaning of this law. Refer to Fig. 1.15a.

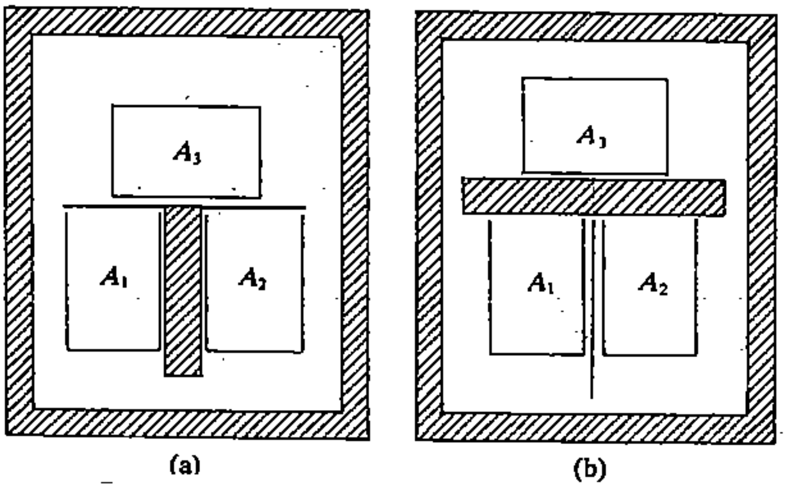


Fig. 1.15 : The Zeroth law of thermodynamics (adiabatic walls are denoted by shading and diathermic walls by solid lines) ; (a) A_1 and A_2 are in thermal contact with A_3. (b) A_1 and A_2 are in thermal contact with one another.

Here A_1 and A_2 are two systems separated by adiabatic walls. They are in thermal contact with another system A_3. Both A_1 and A_2 individually will come in thermal equilibrium with A_3. If now A_1 and A_2 are put in thermal contact with each other (Fig. 1.15b) then according to the zeroth law both A_1 and A_2 will be in thermal equilibrium.

All bodies in thermal equilibrium must have a common property which has the same value for all of them. This property is called the temperature. Thus the temperature of a body is the property which determines whether or not the body is in thermal equilibrium with other bodies. The phenomenon that two things in contact tend towards a common temperature is so common that its importance has been overlooked. When physicists finally did appreciate its significance and fundamental nature, it was decided to have it elevated to the status of a "Law of thermodynamics" By that time the first and second laws were already enunciated. So in order to place it ahead of these laws it is named as the zeroth law.

Now we would like you to look at Eq. (1.1) and read once again the paragraph following it. Eq. (1.1) is quite well known to you. Can such relations, exist for other thermodynamic systems? In fact from the zeroth law it can be established mathematically that a relation does exist between temperature and other thermodynamic variables associated with a system. Such a relation, as you know, is called an equation of state. Let us study about it in some detail before rounding off this unit.

1.6 THE EQUATION OF STATE

You know that the temperature of a system can be expressed as a function of any other two thermodynamic parameters. If the two parameters are x and y then mathematically it can be expressed as

$$T = f_1(x, y) \tag{1.2a}$$

Eq. (1.2a) can be solved for x in terms of T and y and can even be solved for y in terms of T and x so that we have the relations

$$x = f_2(T, y) \tag{1.2b}$$

$$y = f_3(T, x) \tag{1.2c}$$

In other words Eqs. (1.2a, b and c) can be expressed as

$$f(x, y, T) = 0 \tag{1.3}$$

Eq. (1.3) is **parametric** as the form of f is not given. But the equation of state of an ideal gas (Eq. 1.1) is **exact**. Likewise we may have equations of state for a real gas or for several other systems. We will not aim to derive any such equation here. We will only provide a few examples in Table 1.2.

Table 1.2

System (variables)	Equation of State	
	Parametric	**Exact**
Ideal gas (p, V, T)	$f(p, V, T) = 0$	$pV = RT$, where R is the universal gas constant
Real gas (p, V, T)	$f(p, V, T) = 0$	$(p + \frac{a}{V^2})(V-b) = RT$, where a and b are constants
Paramagnetic solid (M, B, T)	$f(M, B, T) = 0$	$M = C\frac{B}{T}$, where M is the intensity of magnetisation and B is the flux density of the magnetic field in which the solid is placed. C is a constant
Stretched wire (L, F, T)	$f(L, F, T) = 0$	$L = L_0[1 + pF + q(T - T_0)]$ where L and L_0 are the lengths of the wire at temperatures T and T_0 respectively. F is the tension in the wire, p and q are constants.

The parametric form of the equation of state may be used to study some typical characteristics like coefficient of thermal expansion, elasticity, compressibility and so on of any substance. We shall do that now. This exercise will make you competent to handle thermodynamic relations involving partial derivatives. You will encounter several such relations, particularly in Block 2 of this course.

1.6.1 Deductions from Equation of State

Before you proceed to study the several characteristics using the equation of state you will need to learn a little about partial differentiation. You will find that it is an extension of the idea of ordinary differentiation. We come across such differentiation when a quantity is a function of more than one variable and it is required to find the change in the quantity when any one of the variables changes by a small amount. For example the temperature of a gaseous system is a function of pressure and volume. Now, we may like to obtain the rate of variation of temperature with respect to an isochoric (volume = constant) variation of pressure. Likewise we may wish to obtain the rate of variation of temperature with respect to an isobaric (pressure = constant) variation of volume. In the former case we are seeking the partial derivative of T with respect to p at constant V, denoted by $\left(\frac{\partial T}{\partial p}\right)_V$, whereas in the latter case the partial derivative of T with respect to V, denoted by $\left(\frac{\partial T}{\partial V}\right)_p$. Notice that instead of using the symbol 'd' as in the case of ordinary differentiation here we are using the symbol '∂' (pronounced 'del'). We shall now work out mathematical relationship between the partial derivatives involving any three variables. These will be very useful in doing the relevant deductions from equation of state.

Let z be a function of x and y :

$$z = z(x, y) \tag{1.4}$$

Then total differential dz is given by the following relation :

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{1.5}$$

Eq. (1.5) expresses the change in z which results from changes in x and y on which z depends.

Now if we take three variables as p, V and T of a gaseous system then we may say that

$$V = V(p, T)$$

Thus using Eq. (1.5) the volume difference dV between two neighbouring equilibrium states may be expressed as

$$dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT \tag{1.6a}$$

and similarly for the pressure difference dp as

$$dp = \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT \tag{1.6b}$$

Now, substituting Eq. (1.6b) in Eq. (1.6a), we get

$$dV = \left(\frac{\partial V}{\partial p}\right)_T \left[\left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT\right] + \left(\frac{\partial V}{\partial T}\right)_p dT$$

$$\text{or } 0 = \left[1 - \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T\right] dV - \left[\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_p\right] dT \tag{1.7}$$

Now, of the three variables p, V, and T only two are independent. Choosing V and T as the independent variables, Eq. (1.7) must be true for all sets of values of dV and dT. Thus for two states which are at the same temperature ($dT = 0$) but having different volumes ($dV \neq 0$) we get from Eq. (1.7)

$$1 - \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T = 0$$

- If $z = z(x, y)$ then total differential dz is expressed as

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

This leads to two important mathematical relations:

$$\text{(i)} \quad \left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{(\partial x/\partial z)_y} \quad \text{(ii)} \left(\frac{\partial z}{\partial x}\right)\left(\frac{\partial x}{\partial y}\right)\left(\frac{\partial y}{\partial z}\right) = -1$$

- In the language of partial derivatives the coefficient of isobaric coefficient of volume expansion (β), isothermal elasticity (E_T) and isothermal compressibility (κ) are defined as follows

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

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

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

1.8 TERMINAL QUESTIONS

1) a) Can a system composed of 200 molecules be called a thermodynamic system? Justify your answer.

   b) Prove that the specific value corresponding to an extensive variable is an intensive property. (**Hint** : Specific value of any variable is its value per unit mass.)

   c) The weight of 2 $m^3$of Hg at 0°C and 1 bar pressure at a place where $g = 9.80\ ms^{-2}$ is 2.67×10^5 N. Give two extensive and five intensive variables of this system.

2. Consider the following statements :

   i) Specific gravity of a substance is an intensive property but density is an extensive property.

   ii) Reversible processes are only an idealisation and all the natural processes are irreversible.

   iii) An isolated system is necessarily adiabatic. Choose your answer.
   (a) if only (i) and (ii) are correct.
   (b) if only (ii) and (iii) are correct.
   (c) if only (i) and (iii) are correct.
   (d) if all the statements are correct.

3) A certain stretch of railway track is laid without expansion joints in Thar desert where day and night temperatures differ by 25 K. The cross-sectional area of rail is $3.6 \times 10^{-3}\ m^2$. The Young's modulus, Y, of its material is $2 \times 10^{11}\ N\,m^{-2}$ and its co-efficient of linear expansion, α, is $8 \times 10^{-6}\ K^{-1}$. (a) If the length of the track is kept constant, what is the difference in the tension in the rails between day and night? (b) If the track is 15 km long, and is free to expand, what is the change in its length between day and night?

(**Hint:** Use $f(L, F, T) = 0$ alongwith $Y = \frac{L}{A}\left(\frac{\partial F}{\partial L}\right)_T$ and $\alpha = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_F$ where L, F and T denote length, tension and temperature respectively.)

1.9 SOLUTIONS AND ANSWERS

SAQs

1) (a) (i) A dice (Fig. 1.16a) (ii) A car (Fig. 1.16b) as its doors, bonnet and dickey can be opened (iii) Smoke coming out of a chimney (Fig. 1.16c).

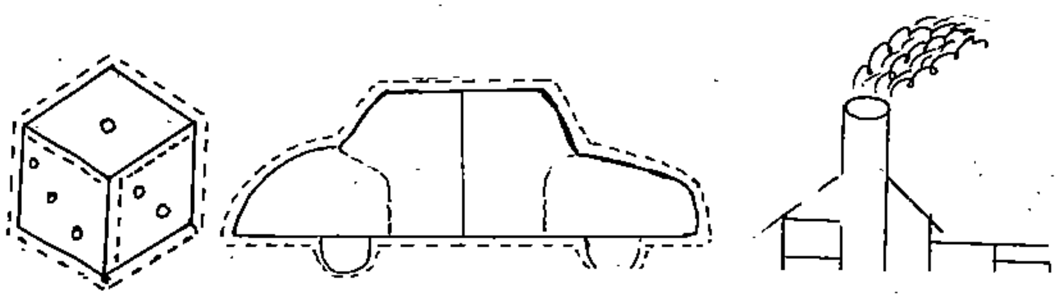


Fig. 1.16 : Diagrams for answer to SAQ 1 (a). In each case the dotted line represents the boundary.

(b) The volume of the system is constant. Hence, it is an open system.

(c) This system has a constant mass so it is a closed system.

(d) When we consider a rose plant in a garden it is a system with other plants, soil and atmosphere as surroundings. In day time it takes up sunlight (energy) and CO_2 (matter) from the atmosphere and gives out O_2. It also takes nutrients (matter) from the soil and increases its own matter content. Thus, exchange of energy and matter both takes place, which makes the rose plant in a garden an open system.

(e) (i) Closed (ii) Open

2) a) Intensive : surface tension (s), e.m.f. (E)
Extensive: length (L), charge (q)

b) Let f be mass and g be volume of a substance then f/g is its density.

c) (i) Pressure, volume, temperature, mass and density.
(ii) Intensity of polarisation, temperature, electric field intensity.

3) a) (i) and (ii) irreversible (iii) reversible.

b) Let us consider the case of expansion of a gas contained in a cylinder. Suppose this is done by pulling the piston outward. If there is a friction between piston and the inner wall of the cylinder the process is definitely irreversible. In this case a portion of mechanical energy provided by the pull goes in heating of the piston and the wall of the cylinder. This illustrates that energy is dissipated during an irreversible process.

Activity

$$\text{Angular speed of second-hand} = \frac{2\pi}{60}\,\text{rad s}^{-1} = \frac{\pi}{30}\,\text{rad s}^{-1} = 3.3\pi \times 10^{-2}\,\text{rad s}^{-1}$$

$$\text{Angular speed of minute-hand} = \frac{2\pi}{60\times60}\,\text{rad s}^{-1} = \frac{\pi}{1800}\,\text{rad s}^{-1} = 5.5\pi \times 10^{-4}\,\text{rad s}^{-1}$$

$$\text{Angular speed of hour-hand} = \frac{2\pi}{12\times60\times60}\,\text{rad s}^{-1} = \frac{\pi}{21600}\,\text{rad s}^{-1} = 4.6\pi \times 10^{-5}\,\text{rad s}^{-1}$$

The movement of second-hand can be perceived. Angular speeds of minute and hour-hand being small their movements cannot be perceived. Hence their movement is quasistatic in nature.

4) Refer to Fig. 1.17. Here i and f represents initial and final state respectively. Note that in V–T diagram for (i) the extrapolated portion of the straight line must pass through the origin as $\frac{V}{T}$ = constant. The case of p–T diagram for (ii) will be similar.

5) a) Putting $dV = 0$ and $dT \neq 0$ in Eq. (1.7) we get

$$\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_p = 0$$

or

$$\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_p$$

$$\text{specific Volume} = \frac{2}{2.72 \times 10^4} = 7.35 \times 10^{-5}\ \mathrm{m^3\ kg^{-1}}$$

(specific volume is defined as volume per unit mass)

2) (b)

3) a) Since, $f(L, F, T) = 0$, from Eq. (1.9) we get,

$$\left(\frac{\partial L}{\partial F}\right)_T \left(\frac{\partial F}{\partial T}\right)_L \left(\frac{\partial T}{\partial L}\right)_F = -1$$

Thus

$$\frac{L}{YA}\left(\frac{\partial F}{\partial T}\right)_L \frac{1}{\alpha L} = -1$$

or

$$\left(\frac{\partial F}{\partial T}\right)_L = -YA\alpha$$

So, if the length of the track is kept constant, the difference in tension corresponding to a difference in temperature ΔT is given by

$$\Delta F = -YA\alpha\ \Delta T$$

Here ΔT is negative when we consider the change from day to night.

Hence, $\Delta F = (2 \times 10^{11}\ \mathrm{N\ m^{-2}})\ (3.6 \times 10^{-3}\ \mathrm{m^2})\ (9 \times 10^{-6}\ \mathrm{K^{-1}})\ (25\ \mathrm{K})$

$$\Delta F = 1.44 \times 10^5\ \mathrm{N}$$

As the temperature changes from day to night, the track contracts. However, the track is not permitted to contract because its length is being kept constant. Therefore, a force would be required to expand the track and restore it to its original length and hence ΔF is positive.

b) $f(L, F, T) = 0$

or $L = L(F, T)$

$$\therefore\ \mathrm{d}L = \left(\frac{\partial L}{\partial F}\right)_T dF + \left(\frac{\partial L}{\partial T}\right)_F dT$$

Putting $dF = 0$ (since the track is free to expand) and

$\alpha = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_F$, the difference in length L corresponding to a difference in temperature ΔT is given by

$$\Delta L = \alpha L \Delta T$$

If we consider the change from day to night, $\Delta T = -25$ K

$$\therefore\ \Delta L = (8 \times 10^{-6}\ \mathrm{K})\ (15 \times 10^3\ \mathrm{m})\ (-25\ \mathrm{K}) = -3\ \mathrm{m}$$

i.e. there is a decrease in the length of the track by 3 m.

UNIT 2 MEASUREMENT OF TEMPERATURE

Structure

2.1 Introduction
  Objectives
2.2 Principle of Measurement of Temperature
  Physical Properties Considered for Measurement of Temperature
  Scale of Temperature
2.3 Gas Thermometer
  Constant Volume Gas Thermometer
  Perfect Gas Temperature Scale
2.4 Resistance Thermometers
  Platinum Resistance Thermometer
  Thermistors
2.5 Thermocouples
  Thermocouples and Thermoelectric Circuits
  Practical Thermocouples
2.6 Radiation Pyrometers
2.7 The International Practical Temperature Scale
2.8 Summary
2.9 Terminal Questions
2.10 Solutions and Answers

2.1 INTRODUCTION

Would you like to remain outdoor on a hot summer afternoon? Preferably not. Likewise you will not like to take bath in ordinary tap water during winter. As you can realise that the above examples are related with the most important thermodynamic variable temperature. You have learnt about the concept of temperature in the previous unit. We can have a feeling of this thermodynamic variable by way of our senses. But it has an element of difference from the senses of smell and taste. We do not go for quantifying these senses. In other words we would never go to measure how much higher is the smell of a rose than that of a sunflower. Nor we question how much is a curry tastier than a salad, whereas for temperature we need to quantify. Everyday you get to know about the temperature of the important cities from the newspaper. If someone has a prolonged fever a temperature chart of his/her body is maintained.

The device used for measurement of temperature, as you know, is called thermometer. For the above measurements we normally use a liquid-in-glass thermometer with which you are familiar. It utilises the property of variation of the volume of a liquid with temperature. However, the temperatures of our interest are not only restricted to that of a place or a man's body. It ranges from as low as 0.01 K, where helium solidifies, to 6000 K, the temperature of sun's surface. How do we measure these temperatures? Certainly not by liquid-in-glass thermometers. In fact there are many other kind of thermometers about which you will read in this unit.

The action of every kind of thermometer is based on the temperature-variation of some physical property. In this unit you will read how gas thermometers, resistance thermometers, thermocouples and radiation pyrometers are used for the measurement of temperature.

You will also learn how a scale is developed for the measurement of temperature. We shall chiefly deal with the perfect gas scale. Finally we shall discuss briefly the International Practical Scale of Temperature.

As you know the change in temperature of a body is brought about by heat. But what is the nature of heat? The answer to this question will lead us to the first law of thermodynamics. In the next unit you will read about that.

Objectives

After studying this unit, you should be able to

- state the principle of measurement of temperature,
- compare different types of methods of measurements of temperature,
- describe the working and relative merits as well as demerits of gas thermometers, resistance thermometers, thermocouples and radiation pyrometers,
- outline the features of a perfect gas scale,
- compute temperature from the given values of a particular thermometric property and vice versa,
- select a thermometer for a specific use.

2.2 PRINCIPLE OF MEASUREMENT OF TEMPERATURE

Measuring temperature is a very familiar experience. You must have seen a clinical thermometer being inserted under the tongue of a patient. What happens in that case? The mercury column increases in length. We then determine the temperature of the body of the patient by noting the reading of the mark upto which the mercury column reaches. In other words, we utilise the properties of variation of the volume of a liquid with temperature for the measurement of temperature.

Incidentally we always measure temperature by observing the variation of certain property with temperature. Let us see what these properties are.

2.2.1 Physical Properties Considered for Measurement of Temperature

Some properties which exhibit variation with small change in temperature are length of a liquid column in a capillary, volume of a fluid, pressure of a gas kept in a container of fixed volume, electrical resistance of a metal or a semiconductor, e.m.f. between the junctions of two dissimilar metals or alloy maintained at different temperatures, and so on. We refer to these properties as **thermometric properties.**

Now, let us again come back to the case of the familiar clinical thermometer. You must have seen that the graduation on it covers a range roughly between 94°F and 108°F. On the other hand the same for a common laboratory thermometer normally ranges between – 10°C and 110°C. In each case the range is equally divided into number of divisions. Selection of the range and its subsequent division is essential for the measurement of temperature. We refer to this as preparing a scale of temperature. Let us learn about it in detail now.

2.2.2 Scale of Temperature

In order to make a thermometer, we select a suitable substance having one of the thermometric properties and assign a set of numbers to the values of the property during its variation in accordance with some rule to define the scale of temperature. When we bring the thermometer into contact with a body and allow it to reach the state of **thermal equilibrium,** the thermometric property attains a specific value, which we read in terms of the number assigned to it. Thus, we get a measure of the temperature of the body. The scale developed will be simple if the thermometric property, we have chosen, has a linear dependence on temperature.

Now suppose that we represent the value of thermometric property by X_T and the temperature corresponding to it by $T(X)$. Assuming the variation of X_T with temperature as linear, we write

$$X_T = aT(X) + b, \tag{2.1}$$

where a and b are constants. We can determine a and b from the value of the thermometric property at two temperatures. For example, if we assign the values X_0 and X_{100} to the thermometric property at temperature 0°C and 100°C, then

$$X_0 = a \times 0 + b = b \tag{2.2}$$

and

$$X_{100} = 100\,a + X_0$$

This gives us

$$a = \frac{X_{100} - X_0}{100} \tag{2.3}$$

so that

$$T(X) = \frac{1}{a}(X_T - b) = \frac{X_T - X_0}{X_{100} - X_0} \times 100 \tag{2.4}$$

You must be familiar with the scale defined by Eq. (2.4). It is the Celsius scale and is a two-point scale because we have used value of X_T at two fixed points, 0°C (ice point) and 100°C (steam point) to determine a and b.

An easily reproducible state of a standard system, chosen arbitrarily, is called a fixed point. The ice point and steam point are the temperatures at which pure water freezes and boils, respectively, at atmospheric pressure at sea-level and 45°. latitude.

Incidentally, the freezing and boiling temperatures are very sensitive to atmospheric pressure, presence of dissolved impurities in the thermometric liquid, nature of the glass used for holding the liquid and so on. So it becomes difficult to reproduce the fixed points. Secondly, the scale established in this method depends upon the physical property and the material used.

The latter problem can be solved by defining a scale in such a way that it does not depend upon any particular property of any particular substance. There are two such theoretical scales

a) The perfect gas scale, which is based on the gas law

$$\frac{pV}{T} = \text{a constant}$$

(You will read more about this scale in Sec. 2.3.2.)

b) Kelvin's thermodynamic scale based on the working of a reversible heat engine.

These above two scales are equivalent. You will learn the proof of this equivalence after studying Carnot's engine and Carnot's theorem in Block 2 of this course.

However, to remove the experimental uncertainties, as regards the reproductivity of the fixed points associated with a two-point scale, a one-point scale was developed at the Tenth Conference of Weights and Measures held at Paris in 1954. It was decided that **the triple point of water—the temperature at which ice, water and water vapour are in equilibrium with each other, be taken as the fixed point. Its value is 273.16 and the unit is called kelvin** (represented by K). You will read about the existence of triple point in Unit 7 of Block 2. On this scale, the ice point is 273.16 K and the steam point is 373.16 K. Since it is not possible to attain a temperature below 0 K, it is referred to as the **absolute zero** and the scale is called **absolute scale.** However, for practical purposes, we use the Celsius scale on which the triple point of water is 0.01°C. Here, we represent temperature by t and it is related to the absolute temperature T(K) through the relation.

$$t = T - 273.15 \tag{2.5}$$

If the value of the thermometric property at the triple point be X_{tp}, Eq. (2.1), with $b = 0$, takes the form

$$X_{tp} = 273.16\, a. \tag{2.6}$$

Now we can easily determine a from the known value of X_{tp}. Rewriting Eq. (2.1) i.e. $X_T = a\, T(X)$ and combining it with Eq. (2.6), we get

$$T(X) = 273.16\,(X_T/X_{tp}). \tag{2.7}$$

From Eq. (2.7), we note that the main step in the development of a thermometer is to determine X_{tp} at the triple point of water. The apparatus used for establishing this temperature is called the triple point cell. A labelled diagram of this apparatus is shown in Fig. 2.1. First water of highest purity is distilled into the vessel. When all air has been removed, the vessel is sealed off. Using a freezing mixture in the inner well, a layer of ice is made to be formed around it. On replacing the freezing mixture by a thermometer bulb a thin layer of ice gets melted near it. Thus, ice, water and water vapour coexist in equilibrium within the U-tube and the device in equilibrium with these is at the triple point.

Thus, we can obtain a one-to-one correspondence between temperature and a thermometric property by multiplying the ratio of the observed value of the property to its value at the triple point by 273.16. Obviously, the scale so obtained depends on the value of X_T/X_{tp}, which, in general, is expected to be different for different properties of the same substance or same property of different substances. For example, the ratio R_T/R_{tp} will be different for copper and nickel, where R represents electrical resistance. You may now ask: What would happen if we consider a property such as resistance or thermo-e.m.f. having a non-linear dependence on temperature? Such thermometers include resistance thermometer, thermocouple etc. and are somewhat complex to use.

You may now like to work out an SAQ on the principle of measurement of temperature

SAQ 1

a) Name three thermometric properties which have linear dependence on temperature.

b) At what temperature, the absolute scale reading is (i) 1.5 times the Celsius scale reading, and (ii) equal to the celsius scale reading?

c) Length of a mercury column in a capillary tube is 3.30 cm. at 0°C and 24.87 cm at 100°C. What is the temperature of a body, in contact with which the column length is found to be 18.53 cm?

Now, you know the basic principles of measurement of temperature. Let us now study about the features of the one-point scale as applied to different methods employed for measuring temperature.

The commonly used thermometric properties are: length of liquid column in a capillary, volume of a gas at constant pressure, pressure of a gas at constant volume, resistance of a metal or a semiconductor and thermo-e.m.f. We name the thermometers based on these properties accordingly and express Eq. (2.7) in terms of corresponding symbols. Thus, for a liquid-in-glass thermometer, we write

$$T(L) = 273.16\,(L/L_{tp}), \tag{2.8}$$

where L represents the length of the liquid column; and in the case of a resistance thermometer, we have

$$T(R) = 273.16\,(R/R_{tp}), \tag{2.9}$$

where R represents the resistance of the material of the thermometer.

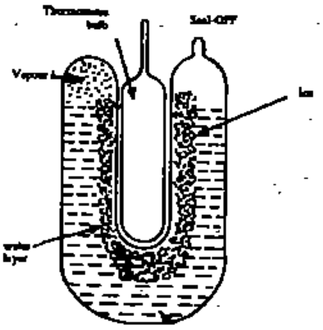


Fig. 2.1 : A triple point cell

You may now like to work out an SAQ on the above concept. For that you will have to recall from your school science courses the basic idea of a thermocouple.

SAQ 2

Write down the relation corresponding to Eqs. (2.8) and (2.9) for a thermocouple.

Now we need to find out whether the value we obtain for the temperature of a system depends on the choice of the thermometer we use to measure it. By defining the one-point scale we have ensured that all the different kinds of thermometers agree at the standard fixed point. But what happens at other points? Experiments show that the value of X_T/X_{tp} at the same temperature for thermometers of different or same kind but using different materials exhibits a significant variation. Hence, for obtaining a definite temperature scale, we must select one particular kind of thermometer as standard. Experiments, however do show that the variation in X_T/X_{tp} values is smallest among the different constant-volume gas thermometers. This suggests that a gas can be a standard thermometric substance.

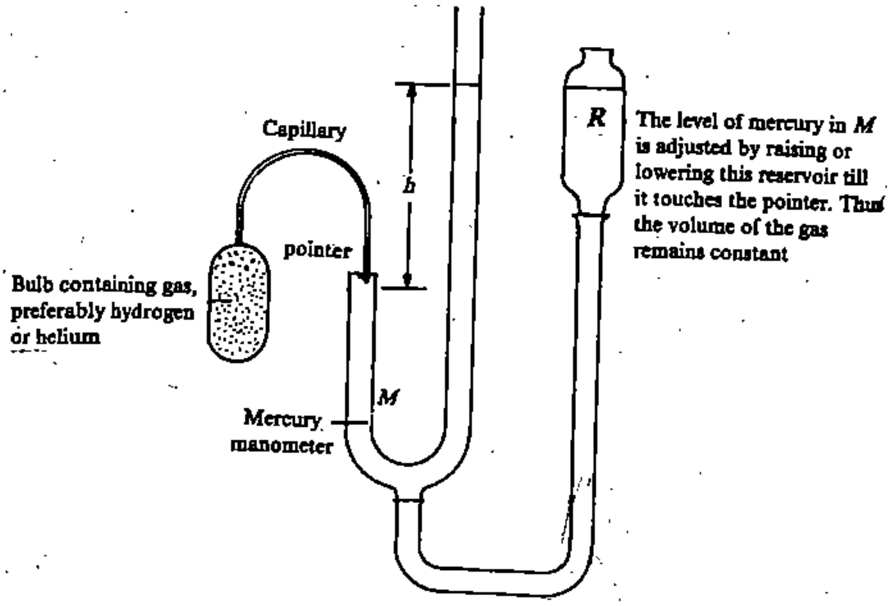
It is seen that as the amount of gas used in such a thermometer is reduced (which means that its pressure is reduced), the variation in readings between gas thermometers using different kinds of gas is also reduced. This indicates that there is something fundamental about the behaviour of this kind of thermometer if the pressure of the gas is low. We use such a thermometer as a reference to calibrate other thermometers with respect to its scale. So let us study about that.

2.3 GAS THERMOMETERS

Here we use the temperature dependence of volume at constant pressure and that of pressure at constant volume as the thermometric properties. Both types of expansion are highly uniform over a wide range of temperature. However, a constant-pressure gas thermometer has a relatively complicated construction and does not give consistent results. Therefore, the constant-volume thermometer is more in use and better suited as a standard device. Consequently, we discuss only the constant volume gas thermometer.

2.3.1 Constant Volume Gas Thermometer

The details of construction of constant volume gas thermometer with regard to its dimensions, shape, materials used, etc. differ from one laboratory to another. However, we have shown the important features of its construction and principle of use in Fig. 2.2.



The level of mercury in *M* is adjusted by raising or lowering this reservoir till it touches the pointer. Thus the volume of the gas remains constant

Fig. 2.2: The constant volume gas thermometer

When the thermometer is in contact with a hot body, the gas expands due to rise in its temperature and pushes mercury down in the tube *M*. The level of mercury in *M* becomes stationary when equilibrium is attained. The height *h* of the mercury level in *M'* with respect to *P* is measured accurately. In contrast, if we use the thermometer to measure the temperature of a cold body, the gas contracts and we have to be careful that mercury is not sucked into the bulb. Otherwise, we adjust the level of mercury in a similar way.

Suppose that the height of mercury in *M'* above (below) p is $\pm h$. Then, pressure of the gas in G is given by

$$p = p_a \pm h\rho g, \qquad (2.10)$$

where p_a is the atmospheric pressure, ρ is density of mercury at ambient temperature and g is local value of acceleration due to gravity. In this case, Eq. (2.7) becomes

$$T(p) = 273.16\,(p/p_{tp}). \qquad (2.11)$$

It may be remarked that before using Eq. (2.11) we have to apply corrections to the value of p or p_{tp} due to the following factors :

i) the temperature gradient along the capillary
ii) the gas pressure in M above p
iii) the change in volumes of the bulb and the capillary with change in temperature and pressure
iv) change in the density of mercury with temperature
v) adsorption or deadsorption of the gas by the walls of the bulb and the capillary.

Of course, some of these can be taken care of by proper choice of materials and the design.

The temperature range of gas thermometers with proper design varies from about 10 K to 1900 K. **Although these are sensitive and accurate, they suffer from the drawbacks of large size and slowness in attaining the equilibrium with the system.** Therefore, these are not practical thermometers. We only use these as standards to calibrate other thermometers. We may also add that the results obtained with the thermometers containing different gases yield the same result if p_{tp} is very small. To obtain this situation, we plot p/p_{tp} versus p_{tp} graph (Fig. 2.3), determine p/p_{tp} for p_{tp} tending to 0 and then use Eq. (2.11).

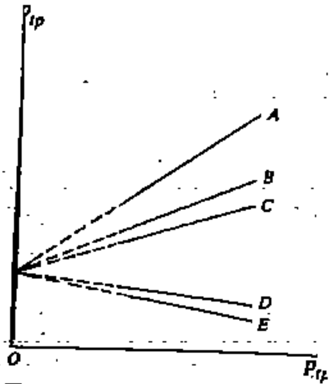


Fig. 2.3 : p/p_{tp} vs. p_{tp} graph for different gases *A*, *B*, *C*, *D* and *E*. *OP* is the extrapolated value of p/p_{tp} for $p/p_{tp} \rightarrow 0$.

You may like to work out an SAQ on the above concept.

SAQ 3

If constant-volume gas thermometers containing different gases in varying quantities are used to determine the normal boiling point of water, the extrapolated curves for the ratio of the gas pressure at the steam point to that at the triple point intersect the ratio axis at 1.36604. Evaluate the steam point.

Now that you have become familiar with Eq. (2.11), we shall work out an example to discuss the use of a constant volume hydrogen thermometer. After that you will work out an SAQ on gas thermometer.

Example 1

A constant-volume hydrogen thermometer is brought into thermal contact with a triple point cell and then with a body whose temperature is to be determined. The heights of mercury column in the two cases are noted as −22.0 cm and −15.0 cm, respectively. What is the temperature of the body? Given, atmospheric pressure = 1 bar, acceleration due to gravity = 9.81 m s^{-2} and density of mercury = 13.59×10^3 kg m^{-3}

Solution

It is given that the atmospheric pressure is 1 bar, i.e.

$$p_a = 1 \text{ bar} = 10^5 \text{ N m}^{-2}.$$

Using Eq. (2.10), we get the values of pressure of the gas at the triple point and the body temperature as

$$p_{tp} = (10^5 - 0.22 \times 13.59 \times 10^3 \times 9.81) \text{ N m}^{-2} = 7.07 \times 10^4 \text{ N m}^{-2}$$

$$p = (10^5 - 0.15 \times 13.59 \times 10^3 \times 9.81) \text{ N m}^{-2} = 8.00 \times 10^4 \text{ N m}^{-2}.$$

Substituting these values in Eq. (2.11), we get

$$T = 273.16 \text{ K} \times (8.00 \times 10^4 \text{ N m}^{-2})/(7.07 \times 10^4 \text{ N m}^{-2}) = 309 \text{ K}$$

SAQ 4

Consider five constant volume gas thermometers, three of which are filled with He at 100 m bar, 50 m bar and 25 m bar and two with N_2 at 20 m bar and 5 m bar at the triple point. Answer the following questions.

i) Will these thermometers yield the same value of temperature for a body?

ii) Will the three He filled thermometers give the same value of temperature?

iii) Which thermometer will give the value closest to the actual one?

iv) How will you determine the actual value of temperature using the three He filled temperatures?

We have already mentioned about the perfect gas temperature scale in Sec. 2.2. You will now see how such a scale can be made to develop through Eq. (2.11).

2.3.2 Perfect Gas Temperature Scale

We have pointed out earlier that all the constant-volume gas thermometers give same results if the pressure of the gas filled at the triple point is extremely small. In fact, this idea is used to define the perfect gas temperature scale, which is universal. We know that when the pressure of a gas is very low, the number of molecules per unit volume becomes very small. Hence the interactions between the molecules can be neglected. Moreover, the actual volume occupied by them can be neglected as compared to the volume of the bulb. So the gas behaves as a perfect gas. Thus the temperature scale, which follows from this concept is referred to as the perfect gas temperature scale. You may recall from Sec. 2.2.1 that with the help of this scale, one can obtain the thermodynamic temperature. It is defined as

$$T(p) = \lim_{p_{tp} \to 0} [273.16 \, (p/p_{tp})] \tag{2.12}$$

and is also referred to as the perfect gas temperature.

From Eq. (2.12), we observe that $T \to 0$ when $p \to 0$, i.e. the zero of this scale is the temperature for which the pressure exerted by the gas is zero. However, at low temperatures, close to 0 K the intermolecular interactions cannot be ignored and all the gases get liquified. Nonetheless, if we plot p as function of T in the temperature range where the variation is linear, the curves for all the gases pass through the origin. However, the temperature $T = 0$ remains as yet unattainable.

You may recall from Sec. 2.2.1 that the kelvin temperature scale, which is independent of the properties of any particular substance, is equivalent to the perfect gas scale. In view of this we use the symbol K after a perfect gas temperature.

You may now work out a simple SAQ on the perfect gas scale.

SAQ 5

Some workers used to define the perfect gas temperature scale with the help of the expression

$$p_t = p_{tp}\,(1 + \alpha t),$$

where t is temperature in °C and $\alpha = 3.661 \times 10^{-3}\ {}^\circ\mathrm{C}^{-1}$. Show that this definition is consistent with Eq. (2.12). Furthermore, obtain the value of the temperature for which $p_t = 0$.

You have learnt that a constant volume gas thermometer is not a practical thermometer. You will now study about practical thermometers. We will not discuss liquid-in-glass thermometers as you have read in details about them in your school science courses. We shall start with resistance thermometer.

2.4 RESISTANCE THERMOMETERS

In these thermometers, we make use of the fact that the resistance of a metallic sample increases and that of a semiconductor decreases with increase in temperature. First we shall study about the Platinum resistance thermometer where the property of a metal is used.

2.4.1 Platinum Resistance Thermometer

We can represent the variation in the resistance of a metal or an alloy over a limited range of temperature, by the relation

$$R_t = R_0\,(1 + at + bt^2); \tag{2.13}$$

where R_t and R_0 are the resistances at t°C and the ice point respectively; and a and b are characteristic constants. We generally use platinum for the construction of a resistance thermometer because of the following reasons.

i) It can be easily purified.

ii) It has a high melting point (1772 °C),

iii) It shows significant variation in resistance with temperature.

iv) Being a noble metal it is less prone to get oxidised. For pure Pt,

$$a = 3.94 \times 10^{-3}\ {}^\circ\mathrm{C}^{-1}$$

and

$$b = -5.8 \times 10^{-7}\ {}^\circ\mathrm{C}^{-2}.$$

over the temperature range −200 °C to 1200 °C.

To construct a Pt-resistance thermometer, we take a suitable length of pure Pt wire. It is then wound in a non-inductive manner (Fig. 2.4) over a thin frame of mica. This is then placed suitably in a cylindrical tube of ebonite. The resistance of the wire is accurately determined by passing a known constant current through it and measuring the potential difference across it with the help of a highly sensitive potentiometer (Fig. 2.5). The current is held constant by adjusting a rheostat so that the potential difference across a standard resistor in series with the thermometer as observed with the help of a monitoring potentiometer, remains constant. The main advantage of the potentiometric method for the measurement of resistance over those using bridges is that we do not have to bother about the resistance offered by the leads.

Fig. 2.4: Non-inductive winding. It is done for minimising the self inductance of the wire. The wire is doubled back on itself before being coiled up.

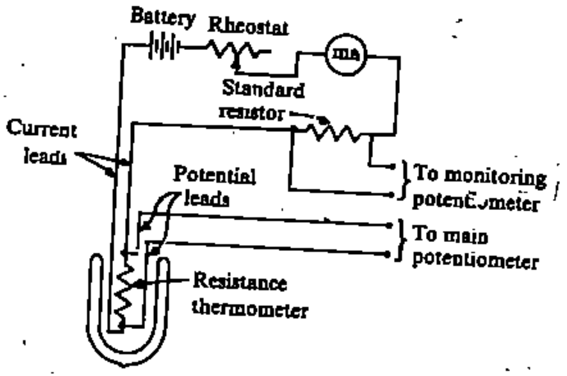


Fig. 2.5: The Pt-resistance thermometer in a potentiometric circuit for the measurement of resistance.

A particular type of Wheatstone bridge, known as the Calendar and Griffith's bridge is also used for measurement of resistance of thermometer.

Now take a look at Eq. (2.13) again. It shows that variation of R_t with t is non-linear. Therefore, every thermometer is provided with a R_t versus t graph obtained by its actual comparison with a standard gas thermometer and can be used for direct reading of temperature.

We shall now work out an example to illustrate the determination of temperature by a platinum resistance thermometer.

Example 2

For a Pt-wire, the co-efficients for variation off resistance with temperature are

$$a = 3.90 \times 10^{-3}\,°C^{-1} \text{ and } b = -5.7 \times 10^{-7}\,°C^{-2}$$

A thermometer is constructed using this wire with $R_0 = 10.00\ \Omega$. Determine the temperature of a heat bath, in contact with which the resistance of the wire is found to be 13.12 Ω.

Solution

If temperature of the bath is t°C, resistance of the thermometer wire is given by

$$R_t = R_0 (1 + at + bt^2).$$

Here,

$$R_t = 13.12\,\Omega,\ R_0 = 10.00\,\Omega,\ a = 3.90 \times 10^{-3}\,°C^{-1}$$

and

$$b = -5.7 \times 10^{-7}\,°C^{-2},$$

so that we have

$$13.12\Omega = 10.00\Omega\,(1 + 3.90 \times 10^{-3}\,t - 5.7 \times 10^{-7}\,t^2)$$

or $$1 + 3.90 \times 10^{-3}\,t - 5.7 \times 10^{-7}\,t^2 = 1.312$$

or $$5.7 \times 10^{-7}\,t^2 - 3.9 \times 10^{-3}\,t + 0.312 = 0.$$

Solving this quadratic in t, we get

$$t = 81°C$$

the second root of the quadratic comes out to be 6.8×10^3 °C, which we have rejected on physical grounds.

The principal merits of a Pt-resistance thermometer are that

i) it can be used from −200°C to 1200°C, with an accuracy of 0.02°C from 0°C to 600°C and of 0.1°C for higher temperatures,

ii) it is very convenient for ordinary use,

iii) its calibration is so reliable that even this can be used as standard.

The main drawbacks of this thermometer are that its thermal capacity is very high so that the system under study is affected and it takes longer time to attain the equilibrium and also to measure the resistance. So can we use it to record continuously varying temperatures as in the experiements on dependence of chemical reaction rate on temperature? The answer is no. For that we require a different kind of resistance thermometer. This is called thermistor:

2.4.2 Thermistors

A thermistor is essentially a crystalline semiconductor. The resistance vs. temperature curve for such a substance is shown in Fig. 2.6. The resistance decreases very steeply with temperature. In other words they have a **negative temperature coefficient of resistance.** The temperature variation of resistance may be expressed as

$$R_T = A \exp (B/T) \tag{2.14}$$

where A and B are constants. B is called the **characteristic temperature** and it lies between 2000 K and 4000 K.

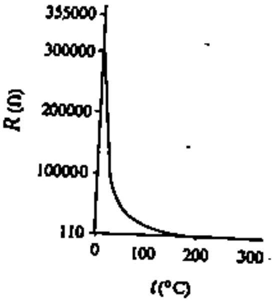


Fig. 2.6: The variation of resistance with temperature for a thermistor.

Now let the resistance of a thermistor be R_0 at temperature T_0. then from Eq. (2.14), we get

$$R_0 = A \exp (B/T_0)$$

or

$$\frac{R_T}{R_0} = \exp\left(\frac{B}{T} - \frac{B}{T_0}\right)$$

$$\therefore \quad R_T = R_0 \exp\left\{ B\left(\frac{1}{T} - \frac{1}{T_0}\right) \right\} \tag{2.15}$$

The materials which we generally use for this purpose are oxides of Mn, Co, Ni, Cu, etc. and ordinary carbon resistances. **These thermometers are useful over the temperature range 1K to 600 K** and yield results with an accuracy of about 10^{-5} K at few K and 10^{-3} K at room temperature and above. The carbon resistor is highly useful below 20 K. In addition to high sensitivity, these thermometers have the advantage of small size. But it has a serious disadvantage. Its resistance is unstable In other words its resistance corresponding to a particular temperature does not remain fixed.

You may now like to work out an SAQ on resistance thermometers.

SAQ 6

a) Fill in the blanks in the following sentences:
   i) Platinum is used for construction of resistance thermometers because its .... varies significantly with ....
   ii) Pt-resistance thermometer can be used as standard because its .... is very reliable.
   iii) Pt-resistance thermometer .... be used in an experiment on dependence of rate of evaporation of a liquid on temperature.
   iv) The temperature coefficient of resistance of a thermistor is ....

b) Suppose Eq. (2.14) is used to define a temperature scale. Establish the relation between this scale and the perfect gas scale.

Now that you have learnt about resistance thermometry, you realise that it provides us with a very sensitive method for measuring temperature. Now suppose you want to determine the temperature coefficient of resistance of a metal. And for that you have taken a plate made out of that metal. Now you cannot use a Pt-resistance thermometer for this purpose because of its size. The size of a thermistor is small, but it cannot be fixed to the plate. For this purpose we use another kind of thermometer which makes use of an electrical property. It is the thermocouple. Let us now study that.

2.5 THERMOCOUPLES

Fig. 2.7: The Seebeck or thermoelectric effect. The arrows show the direction of current. Here the metal *B* is ahead of metal *A* in the thermoelectric series. Such a circuit is called a thermoelectric circuit.

These are essentially thermoelectric thermometers and are based on Seebeck's (1826) discovery that **an emf is developed between the junctions of two dissimilar metals or alloys maintained at different temperatures (Fig. 2.7).** We can express the dependence of thermo-emf (E) on temperature difference (t) between the two junctions as

$$E = C_1 t + C_2 t^2 \tag{2.16}$$

where C_1 and C_2 are thermoelectric constants for the pair of metals or alloys used. The rate of change of E with t is called the thermoelectric power (TEP) of the thermocouple. Suppose that the TEP of a thermocouple is 40 $\mu V°C^{-1}$. This means that 1 μV corresponds to (1/40)°C i.e. 0.025°C. So if the least count of a voltmeter or any arrangement for the measurement of potential difference is 1 μV, then with the help of the above thermocouple, a minimum possible temperature, equal to 0.025°C, can be measured. Thus TEP is a measure of the sensitivity of the thermocouple. It depends on the values of C_1 and C_2.

Let us now study about the construction of a thermocouple and how thermoelectric circuits are made.

2.5.1 Thermocouples and Thermoelectric Circuits

To construct a junction of a thermocouple, say of copper and iron, we take wires of copper and iron, and join together one end of both using gas or arc welding. This end forms a junction and we may keep it as such or seal in a tube of quartz, porcelain or hard glass to protect it from any contamination. The system whose temperature is required should ideally surround the thermocouple junction. For measuring the temperature of a metallic plate such a junction is attached to it using a soft solder made of a zinc-tin alloy. A particular kind of paste is also used to attach the junction.

A thermocouple may be used in the three ways shown in Fig. 2.7 (a, b and c). The emf developed between the two junctions is measured with a milli or micro-voltmeter, or with the help of a very sensitive potentiometric arrangement.

Interpolation is a process used to estimate an intermediate value of one (dependent) variable which is a function of a second (independent) variable when values of the dependent variable corresponding to several discrete values of the independent variable are known.

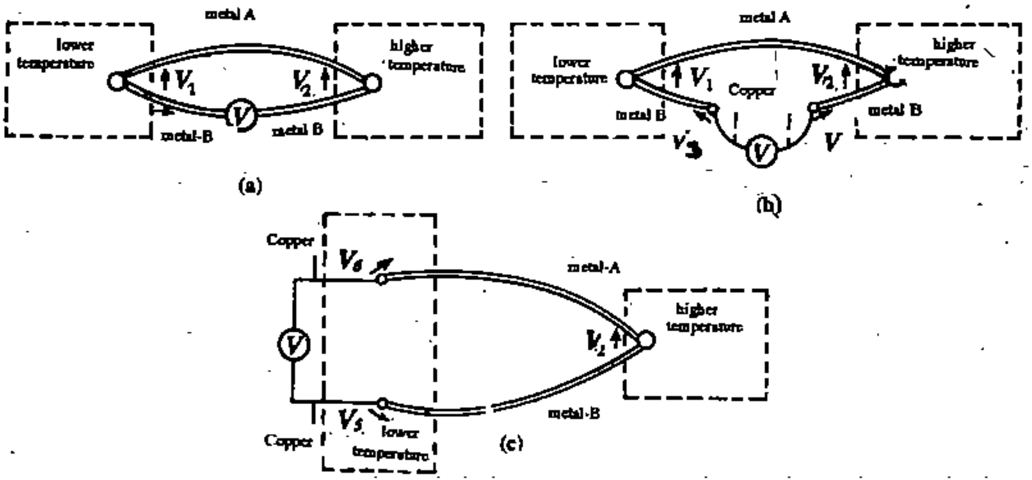


Fig. 2.8: Three ways of using a thermocouple. (a) A basic thermoelectric circuit; (b), (c) Alternative ways of connecting the voltmeter in a thermoelectric circuit.

Now that you have learnt about the thermoelectric circuits, let us discuss about some practical thermocouples.

2.5.2 Practical Thermocouples

The temperature range covered by a thermocouple and its sensitivity depend on the material of the wires used, which we list for some common cases in Table 2.1.

Table 2.1 : Comparison of thermocouple characteristics

Thermocouple	Temperature range °C	TEP $\mu V°C^{-1}$
Iron-constantan	−200 to 760	55
Platinum—Platinum (10−13%) rhodium alloy	0 to 1700	(7−12)
Chromel-alumel	−220 to 1300	40 for $t > 0°C$

From Table 2.1, we note that the thermocouples have nearly same temperature range as that of a Pt-resistance thermometer. However, their **main merits are low cost, small size and quick equilibrium with the system under study. Consequently, we can use thermocouples to study rapid temperature variations also.**

The principal limitations of thermocouples are the following:

i) These need sensitive voltage measuring devices.

ii) They require correction for the emf arising from the temperature gradient along a wire (Thomson emf) and the difference in the amounts of heat absorbed and liberated at the two junctions (Peltier effect).

iii) Their sensitivity is highly affected by the purity of the metals or alloys used.

To reduce the errors due to the last two factors and to take care of the nonlinearity of variation of E with t, each thermocouple is provided with a calibration curve between temperature and thermo-emf.

Let us now work out an example illustrating the measurement of temperature by a thermocouple.

Example 3

Compute the temperature of the hot junction of an iron-constantan thermocouple ($C_1 = 54.8\ \mu V°C^{-2} = 0.05\ \mu V°C^{-2}$) if its cold junction is maintained at the ice point and the thermo emf is 13 μV.

Solution

Since the cold junction is maintained at 0°C, we write down the emf in terms of the hot junction temperature as

$$E = C_1 t + C_2 t^2$$

Here, we are given that $C_1 = 54.8 \times 10^{-6}$ V °C^{-1}, $C_2 = 0.05 \times 10^{-6}$ V °C^{-2} and $E = 13.0 \times 10^{-3}$ V. Substituting these values, we have

$$13 \times 10^{-3} = 54.8 \times 10^{-6}\, t + 0.05 \times 10^{-6}\, t^2$$

or

$$0.05\, t^2 + 54.8\, t - 13.0 \times 10^3 = 0$$

Two roots of this quadratic equation are

$$t = -1.30 \times 10^3 \text{ and } 201.$$

Since we cannot have a temperature of -1.30×10^3 °C we reject the former and find that the temperature of the hot junction is 201 °C.

You may now like to answer the SAQ on thermocouples.

SAQ 7

Complete the following sentences using appropriate words to fill in the blanks:

i) Thermocouples are quite popular for measuring temperature in research laboratories because of ...., ... and attainment of ....

ii) Each thermocouple is provided with a calibration curve because .... does not vary linearly with .... and its values as well as variation depend on nature of the wires used.

A thermocouple makes use of two metals. In your school science course on thermal expansion of solids you must have read about a device, made of two metals, which can be used as a thermometer. Can you recall that? It is the bimetallic strip about which you will briefly study now.

Bimetallic Strip

This makes use of the **different expansion** of two metals. Strips of two different metals are joined together as shown in Fig. 2.9a. When they are allowed to expand freely, they do so by different extents for a given change of temperature. Now, by way of

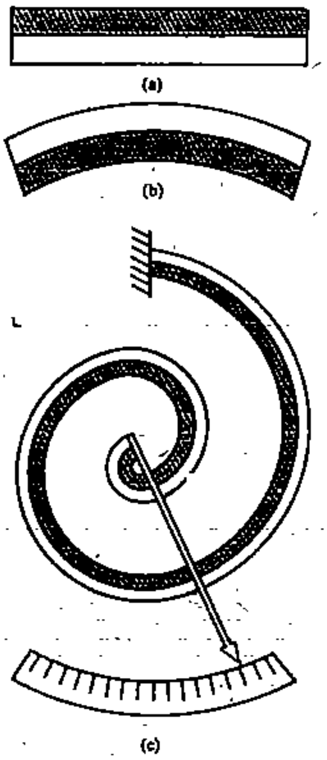


Fig. 2.9 (a,b): A bimetallic strip at two different temperatures (c) A thermometer made of a cited bimetallic strip.

construction these are constrained to be of the same length at their common surface Hence, a temperature change forces the strip to bend into a circular arc (Fig. 2.9b). If one end of the strip is fixed, the temperature change can be calibrated in terms of the deflection of the other end. In order to be used as a thermometer, such strips are made in the shape of spiral and a pointer is attached to its free end (Fig. 2.9c).

It is desirable to have an appreciable difference between the coefficients of linear expansion of the two metals in a bimetallic strip. This causes the strip to bend significantly for a given rise in temperature, thereby increasing its sensitivity. For this reason, one of the metals used is invar, which has a very low coefficient of linear expansion.

So far you have studied about several thermometers. For all of them a physical contact between the temperature sensor and the test object is necessary. But suppose we want to determine the temperature of the sun. How do we do that? This is done by a device called **radiation pyrometer.** It allows us to measure temperature without making any contact between the test object and the sensor. Let us study briefly about that now.

2.6 RADIATION PYROMETERS

These thermometers work by way of detecting the infrared radiation given off by the test object. You must note that infrared radiations are emitted not only by 'hot objects'. Any object whose temperature is above 0 K emits radiation. The amount of radiation depends upon the temperature. So by measuring this amount the temperature of the object can be determined.

You know from your school science course that the best emitters of radiation at any temperature are the black bodies. You will learn in Unit 8 of Block 2 of this course that the radiation emitted by a black body depends on its temperature only. The total power per unit area of the emitted radiation is given by the relation

$$M = \sigma T^4 \qquad (2.17)$$

where σ is known as the Stefan's constant. Its value is given by

$$\sigma = 5.67 \times 10^{-8} \text{ N m}^{-2} \text{ K}^{-4}$$

Let us work out an example to illustrate Eq. (2.17)

Example 4

The surface area of the filament of a 60 W bulb is 13 mm^2. Estimate the temperature of the illuminated filament assuming that the radiation emitted by it is close to that by a black body.

Solution

From Eq. (2.17) we know that

$$T = \left(\frac{M}{\sigma}\right)^{1/4}$$

Here $$M = \frac{60 \text{ W}}{13 \times 10^{-6} \text{ m}^2}$$

$$\therefore \quad T = \left(\frac{60 \text{ W}}{13 \times 10^{-6} \text{ m}^2 \times 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}}\right)^{1/4}$$

$$= 3.0 \times 10^3 \text{ K.}$$

The pyrometers that work on the basis of Eq. (2.17) are called **'total radiation pyrometers'.**

There is another kind of pyrometer called the 'optical pyrometer' which takes care of the measurement of energy emitted in a particular portion of the spectrum. It is given by Planck's radiation law (about which you will read in Block 4 of this course) as

$$u_\lambda = \frac{C_1}{\lambda^5[\exp(C_2/\lambda T) - 1]} \qquad (2.18)$$

where u_λ is the energy emitted per unit time and unit area per unit wavelength and λ is the wavelength.

$$C_1 = 3.74 \times 10^{-16} \text{ W m}^2,\ C_2 = 1.44 \times 10^{-2} \text{ m K}$$

The schematic diagram of a radiation pyrometer is shown in Fig. 2.10.

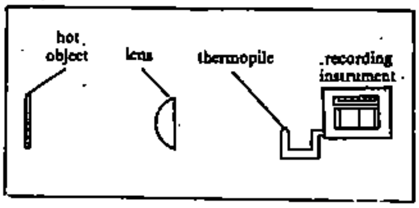


Fig. 2.10: A shematic diagram of a radiation pyrometer. Part of the thermal radiation emitted by a hot object is intercepted by a lens and focussed onto a thermopile, which is a collection of thermocouples. The resultant heating of the thermopile causes it to generate an electrical signal (proportional to the thermal radiation) which can be displayed on a recorder.

Radiation pyrometers have the advantage that they can be used to measure any temperature however high that may be and that too irrespective of the location of the test object. The pyrometer need not be raised to the temperature of the test object. But, it has a serious drawback. In principle it can measure the temperature of black bodies only.

However, a pyrometer is generally used to measure the temperature of any hot source. It then gives the temperature at which the intensity of emission of a perfectly black body would be the same as that of the source. This temperature is known as the **black body temperature** of the substance. This temperature is less than the actual temperature of the substance. Can you tell why? This is because the emitting power of a black body at a particular temperature is higher than that of any other body at the same temperature. So you can realise that always an error will be involved in determining the temperature. Higher the departure from perfect blackness of the body, greater will be the error. Keeping in view this error, the lower practical limit of temperature to be measured by radiation pyrometers is about 1000 K.

You have now learnt about different kinds of thermometers and scales for measuring temperature. You must have noted that none of the properties of materials used for temperature sensing varies strictly linearly with temperature. This poses a problem for the makers of the thermometers as regards their calibration. In order to get rid of this difficulty a practical temperature scale was adopted by the International Committee of Weights and Measures and it is known as the International Practical Temperature Scale. We shall study very briefly about it before rounding-off this unit.

2.7 THE INTERNATIONAL PRACTICAL TEMPERATURE SCALE

This scale enables us to use a specific thermometer over a specific range and get them calibrated in terms of the kelvin or celsius scale. Some temperatures of interest and the different kinds of thermometers along with their corresponding ranges have been shown schematically in Fig. 2.11. A is a linear scale and B is a logarithmic scale.

The international practical temperature scale was adopted in 1968 and is referred to as IPTS-68. The features of this scale are that it:

a) Selects a set of eleven reference points and assigns to these points values of thermodynamic temperature in the light of best available measurements.

b) Selects a set of thermometers for interpolation between the reference points, and

c) Agrees on the interpolation procedures to be used.

These reference points with their assigned temperatures, together with the specified thermometers and interpolation procedures, establish an empirical scale, which is arranged to coincide as closely as possible with thermodynamic temperature. The values of the temperature along with the names of the standard thermometers are shown in Table 2.2. The suffix 68 with T and t indicates that the scale was adopted in 1968.

The variation of the susceptibility of a paramagnetic salt with temperature is used for measurement of very low temperatures.

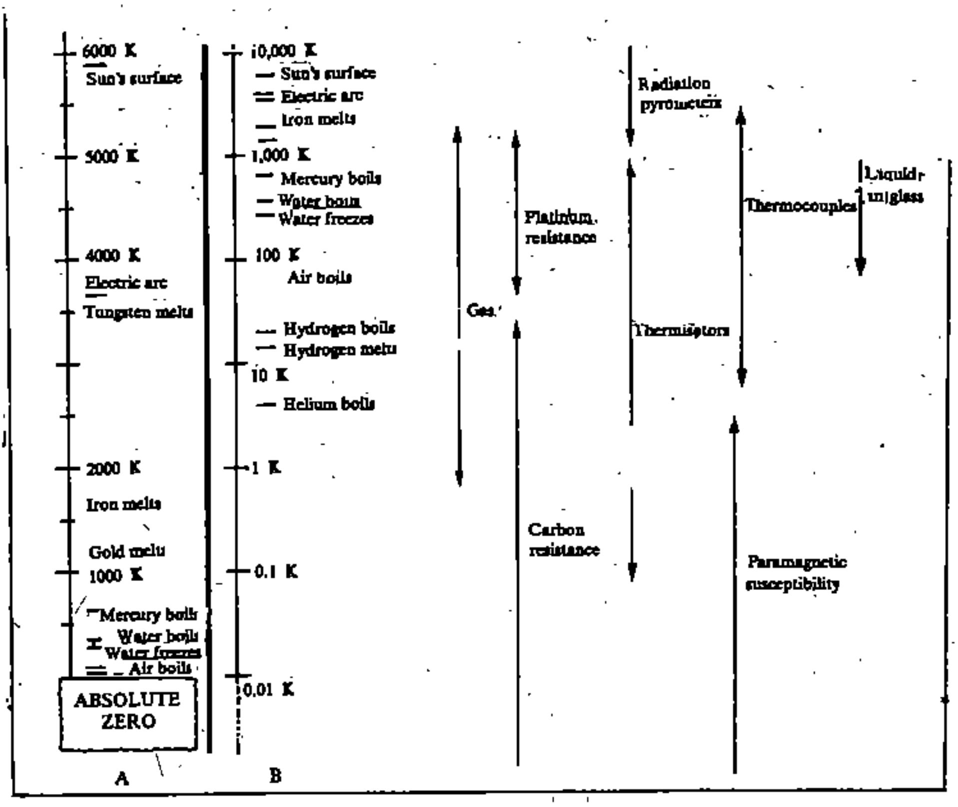


Fig. 2.11 : Some temperature of interest and useful ranges of different kinds of thermometer

Table 2.2 : The International Practical Temperature Scale (IPTS-68)

No.	Fixed Point	Assigned temperature		Standard thermometer
		T_{68} (K)	t_{68} (°C)	
				optical pyrometer (above 1337.58 K)
1.	Freezing point of gold	1337.58	1064.43	
2.	Freezing point of silver	1235.08	961.93	thermocouple (903.89–1337.58 K)
3.	Freezing point of zinc	692.73	419.58	
4.	Boiling point of water	373.15	100	
5.	Triple point of water	273.16	0.01	
6.	Boiling point of oxygen	90.188	−182.962	
7.	Triple point of oxygen	54.361	−218.789	platinum resistance (13.81–903.89 K)
8.	Boiling point of neon	27.102	−246.048	
9.	Boiling point of equilibrium hydrogen	20.28	−252.87	
10.	Equilibrium between the liquid and vapour phases of equilibrium hydrogen at $33\,330.6\ \mathrm{N\,m^{-2}}$	17.042	−256.108	
12.	Triple point of equilibrium hydrogen	13.81	−259.34	

Let us now sum-up what we have read in this unit.

2.8 SUMMARY

- A thermometer is a device which is employed to determine the temperature of a system or an object by bringing this into thermal equilibrium with it, without altering its thermodynamic state.

- In the one-point temperature scale, called absolute temperature scale, the temperature of the system is obtained by multiplying the ratio of the observed value of a thermometric property and its value at the triple point of water by 273.16.
- The problem of dependence of one-point scale on the thermometric property (being used) is solved by using the constant–volume gas thermometers containing gas at extremely low pressures, as standard. The temperature scale so obtained is called the perfect gas scale.
- Temperature on the absolute scale is related to that on the celsius scale through $T = t + 273.15$.
- The gas thermometers are very sensitive and accurate but they are bulky and take time to attain equilibrium. Therefore, these are not used for routine measurements.
- A Pt-resistance thermometer is based on the fact that the resistance of a Pt-wire increases with temperature as

  $$R_t = R_0 (1 + at + bt^2).$$
- A thermistor makes use of decrease of resistance of semiconductors with temperature as $\exp (B/T)$.
- A thermocouple uses the variation of thermo–emf between two junction of dissimilar metals maintained at different temperatures. The variation of E vs. t is given by

  $$E = C_1 t + C_2 t^2$$
- A radiation pyrometer is used for measuring extremely high temperatures. It works by measuring the amount of radiation from the body whose temperature is to be measured. It is not necessary to establish a physical contact between the body and the sensor.
- In the IPTS-68, various fixed points have been precisely defined so that any thermometer can be accurately calibrated.

2.9 TERMINAL QUESTIONS

1) Suppose the triple point of water was assigned the value 491.69 degree instead of 273.16 degree. Write down the expression for $T(X)$ in terms of property X of the substance assumed to be varying in direct proportionality with temperature. How is this scale related to the kelvin scale? Hence calculate the values of the ice point and the steam point on the new scale.

   (**Note** : The new scale is called Rankine and 1°R is equal to 1°F.)

2) What is the thermo–emf across the two junctions of a thermocouple with $C_1 = 40\ \mu V\,°C^{-1}$ and $C_2 = -0.01\ \mu V\,°C^{-2}$ when its hot junction is at 700°C with respect to the cold junction?

3) Which thermometer(s) will you like to use for measuring the temperature given below?

   (i) 60 K (ii) 250 K (iii) 1000 K (iv) 5000 K

4) Complete the following statements by filling in the blanks with appropriate words :

   i) Thermometers generally used as standard for calibration of other thermometers are
   a) .... b) ....

   ii) Thermometers which cannot be used for measurement of continuously varying temperature are
   (a) ....
   (b) ....
   However, such a temperature can be found using
   (c) ....
   (d) ....

   iii) The difference between the coefficients of linear expansion of the metals used in a bimetallic strip should be as .... as possible.

iv) A .... is a thermometer with the help of which the temperature of an object can be measured without bringing the test object in contact with the sensor.

2.10 SOLUTIONS AND ANSWERS

1) a) Length of a liquid column, volume of a block, pressure of a gas in a vessel of constant volume.

b) (i) Since absolute temperature scale reading T is 1.5 times the Celsius scale reading t, we have

$$T = 1.5t = t + 273.15.$$

Solving this, we get

$$t = 546.30°\text{C}$$

and

$$T = 819.45 \text{ K}.$$

b) (ii) This can never happen.

c) Here, length of the mercury column is the thermometric property. Thus, we have

$$X_0 = 3.30 \text{ cm}, X_{100} = 24.87 \text{ cm}, X_T = 18.53 \text{ cm}.$$

Using Eq. (2.4), we get

$$T = \frac{18.53 - 3.30}{24.87 - 3.30} \times 100°\text{C} = 70.6°\text{C}$$

2) $T(E) = 273.16\,(E/E_{tp})$,

where E represents the thermo-emf of the thermocouple, whose hot junction is kept at the temperature to be measured and the cold junction is maintained at the triple point of water.

3) A constant volume thermometer gives most reliable data if gas filled in it has p_{tp} close to zero. Here, it is given that p/p_{tp} value corresponding to p_{tp} close to zero is 1.36604. Now, for a constant volume gas thermometer

$$T = 273.16\,(p/p_{tp})$$

Substituting the given values, we get

$$T = (273.16 \times 1.36604) \text{ K} = 373.15 \text{ K}.$$

4) (i) No

(ii) No

(iii) Thermometer filled with N_2 at 5 m bar will give the value closest to the actual one.

(iv) We shall record p/p_{tp} for all the three thermometers, plot graph between these and p_{tp}. The intercept of p/p_{tp} for $p_{tp} = 0$ gives actual value of p/p_{tp}, which on multiplication with 273.16 will yield actual temperature.

5) It is given that

$$p_t = p_{tp}\,(1 + \alpha t)$$

so that

$$t = (1/\alpha)\left(\frac{p}{p_{tp}} - 1\right)$$

Substituting for α, we get

$$t = \frac{1}{3.661 \times 10^{-3}}\left[\frac{p}{p_{tp}} - 1\right] = 273.15\left(\frac{p}{p_{tp}} - 1\right)$$

or $t + 273.15 = T = 273.15\,(p/p_{tp})$

This is consistent with Eq. (2.12) except that the multiplier is 273.15 instead of 273.16.

Moreover, $p_t = 0$ when

$$1 + \alpha t = 0$$

or

$$t = -1/\alpha = -273.15°\text{C}.$$

6) a) (i) resistance, temperature
   (ii) calibration
   (iii) cannot
   (iv) negative

b) Writing resistance of semiconductor as R, we have

$$T = 273.16\,(R_T/R_{tp})$$

$$= 273.16 \exp\left[B\left(\frac{1}{T} - \frac{1}{T_{tp}}\right)\right]$$

$$= 273.16 \exp\left[B\left(\frac{1}{T} - \frac{1}{273.16}\right)\right]$$

7) (i) low cost, small size, quick equilibrium.
   (ii) thermo emf, temperature

Terminal Questions

1) Assuming a property X of the substance to vary in direct proportionality with temperature, we have

$$X = a\,T(X)$$

At the triple point $T(X) = 491.69°$ so that value of X at this temperature is given by

$$X_{tp} = 491.69\,a.$$

Using symbol R for this scale, we have

$$T°\text{R} = \frac{X}{a} = 491.69\,(X/X_{tp})$$

In order to determine its relationship with kelvin scale, we note that

$$T\,\text{K} = 273.16\,(X/X_{tp})$$

Obviously,

$$\frac{T°\text{R}}{T\,\text{K}} = \frac{491.69}{273.16} = 1.8000$$

Ice point on the new scale = $(273.15 \times 1.8000)°\text{R} = 491.67°\text{R}$
Steam point on the new scale = $(373.15 \times 1.8000)°\text{R} = 671.67°\text{R}$

2) Temperature dependence of thermo-emf for a thermocouple is given by

$$E = C_1 t + C_2 t^2$$

Substituting the given values, we get

$$E = (40 \times 10^{-6} \times 700 - 0.01 \times 10^{-6} \times 700^2)\text{V} = 2.3 \times 10^{-2}\text{V}$$

3) (i) Constant-volume gas thermometer, Thermistor, Chromel-alumel thermocouple
   (ii) Constant-volume gas thermometer, Pt-resistance thermometer, Thermistor, Thermocouple
   (iii) Constant-volume gas thermometer, Pt-resistance thermometer, Thermocouple
   (iv) Pyrometer

4) (i) (a) Constant-volume gas thermometer
       (b) Pt-resistance thermometer
   (ii) (a) Constant-volume gas thermometer
       (b) Pt-resistance thermometer
       (c) Thermistor
       (d) Thermocouple
   (iii) large
   (iv) radiation pyrometer

UNIT 3 THE FIRST LAW OF THERMODYNAMICS

Structure

3.1 Introduction
    Objectives
3.2 Heat
    Nature of Heat
3.3 Work
    Internal and External Work
3.4 Expressions for Work
    A Gaseous System
    Other Systems
3.5 Path Dependence of Work and Heat
3.6 Internal Energy
3.7 The First Law of Thermodynamics
    Differential form of the First Law
3.8 Summary
3.9 Terminal Questions
3.10 Solutions and Answers

3.1 INTRODUCTION

In the previous unit you have read about measurement of temperature. As you know, the change of temperature of a system is an effect caused by way of exchange of heat. Now, what is the nature of heat? This question puzzled many a mind for a long time. The answer to this and many other related questions are contained in the first law of thermodynamics, about which we will study in this unit.

Energy reigns over everything that has been occurring around us, since time immemorial. When ancient people had shot arrows or lighted fire they were unaware that energy was being expended in different forms. Now we know that these are elastic potential energy and chemical energy, respectively. Since then we have come a long way. With the discovery of the principle of conservation of energy we have realised the importance of energy in human life. The first law of thermodynamics is only an extension of this principle.

In the beginning of this unit we shall discuss about the nature of heat. Then you will read about work from the thermodynamic point of view. You will see that work is done when a gas is compressed or expanded or when a wire is under tension or when a paramagnetic material is magnetised.

Then we will establish that work and heat are interconvertible, and hence equivalent forms of energy. This aspect is responsible for the operation of all kinds of engines on which we depend so much. The first law of thermodynamics originates from this idea of equivalence of work and heat. However, in addition to work and heat you will learn about another important function. It is the internal energy of a body. The definition of this function will lead us to the formal statement of the first law of thermodynamics. We shall illustrate this law with the help of a few simple examples. Finally, you will learn about its basic significance.

In the next unit we will discuss important applications of the first law of thermodynamics.

Objectives

After studying this unit, you should be able to

- explain the nature of heat
- explain the thermodynamic concept of work
- compute work for several thermodynamic systems
- define internal energy and appreciate that it is a function of the state of the system
- understand the significance of the first law of thermodynamics.

3.2 HEAT

We know from experience that a glass of ice-cold water left on a table on a hot summer day eventually warms up whereas a cup of hot tea on the same table cools down. It means that when the temperature of the system, water or tea in this case, and its surroundings are different, energy is exchanged between the system and the surrounding medium, until thermal equilibrium is established. That is, energy transfer continues till the body and the surrounding medium are at the same temperature. We also know that in the case of cold water, energy flows from the environment to the glass, whereas in the case of hot tea energy flows from the cup to the environment. In other words, the direction of energy transfer is always from the body at higher temperature towards that at lower temperature. You may now ask: In what form is energy being transferred? In the above cases energy is said to be transferred in the form of **heat.** So, we can say that **heat is the form of energy transferred between two (or more) systems or a system and its surroundings by virtue of temperature difference.** The system at higher temperature is called **source** and the one at lower temperature is called **sink.** But what is the very nature of this form of energy? Let us discuss briefly about that now.

3.2.1 Nature of Heat

Till the beginning of the nineteenth century, predominant view was that heat exists in every body in the form of a material substance, called **caloric.** It was believed that a body at higher temperature contained more caloric than a body at a lower temperature. When a hot body was placed in contact with a cold body, the caloric was believed to flow spontaneously from the hotter to the colder body until they attained thermal equilibrium.

However some observations of Count Rumford and Sir Humphrey Davy did not agree with this idea. Davy rubbed two pieces of ice to get water. Now, how can you explain this on the basis of the caloric concept? Ice must contain less caloric than water and the process of rubbing leads to further squeezing of caloric out of the solid. Thus the water formed due to the friction should contain less caloric than ice. This contradicts the caloric theory.

Thus a need for replacing the caloric theory was felt. It was finally achieved in 1840 through Joule's work on the equivalence of heat and mechanical work. In Joule's experiment heat was produced by churning water contained in a cylinder by means of brass paddles. This means that the mechanical energy of the paddles is converted into heat. Now, how is this heat produced? It is by way of the chaotic motion of the water molecules. Thus it could be established that some kind of molecular motion is associated with heat.

In this connection you must note that in our daily life we often say that a cup of hot coffee has heat, or there is tremendous heat in the sun. But henceforth we will use the word 'heat' only when it crosses the boundary of a system. **Heat is an energy in transit.** It is wrong to say heat in a body. In Sec. 3.6 you will learn that when we speak of heat in a body we essentially mean its internal energy. Internal energy and heat are two different things. You will learn about the difference in this unit itself.

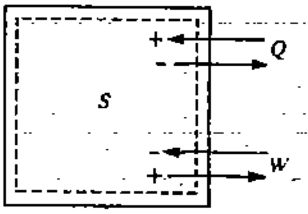


Fig. 3.1: Sign convention for heat. *S* is the system. For *A*, heat flows into *S* and it is positive. For *B*, heat flows out of *S* and it is negative.

Since heat is a directional quantity we adopt a sign convention to represent it. Heat transferred to a system is positive while heat taken from a system is negative (Fig. 3.1). However you may recall from Sec. 1.4.3, that heat transfer for a process may be such that it is neither positive nor negative i.e. it is zero. Such a process is called adiabatic.

Let us now take up an example based on the ideas discussed so far.

Example 1

A potato is initially at room temperature (30°C). It is baked in an oven maintained at 200°C. Considering the potato to be the system of interest, explain whether any heat is transferred during the process.

Solution

The skin of the potato may be considered as the system boundary. Now owing to the difference of temperature between the oven and the potato a part of the energy of the oven will pass through the skin to the potato, in the form of heat.

You may now like to answer the following SAQ:

SAQ 1

A well insultated furnace F is being heated by means of its heating element H shown in Fig. 3.2. Taking the entire furnace, including the heating element, to be a system, can you say if a heat transfer takes place?

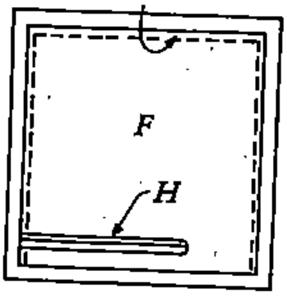


Fig. 3.2

From the answer to SAQ 1, you must have realised that energy transfer can take place through the system boundary in a form other than heat. This form of energy is called work. You will study it now.

3.3 WORK

If energy crosses the boundary of a system and it is not in the form of heat, it must be work. If the cause of transfer of energy is a temperature difference between the system and the surroundings, then that form of energy is heat. So we can say that if the energy interaction is not caused by a temperature difference between the system and the surroundings, it is work.

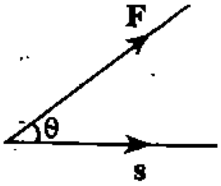


Fig. 3.3: Work done $= F\,s\cos\theta$

You may recall from your school science courses that from the point of view of mechanics work is said to be done when the point of application of a force moves. It is measured by the product of the magnitude of the force and the projection of the displacement of the point of application in the direction of the force. As you know it is given by (see Fig. 3.3)

$$W = \mathbf{F}\cdot\mathbf{s} = F\,s\cos\theta.$$

We follow the same logic in thermodynamics. But here we make a classification of work as follows.

3.3.1 Internal and External Work

If a system as a whole exerts a force on its surroundings so that a displacement takes place, the work that is done either by or on the system is called **external work.** If gas contained in a cylinder at uniform pressure expands it imparts motion to the piston and does external work on its surroundings. On the other hand, the work done by a part of the system on another part is called **internal work.**

Internal work is of no consequence in thermodynamics. In thermodynamics by work we essentially mean external work. Let us take an example. Suppose a rat climbs a staircase. In principle it performs some work. You must have noted that in this case it utilises its own biochemical energy to perform this work. So it is an internal work. In other words, according to thermodynamics it does not perform any work. Similarly if a storage battery is not in operation then the changes that take place in the cell, such as inter-diffusion of chemicals are not accompanied by the performance of work. If, however, the cell is connected to an external circuit, a current will flow in that circuit and may cause a bulb to glow. So in order that an electric cell performs work it must be connected to an external circuit.

The production of work by a system is considered as a desirable effect and the consumption of work is considered undesirable. Accordingly, the following convention is adopted. The work done by a system is positive and the work done on a system is negative. According to this convention, the work produced by car engines or gas turbines is positive. And the work consumed by compressors or mixers is negative.

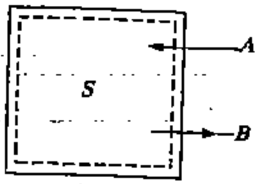


Fig. 3.4: S is the system of interest. A heat input is like a deposit. And work output is like a withdrawal.

We can represent the convention of sign for heat Q and work W in a schematic diagram (Fig. 3.4).

There are many types of forces that can do work on a system. Before you study these, you may like to work out an SAQ. (Please do not get scared by the length of the SAQ. It is indeed easy!).

SAQ 2

a) Choose proper words from the parentheses to fill in the blanks in the statement given below.

(displacement, force, inertia, negative, positive, work) .... is said to be done by a system and taken to be .... if it exerts a net .... on the surroundings, which causes a ....

b) Explain whether any work is done or not in the following processes:

(i) A magnet is brought near an electrical circuit carrying current. A change in magnetisation takes place by way of realignment of the weber elements within the magnet.

(ii) A galvanometer coil is set into motion by sending a current through it.

c) What are the signs of work (i) we get from a steam engine (ii) done on an electric motor attached to a pump.

3.4 EXPRESSIONS FOR WORK

In thermodynamics, we express the work in terms of the state variables of the system. This is done because it makes the analysis simple mathematically. To achieve this, we have to ensure that the system is always near an equilibrium state, i.e., the process involved is quasistatic in nature. With this in mind, we now proceed to determine expressions for work done in various systems.

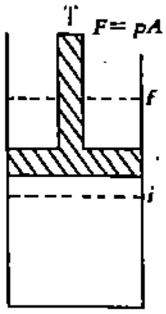


Fig. 3.5: Work done during expansion of a gaseous system. i and f stand respectively for the initial and final states.

3.4.1 A Gaseous System

Suppose we have mass M of a gas filled in a cylinder fitted with a frictionless piston on which both the system and the surroundings can act (Fig. 3.5). Let the area of the cross-section of the piston be A. If at any instant, the pressure exerted by the system on the piston is p, the force on it is pA. This force pushes the piston outward. If the piston moves in the direction of the force through dx, we can write down the work done by the system as

$$\delta W = pA\, dx$$

You will note that Adx is the increase in volume of the system caused by the outward movement of the piston. Writing $Adx = dV$, we have

$$\delta W = pdV. \tag{3.1}$$

Now go back to Sec. 1.4.2 and read its third paragraph. You will realise that we have to assume that the system expands quasistatically, say from volume V_i to V_f. In other words, V_i and V_f are the initial and final volumes, respectively. Then the **total work done by the gaseous system on its surroundings is given by**

$$\Delta W_T = \int_{V_i}^{V_f} pdV \tag{3.2}$$

Now, for evaluating the integral in Eq. (3.2) we need to know how p depends on V. This is given by the nature of the process.

A Convention

You will learn that quantities like work (W) and heat (Q) are not functions of the state, whereas internal energy (U) is a function of the state. An infinitesimal change in the value of a quantity, which is not a state function, is indicated by putting the symbol δ on the left side of the quantity of interest. Some texts use the symbol $đ$. The infinitesimal change in a quantity, which is a state function, is indicated by putting the symbol d on the left side of the concerned quantity. Hence an infinitesimal work is δW or an infinitesimal heat given to a system is δQ, whereas an infinitesimal change in internal energy is dU.

You would recall from Sec. 1.4.3, that at any instant we can show p and V as a point on the indicator diagram. The line joining these points gives the path of the expansion process (Fig. 3.6). The exact shape of this line depends on the nature of the variation of p with V. Refer to Fig. 3.6. You would note that pdV represents the area of the shaded strip. Categorically, ΔW_T **is the sum of the area of the strips obtained for all the infinitesimal changes from the initial to the final state.** This is simply the area under the p–V diagram of the system enclosed by the **V-axis and the values of p corresponding to the initial and final states.**

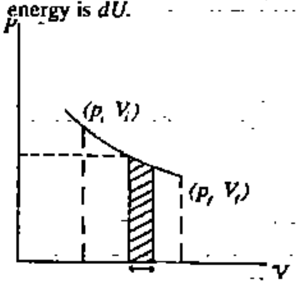


Fig. 3.6: p-V diagram for a gaseous system undergoing expansion.

Let us now calculate the work done by a gaseous system for an isothermal expansion (or compression) of an ideal gas. You would recall that this system obeys the equation of state

$$pV = nRT,$$

where the symbols have their usual meanings.

Substituting for p in Eq. (3.1) and using subscript T to indicate constancy of temperature (isothermal change), we get

$$\delta W_T = (nRT/V)\, dV \tag{3.3}$$

Hence, using Eq. (3.2) we get,

$$\Delta W_T = nRT \ln (V_f/V_i) = 2.303\, nRT \log (V_f/V_i) \tag{3.4}$$

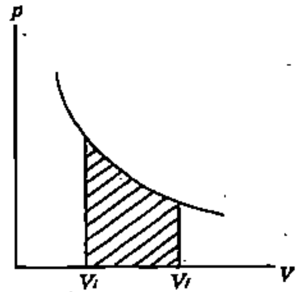


Fig. 3.7: Work done by an ideal gas in isothermal expansion.

This equation tells us that when a **given quantity of gas undergoes isothermal expansion, the work done by it depends on the temperature T and the expansion ratio of final to initial volumes, (V_f / V_i).** During expansion $V_f > V_i$, so that ΔW_T is positive and it is shown by the shaded area in Fig. 3.7. On the other hand when the gas is compressed, $V_f < V_i$ and ΔW_T is negative implying that work is done on the system. This too will be given by the area of the same shaded portion.

Next, suppose that the gas has undergone an isochoric process. In this case, $dV = 0$ so that $\delta W = pdV = 0$, i.e., no work is done in an isochoric process.

To enable you to grasp this concepts, let us work out an example.

Example 2

Two moles of a perfect gas at standard temperature and pressure are first expanded isothermally to 3 times its original volume. Then it is compressed isochorically till its pressure attains the starting value. Calculate the total work done, given $R = 8.3\text{ J K}^{-1}\text{ mol}^{-1}$.

Solution

Work done by the gas during isothermal expansion $= nRT \ln (V_f/V_i)$

Here $V_f/V_i = 3$. Hence,

$\Delta W_T = 2\text{ (mol)} \times (8.3\text{ J K}^{-1}\text{ mol}^{-1}) \times (273\text{K}) \ln 3 = 5.0 \times 10^3\text{ J}$

Work done during isochoric process $= 0$

Hence, total work done by the gas $= 5.0 \times 10^3$ J.

You may now like to work out an SAQ before we discuss work done in several other systems.

SAQ 3

a) Show that Eq. (3.4)

$$\Delta W_T = nRT \ln (p_i/p_f)$$

b) A gaseous system expands from volume V_1 to V_2 under isobaric conditions. Calculate the work done in this process. Also show it on an indicator diagram.

3.4.2 Other Systems

Suppose we have a wire whose one end is fixed and the other end is subjected to an instantaneous tension F. This tension causes the length of the wire to change from L to $L + dL$. Then the work done is given by

$$\delta W_F = FdL \tag{3.5}$$

The minus sign signifies that dL indicates an extension of the wire for which work must be done on the wire.

If the change in the length of the wire is from L_i to L_f in a quasistatic manner, the total work done on the wire is given by

$$\Delta W_F = \int_{L_i}^{L_f} F\, dL \tag{3.6}$$

Analogous to Eqs. (3.1) and (3.5) we can have the expressions of work done for the following cases: (i) by an electric cell during a transfer of charge dq, (ii) on a paramagnetic material placed in a magnetic field in increasing its magnetisation by dM.

For case (i), we have

$$\delta W_E = -Edq, \tag{3.7}$$

where E is the e.m.f. of the cell

For case (ii), we have

$$\delta W_M = -VB_a dM, \tag{3.8}$$

where B_a is the applied magnetic field and V is the volume of the material.

We shall now illustrate the above expressions with a couple of numerical examples.

Example 3

A steel wire of length 2.5 m and area of cross-section 2.5×10^{-6} m^2 is suspended from a torsion head. Its length is increased by hanging a weight of 5 kg with the free end. Determine the work done on the wire. Young's modulus of steel is 2×10^{11} N m^{-2}.

Solution

We know that the longitudinal strain produced in a wire is given by

longitudinal strain = longitudinal stress/Young's modulus

or $$\frac{dL}{L} = \frac{F/a}{Y}$$

Substituting various values, we get

$$dL = \frac{FL}{aY} = \frac{(5 \times 9.8\,\text{N}) \times (2.5\,\text{m})}{(2.5 \times 10^{-6}\,\text{m}^2) \times (2 \times 10^{11}\,\text{N m}^{-2})}$$

$$= 2.45 \times 10^{-4}\,\text{m} = 2.4 \times 10^{-4}\,\text{m}$$

The value of dL has to be rounded off to two significant digits. Here we have a special case as the digit to be discarded is 5. By convention, we have rounded off to the nearest even number.

Hence, the work done by the wire on being stretched is given by

$$\delta W_F = -FdL = -(5 \times 9.8\,\text{N}) \times (2.4 \times 10^{-4}\,\text{m})$$

$$= -1.2 \times 10^{-2}\,\text{J}.$$

Negative sign shows that work is done on the wire.

Example 4

Magnetic susceptibility of a paramagnetic substance varies with temperature as, $\chi = C/T$, where C is a constant (Curie's law). Show that the work done on a paramagnetic material during a quasistatic isothermal change in magnetisation from M_i to M_f is given by

$$\Delta W_M = \frac{CV}{2\,\mu_0 T}\,(B_{af}^2 - B_{ai}^2) = \frac{\mu_0 TV}{2C}\,(M_f^2 - M_i^2)$$

Use this result to evaluate the work done on a sample having $\chi = 9.0 \times 10^{-2}$ N A^{-1} m^{-1} T^{-1} at 2.1 K and volume 2×10^{-4} m^3 when it is magnetised by increasing the applied flux density slowly from 0.7 T to 1.2 T maintaining temperature at 2.1 K.
($\mu_0 = 12.57 \times 10^{-7}$ NA^{-2})

A paramagnetic substance when placed in an external magnetic field has a tendency to get weakly aligned in the direction of the external field. The susceptibility χ of such a substance is given by

$$\chi = \frac{M}{H},$$

where H is the magnetising field and M is the intensity of magnetisation. It has a very low (positive) value.

The notation T is used for temperature in kelvin scale. Its unit is kelvin (K). In Example 4 T stands for tesla which is the unit of magnetic induction or flux density and is equivalent to weber m^{-2}. $\chi = \frac{M}{H}$, where M is the magnetic moment per unit volume. Unit of magnetic moment is equivalent to that of

$$\frac{\text{torque}}{\text{magnetic induction}}$$

Hence it is N m T^{-1}

So unit of M is N m T^{-1} m^{-3}, i.e. N m^{-2} T^{-1} and the unit of H is A m^{-1}.

So the unit of χ is $\frac{\text{N m}^{-2}\,\text{T}^{-1}}{\text{A m}^{-1}}$, i.e. N A^{-1} m^{-1} T^{-1}

Solution

Work done by a paramagnetic sample of volume V in developing magnetisation dM in the applied flux density $B_a = \mu_0 H$ is given by

$$\delta W_M = -V\,B_a\,dM$$

Here, $M = \chi B_a/\mu_0 = \left(\frac{C}{T}\right)\frac{B_a}{\mu_0}$ so that under isothermal conditions $dM = (C/\mu_0 T)\,dB_a$. When B_a is changed from B_{ai} to B_{af}, the work done by the sample is

$$\Delta W_M = -V\int_{B_{ai}}^{B_{af}} B_a \frac{C}{\mu_0 T}\,dB_a$$

$$= -\frac{CV}{2\,\mu_0 T}\,(B_{af}^2 - B_{ai}^2)$$

$$= -\frac{CV}{2\,\mu_0 T}\left\{\left(\frac{\mu_0 T}{C}M_f\right)^2 - \left(\frac{\mu_0 T}{C}M_i\right)^2\right\}$$

$$= -\frac{\mu_0 TV}{2C}\,(M_f^2 - M_i^2)$$

During demagnetisation ($M_i > M_f$) work is done by the substance.

Negative sign shows that work is done on the material during magnetisation ($M_f > M_i$). Note that we started with the expression for work done by the material and ended up with the negative sign. So the required expression for work done on the sample is

$$\frac{\mathrm{N\,A^{-1}\,m^{-1}\,T^{-1}\,m^3\,T^2}}{\mathrm{N\,A^{-2}}}$$
$= \mathrm{A\,T\,m^2}$
$= \mathrm{A}$ (weber)
$= \mathrm{A\,V}-\mathrm{s}$
$= (\mathrm{A\,s})\,(\mathrm{V})$
= coloumb volt
= joule

$$\Delta W_M = \frac{CV}{2\,\mu_0\,T}\,(B_{af}^2 - B_{ai}^2) = \frac{\mu_0\,TV}{2C}\,(M_f^2 - M_i^2)$$

Now, in the given numerical problem,

$$\chi = \frac{C}{T} = 9.0 \times 10^{-2}\,\mathrm{N\,A^{-1}\,m^{-1}\,T^{-1}}, \quad V = 2 \times 10^{-4}\,\mathrm{m^3}$$

$$B_{ai} = 0.7\,\mathrm{T}, \quad B_{af} = 1.2\,\mathrm{T} \text{ and } \mu_0 = 12.57 \times 10^{-7}\,\mathrm{N\,A^{-2}}$$

Therefore, work done on the sample is given by

$$\Delta W_M = \frac{C}{T}\,\frac{V}{2\mu_0}\,(B_{af}^2 - B_{ai}^2)$$
$$= (9.0 \times 10^{-2}\,\mathrm{N\,A^{-1}\,m^{-1}\,T^{-1}}) \times \frac{(2 \times 10^{-4}\mathrm{m^3})}{(2 \times 12.57 \times 10^{-7}\,\mathrm{N\,A^{-2}})} \times (1.2^2 - 0.7^2)\,\mathrm{T^2}$$
$$= 6.8\,\mathrm{J}.$$

You may now like to work out a simple SAQ to understand the handling of the expressions for work done.

SAQ 4

Determine the work done by a Leclanche cell of emf 1.40 V, which supplies a constant current of 150 mA for 1 minute.

In the following table, we have given for your ready reference the expressions for work done for several systems. Symbols have their usual meanings.

Table 3.1: Expressions of work for several systems

System	Infinitesimal work ($đW$)	Work done during a process (ΔW)
Gaseous	pdV	Expansion from volume V_i to V_f: $\Delta W_T = \int_{V_i}^{V_f} pdV$
Paramagnetic substance	$-VB_a dM$	Increase in magnetisation from M_i to M_f: $\Delta W_M = -V\int_{M_i}^{M_f} B_a\,dM$
Surface Film	$-s\,dA$	Increase in surface area from A_i to A_f: $\Delta W_s = -\int_{A_i}^{A_f} s\,dA$
Stretched Wire	$-F\,dL$	Increase in length of a wire from L_i to L_f: $\Delta W_F = -\int_{L_i}^{L_f} F\,dL$
Electric Cell	Edq	Passage of a current i through an electric cell during the interval of time t_i to t_f: $\Delta W_E = -\int_{t_i}^{t_f} Ei\,dt$

$i = \frac{dq}{dt}$, i.e. $dq = idt$

So, now, you are able to determine work done during several thermodynamic processes. Let us now examine whether work and heat are dependent on the path of a process or not.

3.5 PATH DEPENDENCE OF WORK AND HEAT

You have come to know from Sec. 3.4.1 that the work done by a gaseous system can be represented by the area under the p–V diagram of the system from the initial to the final state. Now refer to Fig. 3.8. The work done for the process ACB is equal to the area $ACBFG$, and that during the processes ADB and AEB are the areas $DBFG$ and $AEFG$ respectively. Since these areas are not equal, the work done during these processes are not same. So work done depends on the path taken, i.e. work does not depend **only** on the initial and final state variables of a process. In other words, work is not a function of the state. Is the same true about heat? To understand this let us take a simple example.

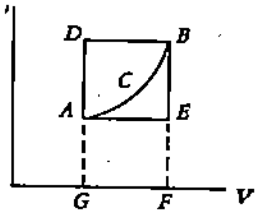


Fig. 3.8: The points A and B, are connected by several paths. The path ACB indicates a general process. The path ADB is the combination of an isobaric and an isochoric process, whereas the path AEB is the combination of an isochoric and an isobaric process.

Suppose you have milk at 30°C in a glass and you wish to raise its temperature by 5°C. This can be done by **adding heat to it, or churning it vigorously, or by doing a combination of heating and churning.** However, in all cases we ultimately arrive at a state which can be defined as milk at 35°C. And in all cases the initial state can be defined as milk at 30°C. The processes connecting these states were different and the quantities of heat given to the system for the three processes were not the same. So we can say that heat given to a system is dependent on the process. So it is dependent on the path taken between the initial and final states and is hence not a function of the state of the system.

You must have observed that in the preceding example work done on the system was also not the same in all cases. This is not unexpected as we have already established that work is not a function of the state. Now, can there be any function whose value changes by the same amount during these processes, so that it is independent of the path between the states? Yes, such a function does exist. It is known as internal energy. Let us now discuss it in some detail.

3.6 INTERNAL ENERGY

The internal energy of a system is the sum of the energies of the individual components of the system. This includes their kinetic energy due to random motion and their potential energies due to interactions amongst themselves. For example, the internal energy of a metallic rod is made up of the kinetic energies of the conduction electrons, the potential energies of atoms of the metal and the vibrational energies about their equilibrium positions (Fig. 3.9).

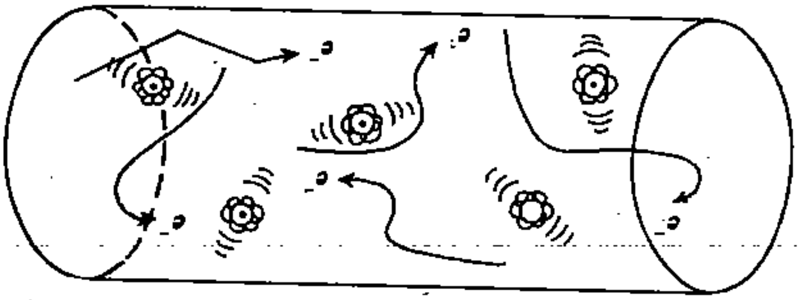


Fig. 3.9 : The internal energy of a metallic rod which includes kinetic energies of the conduction electrons (e^-) and the vibrational energies of the atoms of the metal.

Internal energy is a state function. It depends **only** on the state variables like temperature, pressure and volume. You may say that work done in a gaseous system also depends on these variables. But work done is not a state function. For this you read the second sentence of this paragraph again. The emphasis there is on the word 'only'. Work done depends on the path also. To understand this concept better let us refer back to the example we had considered in Sec. 3.4. By increasing the temperature of milk by 5°C, the movement of the molecules comprising the milk is made more vigorous. In other words, its internal energy is raised. Since in each case the temperature increases by the same amount, the changes in internal energy are also the same. So whatever might the heat and work input be to raise the temperature of milk by 5°C, the change in internal energy is always the same. This suggests that internal energy is a function of the state of the system. You may now like to work out an SAQ on this concept.

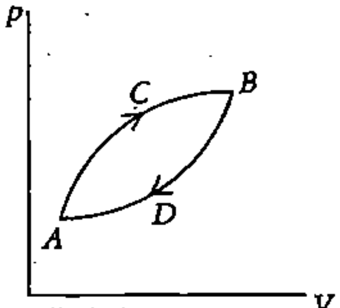


Fig. 3.10 : A cyclic process

SAQ 5

a) From the kinetic theory of gases we know that there is no intermolecular force between the molecules of an ideal gas. Use this idea to prove that the internal energy of an ideal gas depends on temperature only.

b) Show that the change in internal energy during a cyclic process (Fig. 3.10) is zero.

So far we have seen that heat and work inputs into a system cause its internal energy to rise. Likewise, if heat is taken out of the system or some work is done by the system its internal energy is lowered. In Fig. 3.11 we have shown schematically the different methods by way of which internal energy of a system may be made to change. We have discussed quite a few examples related to Figs. 3.11 a and b. The case of Fig. 3.11c is referred to as diffusive interaction. It will not be of much interest for systems we shall be dealing with in this block. So we shall not touch upon it.

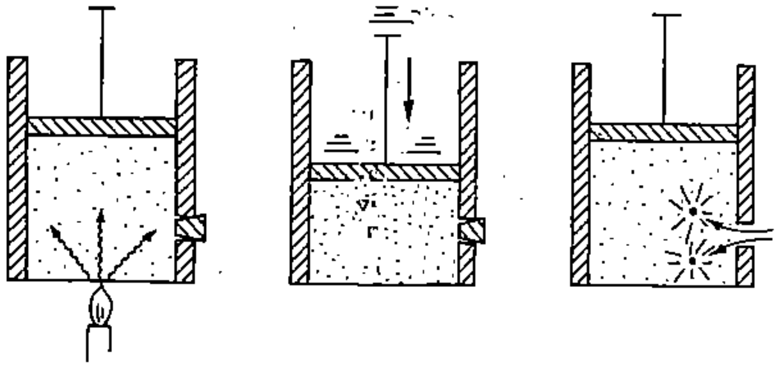


Fig. 3.11 : The three kinds of processes through which the internal energy of a system may be changed, (a) Adding heat energy (b) Doing work on it and (c) Adding particles to it.

We shall now invoke the good old principle of conservation of energy to analyse the aspect of change of internal energy and in the process we shall arrive at the first law of thermodynamics.

3.7 THE FIRST LAW OF THERMODYNAMICS

The principle of conservation of energy states that 'Energy can neither be created nor destroyed; it can be transformed from one form to another, the total amount of energy (in this universe) remaining constant.' Now according to this principle, we cannot get energy out of nowhere. **If energy of a system increases, there ought to have been an equivalent expenditure of energy.**

Let us again consider the example of raising the temperature of milk. You can say that internal energy of the milk can be increased in three ways (i) only by way of heat input, (ii) only by way of work input and (iii) a combination of heat and work input. For (i), let the heat absorbed by the system be $\Delta Q'$. The work done on the system is zero and so the work done by the system is also zero. For (ii) the heat absorbed is zero. Let the work done by the system be $\Delta W'$ so that the work done on the system is $-\Delta W'$. For (iii) let the heat absorbed be ΔQ and let the work done by the system be ΔW so that the work done on the system is $-\Delta W$.

We know that the change in internal energy is same in all cases. Let that be ΔU. Here all the quantities are expressed in heat units. Now, from the principle of conservation of energy, we must have :

Increase in internal energy = (Heat absorbed) + (work done on the system)

i.e. $\Delta U = \Delta Q' = -\Delta W' = \Delta Q + (-\Delta W)$

or $\Delta U = \Delta Q - \Delta W$ (3.9)

Whenever heat is converted into any other form of energy (as in a steam engine) or vice versa (as in an electrical heater) in each form it is equivalent. If a quantity of heat, Q is completely converted into work, W, then W is equivalent to Q and

$\frac{W}{Q}$ = a constant is known as the *mechanical equivalent of heat*. It is denoted by J and its value is approximately equal to 4.2 joules cal^{-1}. Thus 1 calorie of heat can be expressed as 4.2J. We say that 1 cal. of heat expressed in work unit is 4.2J. Likewise work can be expressed in heat units. In our blocks, while discussing a particular problem, we shall express work and heat in the same units, i.e. either both in work units or both in heat units.

Eq. (3.9) can be considered as the mathematical form of the first law of thermodynamics when diffusive interaction is neglected. Unless otherwise stated, we shall assume that diffusive interaction is absent. The formal statement of the first law is as follows: **'Internal energy of a system is a function of the state of the system and its change during a thermodynamic process is equal to the sum of the heat given to the system and the work done on the system.'** Thus, according to this law, we can say that for thermodynamic processes taking place between two particular states, the difference between the heat absorbed and the work done by the system is always a constant and is equal to the change in internal energy of the system.

Now look at Fig. 3.12 and read its caption carefully to understand an illustration of the first law of thermodynamics.

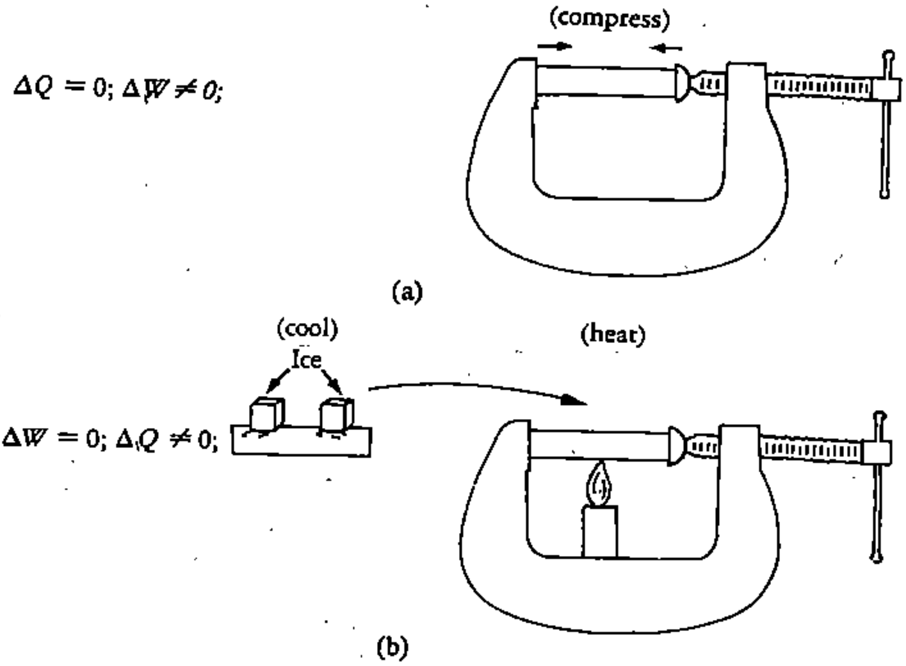


Fig. 3.12: Illustration of two quite different paths for getting from the same initial state to the same final state. (a) The iron bar is put into the clamp and then compressed. In this process, work is done on the iron bar, but no heat energy is added or removed. ($\Delta W \neq 0$; $\Delta Q = 0$). (b) The iron bar may first be cooled so that it contracts and can be slipped into the clamp that has been already adjusted for the desired final length. Then heat can be added to bring the temperature up to the desired final temperature. In doing this, the bar expands and gets stuck in the clamp. In this process, no work is done on the bar, but there is some net heat transfer. ($\Delta W = 0$; $\Delta Q \neq 0$). In both processes the iron bar ends up at the same final temperature and pressure.

Let us now take two numerical examples to illustrate the first law of thermodynamics.

In the first example you will have to apply the idea that the change in internal energy between two states is independent of the path connecting the states.

Example 5

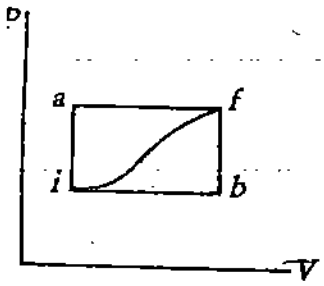


Fig. 3.13

Refer to Fig. 3.13 when a system is taken from state *i* to state *f* along the path *iaf*, it is found that $\Delta Q = 45$ cal and $\Delta W = 20$ cal. Along the path *ibf*, $\Delta Q = 30$ cal.

a) what is ΔW along the path *ibf*?
b) If $\Delta W = -13$ cal for the curved return path *fi*, what is ΔQ for this path?
c) Taking $U_i = 10$ cal, what is U_f?
d) If $U_b = 21$ cal, what are ΔQ's for the processes *ib* and *bf*?

Solution

a) We know that, $U_f - U_i$ = a constant independent of the path joining *i* and *f*.

For *iaf*, $\Delta Q = 45$ cal, $\Delta W = 20$ cal. So from Eq. (3.9), we get

$\Delta U = (45-20)$ cal $= 25$ cal.

$\therefore\ U_f - U_i = 25$ cal.

Eq. (3.12) is called the **differential form of the first law. Let us illustrate this with an** example.

Example 7

a) Using the symbols used in the text. write down the differential form of the first law of thermodynamics for the following systems :
   (i) A gas in a cylinder filled with a piston
   (ii) A wire under tension

b) A sample of a perfect gas is subjected to a series of quasistatic changes shown in the p–V diagram (Fig. 3.15) and explained below :
   (i) along AB: isothermal, (ii) along BC: isochoric, (iii) along CD: adiabatic

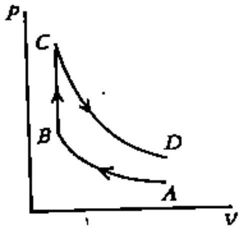


Fig. 3.15

Let dV, dp, dT, and dU, respectively be the changes in volume, pressure, temperature and internal energy, and let δW and δQ, respectively be the work done by and heat added to the system. Complete the following Table (3.2) with 0, − or + in the blanks to indicate no change, decrease or increase in the appropriate quantity.

Table 3.2

Path	dV	dp	dT	δW	δQ	dU
AB						
BC						
CD						

Solution

a) (i) $\delta Q = dU + pdV$
   ii) $\delta Q = dU + FdL$

b) i) Path AB: Along this path the gas is compressed isothermally so that dT *is* 0. Again as U is a function of T only for a perfect gas, dU is also 0, dp is + and dV as well as δW are −. Clearly, δQ (= δW) is also −.

   ii) Path BC: Along this path pressure increases at the same volume so that dV = 0 and dp is +. Also $\delta W = pdV = 0$. Now, pressure can be increased isochorically only by heating the gas so that δQ is +, which makes dT + and from $dU = \delta Q - \delta W$, dU is also +.

iii) Path CD: This being the path for an adiabatic expansion of the gas, dV is +, dp is − and δW is + while $\delta Q = 0$. Heat given to the system is zero and moreover, work is done by the system. So, energy flows out of the system boundary. This causes cooling of the gas so that dT is − and dU is also −.

The complete Table (3.3) will hence be as follows :

Table 3.3

Path	dV	dp	dT	δW	δQ	dU
AB	−	+	0	−	−	0
BC	0	+	+	0	+	+
CD	+	−	−	+	0	−

You may now work out an SAQ on the above concept. The SAQ may appear to be lengthy. But do not get scared by that. It is very simple.

SAQ 7

a) Write down the mathematical form for the first law of thermodynamics applied to a thermally insulated system and comment on the nature of change in its internal energy.

b) Using the symbols employed in the text, write down the mathematical form of the first law of thermodynamics for the following systems.

(i) A paramagnetic substance in a region of magnetic flux density B_a, (ii) An electric cell, and (iii) a perfect gas expanding into vacuum under isothermal conditions.

c) **Fill in the blanks in the following sentence:**
A process is .... if $\delta Q = dU$,........... if $dU = -\delta W$ and .... if $\delta Q = \delta W$.

d) **Suppose you place a tray filled with water in a freezer. What will be the signs of δW, δQ and dU for the contents of the tray? Justify your answer.**

We shall now wind up this unit. But before we do so let us see what are the significances of the first law.

The first law is not a new law. It is an extension of the principle of conservation of energy. If a machine could have been built so that it would have been able to do work without any input of energy then it could have run perpetually. For making it work, it would have just been required to give it a start. Such a machine is called a **perpetual motion machine of the first kind.** The first law rules out such a machine. The fact that it has not yet been possible to build such a machine, forms an experimental basis of the first law.

However, the first law takes into account a function of state of the system, i.e. internal energy. It shows that the difference of two inexact differentials of heat and work is equal to an exact differential, that of internal energy.

In this unit we have introduced the first law and have studied a few illustrations. You will learn about a wide variety of applications of this law in the next unit.

3.8 SUMMARY

- Heat is the form of energy that is transferred between systems or a system and its surroundings by virtue of temperature difference.
- Heat added to a system is considered positive and heat taken away is considered negative.
- If an energy interaction between a system and its surroundings takes place not by way of difference of temperature then it is called work.
- Work done by a thermodynamic system is taken to be positive and that done on it as negative.
- A thermodynamic system of constant mass that exerts pressure on its surroundings is called a chemical system.
- The following are the expressions for work done in different systems, which have undergone a finite change.

Expansion of a gaseous system : $\Delta W_T = \int_{V_i}^{V_f} p\,dV$.

Isothermal expansion of a perfect gas : $\Delta W_T = nRT \ln (V_f/V_i)$.

A wire under tension : $W = -\int_{L_i}^{L_f} F\,dL$.

Paramagnetic substance placed in a region of flux density B_a : $\Delta W_M = -V\int_{M_i}^{M_f} B_a\,dM$

An electric cell supplying current i at constant emf E: $\Delta W_E = -\int_{t_i}^{t_f} E\,i\,dt$

- Work done by or on the system during a process or heat absorbed or evolved by a system during a process are path dependent. Work and heat are not functions of the state of the system.

- The internal energy of a system is the sum of the energies of the individual elements of the system. It is a function of the state of the system.
- First law of thermodynamics states that when a system undergoes a process, its internal energy changes by an amount equal to the difference in the quantity of heat transferred to and the work done by it and the change in internal energy is the same for all process connecting the same initial and final states.
- The differential form of the first law is given by

$$\delta Q = dU + \delta W$$

3.9 TERMINAL QUESTIONS

1. Use the definition of heat learnt in Sec. 3.2 to define a source of heat at temperature T_1 and a sink of heat at temperature T_2.
2. Two moles of a perfect gas occupy a volume of 0.050 m^3 and exert a pressure of 2.6×10^5 N m^{-2}. It is compressed isobarically to 0.035 m^3. Determine the work done by the gas and the fall in its temperature. (Given $R = 8.3$ J K^{-1} mol^{-1}).
3. A perfect gas at 300 K occupies a volume of 0.2 m^3 at a pressure of 5×10^6 N m^{-2}. It is allowed to expand isothermally until its volume is 0.5 m^3. Next, the gas is compressed isobarically upto its original volume. Finally, the pressure is increased isochorically until the gas returns to its initial state. Plot the process on the indicator diagram and determine the work done during the cycle.
4. For normal growth of a child, internal energy must increase. Comment on this statement.
5. Suppose you have 500 g of water in a perfectly insulated container and stir it gently. Assuming it to be a thermodynamic system, fill in the blanks in the following sentences by choosing appropriate word(s) from the bracket after each statement.
   i) Heat .... from or to the system (flows, does not flow)
   ii) Work is done .... the system (on, by)
   iii) Temperature of the system .... (rises, falls)
   iv) Change in internal energy of the system is .... (positive, negative).
6. A system is subjected to four types of processes depicted in the Table 3.4. Fill up the blanks for each process if the entries already made are in joules.

Table 3.4

Process	Heat added δQ	Work done δW	Internal energy		Change in internal energy dU
			Initial U_i	Final U_f	
I	30	0	—	30	—
II	—	30	30	—	20
III	60	—	0	—	40
IV	–20	—	15	40	—

3.10 SOLUTIONS AND ANSWERS

SAQs

1. For this problem the interior surfaces of the oven form the system boundary. The energy content of the oven increases as evidenced by a rise in its temperature. This energy transfer to the furnace is not caused due to a temperature difference between the furnace and the surrounding air. So the energy transfer is not heat.

   Here, the energy transfer is caused by the flow of electrons along the heating element and this takes place across the system boundary. So this is an energy transfer of a different kind.

2. a) Work, positive, force, displacement.
   b) i) Here the system of interest is the magnet. In this case some internal adjustments take place within the magnet. So no work is done.
      ii) In this case current flows into the coil from its surroundings and the coil is set into rotation. So work is done.
   c) (i) +, (ii) −.

3. a) For an ideal gas undergoing isothermal process from state (p_i, V_i) to state (p_f, V_f) we have $p_fV_f = p_iV_i$. Therefore, $V_f/V_i = p_i/p_f$ and this on substitution into Eq. (3.4) yields

$$\Delta W_T = nRT \ln (p_i/p_f)$$

   b) Since the system expands from volume V_1 to V_2 at constant pressure, we have

$$\Delta W_p = \int_{V_1}^{V_2} \delta W = \int_{V_1}^{V_2} p dV = p (V_2 - V_1) = p\Delta V$$

   On the indicator diagram, the path is a straight line parallel to the V-axis and the work done by the system is indicated by the shaded area in Fig. 3.16.

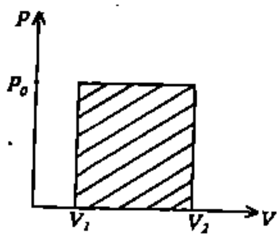


Fig. 3.16

4. We know that current is given by $i = \frac{dq}{dt}$ or $dq = idt$. Hence, the work done by an electric cell of emf E in supplying constant current i from time t_i to t_f is

$$\Delta W = -\int_{t_i}^{t_f} Eidt = -Ei(t_f - t_i)$$

Substituting different values, we get

$$\Delta W = -1.40 \text{ V} \times 0.15 \text{ A} \times 60 \text{ s} = 12.6 \text{ J}.$$

(volt) (ampere) (sec)
= (volt) (coulomb)
= joule

5. a) U is a function of state, and is in general a function of p, V, T. We have to prove that for an ideal gas U depends on T only. If U depends on V, then on increasing the volume of the system, U should change. Now on increasing the volume, the intermolecular spacing increases. Had there been an attractive intermolecular force, this increase of spacing would have led to work being done against that force and the internal energy of the system would have increased. Had there been a repulsive intermolecular force, U would have decreased. But since there is no force, U will not change at all. Hence U does not depend on V. Similarly, it can be proved that U does not depend on p. So it depends on T only.
   b) Refer to Fig. 3.17. It is the replica of Fig. 3.10. During the process ACB, the change in internal energy is $(U_B - U_A)$ and that during the process BDA is $(U_A - U_B)$. So the overall change during the cyclic process $ACBDA$ is given by $(U_B - U_A) + (U_A - U_B) = 0$.

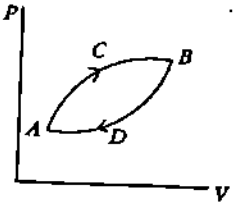


Fig. 3.17

6. The diet consumed is like heat supplied and energy spent is the work done by the system. Thus,

$$\delta Q = 10^4 \text{ J per day}$$
$$\delta W = 1.2 \times 10^4 \text{ J per day}$$

Therefore, change in internal energy per day is given by

$$\begin{aligned} dU &= \delta Q - \delta W \\ &= (1.0 \times 10^4 - 1.2 \times 10^4) \text{ J} \\ &= -2.0 \times 10^3 \text{ J} \end{aligned}$$

This decrease corresponds to loss of sucrose. Therefore, sucrose lost per day

$$\begin{aligned} &= \frac{2.0 \times 10^3}{1.6 \times 10^4} \text{ kg} \\ &= 0.125 \text{ kg} \end{aligned}$$

Hence, number of days required for the loss of 1 kg $= \frac{1}{0.125} = 8$.

7. a) For a thermally insulated or adiabatic system $\delta Q = 0$ so that Eq. (3.12) becomes $dU = -\delta W$. Thus, decrease in internal energy of a thermally isolated system is equal to the work done by the system and the increase in internal energy is equal to work done on the system. Moreover, since dU depends only

UNIT 4 APPLICATIONS OF THE FIRST LAW OF THERMODYNAMICS

Structure

4.1 Introduction
  Objectives
4.2 Difference of Heat Capacities of a Gas
4.3 Equation of State for Adiabatic Processes
  The Adiabatic Lapse Rate: Convective Equilibrium
  The Speed of Sound
  Adiabatic and Isothermal Elasticities
4.4 The Enthalpy
  4.4.1 Enthalpy and Chemical Processes
  4.4.2 Standard Enthalpy Changes
  4.4.3 Enthalpy of Reaction
4.5 Hess's Law
4.6 Summary
4.7 Terminal Questions
4.8 Solutions and Answers

4.1 INTRODUCTION

In Unit 3 you have learnt the first law of thermodynamics. It is essentially an extension of the principle of conservation of energy for thermodynamic processes. It tells us that heat and other forms of energy are equivalent. Do you know that much of our world works because of this equivalence? Most of the electrical energy that lights our houses, operates machines and runs trains originates in heat. This heat is released in burning of coal, oil, gas or fissioning of uranium.

In a sense, this law is universal and explains phenomena observed in nature as well as in a laboratory. The fall in temperature as we move upward in outer atmosphere — a very large scale phenomenon — is explained rather well. Using this law we can also explain the pressure oscillations in a sound wave. Its application to flow processes and chemical reactions is also very interesting. In spite of its wide utility, this law has inherent limitations. It gives us no information about the direction of flow of heat. This information is contained in the second law of thermodynamics, which you will study in Block 2 of this course.

In this unit you will learn to apply the first law to diverse thermodynamic systems. In Sec. 4.2 we start by computing the heat capacities at constant pressure and constant volume for an ideal gas. For any substance, this difference can be related to measurable quantities like volume expansion coefficient and bulk modulus of elasticity. In Sec. 4.3 we have used this law to derive the equation of state for adiabatic processes. Using this equation, we have computed an expression for the adiabatic lapse rate. In Sec. 4.4 we have introduced the concept of enthalpy — a function of state. It is useful in discussing production of low temperatures and regenerative cooling as well as chemical reactions. You will learn more about enthalpy in the next block.

Objectives

After studying this unit, you will be able to

- compute the difference between heat capacities at constant pressure and at constant volume
- derive the equation of state for an adiabatic process
- explain adiabatic lapse rate
- compute expressions for velocity of sound in air
- define enthalpy and use it to study chemical reactions
- State Hess's Law.

In Unit 3 you learnt to establish the first law of thermodynamics and compute changes in internal energy when a substance undergoes a change of state. In this unit we will apply this law to diverse physical systems. Let us first consider a gaseous system. You would recall that the heat capacity of ideal gases is independent of the nature of the gas. But physical conditions under which heat is given change the value of heat capacity of a gas. Is the same true for liquids and solids? To discover the answer to this question let us calculate the difference between heat capacities of gases at constant pressure and at constant volume.

4.2 DIFFERENCE OF HEAT CAPACITIES OF A GAS

From Unit 3 you would recall that in the absence of diffusive interactions, the first law of thermodynamics for a gaseous system has the form

$$\delta Q = dU + pdV \tag{4.1}$$

This means that heat δQ given to a system at constant pressure (isobaric process) changes its internal energy by dU and volume by dV.

Since heat is not a state variable, we have put δ before Q to denote changes in heat content of a system.

Let us assume that one mole of a gas is contained in a cylinder fitted with a piston. In Unit 1 you learnt that the state of a gas can be described in terms of any two thermodynamic coordinates out of p, V and T. Let us choose T and V as independent variables. Since internal energy is a function of state, we can write

$$U = U(T, V)$$

Then the differential of U can be written as

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{4.2}$$

The symbol ∂ is pronounced as del. It denotes a partial derivative.

On combining Eqs. (4.1) and (4.2), you can write

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \tag{4.3}$$

You can now imagine that the piston is tightly clamped. As we heat the gas, it cannot expand, i.e. it cannot do any work and all the heat goes to raise its internal energy and hence temperature. **The heat required to raise the temperature of one mole of a gas through one degree when its volume is kept constant is termed as molar heat capacity at constant volume.** It is denoted by the symbol C_V and is generally expressed in J mol $^{-2}$ K^{-1}. For such a system Eq. (4.3) reduces to

$$C_V = \left(\frac{\delta Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{4.4}$$

The different symbols have been used to depict changes in heat and temperature. We have done so because heat is not a function of state.

You may recall that heat capacity varies from substance to substance. It varies with temperature and amount of the substance as well. The latter is **measured in kg or by the number of moles. The corresponding measures of heat capacity are specific heat and molar heat capacity.** The specific heat is the heat capacity per kilogram and molar heat capacity is the heat capacity per mole. At constant volume the specific heat is denoted by small letter c_v :

$$c_v = \frac{C_V}{m}$$

where m is the number of kilograms per mole in the substance with molar heat capacity C_V at constant volume. The specific heat capacity is measured in cal g^{-1} K^{-1}. When heat is measured in joules (1 cal = 4.184 J), molar heat capacity is measured in J mol^{-1} K^{-1}.

Now suppose that the piston is allowed to move in or out so that the gas is kept at constant pressure. The gas does work on the piston and some of the heat ends up as mechanical energy of the surroundings. So to achieve a given change in temperature, more heat has to be supplied to the gas in a constant pressure process. **The molar heat capacity of a gas at constant pressure is defined as the amount of heat required to raise the temperature of one mole of gas by one degree. It is denoted by the symbol** C_p. Mathematically, we can write

$$C_p = \left(\frac{\delta Q}{\partial T}\right)_p \tag{4.5}$$

On combining Eqs. (4.3) and (4.5), you will get

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

Using Eq. (4.4) we find that

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p \tag{4.6}$$

SAQ 2

Show that the first law of thermodynamics can also be written as

$$\delta Q = C_V\, dT + p dV$$

and

$$\delta Q = C_p\, dT - V dp$$

Let us pause for some time and ask: What have we achieved so far? Do we distinguish heat capacities at constant volume and constant pressure for solids and liquids as well? For these substances such a distinction is less significant because they are incompressible. That is, their coefficient of volume expansion is much less compared to that for gases. In fact, for solids and liquids, measured values are quoted at constant pressure.

So far you have learnt to compute the difference between heat capacities at constant pressure and constant volume. Let us now consider a process in which no heat is exchanged between the system and surroundings. You may have experienced sometimes that if you let air out of a tyre, you feel that the air is cool. Blow on the back of your hand with your mouth wide open. You will feel that your breath is warm. Now close your lips into a small opening and blow again. Your breath now feels cool. Does this mean that your body temperature is different in the two cases or do the conditions induce this apparent change? It happens because in the latter case, air undergoes adiabatic expansion. From Unit 1 you know of many adiabatic processes occurring around you. But in this unit we will consider the particular cases of the propagation of sound in air and expansion of air as it rises in the troposphere. In a physics laboratory, you can realise an adiabatic transformation by expanding or compressing a gas in a cylinder having non-conducting walls and fitted with an insulated piston. Let us now derive the equation of state for an adiabatic process using the first law of thermodynamics.

4.3 EQUATION OF STATE FOR AN ADIABATIC PROCESS

In an adiabatic process, the system and the surroundings are not in thermal contact. That is, no heat exchange takes place and $\delta Q = 0$. Then the first law of thermodynamics tells us that

$$dU + \delta W = 0 \tag{4.9}$$

This shows that in an adiabatic expansion, internal energy decreases. Since U is a function of T, a fall in internal energy implies drop in temperature, i.e. the system cools. What happens in an adiabatic compression? We expect that the temperature will increase as work is done **on** the system. From this you may conclude that adiabatic expansion produces cooling and adiabatic compression produces heating. This finds an important application in the production of low temperatures. You will learn its details in Unit 8 of Block 2.

Suppose that one mole of a perfect gas is subject to a quasistatic adiabatic expansion. From SAQ 2 you can write

$$C_V dT + p dV = 0 \tag{4.10}$$

During the expansion, the gas passes through an infinite number of equilibrium states. This means that the equation of state ($pV = RT$) will hold for each state. On substituting $p = RT/V$ and dividing throughout by $C_V T$, you can arrange the resulting expression in the form

$$\frac{dT}{T} = -\frac{R}{C_V}\frac{dV}{V} \tag{4.11a}$$

In general, the heat capacity at constant volume changes with temperature. But this is significant only when the change in temperature is very large (~ 1000K). So for processes under consideration C_V may be assumed to be independent of temperature.

For a quasistatic process, V and T are well defined for each state. So if we assume that C_V is independent of temperature, we can readily integrate Eq. (4.11a) to obtain

$$\ln T = -\frac{R}{C_V}\ln V + \ln K \tag{4.11b}$$

where $\ln K$ is constant of integration.

Taking antilog, we obtain

$$TV^{R/C_V} = K$$

Using Eq. (4.8) we can also write

$$TV^{(C_p - C_V)/C_V} = K$$

In your earlier physics classes you must have learnt that the ratio of heat capacity at constant pressure to that at constant volume is usually denoted by the greek symbol gamma; $\gamma = C_p/C_V$. So we can rewrite the equation for an adiabatic transformation as

$$TV^{\gamma - 1} = K \qquad (4.12)$$

This relation tells us that as temperature increases volume decreases and vice versa when a perfect gas undergoes a quasistatic adiabatic change. This is an important result. Before proceeding further, let us pause for a minute and ask: Can we similarly relate pressure and temperature or pressure and volume? To discover answer to this question, we would like you to solve SAQ 3.

SAQ 3

Starting from Eq. (4.12), show that

$$\frac{T^\gamma}{p^{\gamma-1}} = K_1 \qquad (4.13a)$$

and

$$pV^\gamma = K_2 \qquad (4.13b)$$

where K_1 and K_2 are constants.

[**Hint**: Use Equations of state $pV = RT$.]

Eq. (4.13a) predicts that during an adiabatic process, increase/decrease in pressure is accompanied by a corresponding increase/decrease in temperature. Can you say the same about Eq. (4.13b)?

You will note that Eqs. (4.12) and (4.13) are equivalent forms of the so-called **adiabatic equation.** This equation will hold provided

i) the initial and final states are equilibrium states,

ii) the perfect gas equation $pV = RT$ is valid, and

iii) the internal energy of the gas is proportional to temperature only.

SAQ 4

Differentiate Eq. (4.13b) w.r.t. V and compute $(dp/dV)s$. Also calculate the corresponding quantity for an isothermal change (pV = constant). What do you conclude?

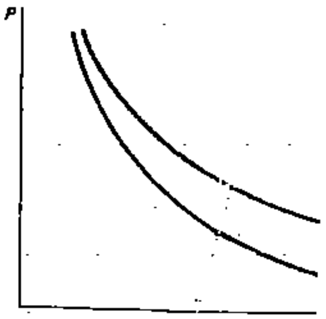


Fig. 4.1 Plot of Eq. (4.13 b)

Now refer to Fig. 4.1. It shows a plot of Eq. (4.13b) on a $p - V$ diagram. You will observe that the adiabat is a part of hyperbolae. The slope of the adiabat is $\gamma(p/V)$. (You must have seen it on working out SAQ 4.) Compare it with the slope of an isotherm. You will note that the slope of an adiabat is γ times the slope of an isotherm. That is, an adiabat is steeper than an isotherm. This is because the gas loses internal energy as it expands. This also implies that relative change in volume in an adiabatic process is less than that in an isothermal change.

Example 3

The nozzle of a bicycle is blocked. With no force on the handle, the pump contains a volume V of air at 300K and atmospheric pressure. The handle is pushed down with a constant force **F** reducing the volume to half. No air escapes from the pump. Assume the change to be adiabatic. Taking γ for air to be 1.4, compute the final temperature of air in the pump.

Solution

Since the change is adiabatic, we can use Eq. (4.13b):

$$pV^\gamma = \text{constant}$$

or

$$p_i V^\gamma = p_f \left(\frac{V}{2}\right)^\gamma$$

where p_f is the pressure of the gas when the handle is in final equilibrium state. On simplifying this equation, we get

$$p_f = p_i\, 2^\gamma = 2.64\, p_i$$

Applying the perfect gas equation of state, you can write

$$\frac{p_i V}{T_i} = \frac{p_f (V/2)}{T_f}$$

or

$$T_f = \frac{p_f}{2\, p_i}\, T_i$$

$$= \frac{2.64}{2}\, T_i$$

$$= 1.32 \times (300\ \text{K})$$

$$= 396\text{K}$$

Beware, this temperature is higher than the boiling point of water! So you are advised not to touch the nozzle of a blocked pump after you have used it. Physically this means that adiabatic compression produces heating.

SAQ 5

The pressure inside a scooter tyre is 2 atm. at 300K. It bursts suddenly. Regarding the change to be adiabatic, compute the final temperature. Use $\gamma = 1.4$.

You may think that Eq. (4.13) contradicts the ideal gas law. It is not so because the ideal gas law does not imply pV = constant except for an isothermal process. Since a reversible process cannot be both adiabatic and isothermal, there is no contradiction.

Example 4

Two identical gaseous systems, each containing 0.06 mol of ideal gas, are at 300K and 2.0 atm pressure. The ratio of heat capacities of the gas is 1.4. One of the gases is made to expand adiabatically and the other isothermally until they are at normal pressure. Calculate the final volumes in each case.

Solution

The initial volume of both gases may be obtained from the ideal gas law, $pV = nRT$. Solving for V, we get

$$V = \frac{nRT}{p} = \frac{(0.06\ \text{mol}) \times (8.3\ \text{J K}^{-1}\,\text{mol}^{-1})(300\text{K})}{(2.0\ \text{atm})\,(1.0 \times 10^5\,\text{Pa atm}^{-1})}$$

$$= 7.5 \times 10^{-4}\,\text{m}^3$$

For the isothermal process, T remains constant at 300K. So when pressure drops to half, the equation pV = constant implies that the volume doubles. So the final volume should be 1.5×10^{-3} m^3. That is,

$$V_f = 1.5 \times 10^{-3}\,\text{m}^3 \qquad \text{(i)}$$

For the adiabatic process, we have

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

Solving for V_f, we get

$$V_f = \left(\frac{p_i}{p_f}\right)^{1/\gamma} V_i$$

$$= \left(\frac{2.0\,\text{atm}}{1.0\,\text{atm}}\right)^{1/1.4} \times (7.5 \times 10^{-4}\ \text{m}^3)$$

$$= 1.2 \times 10^{-3}\ \text{m}^3 \qquad \text{(ii)}$$

On comparing (i) and (ii) you will note that the volume of the gas undergoing an adiabatic expansion is less than that when it undergoes isothermal expansion.

An important manifestation of adiabatic process is found in the troposphere. We know that as we move up, the temperature gradually drops. This is referred to as **adiabatic lapse rate.** Let us now understand the physics involved in it.

4.3.1 The Adiabatic Lapse Rate : Convective Equilibrium

The heat from the sun, on being absorbed by the ground, heats up the air in immediate contact. The heated air rises upward and a vertical density gradient is established. This gives rise to convection currents which transport cooler air downwards and hot air upwards. As hot air rises, it expands. Will it exchange heat with its environment? It may not do so because air is a poor conductor of heat. This means that in intermixing of air we have an adiabatic expansion.

To calculate the drop in temperature with height, we assume that air behaves as a perfect gas. That is, we ignore the presence of water vapour in atmosphere. This means that we can use Eq. (4.13a). For one mole of the gas, Eq. (4.13a) in logarithmic form becomes

$$\gamma \ \ln T - (\gamma - 1)\ln p = \ln K_1$$

On differentiation, we get

$$\frac{dT}{T} - \frac{\gamma - 1}{\gamma}\frac{dp}{p} = 0$$

which can be rearranged as

$$\frac{dp}{p} = \frac{\gamma}{\gamma - 1}\frac{dT}{T} \qquad (4.14)$$

Let us now pause for a minute and ask: What are we looking for? We wish to calculate variation of temperature with height, i.e. dT/dh. To do so, we must relate pressure with height. For this, we recall that as we go up, pressure decreases. Mathematically, this is expressed as

$$dp = -\rho g\, dh$$

where ρ is average density of air and g is acceleration due to gravity. The negative sign signifies that pressure decreases as we move up.

Since we have assumed that air behaves as perfect gas, we can use the equation of state $p = RT/V$ in the above expression. This gives

$$\frac{dp}{p} = -\frac{Mg}{RT}\,dh \qquad (4.15)$$

where $M = \rho V$ is the average molecular weight (=28.9u) of air. On combining Eqs. (4.14) and (4.15), we get

$$\frac{dT}{dh} = -\frac{\gamma - 1}{\gamma}\frac{Mg}{R} \qquad (4.16)$$

μ signifies atomic mass unit : $1\ \mu = 1.673 \times 10^{-27}$ kg.

This is the required expression for adiabatic lapse rate. The negative sign on the RHS indicates that temperature decreases as we move upwards. To obtain an estimate of the lapse rate, we would like you to solve the following SAQ.

SAQ 6

Insert appropriate values of M, g, R and ρ for air and compute the lapse rate.

From Eq. (4.19) you would recall that

$$E_s = \gamma p$$

and while solving SAQ 7 you must have proved that isothermal elasticity is numerically equal to pressure :

$$p = E_T.$$

On combining these results, you can establish the required expression.

You may recall from Sec. 4.2 that C_V is a perfect differential of U. Now you may ask: Can we define a function of state which corresponds to C_p? Alternatively, is there a class of processes where U and pV are grouped together? This does happen in the isobaric chemical reactions as well as flow processes. You will learn the details of flow processes with particular reference to Joule-Thomson effect and regenerative cooling in Unit 7. For the present, it is sufficient to discover the function which governs these changes/processes.

4.4 THE ENTHALPY

Let us express U as a function of T and p:

$$U = U(T, p)$$

Then we can write

$$dU = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T dp$$

Substituting this in Eq.(4.3), we find that the first law of thermodynamics takes the form

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T dp + p\, dV \tag{4.23}$$

Hence, heat capacity at constant pressure is given by

$$C_p = \left(\frac{\delta Q}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$

which can be rewritten as

$$C_p = \frac{\partial}{\partial T}(U + pV) \tag{4.24}$$

The sum $(U + pV)$ is represented by a new function, called **enthalpy**. It is denoted by the symbol H. Thus

$$H = U + pV \tag{4.25}$$

so that

$$C_p = \left(\frac{\delta Q}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{4.26}$$

We expect that enthalpy will also be a function of state of the system. Moreover, it is an extensive property of the system.

In the literature you may also encounter alternative nomenclature for enthalpy — the total heat content and total energy. However, we will use the term enthalpy.

4.4.1 Enthalpy and Chemical Processes

So far we have considered only physical processes. You may now ask: Is there any other class of processes where the first law of thermodynamics is seen in action? We know that biological and chemical reactions also involve energy changes. For instance, we may need to know energy required to keep a cell alive. Similarly, energy is evolved when magnesium is put in dilute hydrochloric acid. But energy is absorbed when hydrochloric acid combines with sodium hydroxide. The study of energy changes that occur during chemical reactions is known as **thermochemistry.** Since energy changes in a chemical reaction occur as heat, which is a function of path, it is important to know how the reaction is carried out. For this reason, we usually discuss energy changes in chemical reactions in terms of enthalpy — which is a state function.

We will now discuss it briefly. The details are to be found in the course on Atoms and Molecules CHE-01. Reactions for which $\Delta H > 0$ are called **endothermic** or heat absorbing, whereas those for which $\Delta H < 0$ are called **exothermic** or heat releasing. When a reaction takes place in an adiabatic container, an endothermic reaction results in cooling, i.e. lowering of temperature and an exothermic reaction results in heating, i.e. rise of temperature. Common laboratory glassware like a test-tube or beaker are poor heat insulators. As a result, in an exothermic reaction heat leaves the system as soon as temperature rises above that of surroundings. But we can definitely say that as long as initial and final temperatures are same, heat leaves the system in an exothermic reaction and enters the system in an endothermic reaction. It is important to note that an exothermic reaction results in products of lower energy than the reactants. But this does not mean that exothermic reactions can occur spontaneously. On the other hand, endothermic reactions never occur on their own.

4.4.2 Standard Enthalpy Changes

The enthalpy change accompanying a reaction is called the reaction enthalpy. It is denoted as ΔH. The standard enthalpy of reaction is the change of enthalpy when reactants in their standard states, i.e. pure form at a pressure of 1 bar at 25°C, change to products in their standard states. We often specify the physical state of the substance (s for solids, l for liquids and g for gases), temperature and concentration (by writing the number of moles). For example, the reactions for dissolution of gaseous hydrogen chloride in water for different concentrations are written as

$$\mathrm{HCl}\,(g) + 10\mathrm{H_2O} \longrightarrow \mathrm{HCl}\,(10\mathrm{H_2O});\quad \Delta H_{10} = -69.5\,\mathrm{kJ\ mol^{-1}}$$

$$\mathrm{HCl}\,(g) + 50\mathrm{H_2O} \longrightarrow \mathrm{HCl}\,(50\mathrm{H_2}O);\quad \Delta H_{50} = -73.3\,\mathrm{kJ\ mol^{-1}}.$$

$$\mathrm{HCl}\,(g) + 200\mathrm{H_2O} \longrightarrow \mathrm{HCl}\,(200\mathrm{H_2O});\quad \Delta H_{200} = -74.2\,\mathrm{kJ\ mol^{-1}}.$$

You will note that as the solution is gradually diluted, enthalpy changes. The change of enthalpy with dilution is referred to as **enthalpy of dilution.**

What is the enthalpy of dilution when water content is changed from 10 to 50 mole? You can easily compute that it is $-3.8\,\mathrm{kJ\ mol^{-1}}$.

You will also note that enthalpy decreases as the solution is gradually diluted. When dilution causes essentially no change in enthalpy, the solution is referred to as **aquous solution**. Thermochemical equations for some aquous solutions are given below :

$$\mathrm{HCl}\,(g) + \mathrm{aq} \rightarrow \mathrm{HCl}\,(\mathrm{aq});\quad \Delta H_{aq} = -74.9\,\mathrm{kJ\ mol^{-1}}$$

$$\mathrm{NaCl}\,(s) + \mathrm{aq} \rightarrow \mathrm{NaCl}\,(\mathrm{aq});\quad \Delta H_{aq} = 335\,\mathrm{kJ\ mol^{-1}}.$$

$$\mathrm{AqNO_3}\,(s) + \mathrm{aq} \rightarrow \mathrm{AqNO_3}\,(\mathrm{aq});\quad \Delta H_{aq} = 22.6\,\mathrm{kJ\ mol^{-1}}.$$

4.4.3 Enthalpy of Reaction

We know that in a chemical reaction, one or more substances (reactants) give rise to entirely different substance(s) (products). Thermodynamically, we say that the chemical system has undergone a change from its initial state to the final state subject to external conditions. The change involves rearrangement of chemical bonds; breaking of existing bonds in reactants and formation of new ones in products. This s invariably accompanied by evolution or absorption of energy in the form of heat. This is referred to as enthalpy of reaction.

> Enthalpy of reaction is the total energy absorbed or given out in the reaction when the reactants have completely changed into products under given external constraints.

For a reaction taking place at a given temperature and volume, first law tells us that t constant volume enthalpy of reaction is equal to the difference in the internal nergies of products and reactants, i.e.

$$\delta Q_V = dU = U_p - U_R.$$

On the other hand, for a reaction carried out isobarically, the constant-pressure nthalpy of reactions is equal to the difference in the enthalpies of the products and the reactants, i.e.

$$\delta Q_p = dH = H_P - H_R$$

SAQ 8

Interpret the equation

$$NaOH\,(s) + HCl\,(g) \rightarrow NaCl\,(s) + H_2O\,(l);\ \Delta H = -177.8\text{kJ}$$

Since enthalpy of a chemical reaction is essentially the energy involved in breaking of bonds in reactants and formation of bonds in products, it is desirable to say something about the enthalpy of dissociation of a bond. The mean enthalpy change in dissociation of all bonds of a particular type in 1 mole of the substance in gaseous state is termed as **bond enthalpy or bond energy.** The enthalpies of dissociation of bonds for some typical cases are listed in Table 4.2.

Table 4.2 : Typical Values of Enthalpies of Dissociation of Bonds

Bond	ΔH (kJ mol^{-1})	Bond	ΔH (kJ mol^{-1})
H—H	436.0	C = C	615.0
H—Cl	431.4	C ≡ C	811.7
O—H	462.8	C—O	351.5
O—O	138.9	C = O	728.0
O = O	497.3	C—N	291.6
C—H	413.4	C—Cl	326.4
C—C	347.7	Cl—Cl	242.7

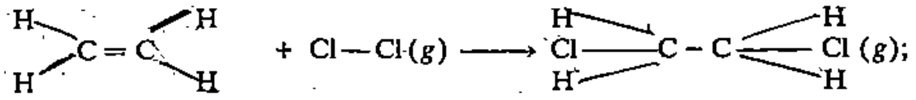
Example 5

Using the values of bond energies from Table 4.1. compute the enthalpy of the reaction

$$C_2H_4(g) + Cl_2(g) \rightarrow C_2H_4Cl_2(g)$$

Solution

The above reaction can be expressed as



We note that in this reaction

i) a Cl — Cl bond breaks in $Cl_2(g)$,

ii) a C = C bond breaks in C_2H_4 while four C – H bonds are unaffected, and

iii) a C – C and two C – Cl bonds are formed in $C_2H_4\ Cl_2$.
Therefore, enthalpy of the reaction is

ΔH = Energy of formation of one C – C bond and two C – Cl bonds + Energy of breaking of a Cl – Cl bond and a C = C bond

$$= (-347.7\text{kJ mol}^{-1}) - 2 \times (326.4\text{kJ mol}^{-1}) + (242.7\text{kJ mol}^{-1}) + (615.0\text{kJ mol}^{-1})$$

$$= -142.8\text{kJ mol}^{-1}.$$

Obviously, it is an exothermic reaction.

4.5 HESS'S LAW

Hess's law is a corollary of the first law of thermodynamics. According to Hess's law, the total heat absorbed or given out in a chemical change at constant volume or constant pressure does not depend on the path followed for the process. This means that when the evolution of a chemical system from the initial state to the final state occurs in one step or a series of stages, the total enthalpy of the reaction remains the same. To illustrate this, let us consider the formation CO_2 gas. We can do so by burning graphite in oxygen directly as well as by oxidation of carbon monoxide produced first. The thermochemical reactions of interest are

$$C(s) + O_2(g) \rightarrow CO_2(g); \ \Delta H = -393.4 \text{ kJmol}^{-1}$$
$$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g); \ \Delta H_1 = -110.5 \text{ kJmol}^{-1}$$
$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g); \ \Delta H_2 = -283.2 \text{ kJmol}^{-1}$$

You will note that ΔH is almost equal to the sum of ΔH_1 and ΔH_2. This shows that Hess's law enables us to add or subtract thermochemical equations in the same way as we do with ordinary algebraic equations.

4.6 SUMMARY

- For one mole of a perfect gas, the difference of heat capacities at constant pressure and constant volume is equal to R; the molar gas constant:

  $$C_p - C_V = R$$

- The equation of state for an adiabatic process in terms of temperature and volume is

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

  In terms of temperature and pressure, we can rewrite it as

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

  In terms of pressure and volume, we have

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

- The adiabatic lapse rate in the stratosphere is brought about by convective currents. It is given by

  $$\frac{dT}{dh} = -\frac{\gamma-1}{\gamma}\frac{Mg}{R}$$

- The propagation of sound in air is an adiabatic process. The expression for the velocity of sound is

  $$v = \sqrt{\frac{E_s}{\rho}} = \sqrt{\frac{\gamma RT}{M}}$$

  where E_s is adiabatic elasticity and ρ denotes average density of air.

- The ratio of adiabatic to isothermal elasticities of a substance is equal to γ; the ratio of heat capacities of a gas at constant pressure and constant volume:

  $$\frac{E_s}{E_T} = \gamma = \frac{C_p}{C_V}$$

- The sum $U + pV$ is called enthalpy:

  $$H = U + pV$$

  The enthalpy is a function of state.

- Enthalpy of a reaction is the total energy absorbed or given out when the reactants have completely changed into products under given external conditions.

- For endothermic reactions $\Delta H < 0$ whereas for exothermic reactions $\Delta H > 0$.

4.7 TERMINAL QUESTIONS

1) Starting from the first law of thermodynamics, show that

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_p - C_V}{V\alpha} - p$$

$$\left(\frac{\partial U}{\partial T}\right)_p = C_p - pV\alpha$$

Hence,

$$E_T = -V\left(\frac{\partial p}{\partial V}\right)_T = \frac{RT}{V} = p$$

and $$v = \sqrt{\frac{RT}{V\rho}} = \sqrt{\frac{p}{\rho}}$$

On substituting for p and ρ, we find that

$$v = \sqrt{\frac{1.01 \times 10^5 \mathrm{N\,m^{-2}}}{1.29 \mathrm{\,kg\,m^{-3}}}}$$

$$= 280 \mathrm{\,ms^{-1}}$$

The difference between the values obtained by Laplace and Newton is

$$v = (331 - 280) \mathrm{\,ms^{-1}} = 51 \mathrm{\,ms^{-1}}$$

% difference with respect to the standard (Laplace's) value $= 15.4\%$

8) From this we understand that one mole of solid NaOH reacts with one mole of HCl at STP to give one mole of solid NaCl and one mole of liquid water. The heat of reaction is -177.8 kJ. The negative sign implies that the reaction is **exothermic.**

TQs

1) From Eq. (4.6) we recall that

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

By definition, the volume expansion coefficient α is given by

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

Hence, $$C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] V\alpha$$

On re-arranging terms, we get the required result:

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_p - C_V}{V\alpha} - p \qquad \text{(i)}$$

To prove the second result, we take U as a function of p and T, i.e.

$$U = U(p, T)$$

Then

$$dU = \left(\frac{\partial U}{\partial P}\right)_T dp + \left(\frac{\partial U}{\partial T}\right)_p dT.$$

so that

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial P}\right)_T dp + p dV$$

On dividing throughout by dT and keeping pressure constant, we find that

$$\left(\frac{\delta Q}{\partial T}\right)_p = C_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$

Hence,

$$\left(\frac{\partial U}{\partial T}\right)_p = C_p - pV\alpha \qquad \text{(ii)}$$

To know pressure variation of internal energy you have to rewrite (i) as

$$\left(\frac{\partial U}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T = \frac{C_p - C_V}{\alpha V} - p \qquad \text{(iii)}$$

By definition, isothermal elasticity

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

or

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

Using this result in (iii), we get pressure variation of internal energy :

$$\left(\frac{\partial U}{\partial p}\right)_T = \frac{pV}{E_T} - \frac{C_p - C_V}{\alpha E_T} \qquad \text{(iv)}$$

2) For a pure paramagnetic substance

$$\delta Q = dU - BdM \qquad \text{(i)}$$

Taking U as a function of T and M, we can write

$$U = U(T, M)$$

so that

$$dU = \left(\frac{\partial U}{\partial T}\right)_M dT + \left(\frac{\partial U}{\partial M}\right)_T dM$$

Substituting this in (i), we find that

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_M dT + \left[\left(\frac{\partial U}{\partial M}\right)_T - B\right] dM$$

Following the procedure used in arriving at Eq. (4.6), you can write

$$C_B - C_M = \left[\left(\frac{\partial U}{\partial M}\right)_T - B\right]\left(\frac{\partial M}{\partial T}\right)_B \qquad \text{(ii)}$$

For a pure paramagnetic substance

$$\left(\frac{\partial U}{\partial M}\right)_T = 0$$

so that

$$C_B - C_M = -B\left(\frac{\partial M}{\partial T}\right)_B \qquad \text{(iii)}$$

From Curie's law

$$M = \frac{kB}{T}$$

where k is a constant.

We can now write

$$\left(\frac{\partial M}{\partial T}\right)_B = -\frac{kB}{T^2} \qquad \text{(iv)}$$

This result is useful in understanding the operating principle of production of low temperatures using adiabatic demagnetization. You will learn to apply it in Unit 7.

3) For an ideal gas, the equation of state is

$$pV = RT \qquad \text{(i)}$$

Hence

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{RT}{p^2 T} = \frac{1}{p} \qquad \text{(ii)}$$

That is, β_T is inverse of pressure for an ideal gas. You should have expected this result from Eq. (4.19). Similarly, for a van der Waals' gas

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \qquad \text{(iii)}$$

or

$$p = \frac{RT}{V - b} - \frac{a}{V^2}$$

NOTES

Utter Pradesh
Rajarshi Tandon Open University

UGPHS-06
THERMODYNAMICS AND STATISTICAL MECHANICS

Block

2

THE SECOND AND THE THIRD LAWS OF THERMODYNAMICS

UNIT 5
Entropy and the Second Law of Thermodynamics 5

UNIT 6
The Thermodynamic Potentials 23

UNIT 7
Phase Transitions 41

UNIT 8
Production of Low Temperatures and the Third Law 52

BLOCK INTRODUCTION

In Block 1, you have studied the basic concepts of thermodynamics, measurement of temperature, the first law of thermodynamics and its applications. Block 2 deals with entropy, the second law of thermodynamic, thermodynamic potentials, phase transitions, production of low temperature and the third law of thermodynamics. In Unit 5, we have introduced the concept of entropy and established its intimate connection with the second law of thermodynamics. You will learn to derive expressions for change in entropy of an ideal gas and efficiency of a reversible engine. In this unit, you will realise why soon after Clausius introduced the concept of entropy, thermodynamics became such a powerful science. This is essentially because it connects thermodynamics with statistical mechanics. That is, entropy is a tool by which we can correlate the macroscopic and microscopic behaviour of a system.

In Unit 6, we have discussed thermodynamic potentials whose knowledge is essential to determine the general condition of thermodynamic equilibrium. You would learn that they are a treasure of information for all important thermodynamic relations. They are handy in obtaining Maxwell's relations and can be used to study phase transitions and physics of low temperatures. You will study these in Units 7 and 8, respectively.

The units in this block are essentially of equal length. To facilitate your work, we are suggesting the following estimates for the study time required for each unit:

Unit 5	6 h
Unit 6	6 h
Unit 7	5 h
Unit 8	6 h

The mathematics used in these units is quite simple and you are advised not to memorise relations. Our emphasis will be on the use of mnemonic diagrams for deriving a relation of interest. Some illustrations to this effect are given in the text. You will see many more in the video programme entitled "Mnemonics in Thermodynamics". We hope that you will enjoy the subject.

We wish you success.

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UNIT 5 ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

Structure

5.1 Introduction
  Objectives
5.2 What is Entropy?
5.3 The Second Law of Thermodynamics
5.4 Entropy Change of an Ideal Gas
  Entropy of Mixing
  Entropy of Phase Transition
5.5 The Carnot Cycle
  Heat Engines
  Refrigerators
5.6 Summary
5.7 Terminal Questions
5.8 Solutions and Answers

5.1 INTRODUCTION

n Block 1, you have learnt that the first law of thermodynamics is essentially the law of onservation of energy for thermodynamic systems. Though this law is universal in a sense, has some inherent limitations. Let us consider a cup of hot tea. The first law tells us that he total energy of the tea, cup and the surroundings is constant. From experience we know hat tea will lose energy (heat) to the surroundings and get cooled. But the first law does not ule out the possibility of the surroundings (at a lower temperature) transferring some of its nergy to the tea (at a higher temperature). (If this were true, we could have generated energy vith no fuel and avoided all accompanying hazards!) In spite of the fact that total energy emains constant in both processes and that the first law is not violated, we all are convinced hat heat does not flow on its own from a body at lower temperature to a body at higher emperature. But why? This is because cooling is a **unidirectional** natural process. You nay be familiar with many other unidirectional processes occurring in physically diverse ystems. We may mention spontaneous expansion of a gas into fixed volume (free expansion), ischarging of a battery when in operation (chemical process), and intermixing of two fluids liffusion), among others.

re you convinced why natural processes take place in a particular direction? The question ow arises: What determines the direction of a natural process? Can we give a quantitative ermodynamic criterion which governs this change? The answer to these and many other ich questions was given by Clausius in 1850 when he introduced a new thermodynamic nction called **entropy** (from the Greek word **trope**). Clausius showed that for natural ocesses, entropy of the universe can never decrease. That is, natural processes evolve in e direction of increase of entropy. But what is entropy? To seek answer to this question, e begin this unit by defining entropy with reference to a reversible process, though natural ocesses are irreversible. How do we define entropy and compute entropy change r irreversible processes? You will discover the answer to this question as you go through is unit. In Sec. 5.3, we postulate the second law of thermodynamics in terms of entropy. xpressions for change in entropy of an ideal gas are derived in Sec. 5.4. Next, we calculate e efficiency of a reversible engine using *T-S* diagram. This discussion is followed by the nventional statements of the second law of thermodynamics and their equivalence.

bjectives

fter going through this unit, you will be able to :

That is, when heat transfer is reversible, the changes in entropies of blocks A and B are numerically equal. But they have opposite signs. As a result, there is no net change in entropy and you can say that in a reversible process, total entropy is conserved.

---

iv) Eq. (5.4) has been derived for a reversible process. What about natural processes like free expansion or heat flow? Refer to Fig. 5.1 and consider heat flow along the path $1C2$. It is an irreversible process. You would now like to know how to compute entropy change for an irreversible process. To this end, we assume that heat is given in infinitesimal steps so that irreversible process between states 1 and 2 can be replaced by a reversible process through infinite quasistatic equilibrium states. Then we use Eq. (5.4) to compute the entropy change for each quasistatic state. And we can say that, between the same initial and final states, the change in entropy is given by the same equation (Eq. (5.4)) for reversible as well as irreversible processes. This is because entropy is a property of state and the entropy difference does not depend on how a system got into that state.

To clarify these ideas, we wish you to go through the following example carefully

---

Example 2

A block of copper weighing 1.5 kg is heated from 300K to 350K. Calculate the entropy change of the block. The specific heat capacity of copper is 389J $\text{kg}^{-1}\,\text{K}^{-1}$. Assume that heat is added irreversibly.

Solution

Although the heat has been added irreversibly, we can calculate ΔS using Eq. (5.4):

$$\Delta S = \int_{300\text{ K}}^{350\text{ K}} \frac{\delta Q_{\text{rev}}}{T}$$

The heat absorbed for an infinitesimal rise in temperature is given by

$$\delta Q_{\text{rev}} = m \times s \times \Delta T$$

You should not confuse S with specific entropy

where m is the mass and s is the specific heat of the block. On inserting the given data, we find that

$$\delta Q_{\text{rev}} = (1.5\text{ kg}) \times (389\text{ J kg}^{-1}\text{K}^{-1}) \times \Delta T$$

so that

$$\begin{aligned}\Delta S &= \int_{300\text{ K}}^{350\text{ K}} \frac{(1.5\text{ kg}) \times (389\text{ J kg}^{-1}\text{K}^{-1}) \times \Delta T}{T}\\ &= 583.5 \ln\left(\frac{350}{300}\right)\text{ JK}^{-1}\\ &= 583.5 \times 2.3 \times \log_{10}(1.67)\text{ JK}^{-1}\\ &= 583.5 \times 2.3 \times 0.0671\\ &= 90.0\text{ JK}^{-1}\end{aligned}$$

You may now like to work out an SAQ to check your progress.

SAQ 1

10 g of steam at 100°C and 1 atm pressure condense at the same temperature and pressure. Calculate the entropy change. Latent heat of steam = 2.238×10^6 J kg^{-1}.

What is the physical significance of entropy? To discover this, let us recall as to what happens when heat is added to ice. You know that every substance is made up of atoms/molecules. Addition of heat causes ice to melt. As a result, molecular arrangement (in water) is somewhat loosened. If you add more heat, water changes into the vapour state. In this state, molecular motion is quite disordered. So we can say that **addition of heat (or increase in entropy) creates chaos or disorder**. On the other hand, when a gas condenses or a liquid solidifies (giving out heat), the molecular arrangement becomes more ordered. That is, disorder decreases when a gaseous substance changes into the solid state and vice versa. So you can say that **entropy is a measure of disorder** in the system.

So far we have introduced the concept of entropy and computed entropy change in a reversible/irreversible process. How does such a change influence the system, its surroundings and hence the universe? This study leads us to the second law of thermodynamics, which is a universal law. It applies to processes taking part in our body, to combustion of fuel in an automobile, an aeroplane and a rocket as well as working of refrigerators. It enables us to specify the direction of evolution of all natural processes. We will now discuss it in detail.

5.3 THE SECOND LAW OF THERMODYNAMICS

Consider that an infinitesimal amount of heat δQ flows from the surroundings at temperature T_{surr} to the system under consideration at temperature T_{sys}. The net change in the entropies of the system and surroundings is given by

$$\Delta S = \Delta S_{sys} + \Delta S_{surr} = \delta Q\left(\frac{1}{T_{sys}} - \frac{1}{T_{surr}}\right) \geq 0 \qquad (5.6)$$

You would note that the equality sign holds for reversible heat flow, whereas greater than sign signifies irreversible heat flow. Since all natural processes are irreversible, you may be tempted to conclude that entropy of the universe is continuously increasing. If you think so, you are on the right track. This continuous increase of entropy in natural processes is known as the **principle of increase in entropy**. And the second law of thermodynamics may be stated as follows:

The second law has been stated in somewhat different but essentially equivalent forms by Kelvin-Planck and Clausius. You will learn these in Sec. 5.5.

> The entropy of the universe can never decrease.

Consider the construction of a building from materials that were initially dispersed about the earth. In this process, matter goes from a highly disorganised state to a very ordered state. That is, the entropy decreases. In Unit 3 of Block 1, you have learnt that the internal energy of a growing child or a plant increases. But the growth of a living organism from a random mix of molecules is accompanied by entropy decrease. This seems to contradict the first as well as the second law of thermodynamics. To understand that this is not so, you may enquire: What is responsible for life on the earth? We can retrace it to the energy generated in sun's core by nuclear fusion. For example, plants use solar energy for photosynthesis and create food. Similarly, humans receive this energy via food chain. So to answer the above question, you have to consider the earth-sun system. If you do so, you will find that the magnitude of entropy decrease associated with life on earth is less than the entropy increase associated with nuclear fusion in the core of the sun. That is, the organisation of matter is governed by a tendency towards greater disorder elsewhere (sun) in the universe. This means that entropy of the earth-sun system increases.

Thus a more formal statement of the second law in terms of entropy reads as follows:

> When an isolated (closed) system undergoes a change, its entropy cannot decrease; it increases or remains constant.

You may now ask: How long will entropy continue to increase? What is the future of the natural world? We expect that entropy of the universe must have some upper limit, marching towards a stagnant stage.

You must now be convinced that the first law of thermodynamics is a statement of the law of conservation of energy and the second law relates (available) energy to entropy. You can use the integrated statement of these laws to compute entropy difference for any process. Let us learn to do so now.

The Entropy Form of the First Law

The first law of thermodynamics establishes the existence of internal energy (U) as a function of state. Similarly, the second law introduces entropy(S) as a state function. Now the question arises: Can we relate these functions? If so, how? To discover the answer to this question, you may recall from Unit 3 that for any change of state not involving diffusive interactions, the change in U is given by

$$dU = \delta Q - \delta W \tag{5.7}$$

For an infinitesimal reversible process between two equilibrium states, the second law of thermodynamics tells us that

$$dS = \frac{\delta Q}{T} \tag{5.8}$$

These equations may be combined to give

$$T\,dS = dU + \delta W \tag{5.9}$$

This is one of the most important thermodynamic relations. In the next unit, you will use it to derive many useful thermodynamic relations.

Proceeding further, we note that for a pVT system, $\delta W = p\,dV$ so that Eq. (5.9) takes the form

$$T\,dS = dU + p\,dV \tag{5.10}$$

You will recognise that this equation relates all thermodynamic variables.

Following Eq. (4.13), we can write it in three equivalent forms:

$$T\,dS = nc_V\,dT + p dV \tag{5.11a}$$

$$T\,dS = nc_p\,dT - V dp \tag{5.11b}$$

and

$$T\,dS = \frac{1}{R}\,[\,c_p\,p\,dV + c_V\,V\,dp\,] \tag{5.11c}$$

where c_p and c_V denote specific heats per mole at constant pressure and constant volume, respectively.

You can use Eqs. (5.11a, b,c) to compute entropy changes for an ideal gas under different physical conditions. Before we do so, we wish that you should answer the following SAQ

SAQ 2

Write the combined mathematical forms of the first and second laws of thermodynamics for

a) a stretched wire,

b) a surface film, and

c) a paramagnetic substance.

5.4 ENTROPY CHANGE OF AN IDEAL GAS

Let us consider that n moles of an ideal gas at temperature T are contained in a cylinder. Depending on the conditions, its state will be described by one equation out of the set of Eqs.(5.11a, b, c). Let us first consider Eq. (5.11a). If you divide throughout by T and use the equation of state ($pV = nRT$), you will get

$$dS = n\,c_V\frac{dT}{T} + n\,R\,\frac{dV}{V} \tag{5.12}$$

Hence, the change in entropy of an ideal gas between states characterised by temperatures T_1 and T_2, and volumes V_1 and V_2 is obtained by integrating this expression. If C_V is independent of temperature, you will find that

$$\Delta S = nc_V \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right) \tag{5.13}$$

which is the same as Eq. (5.2).

To learn to apply this equation, you should study the following example.

Example 3

Calculate the increase in entropy of 1 g of hydrogen when its temperature is raised from –173 °C to 27 °C and its volume becomes four times. Given $C_V = 2.43$ cal g^{-1} K^{-1}, $R = 2.01$ cal mol^{-1} K^{-1} and $M_H = 2$.

Solution

For n moles of an ideal gas, the entropy change is calculated from Eq.(5.13). However, for 1 g of the gas, you have to replace R by $r = R$ /Mol.weight:

$$r = \frac{2.01 \text{ cal mol}^{-1}\text{K}^{-1}}{2 \text{ g mol}^{-1}} = 1.005 \text{ cal g}^{-1}\text{K}^{-1}$$

On inserting the given data, you will get

$$\begin{aligned}\Delta s &= 2.303\left[c_V \log_{10}\left(\frac{T_2}{T_1}\right) + (1.005 \text{ cal g}^{-1}\text{K}^{-1})\log_{10}\left(\frac{V_2}{V_1}\right)\right]\\ &= 2.303 \times [\,(2.43 \text{ cal g}^{-1}\text{K}^{-1}) \times \log_{10} 3 + (1.005 \text{ cal g}^{-1}\text{K}^{-1}) \times \log_{10} 4\,]\\ &= 2.303\,[2.43 \times 0.4771 + 1.005 \times 0.6021\,] \text{ cal g}^{-1}\text{K}^{-1}\\ &= (2.669 + 1.393) \text{ cal g}^{-1}\text{K}^{-1}\\ &= 4.062 \text{ cal g}^{-1}\text{K}^{-1}\end{aligned}$$

Starting from Eqs. (5.11b,c), you can show that entropy change between states defined by (T_1, p_1) and (T_2, p_2) is given by

$$\Delta S = nc_p \ln\left(\frac{T_2}{T_1}\right) - nR \ln\left(\frac{p_2}{p_1}\right) \qquad (5.14)$$

If reference states are defined by (p_1, V_1) and (p_2, V_2), the entropy change is

$$\Delta S = nc_p \ln\left(\frac{V_2}{V_1}\right) + nc_v \ln\left(\frac{p_2}{p_1}\right) \qquad (5.15)$$

A gas may be made to expand or compress isothermally. When one mole of an ideal gas undergoes an isothermal change, Eqs. (5.13) and (5.14) predict that entropy change is given by

$$\Delta S_T = R \ln\left(\frac{V_2}{V_1}\right) = R \ln\left(\frac{p_1}{p_2}\right) \qquad (5.16)$$

The subscript T in Δs_T signifies that temperature remains constant.

That is, *when an ideal gas undergoes an isothermal expansion* ($V_2 > V_1, p_1 > p_2$; $T =$ constant), *its entropy increases.* What change in entropy occurs when a gas undergoes isothermal compression? We expect that entropy will decrease.

Example 4

One mole of an ideal gas expands isothermally to four times its initial volume. Calculate the entropy change in terms of R, the gas constant.

Solution

From Eq. (5.16), we have

$$\begin{aligned}\frac{\Delta s_T}{R} &= \ln(V_2/V_1)\\ &= 2.303 \log_{10}(V_2/V_1)\end{aligned}$$

Since $V_2/V_1 = 4$, the entropy change during isothermal expansion, in terms of R, is

$$\begin{aligned}\frac{\Delta s_T}{R} &= 2.303 \log_{10} 4\\ &= 2.303 \times 0.6020\\ &= 1.386\end{aligned}$$

$$\Delta s_{evap} = \frac{\Delta h_{evap}}{T_{evap}} \tag{5.23}$$

where h_{evap} is the molar enthalpy of vaporisation and T_{evap} is the boiling point.

In the following example, we have illustrated the use of some of these relations to compute entropy changes.

Example 6

The enthalpy of vaporisation of ethanol is 43.5kJ mol^{-1} at its normal boiling point of 351.5K. Compute the entropy of vaporisation.

Solution

From Eq. (5.23),

$$\Delta s_{vap} = \frac{43500\ \text{J mol}^{-1}}{351.5\ \text{K}} = 124\ \text{J K}^{-1}\text{mol}^{-1}$$

To enable you to get an idea about the relative magnitudes of Δs_{vap} and Δs_{fusion}, we have computed Δs_{fusion} also. The enthalpy of fusion of ethanol is 4.6kJ mol^{-1} at its normal melting point of 156K so that

$$\Delta s_{fusion} = \frac{4600\ \text{J mol}^{-1}}{156\ \text{K}} = 29.5\ \text{J K}^{-1}\text{mol}^{-1}$$

You will note that Δs_{vap} is considerably greater than Δs_{fusion}. This difference implies that entropy increases as a system becomes less restricted. When a solid melts, its atoms become less ordered in their locations and motion. When a liquid vaporises, molecules find much greater freedom of movement in the gaseous state.

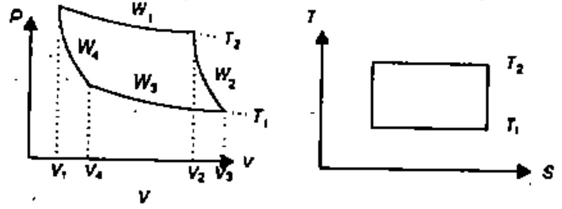
SAQ 4

The melting point of water at 1 bar is 273.16K and the latent heat of melting is 334.4 Jg^{-1}. Calculate the entropy of solidification for one mole of water.

You now know that entropy is conserved in a cyclic reversible process. The simplest yet most important reversible cycle which has great practical utility is the Carnot cycle. Let us now discuss it in some detail.

5.5 THE CARNOT WORD CYCLE

Refer to Fig. 5.3a. It is a schematic representation of the Carnot cycle on the indicator diagram. You will note that this cycle consists of four reversible processes (steps):



(a) (b)

Fig. 5.3: (a) Carnot cycle on p-V diagram. (b) Carnot cycle on T-S diagram

i) isothermal expansion

ii) adiabatic expansion

iii) isothermal compression, and

iv) adiabatic compression.

An indicator diagram depicts a process in terms of p and V. Similarly, a T-S diagram represents a process is terms of T and S variables.

In Fig. 5.3b, we have depicted the Carnot cycle on a T-S diagram. (It is another way of representing thermodynamic behaviour of a substance.) For an ideal gas, the isotherms are straight lines of constant T whereas the adiabatics are straight lines of constant S ($\delta Q = 0 = dS$). To compute net entropy change in one cycle, let us take one mole of an ideal gas enclosed in a cylinder.

Step I

The gas absorbs heat Q_1 reversibly and is allowed to expand isothermally from volume V_1 to V_2. The pressure decreases from p_1 to p_2. Using Eq. (5.3), you can calculate the increase in entropy of the gas. The result is

$$\Delta s_1 = \frac{Q_1}{T_1} \tag{5.24a}$$

Step II

Now the gas in the cylinder is made to expand adiabatically from volume V_2 to V_3. The pressure falls from p_2 to p_3.

From Unit 4, you would recall that in an adiabatic process, no heat exchange takes place between the system and its surroundings. The first law of thermodynamics tells us that in such a case, internal energy of the system decreases and its temperature falls. Let us assume that temperature drops from T_1 and T_2. But since no heat transfer occurs, entropy does not change, i.e.,

$$\Delta s_2 = 0 \tag{5.24b}$$

Step III

The gas at temperature T_2 is now compressed isothermally till its volume is reduced to V_4. In this process, the gas rejects heat Q_2 to its environment and the change in entropy is given by

$$\Delta s_3 = -\frac{Q_2}{T_2} \tag{5.24c}$$

Step IV

Finally, the gas is compressed adiabatically to its original volume and pressure. As a result, its original temperature is also restored but its entropy is conserved during the process:

$$\Delta s_4 = 0 \tag{5.24d}$$

Since the Carnot cycle is reversible, $\Delta s = 0$. That is, no net entropy change occurs and you can write

$$\Delta s_1 + \Delta s_2 + \Delta s_3 + \Delta s_4 = 0$$

In deriving the expression for efficiency, we have not followed the historical development for elegance and ease.

On using Eqs. (5.24 a-d), you will get

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

You can rewrite it as

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \tag{5.25}$$

This result shows that the amount of heat absorbed (rejected) in a reversible cycle is proportional to the temperature of source (sink).

Heat Engines

From your school physics curriculum, you would recall that $Q_1 - Q_2 = W$ is the maximum heat available for doing work (measured in heat units). In a power plant (automobile or a steam engine) we burn fuel for generating Q_1 which, in turn, results in W through the motion of a turbine (piston). The difference is released to surroundings (and is partly responsible for thermal pollution and ecological disturbance). The ratio $\frac{W}{Q_1}$ characterises the efficiency of a machine which converts heat into work. A machine responsible for conversion of heat into work is called a **heat engine**. The efficiency of a machine operating between fixed temperatures T_1 and T_2 is given by

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

Using Eq. (5.25), you can write

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

so that

$$\boxed{\eta = 1 - \frac{T_2}{T_1}} \qquad (5.26)$$

Eq. (5.26) shows that

i) η depends on $T_1 - T_2$; greater the temperature difference, more will be η. In practice, T_2 is limited to the temperature of the surroundings and the only way to increase η is to raise T_1. That is, heat is more useful when it is supplied at a higher temperature. This explains why saturated steam at high pressure is a more efficient working substance. Does this not mean that when heat flows from hotter to colder bodies, it is degraded? Certainly, its usefulness is reduced.

ii) η is always less than one. This is a fundamental limitation imposed by the second law of thermodynamics. We know that most of the electricity is generated in large fossil (coal, oil, gas) or nuclear power plants. These are basically heat engines (where energy is released in chemical or nuclear reactions). The working substance, water, is heated in a boiler and converted into steam at high pressure. It expands adiabatically in a turbine, which is coupled to a generator and converts mechanical energy into electrical energy. The maximum efficiency of a fossil fuel plant is about 50% whereas this figure is 40% for a nuclear plant. That is, only half of the heat generated in a plant is utilised in getting useful work. You may now ask: What happens to the remaining heat? It is not available for any useful purpose. That is, a substantial amount of our expensive fuel ends up as waste heat. It is released in the environment and causes thermal pollution which is responsible for various ecological problems. Today, it has acquired menacing proportions leading to rise in earth's temperature threatening our survival on this planet.

iii) $\eta = 0$ for $T_1 = T_2$. That is, we cannot operate a cycle (and convert heat into work) if there is no temperature difference. To understand this, you may imagine the following situation:

You take your motor boat to sea and run out of fuel. (If you are lucky, you may be rescued by another boat.) The first law of thermodynamics permits your safe return as the ocean has a vast amount of thermal energy. But the second law tells us that this energy cannot be converted into useful work because the ocean is at a uniform temperature. This fact is contained in Kelvin-Planck statement of the second law of thermodynamics:

> It is not possible to construct an engine, no matter how ideal, which working in a cycle will transform entire heat into work.

iv) The efficiency of a Carnot engine is independent of the nature of the working substance. You may expect that real engines will also be independent of the working substance. We may ask: Why are we then so concerned about particular fuels? The answer to this question lies in their availability, economics, technological feasibility and environmental factors. That is, thermodynamic considerations alone cannot decide between various methods of harnessing energy sources.

Example 7

The cluster of nuclear power plants at Tarapur produces 540 MW of electric power. In the reactor core, energy is released (as heat) at the rate of 1600 MW. Steam produced in the reactor enters the turbine at a temperature of 560K and leaves it at 350K. Calculate the efficiency of the power plant.

Solution

The thermodynamic efficiency is given by Eq. (5.26):

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{350\text{K}}{560\text{K}} = 0.375$$

That is, the system is only 37.5% efficient.

The actual efficiency of a power plant is defined as the ratio of electric power output to the thermal power produced:

$$\eta = \frac{540\ \text{MW}}{1600\ \text{MW}} = 0.337$$

The waste heat of 1060 MW is normally discharged in a river (or a sea). This is a huge amount of energy. To reduce problems arising out of this, the designers of the power plant at Narora (UP) have made use of cooling towers where expanding steam is cooled. As a result, heat is released to the atmosphere (air) rather than to water.

Diesel engines used in vehicles constitute another example of heat engines. A typical automobile engine operates at about 800K and rejects exhaust gases to the environment at about 300K. The maximum possible efficiency is then

$$\eta = 1 - \frac{300\text{K}}{800\text{K}} = 0.63$$

In practice, the actual efficiency is much lower and emanating hot gases are responsible for greenhouse effect and pollution of environment. This has increased to alarming proportions, particularly in cities like Delhi, Calcutta, Bombay, Bangalore, Madras, Ahmadabad, Kanpur, etc. So to keep air clean, we should get our vehicles tuned regularly.

SAQ 5

a) In the tropics, the temperatures at the surface of the ocean and at a depth of 300m are 25°C and 5°C, respectively. Will you recommend to tap this energy?

b) A Carnot engine is made to work between ice point (273K) and nitrogen temperature (77K). Calculate its efficiency. Is it possible to attain this figure in actual practice?

v) You would note that the thermodynamic efficiency given by Eq. (5.26) is maximum. This is because all the processes involved in operation are reversible. This result is known as **Carnot's theorem**. It may be stated as follows:

> Of all heat engines working between same temperatures, the reversible Carnot engine has the maximum efficiency.

Carnot's theorem tells us that :

i) all reversible engines working between the same temperature limits have the same efficiency, and

ii) the nature of the working substance is not important.

The beauty of Carnot cycle lies in the fact that all its stages are completely reversible. So if you invert the sequence of processes occurring in a heat engine, you will obtain a refrigerator. Do you know that an air conditioner is also a refrigerator designed to cool a room? Let us now know the physics of this device.

Refrigerator

On your TV set, you may have seen a penguin advertising for a refrigerator: **It is the coolest one.** Have you ever thought as to how cooling is achieved in a refrigerator? Thermodynamically, a refrigerator makes heat to flow in a direction it does not spontaneously go, i.e., from a lower temperature to a higher temperature. You can feel it by putting your hand near the coils of the refrigerator. This observed fact is contained in the statement of second law of thermodynamics due to Clausius:

> It is impossible to make a refrigerator, operating in a cycle, whose sole result is the transfer of heat from a cooler body to a hotter body.

At first, you may think that the Clausius and Kelvin-Planck statements of the second law are unrelated. But it is not true. Both statements are equivalent and their consequences are identical. In fact, each statement implies the other. If either of these statements is proved false, the other one will necessarily be not true. To understand this, let us suppose that Kelvin-Planck statement is not true. This means that you can completely convert a given amount of heat taken from a body into work. From experience, we know that this work (order) can be changed into heat (chaos or disorder) through friction or other dissipative mechanisms. In this process, you can raise the temperature of a body. A continuous repetition will enable you to raise the temperature indefinitely. The net result of this activity will be to transfer heat from a body at lower temperature to a body at higher temperature without any external effort. But this violates the statement of second law due to Clausius.

Similarly, you can argue that if Clausius statement is false, Kelvin-Planck statement will necessarily be violated.

Having learnt the guiding principle of a refrigerator, you may ask: How is its effectiveness measured? It is usually expressed as **coefficient of performance** (*COP*) or **figure of merit**. Let us discuss it now.

The coefficient of performance of a refrigerator is defined as the ratio of total heat extracted at lower temperature to the amount of input work done. Mathematically, we can write it as

$$COP = \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c} \tag{5.27}$$

where Q_c is heat extracted at lower temperature (cooler body) and Q_h is heat rejected at higher temperature (kitchen environment). Using Eq. (5.25), you can rewrite it as

$$COP = \frac{T_c}{T_h - T_c} \tag{5.28}$$

You can derive following conclusions from this result:

(i) *COP* is directly proportional to T_c. That is, the coefficient of performance will be small when T_c is low. In fact, *COP* approaches zero as $T_c \rightarrow 0$. This means that more work will have to be done, i.e., more energy will be used up by the refrigerator for transferring the same amount of heat as T_c decreases. So you can say that the quality of heat is degraded at lower temperatures. If $T_c = 0$, infinite work will be required to produce cooling. Is it possible to attain this temperature?

(ii) *COP* is inversely proportional to $T_h - T_c$, i.e., lower the difference between hot and cold bodies, greater will be the coefficient of performance. As $T_h - T_c$ approaches zero, *COP* approaches infinity. This means that a refrigerator will be most effective when eatables/chemicals placed inside are close to the temperature of surroundings. So to conserve energy, we should not put eatables in the kitchen refrigerator while they are very hot.

Example 8

A typical home freezer operates between –18°C and 30°C. Calculate the maximum value of *COP* of this refrigerator. With this *COP*, how much electrical energy would be required to freeze 0.5 kg of water, initially at 0°C. Given latent heat of fusion = 334kJ kg^{-1}.

Solution

The coefficient of performance is given by

$$COP = \frac{T_c}{T_h - T_c} = \frac{255\text{K}}{303\text{K} - 255\text{K}} = \frac{255\text{K}}{48\text{K}} = 5.3$$

To produce 0.5 kg of ice, you have to extract heat from water. It is given by

$$Q = mL$$

where L is latent heat of fusion. Hence

$$Q = (0.5\text{ kg}) \times (334\text{ kJ kg}^{-1}) = 167\text{ kJ}$$

Using Eq. (5.27), you can write

$$W = \frac{Q_c}{COP} = \frac{167\text{ kJ}}{5.3} = 31.5\text{ kJ}$$

In actual practice, *COP* would be lower and the corresponding work input would be higher because of irreversible processes.

You would recall that when we discussed temperature measurement in Unit 2, we faced the problem that no single method works for all temperatures. Ultimately, we recognised that gas thermometer is the best laboratory standard. But even a helium gas thermometer fails to work below about 1K. Does this mean that we cannot measure temperature below 1K? The operation of a reversible heat engine provides a way of measuring temperature, that is, independent of the particular device and can be used for any value/range. All that you have to do is to operate any thermodynamic device through a completely reversible cycle. If you are able to measure heats absorbed and rejected by the working substance, you can easily calculate the ratio of two temperatures. Knowing one of these temperatures, you can determine the other. As such, it may seem to be a rather obscure way to measure temperature. But it is particularly useful at very low temperatures. In fact, it provides us an absolute way of defining temperature. The temperature so defined is called the **thermodynamic temperature** and the scale on which it is measured is called the **absolute or thermodynamic temperature scale.**

Thermodynamically, the zero of the absolute scale—**absolute zero**–represents a state of maximum order. It corresponds to – 273°C. (It means that ice point corresponds to 273.16K.) The magnitude of each degree on absolute scale is equal to the size of one degree of celsius scale.

Let us now sum up this unit.

5.6 SUMMARY

- Entropy is defined through the relation

$$dS = \frac{\delta Q_{rev}}{T}$$

Entropy is an extensive variable. Moreover, entropy is a state function.

- Entropy is a measure of disorder in the system; more chaotic the system, greater will be its entropy.

- The second law of thermodynamics is essentially the principle of increase of entropy. It states that, when a closed system undergoes a change, its entropy cannot decrease; it either increases or remains constant. Mathematically, it may be expressed as:

$$\Delta S \geq 0$$

- Two other equivalent statements of second law of thermodynamics are due to Kelvin and Planck, and Clausius. The Kelvin-Planck statement governs the working of a heat engine.

It states that we cannot construct an engine, no matter how ideal, which, working in a cycle, will transform the entire heat into work. The efficiency of a heat engine is given by:

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

- The efficiency of Carnot's engine is maximum.

- The Clausius statement of second law governs the working of a refrigerator. It may be stated as: It is impossible to make a refrigerator operate in a cycle so that its sole result is the transfer of heat from a cooler body to a hotter body.

The coefficient of performance of a refrigerator is given by:

$$COP = \frac{Q_c}{Q_h - Q_c} = \frac{T_c}{T_h - T_c}$$

- The entropy change of an ideal gas can be calculated using the relations

$$S = n\,c_V \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)$$

$$= n\,c_p \ln\left(\frac{V_2}{V_1}\right) + n\,c_V \ln\left(\frac{p_2}{p_1}\right)$$

$$= n\,c_p \ln\,(T_2/T_1) - nR \ln\,(p_2/p_1)$$

5.7 TERMINAL QUESTIONS

1) A huge copper block at 1000K is joined to another huge copper block at 500K by a copper rod. The rate of heat conduction is 10^4 Js^{-1}. Calculate the increase in entropy of the universe due to this process.

2) Eddington proposed that entropy is the arrow of time. Comment.

3) m gram of water at temperature T_1 are mixed with an equal mass of water at temperature T_2. Show that the change in entropy is $2m\,C_p \ln\,(T_{av}/T_1 T_2)$, where $T_{av} = \frac{T_1+T_2}{2}$.

5.8 SOLUTIONS AND ANSWERS

SAQ's

1.
$$\delta Q = ml$$
$$= 10^{-2}\text{ kg} \times 2.238 \times 10^{6}\text{ J kg}^{-1}$$
$$= 2.238 \times 10^{4}\text{ J}$$

Hence

$$\Delta S = \frac{\delta Q}{T} = \frac{2.238 \times 10^4\text{ J}}{373\text{ K}}$$
$$= 60\text{ JK}^{-1}$$

2.
a) $T\,dS = dU - F\,dl$

b) $T\,dS = dU - \sigma\,dA$

c) $T\,dS = dU - B\,dM$

3.
$$\Delta s_V = n\,c_V \ln\left(\frac{T_2}{T_1}\right)$$
$$= c_V \ln 2$$

Since $c_V = \frac{3}{2}R$, we find that

$$\Delta s_V = \frac{3}{2} \times \left(8.314\text{ JK}^{-1}\text{mol}^{-1}\right)\ln 2$$
$$= 8.64\text{ J K}^{-1}$$

4.
$$\Delta s_{\text{melt}} = \frac{m\,\Delta l}{T_{\text{melt}}}$$
$$= \frac{18\text{ g} \times 334.4\text{ Jg}^{-1}}{273.16\text{ K}}$$
$$= \frac{6019.2\text{ J}}{273.16\text{ K}}$$
$$= 22\text{ J K}^{-1}$$

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

$$= 1 - \frac{278}{298}$$

$$= \frac{20}{298}$$

$$= 0.07$$

$$= 7\%.$$

This is a highly inefficient system and it is not advisable to tap this source of energy.

b) $\eta = 1 - \frac{77}{273} = \frac{196}{273}$

$$= 0.72$$

$$= 72\%$$

It is too high to be attainable in practice.

TQ's

1. By carrying out the heat transfer reversibly, we can calculate that

$$\Delta S = (q/T_1) - (q/T_2) = 10^4\ \mathrm{J\,s^{-1}}[(1/500\ \mathrm{K}) - (1/1000\ \mathrm{K})] = 10\ \mathrm{J\,K^{-1}s^{-1}}$$

Thus, the entropy of the universe increases by 10 J K^{-1} per second.

2. The statement is justified. If you calculate entropy of the universe at two different times, the point of higher entropy would correspond to the point of later time. This statement is further justified by the fact that the universe has been expanding uniformly ever since its creation. Even if one observes the motion of galaxies, these are found receding with respect to any point of observation. This means that the entropy of the universe is increasing continuously, as does time.

3. Since the masses of water being mixed are equal, the temperature of the mixture will be the arithmetic mean of T_1 and T_2:

$$T_{\text{mix}} = \frac{T_1 + T_2}{2} = T_{av}$$

Since the process is isobaric, the change in entropy of water sample whose temperature rises from T_1 to T_{av} is given by

$$\Delta S_1 = \frac{\delta Q}{T}$$

$$= m\,C_p \ln\left(\frac{T_{av}}{T_1}\right) \qquad \text{(i)}$$

Similarly, the change in entropy of water sample whose temperature falls from T_2 to T_{av} is

$$\Delta S_2 = m\,C_p \ln\left(\frac{T_{av}}{T_1}\right) \qquad \text{(ii)}$$

Hence, the net change in entropy is

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

$$= m\,C_p \ln\left(\frac{T_{av}}{T_1}\right) + m\,C_p \ln\left(\frac{T_{av}}{T_2}\right) \qquad \text{(iii)}$$

Since $\ln a + \ln b = \ln\ (ab)$, you can rewrite it as

$$\Delta S = m\,C_p \ln\left(\frac{T_{av}^2}{T_1 T_2}\right)$$

$$= m\,C_p \ln\left(\frac{T_{av}}{\sqrt{T_1 T_2}}\right)^2$$

$$= 2m\,C_p \ln\left(\frac{T_{av}}{\sqrt{T_1 T_2}}\right) \qquad \text{(iv)}$$

ince $\ln x^n = n\ \ln\ x$.

6.2 THE THERMODYNAMIC POTENTIAL FUNCTIONS

Consider a gas contained in a cylinder fitted with frictionless piston. You would agree that the behaviour of this gas can be described in terms of any two variables amongst p, V and T. The third one is automatically fixed in view of the equation of state. Such a system is said to be a two coordinate system. But even for such a system, we need a much greater number of functions of state: p, V, T, S, U and H. (Of these, U and H have dimensions of energy.) In principle, we can construct several functions of state by combining these functions. However, all such functions may not have physical significance but some do have. In particular, we define Helmholtz and Gibbs functions by adding a combination of p, V, T and S having dimensions of energy, to internal energy or enthalpy. As you proceed, you will learn that a knowledge of the behaviour of a two-coordinate system can be obtained from either of the four thermodynamic potentials. With reference to a system subject to work by pressure only, these functions are defined as

$$\left.\begin{array}{lll} \bullet\ \text{internal energy} & : & U \\ \bullet\ \text{enthalpy} & : & H = U + pV \\ \bullet\ \text{Helmholtz potential} & : & F = U - TS = H - pV - TS \\ \bullet\ \text{Gibbs potential} & : & G = U - TS + pV = F + pV \end{array}\right] \qquad (6.1)$$

The Helmholtz potential is particularly important as it provides a vital connection between thermodynamics and statistical mechanics. That is, it provides a bridge between macroscopic and microscopic viewpoints. You will know these details in Block 4 of this course. Gibbs potential finds wide applications in the study of phase transitions, which you will study in the next unit.

For systems which cannot be described by p and V, these potentials are defined by replacing $-p$ and V by a suitable pair of variables out of σ, A, F and, L (see Table 3.1).

The physical significance of the potential functions becomes clearer from their differential forms. Let us learn about these now.

The Differentials of Potential Functions

Let us consider a gaseous system undergoing an infinitesimal reversible process. From Eq. (5. 10), you would recall that change in internal energy can be expressed as

$$dU = T\,dS - p\,dV \qquad (6.2a)$$

Also, a small change in enthalpy, defined as $H = U + pV$, can be written in terms of changes in internal energy, volume and pressure as

$$dH = dU + p\,dV + V\,dp$$

On combining this with Eq. (6.2a), you can write

$$dH = T\,dS + V\,dp \qquad (6.2b)$$

Likewise you can show that

$$dF = -S\,dT - p\,dV \qquad (6.2c)$$

and

$$dG = -S\,dT + V\,dp \qquad (6.2d)$$

Each of the Eqs.(6.2a) to (6.2d) has two terms on the right hand side. And each term consists of a pair of thermodynamic variables such that their product has dimensions of energy. Moreover, each potential has a different pair of natural variables :

$U = U(S,V)$; $H = H(S,p)$; $F = F(T,V)$ and $G = G(T,p)$

SAQ 1

Prove Eqs. (6.2c) and (6.2d).

Proceeding further, let us suppose that only one of the potentials is known explicitly. Now the question arises: Is it sufficient to get complete information about the system? To discover answer to this question, we have to calculate parameters of state from that function. We illustrate this by considering the Helmholtz potential.

The natural variables associated with F, as you have seen, are T and V. If F is explicitly known in terms of these, Eq. (6.2c) can be used to calculate S and p using the relations

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \tag{6.3a}$$

and

$$p = -\left(\frac{\partial F}{\partial V}\right)_T \tag{6.3b}$$

As entropy of a substance is a positive definite quantity, we can say from Eq. (6.3a) that Helmholtz potential decreases as temperature rises. Moreover, the rate of decrease will be greater for a substance having higher entropy. This explains why gases show maximum loss in F. And Eq. (6.3b) shows that Helmholtz function decreases as the system expands, i.e., volume of the system increases.

The expressions for U, H and G can also be rewritten in terms of F starting from their definitions. For example, by substituting for S from Eq. (6.3a), the internal energy can be expressed as

$$U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2\left[\frac{\partial}{\partial T}\left(\frac{F}{T}\right)\right]_V = \left[\frac{\partial(F/T)}{\partial(1/T)}\right]_V \tag{6.4}$$

since $\frac{d}{dT}\left(\frac{1}{T}\right) = -\frac{1}{T^2}\, dT.$

This is known as the **Gibbs - Helmholtz equation**. It finds great use in thermochemistry.

Similarly, on substituting for S and p from Eqs. (6.3a) and (6.3b) respectively, you can write

$$H = F + TS + pV = F - T\left(\frac{\partial F}{\partial T}\right)_V - V\left(\frac{\partial F}{\partial V}\right)_T \tag{6.5}$$

and

$$G = F + pV = F - V\left(\frac{\partial F}{\partial V}\right)_T = -V^2\left[\frac{\partial}{\partial V}\left(\frac{F}{V}\right)\right]_T \tag{6.6}$$

Eqs.(6.4), (6.5) and (6.6) clearly show that the entire information about a thermodynamic system can be obtained once we know Helmholtz potential. You may now logically ask: Can we say the same for other thermodynamic potentials? Definitely, yes. To convince yourself, you should solve the following SAQ.

SAQ 2

a) Obtain first order derivatives of H and G which justify the following statements:

   i) At constant entropy, the rate of increase of enthalpy with pressure is greater for a gas than that for a solid.

   ii) Under isothermal conditions, the Gibbs energy increases more rapidly with pressure for a gas than for a liquid or a solid.

b) Prove that

   i) $p = -\left(\frac{\partial U}{\partial V}\right)_T + T\left(\frac{\partial S}{\partial V}\right)_T$

   ii) $H = \left[\frac{\partial(G/T)}{\partial(1/T)}\right]_p$

   iii) $F = \left[\frac{\partial(G/p)}{\partial(1/p)}\right]_T$

You have learnt how thermodynamic potentials can be used to get information about basic properties of a system. One of the basic facts about every system is that it exchanges energy with its surroundings and has inherent tendency to approach equilibrium. We are invariably interested in deriving properties of the system without reference to the surroundings. You since T is constant. Thus, at constant volume and temperature, Eq. (6.10) takes the form

$$d(U-TS) = dF = 0$$

That is, the Helmholtz potential governs the equilibrium state of a system for changes at constant T and V. There is another way of looking at this relation. The change dF is less than the change dU by the amount $T\,dS$, which is the **non-available energy** arising from entropy changes in the system. Thus, the energy that we can extract from a system is always less than the internal energy. For this reason, F is also called the **free energy**. For changes at constant V and T, the appropriate conditions of thermodynamic equilibrium are

$$dT = 0, \quad dV = 0, \quad dF = 0 \qquad (6.14)$$

d) Thermally conducting–Isobaric System

As in case (c), we must have $dT = 0$. Similarly, following the argument of case (b), equilibrium requires $p = p_0$ or $dp = 0$.

Thus, Eq. (6.10) now reduces to

$$dA = dU - T\,dS + p\,dV = dU - d(TS) + d(pV) = 0$$

since T and p are constant. We can rewrite it as

$$d(U-TS+pV) = dG = 0$$

That is, Gibbs potential remains unchanged in equilibrium at constant p and T. Just like Helmholtz potential, the maximum work that a system can perform at constant T and p is equal to the change in enthalpy minus the unavailable energy $T\,dS$. (For an irreversible process, the available energy will be still less.) The non-availability of thermal energy is associated with the random nature of heat.

The appropriate conditions for such a system are

$$dT = 0, \quad dp = 0, \quad dG = 0 \qquad (6.15)$$

Thus, the four sets of conditions for thermodynamic equilibrium are:

$$\boxed{\begin{array}{lll} dS = 0, & dV = 0, & dU = 0 \\ dS = 0, & dp = 0, & dH = 0 \\ dT = 0, & dV = 0, & dF = 0 \\ dT = 0, & dp = 0, & dG = 0 \end{array}} \qquad (6.16)$$

You must note that each potential appears with its natural set of variables. These four sets of conditions are entirely equivalent in the sense that they lead to identical physical results. The use of a particular set is entirely a matter of convenience. For example, if a system is kept at constant temperature and pressure, the obvious choice is to minimise the Gibbs potential since its accompanying conditions are automatically fulfilled.

The nature of the conditions implied by Eq. (6.16) are easily identified by reference to Eq. (6.8) and the basic definitions of respective potentials. For example, let us consider the third condition. F is defined by the equation

$$F = U - TS$$

In general, an infinitesimal change in F is given by

$$dF = dU - S\,dT - T\,dS = dU - S\,dT - T_0\,dS \quad (\because T = T_0)$$

On combining this result with Eq. (6.10), we find that

$$dA = dF + S\,dT + p_0\,dV$$

From this, we note that for given values of T and V, A will be minimum if F is minimum. Similarly, when F and T are given, V must be minimum for A to be minimum. When will A be minimum if F and V are given? It can happen only when T is minimum.

In this way, we can list twelve conditions in all for a system to be in equilibrium. These are given in Table 6.1.

Table 6.1 : Conditions for Stable Thermodynamic Equilibrium

	Variables specified		Equilibrium condition
	U	V	S ------> maximum
Often used	T	p	G ------> minimum
	T	V	F ------> minimum
	S	V	U ------> minimum
	S	p	H ------> minimum
	U	S	V ------> minimum
Rarely useful	H	S	p ------> maximum
	H	p	S ------> maximum
	F	T	V ------> minimum
	F	V	T ------> minimum
	G	T	p ------> maximum
	G	p	T ------> minimum

All these conditions supplement the law of increase of entropy. Yet each one of these conditions represents the simplest way of applying the law under given conditions.

Before you go over to the next section, you should work out the following SAQ.

SAQ 3

Suppose that a flask having chemical reactants is heated at atmospheric pressure. Reaction begins to take place at some temperature. Which potential will govern the change? Justify your answer.

Now that you have learnt about themodynamic potentials (F, G, H and U), you can use these to get several thermodynamic relations. We first illustrate it by deriving Maxwell's relations. As you proceed, you will learn that usefulness of these relations stems from the fact that they frequently relate quantities which apparently seem unrelated. The actual beauty of Maxwell's relations lies in that they simplify thermodynamic analysis.

6.4 MAXWELL'S RELATIONS

You have read about exact differentials in Unit 3 of Block 1. We will now use this concept for deriving Maxwell's relations. You may recall from Sec. 3.7 that for a function of two variables

$$Z = Z(x, y)$$

the exact differential can be written as

$$dZ = M\,dx + N\,dy$$

where $M = \left(\frac{\partial Z}{\partial x}\right)_y$ and $N = \left(\frac{\partial Z}{\partial y}\right)_x$.

Hence, the rate of change of M with respect to y at constant x is given by

$$\left(\frac{\partial M}{\partial y}\right)_x = \left[\frac{\partial}{\partial y}\left(\frac{\partial Z}{\partial x}\right)_y\right]_x = \frac{\partial^2 Z}{\partial y\,\partial x}$$

Similarly, you can write the rate of change of N with respect to x as

$$\left(\frac{\partial N}{\partial x}\right)_y = \left[\frac{\partial}{\partial x}\left(\frac{\partial Z}{\partial y}\right)_x\right]_y = \frac{\partial^2 Z}{\partial x\,\partial y}$$

Solution

For one mole, we have

$$T\,ds = c_v\,dT + T\left(\frac{\partial p}{\partial T}\right)_v dv$$

where s, c_v and v are the molar entropy, molar heat capacity at constant volume, and molar volume respectively of the gas.

The van der Waals' gas is said to obey the following equation of state:

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

From this, you can easily write

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b}$$

Using this result in the first TdS-equation, we get

$$T\,ds = c_v\,dT + RT\;\frac{dv}{v-b}$$

Since the gas undergoes an isothermal expansion, $dT = 0$. Also, as the process is reversible, the heat transferred $q = T\,ds$

$$\therefore\; q = RT\int_{v_i}^{v_f}\frac{dv}{v-b} = RT\,\ln\left[\frac{v_f-b}{v_i-b}\right]$$

You can obtain two other TdS equations by taking

$$S = S(T,p) \quad\text{and}\quad S = S(p,V)$$

and following the procedure used in arriving at Eq. (6.19a):

$$\boxed{\begin{aligned} T\,dS &= nc_p\,dT - T\left(\frac{\partial V}{\partial T}\right)_p dp && (6.19\text{b})\\ T\,dS &= nc_V\left(\frac{\partial T}{\partial p}\right)_V dp + nc_p\left(\frac{\partial T}{\partial V}\right)_p dp && (6.19\text{c})\end{aligned}}$$

You will note that $T\,dS$ equations enable us to relate entropy, which is not physically measurable, to directly measurable quantities like heat capacities, temperature, pressure and volume. However, the knowledge of the equation of state is a must for extracting any useful information from these equations.

You may now like to work out an SAQ on $T\,dS$-equations.

SAQ 4

Prove Eqs. (6.19b) and (6.19c).

Use Eq. (6.19b) to calculate the heat transfer if the pressure on 0.015 litre of mercury at 0°C is increased reversibly and isothermally from zero to 1000 atm. It is given that β for mercury = $178 \times 10^{-6}\,\text{K}^{-1}$. Take 1 atm = $10^5\,\text{Nm}^{-2}$. (Assume that V and β remain constant during the process.)

6.5.2 Energy Equations

Just as Maxwell's relations enable us to compute heat transfer, we can also study how internal energy changes with volume, temperature or pressure. The resulting relations are known as **energy equations**. To derive first of these, we divide Eq. (6.2a) by dV. This gives

$$\frac{dU}{dV} = T\,\frac{dS}{dV} - p$$

You may consider each of U, S and p as a function of T and V. If T is held constant, the derivatives in the above equation will have to be treated as partial derivatives, so that you can write

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

Using Eq. (6.18c), we get

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \qquad (6.20a)}$$

Eq. (6.20a) is the so-called **first energy equation**. To illustrate its use, we consider a simple example. For an ideal gas, we know that

$$p = \frac{nRT}{V} \quad \text{and} \quad \left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V}$$

Substituting this in Eq. (6.20a), we have

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{nRT}{V} - p = 0$$

which indicates that the internal energy of an ideal gas is independent of its volume. So we may say that for an ideal gas U depends on T only. But, in general, U is a function of both T and V. You will understand this by solving the following SAQ.

SAQ 5

Using Eq. (6.20a), show that for one mole of a van der Waals' gas, $\left(\frac{\partial u}{\partial v}\right)_T = \frac{a}{v^2}$

The pressure dependence of internal energy can be obtained by dividing Eq. (6.2a) by dp and following the procedure used above. The result is the so-called **second energy equation:**

$$\boxed{\left(\frac{\partial U}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial p}\right)_T \qquad (6.20b)}$$

Before we derive heat capacity equations, we would like you to work out an SAQ.

SAQ 6

Prove Eq. (6.20b).

In Unit 4, you learnt to compute the relation involving the difference of heat capacities for a gas. The general result applicable to any substance was just quoted. We will now prove it using Maxwell's relations.

6.5.3 Heat Capacity Equations : Difference of Heat Capacities

To derive heat capacity equations, let us take S as a function of T and V:

$$S = S(T, V)$$

so that

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Now, starting from the above equation write for a magnetic system

a) the four Maxwell's relations

b) the second TdS-equation

2) A gas obeys the equation $p(v-b) = RT$, where b is constant. Show that

a) u is a function of T only

b) γ is constant

c) $p(v-b)^{\gamma}$ = constant for the gas undergoing a reversible adiabatic process.

6.8 SOLUTIONS AND ANSWERS

SAQs

1. $F = U - TS$

An infinitesimal change in F can be expressed as

$dF = dU - T\,dS - S\,dT$

We know from Eq. (6.2a) that $dU = T\,dS - p\,dV$ or $dU - T\,dS = -p\,dV$

$\therefore\; dF = -S\,dT - p\,dV$, which is Eq. (6.2c).

Similarly,

$G = U - TS + pV = F + pV$

$\therefore\; dG = dF + p\,dV + V\,dp = -S\,dT - p\,dV + p\,dV + V\,dp$

or $dG = -S\,dT + V\,dp$, which is Eq. (6.2d).

2.a) (i) From Eq. (6.2b), we have

$$V = \left(\frac{\partial H}{\partial p}\right)_S$$

For a fixed mass, V is greater in the case of a gas than that for a solid. So, at constant entropy, the rate of increase of H with p is greater for a gas than a solid.

(ii) From Eq. (6.2d), we have

$$V = \left(\frac{\partial G}{\partial p}\right)_T$$

Now, owing to reasons as stated in the case of (i), we can say that at constant temperature, G increases with p more rapidly for a gas than that for a liquid or a solid.

b) From Eq. (6.2c), we know that

$$p = -\left(\frac{\partial F}{\partial V}\right)_T$$

On substituting for F, we set

$$p = -\left[\frac{\partial}{\partial V}(U - TS)\right]_T = -\left(\frac{\partial U}{\partial V}\right)_T + T\left(\frac{\partial S}{\partial V}\right)_T$$

This relation signifies that pressure arises out of two contributions. These are due to the isothermal variations of internal energy with volume and the entropy with volume. The first term is dominant in the case of solids and the second in the case of elastic polymers such as rubber.

The variation of entropy of a system with volume may also contribute to pressure when its energy remains constant. This is exactly what happens in the case of an ideal gas at constant temperature.

c) We know that $G = H - TS$ and $S = -\left(\frac{\partial G}{\partial T}\right)_p$.

Therefore, we can invert this relation to write

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_p$$

$$= T^2\left[\frac{T\left(\frac{\partial G}{\partial T}\right)_p - G}{T^2}\right] = -T^2\left[\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right]_p$$

But $\left[\frac{\partial}{\partial T}\left(\frac{1}{T}\right)\right]_p = -\frac{1}{T^2}$. $\therefore\ H = \left[\frac{\partial(G/T)}{\partial(1/T)}\right]_p$

3. $G = U - TS + pV$

$\therefore dG = dU - T\,dS - S\,dT + p\,dV + V\,dp$

Now $T = T_1$, and $p = p_0$. Then, we have

$dG = dU - T_0\,dS - S\,dT + p_0\,dV + V\,dp$

or $\quad dU + p_0\,dV - T_0\,dS = dG + S\,dT - V\,dp$

or $\quad dA = dG + S\,dT - V\,dp$

As T and p are given, $dT = 0 = dp$. So we have $dA = dG$. Hence, for A to be minimum, G must be a minimum.

4.a) $S = S(T, p)$

$$\therefore dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

Multiplying throughout by T and using Eq. (6.18d), we get

$$T\,dS = nc_p\,dT - T\left(\frac{\partial V}{\partial T}\right)_p dp, \text{ which is Eq. (6.19b).}$$

Next, we choose entropy to be a function of p and V, i.e.,

$$S = S(p, V)$$

$$\therefore\ dS = \left(\frac{\partial S}{\partial p}\right)_V dp + \left(\frac{\partial S}{\partial V}\right)_p dV$$

or $$T\,dS = T\left(\frac{\partial S}{\partial p}\right)_V dp + T\left(\frac{\partial S}{\partial V}\right)_p dV$$

You can rewrite it as

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial p}\right)_V dp + T\left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial V}\right)_p dV$$

or $$T\,dS = nc_V\left(\frac{\partial T}{\partial p}\right)_V dp + nc_p\left(\frac{\partial T}{\partial V}\right)_p dV, \text{ which is Eq. (6.19c).}$$

b) Since the process is reversible and isothermal ($dT = 0$), we have from Eq. (6.19b)

$$\delta Q = T\,dS = -T\left(\frac{\partial V}{\partial T}\right)_p dp = -TV\beta\,dp$$

$$\therefore\ Q = -\int TV\beta\,dp = -T\int V\beta dp \quad (\because T \text{ is a constant})$$

Since V and β remain constant during the process, we have

$$Q = -TV\beta\int dp = -TV\beta(p_f - p_i),$$

where p_i and p_f are the initial and the final pressures.

On substituting the values

$T = (0 + 273)\,\text{K} = 273\,\text{K}$, $V = 0.015$ litre, $\beta = 178 \times 10^{-6}\,\text{K}^{-1}$,
$p_f = 1000$ atm, and $p_i = 0$ atm, we find that

$Q = -(273\text{K}) \times (0.015 \text{ litre}) \times (178 \times 10^{-6}\,\text{K}^{-1}) \times (1000 \text{ atm})$
$= -0.729$ litre atm

iii) We know from Eqs. (6.19a and b) that

$$T\,ds = c_v\,dT + T\left(\frac{\partial p}{\partial T}\right)_v dv$$

and

$$T\,ds = c_p\,dT - T\left(\frac{\partial v}{\partial T}\right)_p dp$$

For a reversible adiabatic process, $Tds = 0$

$$\therefore\ c_v\,dT = -T\left(\frac{\partial p}{\partial T}\right)_v dv \quad \text{and} \quad c_p\,dT = T\left(\frac{\partial v}{\partial T}\right)_p dp$$

or $$c_v\,dT = -\frac{RT}{v-b}\,dv \quad \text{and} \quad c_p\,dT = \frac{RT}{p}\,dp$$

Hence,

$$\frac{c_p\,dT}{c_v\,dT} = \frac{\dfrac{RT}{p}\,dp}{-\dfrac{RT}{v-b}\,dv} = -\frac{v-b}{p}\,\frac{dp}{dv}$$

UNIT 7 PHASE TRANSITIONS

Structure

7.1 Introduction
  Objectives
7.2 Phase Equilibrium
  Condition for Equilibrium between Phases
  Phase Diagrams
7.3 First Order Phase Transitions
  Latent Heat Equations
7.4 Higher Order Phase Transitions
7.5 Gibbs Phase Rule
7.6 Summary
7.7 Terminal Questions
7.8 Solutions and Answers

7.1 INTRODUCTION

Matter exists in three distinct phases—solid, liquid and gas—around us. Most substances in our environment can be made to undergo change in phase by varying temperature and/or pressure. The melting of ice to form water and evaporation of water to form water vapour are the best known examples of phase transitions. The phase change from solid to liquid is marked by a discontinuous change in their strength to withstand a deforming force. The transition from liquid to gaseous phase involves a discontinuous change in density. Some phase transitions are accompanied by discontinuous changes in electrical conductivity. The most important examples include transition from normal conductor to superconductor, where a substance loses all resistance to flow of current, and gas to plasma— the fourth state of matter. Yet some other phase transitions exhibit change in magnetism (paramagnetism to ferromagnetism) and viscosity/heat capacity (normal helium to superfluid helium). Thus, we can say that a **phase transition always brings about an abrupt change in some physical property.**

You may like to know: What is good about phase transitions? First of all, they occur frequently around us. Moreover, many phase transitions are technologically important and physically interesting. The recent discovery of high temperature superconducting phase transition in the range 35-120K holds great promise in areas of information technology (computers, space satellites, etc.), surface transport as well as electronics. It is, therefore, important to know the physics of a phase transition. You have an opportunity to study it in this unit.

If you have been to a hill station like Manali and Darjeeling, particularly in rainy season or winter, you must have seen clouds accumulating around snow-capped peaks. This signifies coexistence of solid and vapour phases. You may now ask: What parameters determine this coexistence? Why and how does it happen like that? You will learn answers to these questions in Sec. 7.2. The equation governing first order phase transitions is given in Sec. 7.3. Higher order phase transitions are discussed in Sec. 7.4. In this study, you will use the knowledge of the previous unit. Therefore, you should ensure that you are thorough with that. If the system of interest consists of more than one chemical substance and each constituent can exist in several phases, their co-existence is described by **Gibbs phase rule**. We have discussed its applications in Sec.7.5.

Objectives

After studying this unit, you will be able to

- define the term phase equilibrium

From this you may be tempted to conclude that every substance that can exist in different phases necessarily has a triple point. This is not always true. Can you name a substance which exists in different phases but does not possess a triple point? In Block 4, you will learn that helium can exist in three different phases. But it has no triple point. This is because solid phase is obtained only under a pressure of about 25 atm.

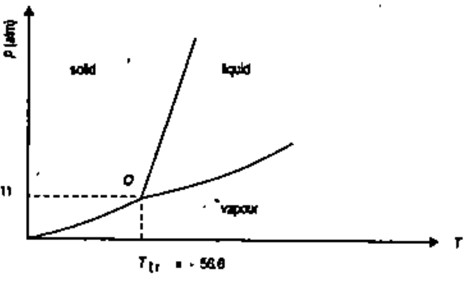


Fig. 7.2 Phase diagram of CO_2

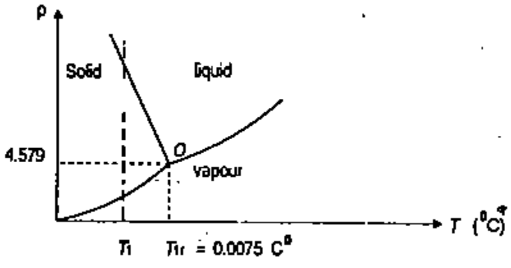


Fig 7.3 Phase diagram of water

Again refer to Fig. 7.2. You will note that :

1) Higher pressures favour the denser phase. Physically, this implies that the melting and boiling points of most substances increase with pressure. This explains why pressure cookers cook food faster and it is difficult to make a good hot cup of tea or coffee at higher altitudes.

2) The lines dividing solid-gaseous, solid-liquid and liquid-gaseous phases tend to slope upward to the right.

3) If you compare this diagram with phase diagram for water shown in Fig. 7.3, you will note that in case of water solid-liquid boundary has a negative slope. It signifies that water expands on freezing and increased pressure melts ice. This is the reason why, unlike other solids, ice becomes slippery when pressure is applied and makes skating possible.

4) You will note that the line separating the gaseous and liquid phase does not continue indefinitely. In fact, beyond the **critical point**, defined by T_c and p_c, there is no clear distinction between liquid and gaseous phases for any substance. It means that there is no change in density, i.e., no phase change occurs in this region.

Let us now learn about familiar phase transitions like melting, vaporisation and sublimation. These are characterised by discontinuous changes in entropy and volume at a particular temperature and are called first-order phase transitions.

7.3 FIRST ORDER PHASE TRANSITIONS

You know that to melt 1g of ice at 0°C, you require 80 cal of heat. This suggests that entropy will show a discontinuous change. Also you know that the specific volumes of ice and water are different. That is, we observe a discontinuous change in volume as well. Such a change is an example of first order phase transition characterised by constant T and p. Mathematically, the condition for co-existence of two or more phases is governed by Gibbs potential. For one-component system, which can exist in two phases, from Eq. (6.2d), you can express specific Gibbs potential $g = \frac{G}{m}$, where m is mass of either phase as

$$dg = -s\,dT + v\,dp \tag{7.5}$$

where $s = \frac{S}{m}$, and $v = \frac{V}{m}$ are the specific entropy and specific volume respectively.

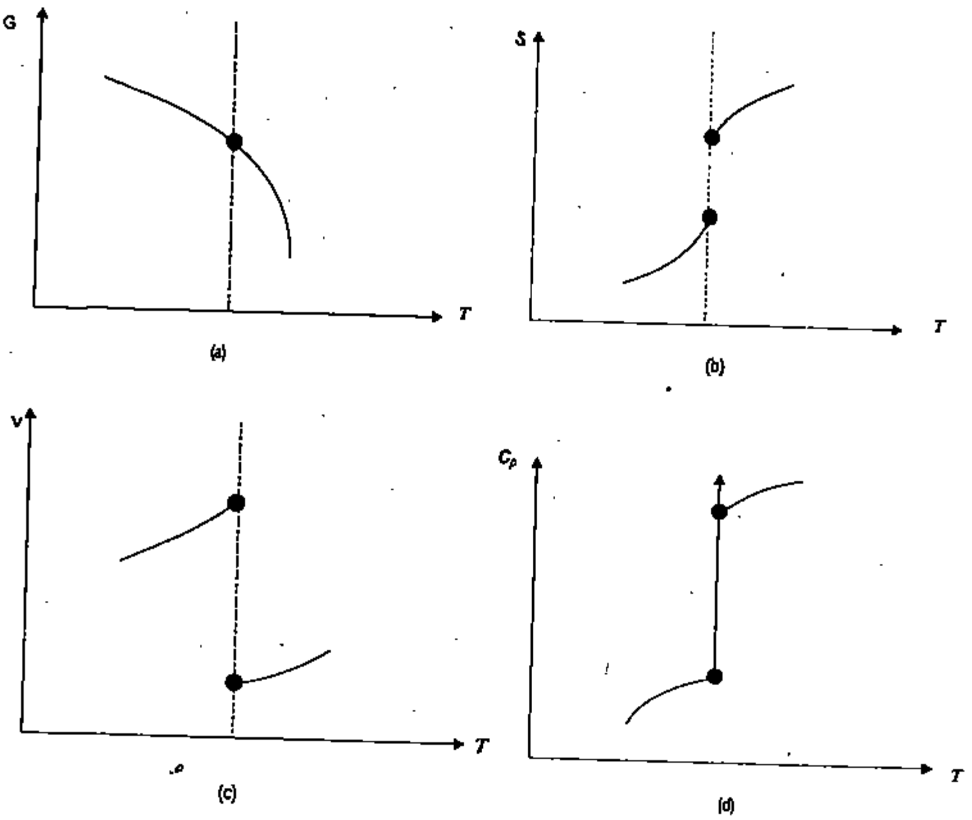


Fig. 7.4: Plot of (a) Gibbs function (b) entropy (c) volume and (d) C_p as a function of temperature for a first order phase transition

These can readily be expressed as the first order derivatives of g:

$$s = -\left(\frac{\partial g}{\partial T}\right)_p \quad \text{and} \quad v = \left(\frac{\partial g}{\partial p}\right)_T$$

Fig. 7.4 schematically depicts variation of G, S, V and C_p with temperature for a first order phase transition.

The behaviour of C_p depicted in Fig. 7.4d is particularly significant. During a phase transition, temperature remains constant and, hence, $dT = 0$. But $C_p = T\left(\frac{\partial S}{\partial T}\right)_p \to \infty$.

Let us consider that water at 100°C boils under atmospheric pressure and two phases — liquid and vapour — are in equilibrium. Is it posible for us to predict the boiling point if pressure were reduced? Or could we predict the pressure under which the boiling point may be lowered or raised? To answer these questions, you should know how changes in temperature and pressure are inter-related when two phases coexist in equilibrium. This information is contained in the Clausius-Clapyron latent heat equation. Let us now learn to derive it.

7.3.1 The First Latent Heat Equation

You know that thermodynamic behaviour of any substance is normally specified by two thermodynamic variables, which are independent of each other. You may choose pressure and temperature as independent variables. But when water is in equilibrium with its vapour, the pressure then equals the vapour pressure and it becomes a unique function of the temperature. This means that pressure and temperature are no longer independent. If the pressure is increased above the vapour pressure, the vapour will condense. On the other hand, if pressure is reduced below the equilibrium value, the liquid will evaporate. To relate the changes Δp and ΔT, we use the fact that the specific Gibbs potentials (or chemical potentials) of two phases must always be equal for their co-existence:

$$g_1 = g_2 \qquad (7.6)$$

Since specific volume is the same in both phases, we can write

$$\frac{c_p}{T}\Delta T - v\beta_1\Delta p = \frac{c_p}{T}\Delta T - v\beta_2\Delta p$$

or

$$\frac{\Delta p}{\Delta T} = \frac{c_{p_2} - c_{p_1}}{T v(\beta_2 - \beta_1)} \tag{7.12a}$$

This is known as **Ehrenfest's equation.** It describes the dependence of pressure on temperature during a second order phase transition.

Since a second order phase transition is characterised by equalities of specific volumes as well, you must expect another Ehrenfest equation which defines the ratio $\Delta p/\Delta T$. If you start with

$$v_1 = v_2$$

as the necessary condition for the co-existence of phases and follow the steps outlined above, you will obtain

$$\frac{\Delta p}{\Delta T} = \frac{\beta_2 - \beta_1}{\kappa_{T_2} - \kappa_{T_1}} \tag{7.12b}$$

where $\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T$ denotes isothermal compressibility.

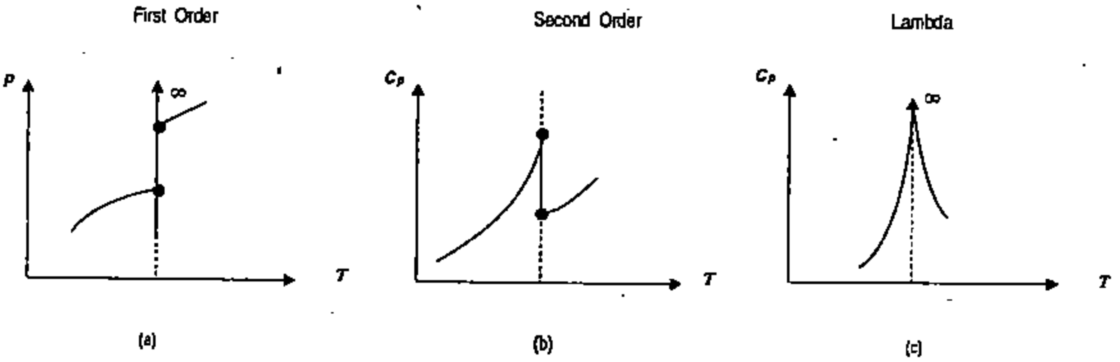
There is another interesting higher order phase transition. It is called the lambda transition. It is characterised by the following:

i) T, p and G remain constant

ii) S and V (also U, H and F) are constants

iii) c_p, and κ_T are infinite.

Now refer to Fig. 7.5. It depicts plots of c_p vs. T for first order, second order and lambda transitions. Can you distinguish the three types of transitions by examining these graphs? The shape of the graph in Fig. 7.5c resembles the Greek letter lambda (λ). (That is why this transition is called a lambda transition.) Important examples of a λ- transition are: (i) the transition from ferromagnetism to paramagnetism at the Curie point, and (ii) the superfluid transition in liquid helium.



(a) (b) (c)

Fig.7.5 Comparison of temperature variation of heat capacity for first order, second order and lambda transitions.

Having learnt the details of first order, second order and lambda transitions for one-component system, let us enquire: How can we determine the co-existence of a number of phases in a multi-component system? How thermodynamic variables influence such a system? The answer to these question is contained in a relation known as the **Gibbs Phase Rule.** We shall quote the relation without going into details. However, its applications to specific systems will be considered to enable you to grasp the idea.

7.5 GIBBS PHASE RULE

We assume that equilibrium between various phases of a multi-component system is influenced by temperature, pressure and concentration rather than external factors, such as gravitational, electric or magnetic field. Then, the number of degrees of freedom F of the system is connected to the components C and phases P by the relation

$$F = C - P + 2$$

or

$$F + P = C + 2 \qquad (7.13)$$

To illustrate this rule, let us first consider the existence of triple point of water. As you know, this point signifies co-existence of ice, water and vapour. Here $C = 1$ because ice, water and vapour have the same composition (H_2O) and $p = 3$. So $F = 1 - 3 + 2 = 0$ That is, there is no freedom. This means that the values of temperature and pressure are fixed at the triple point of water. Moreover, this system cannot exist in more than three phases. You have seen this in Sec. 7.3.

The degrees of freedom of a system is the number of independent variables, such as temperature, pressure and concentration, etc, which must be specified in order to define the system completely. In other words, it is the number of variables which can be varied independently without altering the number of phases.

Let us consider another example, which has three parts. We shall discuss only two parts. The third one has been left as an SAQ for you.

i) A bell jar is placed over a water beaker. The air under the jar gets saturated with water vapour. Here $C = 2$ (H_2O and air), $P = 2$ (liquid water and air-vapour mixture). So $F = 2 - 2 + 2 = 2$. It means that you can vary two variables without affecting the system. The variables may be temperature and pressure. The latter can be varied by connecting the bell jar to a pump.

ii) If in (i), the air is kept at atmospheric pressure, and alcohol is added to water then $C = 3$ (H_2O, alcohol and air), $P = 2$ (water-alcohol mixture, and air-vapour mixture). So $F = 3 - 2 + 2 = 3$. The variables can be temperature, pressure and the concentration of alcohol in water.

SAQ 3

Suppose that some ice is in equilibrium with the water and alcohol mixture in (ii) above. Compute F and identify the possible variables.

We now sum up what you have learnt in this unit.

7.6 SUMMARY

- The condition for equilibrium between two phases is given by

$$g_1 = g_2$$

- The characteristics of first and second order phase transitions are listed below:

Order	Discontinuity appears in			
	Differentials of g		Corresponding experimental quantities	
First	s	v	s	v
Second	$\left\{\begin{matrix} \left(\frac{\partial s}{\partial T}\right)_p & \left(\frac{\partial v}{\partial T}\right)_p \\ \left(\frac{\partial s}{\partial p}\right)_T & \left(\frac{\partial v}{\partial p}\right)_T \end{matrix}\right\}$		c_p β κ	

- The equation governing temperature variation of pressure when phase transition of first order exists is

$$\frac{\Delta p}{\Delta T} = \frac{l}{T(v_2 - v_1)}$$

- The co-existence of phases in a second order phase transition is governed by the equations

$$\frac{\Delta p}{\Delta T} = \frac{c_{p_2} - c_{p_1}}{T v (\beta_2 - \beta_1)}$$

and

$$\frac{\Delta p}{\Delta T} = \frac{\beta_2 - \beta_1}{\kappa_{T_2} - \kappa_{T_1}}$$

- When the equilibrium between various phases is influenced by temperature, pressure and concentration rather than gravitational, magnetic or electric fields, the number of degrees of freedom F of the system is related to the components C and phases P by the Gibbs phase rule:

$$F = C - P + 2$$

7.7 TERMINAL QUESTIONS

1) You know that in a second order phase transition $s_1 = s_2$, and $v_1 = v_2$ at a particular temperature and pressure where 1 and 2 denote the initial and the final phases, respectively. Show that, for such a transition

$$\frac{\Delta p}{\Delta T} = \frac{1}{Tv}\,\frac{c_{p_2} - c_{p_1}}{\beta_2 - \beta_1} = \frac{\beta_2 - \beta_1}{\kappa_2 - \kappa_1}$$

where $\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$, $\kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T$ and $v_1 = v_2 = v$.

2) Salt (NaCl) is gradually added to a beaker (by using some mechanism) containing ice and water in equilibrium under a bell-jar. (The jar contains air at atmospheric pressure.) Compute F and identify the possible variables when

   i) all the salt goes into solution

   ii) some salt remains undissolved.

7.8 SOLUTIONS AND ANSWERS

SAQ's

1. $m_1 v_1 + m_2 v_2 = \text{constant}$

$$d\,(m_1 v_1 + m_2 v_2) = 0$$

or $m_1\,dv_1 + m_2\,dv_2 + v_1\,dm_1 + v_2\,dm_2 = 0$ (i)

Since

$$F = m_1 f_1 + m_2 f_2$$

and the condition of equilibrium is $dF = 0$, you can write

$$m_1\,df_1 + m_2\,df_2 + f_1\,dm_1 + f_2\,dm_2 = 0 \qquad \text{(ii)}$$

Now multiplying (i) by p and adding to (ii), we get

$$(f_1 + pv_1)\,dm_1 + (f_2 + pv_2)\,dm_2 + m_1\,(df_1 + p\,dv_1) + m_2\,(df_2 + p\,dv_2) = 0$$

We know that

$$df = -s\,dT - p\,dv$$

so that

$$df + p\,dv = -s\,dT = 0, \text{ for a reversible isothermal change. Hence}$$

$$df_1 + p\,dv_1 = df_2 + p\,dv_2 = 0$$

So, we have

$$(f_1 + pv_1)\,dm_1 + (f_2 + pv_2)\,dm_2 = 0$$

i.e., $g_1\,dm_1 + g_2\,dm_2 = 0$ $\qquad (f + pv = g)$

But $dm_1 = -dm_2 \neq 0 \Rightarrow g_1 - g_2 = 0$

2. a) You know that the specific volume of ice is greater than that of water. So, when ice melts, we have $v_2 < v_1$, i.e., $v_2 - v_1$ is negative. It implies that $\frac{\Delta p}{\Delta T}$ is negative. Hence, when pressure increases (Δp positive), ΔT is negative implying that melting point is lowered.

b) $l = 35.6 \text{ cals g}^{-1} = 35.6 \times 4.2 \text{ Jg}^{-1}$ $T = (80 + 273)\text{ K} = 353\text{K}$

$v_2 - v_1 = 0.146 \text{ cm}^3 \text{ g}^1 = 0.146 \times 10^{-6} \text{ m}^3\text{g}^{-1}, \Delta p = 1 \text{ atm} = 10^5 \text{ Nm}^{-2}$

Hence,

$$\Delta T = \frac{T\Delta p(v_2 - v_1)}{l} = \frac{(353\text{K}) \times (10^5 \text{ Nm}^{-2}) \times (0.146 \times 10^{-6} \text{ m}^3\text{g}^{-1})}{35.6 \times 4.2 \text{ Jg}^{-1}}$$

$$= 0.345 \text{ K}$$

That is, the increase in melting point per atmospheric pressure is 0.345°C.

3. Here $C = 3$ (H_2O, alcohol and air); $P = 3$ (ice, water-alcohol mixture and air-vapour mixture). So $F = 3 - 3 + 2 = 2$. One of the variables is p, the atmospheric pressure. The other variable, which determines T is, therefore, alcohol concentration. This means that temperature is not an independent variable in this case.

TQ's

1. $$v = v(p, T)$$

or

$$\Delta v = \left(\frac{\partial v}{\partial T}\right)_p \Delta T + \left(\frac{\partial v}{\partial p}\right)_T \Delta p$$

$$\Delta v_1 = \left(\frac{\partial v_1}{\partial T}\right)_p \Delta T + \left(\frac{\partial v_1}{\partial p}\right)_T \Delta p = v_1 \beta_1 \Delta T - v_1 \kappa_1 \Delta p$$

and

$$\Delta v_2 = \left(\frac{\partial v_2}{\partial T}\right)_p \Delta T + \left(\frac{\partial v_2}{\partial p}\right)_T \Delta p = v_2 \beta_2 \Delta T - v_2 \kappa_2 \Delta p$$

But $v_1 = v_2$ and $\Delta v_1 = \Delta v_2$

$$\therefore \ \beta_1 \Delta T - \kappa_1 \Delta p = \beta_2 \Delta T - \kappa_2 \Delta p$$

or $(\kappa_2 - \kappa_1)\Delta p = (\beta_2 - \beta_1)\Delta T$

$$\therefore \ \frac{\Delta p}{\Delta T} = \frac{\beta_2 - \beta_1}{\kappa_2 - \kappa_1}$$

Again $s = s(p, T)$

$$\therefore \ \Delta s = \left(\frac{\partial s}{\partial p}\right)_T \Delta p + \left(\frac{\partial s}{\partial T}\right)_p \Delta T$$

Using Maxwell's relation, you can write

$$\Delta s = -\left(\frac{\partial v}{\partial T}\right)_p \Delta p + \frac{c_p}{T}\Delta T$$

$$= -v\beta\Delta p + \frac{c_p}{T}\Delta T$$

where β is volume expansion coefficient. Hence,

$$\Delta s_1 = -v_1\beta_1\Delta p + \frac{c_{p_1}}{T}\Delta T$$

and $$\Delta s_2 = -v_2\beta_2\Delta p + \frac{c_{p_2}}{T}\Delta T$$

But $\Delta s_1 = \Delta s_2$ and $v_1 = v_2 = v$

$$\therefore \ v(\beta_2 - \beta_1)\Delta p = \frac{1}{T}(c_{p_2} - c_{p_1})\Delta T$$

or $$\frac{\Delta p}{\Delta T} = \frac{c_{p_2} - c_{p_1}}{Tv(\beta_2 - \beta_1)}$$

2.i) $C = 3$ (H_2O, NaCl and air), $P = 3$ (solid, liquid solution of NaCl in water and air-vapour mixture). $\therefore$ $F = 3 - 3 + 2 = 2$. The variables which will determine temperature are pressure and the concentration of the salt in the solution.

ii) $C = 3$, as before. $P = 4$, the additional phase being that of solid salt. $\therefore$ $F = 3 - 4 + 2 = 1$. If we take pressure as the variable, the concentration of solution and temperature get fixed. This happens with a freezing mixture.

UNIT 8 PRODUCTION OF LOW TEMPERATURES AND THE THIRD LAW

Structure

8.1 Introduction
    Objectives
8.2 Ordinary Methods of Cooling
8.3 Joule-Thomson Effect
    Liquefaction of Gases
8.4 Adiabatic Demagnetization
8.5 The Third Law of Thermodynamics
    Consequences of the Third Law
    Unattainability of Absolute Zero
8.6 Summary
8.7 Terminal Questions
8.8 Solutions and Answers

8.1 INTRODUCTION

During summer you often feel thirsty. To quench your thirst you may either take a glass of cold pitcher water or a cold drink. Do you know that water is cooled in a pitcher by evaporation. But by this method you cannot go below about 20°C. In a refrigerator you can attain 0°C. You must have seen some vendors preparing ice-cream by putting a vessel (filled with sweetened milk and other ingredients) in a box containing a freezing mixture of ice and common salt. This arrangement enables them to attain temperature as low as -21°C. In fact, adding various salts (NH_4Cl, $NaNO_3$, $CaCl_2$, KOH, etc) to ice is the oldest method of producing sub-zero temperatures. This method was used by Faraday to liquefy many gases including Cl_2, H_2S, NO_2, etc. As you may recall from Unit 7, many important phenomena are observed at temperatures of the order of a few kelvin. In this unit, you will learn methods to produce such low temperatures. In particular, we will discuss Joule-Thomson method of regenerative cooling and adiabatic demagnetisation in detail. This study has given birth to a new branch of physics called Low Temperature Physics or Cryogenics.

We begin by discussing the use of evaporation and adiabatic cooling techniques to produce low temperatures. Next we discuss the physics of Joule-Thomson effect. Its use for liquefaction of gases is also illustrated in this Section. The adiabatic demagnetisation method is discussed in Sec. 8.4.

In the course of discussion you will realise that it becomes progressively difficult to achieve lower temperatures. This fact is postulated as the third law of thermodynamics. The third law and its consequences are discussed in Sec. 8.5.

Objectives

After going through this unit, you should be able to :

- explain the method of adiabatic cooling
- obtain expression for Joule-Thomson coefficient
- define inversion temperature

- explain the principle of adiabatic demagnetization and describe the experimental arrangement, and
- state the consequences of the third law of thermodynamics.

8.2 ORDINARY METHODS OF COOLING

We live in an environment whose temperature is around 30°C. Quite often we need to cool things by a few degrees below this value. For this we need to extract heat from the body, we intend to cool. This is why an ice-cream vendor puts a freezing mixture around the box containing the ice-creams. In the household refrigerator also, heat is extracted from eatables kept inside. But these techniques cannot be used to cool things off much below 0°C.

Another method employed for cooling is evaporation. This fact is used to cool water in earthen pots. Similarly, if you apply ether on your body, you will have a cooling sensation. In general, the extent of cooling depends on the nature of the liquid and the rate of evaporation. We can increase the rate of evaporation by: (i) using high speed suction pumps, (ii) allowing the vapour to be absorbed by another liquid, and (iii) executing the process in a low pressure atmosphere. If we put liquid N_2, H_2 or He at extremely low temperatures in partial vacuum, some of the liquid vaporizes very quickly and cools the rest. Kammerlingh Onnes achieved a temperature of 0.82 K when he allowed liquid He to boil ($T = 4.2$ K) at a pressure of 0.013 mm. of Hg.

Yet another method commonly used to accomplish cooling is that of adiabatic cooling. It is illustrated schematically in Fig. 8.1.

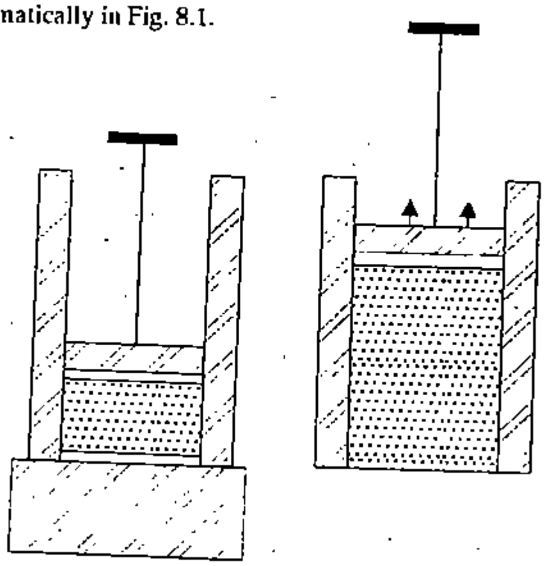


Fig. 8.1: (a) First the gas is brought into thermal equilibrium with the coldest thing around. (b) It is then insulated and allowed to expand against a moving piston. In doing the work, it cools still further.

A gas is first compressed. Next it is cooled as far as possible. It is then insulated and made to expand (against the movable piston). In this process it does some work, say, ΔW. From Unit 4 you would recall that this work is done at the cost of internal energy which results in drop in temperature.

From the first law of Thermodynamics

$$\delta Q = dU + \delta W$$

Here $\delta Q = 0$ because of the insulation.

$$\therefore \; dU = -\delta W.$$

The negative sign indicates that there is a loss of internal energy.

This method fails in practice because the insulation is not always proper. Moreover, the heat capacity of the containers is much greater than that of the gas and a lot of energy expended in the expansion of the gas is returned to it by the walls of the container. As a result, the purpose of expanding the gas gets defeated. Therefore, we need an expansion process where the walls of the container do not give heat to the gas inside. This is accomplished by **adiabatic throttling** in the Joule-Thomson experiment. Let us now learn about it.

8.3 JOULE-THOMSON EFFECT

Joule and Thomson performed a series of experiments in which a gas was allowed to pass through a porous plug from a pressure p_1 to pressure p_2 ($< p_1$) under adiabatic conditions (Fig. 8.2). (We use cotton wool and silk wool as porous materials.) Such a process induces a change in the temperature of the gas. This is known as **Joule-Thomson effect.**

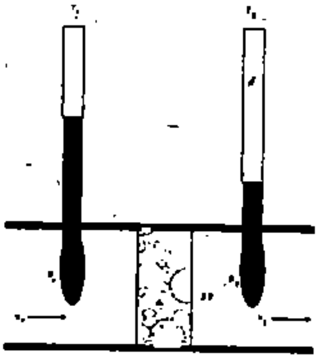


Fig. 8.2: The elements of Joule-Thomson experiment.

Refer to Fig. 8.2 again. The pores in the porous plug placed between the regions of high and low pressures provide a large number of narrow and long orifices for the passage of the gas. This, in turn, ensures that

i) The gas expands slowly. (A quick expansion would result in dissipation of energy.)

ii) During their passage through the orifices, the gas molecules are gradually drawn apart.

That is, the gas is partially obstructed by the pores. We refer to this type of flow as throttling. (The porous plug is termed as throttling valve.) Since this process takes place in a thermally insulated region, it constitutes adiabatic throttling of gases.

The Joule-Thomson experiment has been carried out with a very large number of gases at different pressures p_1 and p_2 and various initial temperatures (T_1). The final temperature T_2 is always different from T_1. We refer to the change in temperature ΔT ($= T_2 - T_1$) as Joule-Thomson effect. It is measured in terms of change in temperature per unit change in pressure across the porous plug: $\mu = \Delta T/\Delta p = (T_2 - T_1)/(p_2 - p_1)$. μ is called Joule-Thomson coefficient. Since $p_2 < p_1$, sign of μ is opposite to that of T. Physically, it means that a gas heats up when μ is negative and vice versa.

You may now like to check your progress. To facilitate this, we have given an SAQ.

SAQ 1

a) Complete the following statement by filling the blank with appropriate words chosen from those given in the brackets. Adiabatic throttling of a gas is its ..... expansion from a region of .... high pressure to that of .... low pressure through a .... (constant, fast, porous plug, slow).

b) Draw a labelled graph showing variation of pressure along the length of the pipe in Joule-Thomson experiment.

c) Is Joule-Thomson experiment a reversible or an irreversible process? Justify your answer.

Theory

You now know that Joule-Thomson effect is an irreversible process. However, we can apply the laws of thermodynamics to the gas before and after throttling as these are equilibrium

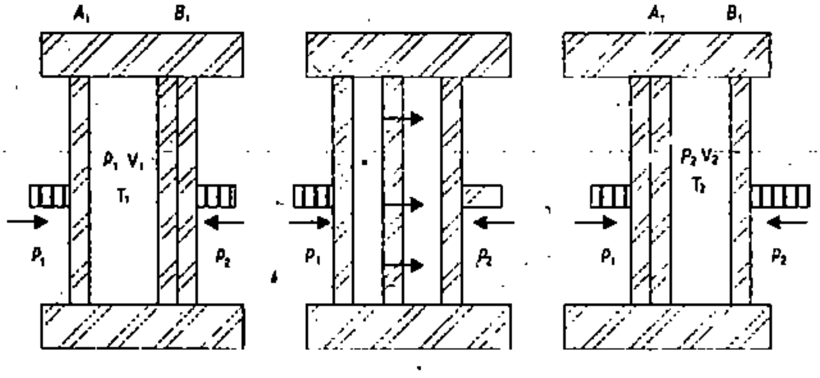


Fig. 8.3: Schematics of (a) initial equilibrium state (b) throttling in progress (c) final equilibrium state during Joule-Thomson expansion.

states. For this purpose, we consider its schematic representation consisting of an adiabatic tube (shown shaded), porous plug and two frictionless pistons (Fig 8.3).

Suppose that we have n moles of a gas between a frictionless piston at A_i and the porous plug PP placed in a nonconducting cylinder. Suppose that the thermodynamic parameters of the gas in this state are p_1, V_1 and T_1. Consider that the second piston is at B_i. We slowly push the first piston and gradually pull the second so that they experience constant pressures p_1 and p_2, respectively. In this way we gradually force the gas through the porous plug from a region of constant pressure p_1 to a region of constant pressure p_2. We assume that the movement of the gas is so slow that kinetic energy of its flow can be ignored.

When the whole gas has been throttled, the two pistons reach the positions A_f (in contact with PP) and B_f, respectively. Let the volume and temperature of the gas between PP and B_f be V_2 and T_2. Since the pistons are frictionless and walls of the cylinder are thermally insulated, we can regard the process to be quasistatic adiabatic in nature. Therefore, from the first law of thermodynamics, you can write

$$\Delta U + \Delta W = 0 \tag{8.1}$$

Here, $\Delta U = U_2 - U_1$, where U_1 and U_2 are internal energies of the gas in initial and final equilibrium states. Furthermore, ΔW is the net work done by the gas on the pistons and we can write it as

$\Delta W =$ (Work done by the gas in expanding against constant pressure p_2)

— (Work done on the gas in compressing it at constant pressure p_1)

$$= \int p_2 \, dV_2 - \int p_1 \, dV_1 = p_2 \int dV_2 - p_1 \int dV_1 \quad (\because p_1 \text{ and } p_2 \text{ are constants})$$

$$= p_2 V_2 - p_1 V_1 \tag{8.2}$$

Substituting the values of ΔU and ΔW in Eq. (8.1), we get

$$U_2 - U_1 + p_2 V_2 - p_1 V_1 = 0$$

or

$$U_1 + p_1 V_1 = U_2 + p_2 V_2 \tag{8.3}$$

Since $H = U + pV$, we find that

$$H_1 = H_2 . \tag{8.4}$$

That is, the initial and the final enthalpies are equal and Joule-Thomson expansion is an isoenthalpic process. However, you must note that when throttling is taking place, the gas is not in equilibrium and enthalpy is not defined.

From Sec. 6.2, you would recall that enthalpy is a function of temperature and pressure. So we can write

$$dH = \left(\frac{\partial H}{\partial p} \right)_T dp + \left(\frac{\partial H}{\partial T} \right)_p dT \tag{8.5}$$

In Joule-Thomson experiment, H is constant and $dH = 0$. Therefore,

$$\left(\frac{\partial H}{\partial T} \right)_p dT_H = - \left(\frac{\partial H}{\partial p} \right)_T dp_H$$

The suffix H indicates that enthalpy is constant. On slight re-arrangement, we can write

$$\left(\frac{\partial T}{\partial p} \right)_H = - \frac{\left(\frac{\partial H}{\partial p} \right)_T}{\left(\frac{\partial H}{\partial T} \right)_p} \tag{8.6}$$

Differentiating both sides with respect to T at constant p, we get

$$-\frac{2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{V-b} - \frac{RT}{(V-b)^2}\left(\frac{\partial V}{\partial T}\right)_p$$

$$\therefore \left[-\frac{2a}{V^3}+\frac{RT}{(V-b)^2}\right]\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{V-b}$$

From Eq. (7.8b), we have

$$\mu = \frac{1}{C_p}\left[\frac{RT}{V-b}\,\frac{1}{\left\{-\frac{2a}{V^3}+\frac{RT}{(V-b)^2}\right\}} - V\right]$$

$$= \frac{1}{C_p}\left(\frac{2a}{RT}-b\right) \qquad (8.9)$$

$$\frac{RT}{V-b}\,\frac{1}{\left[-\frac{2a}{V^3}+\frac{RT}{(V-b)^2}\right]} - V$$

$$= \frac{RT}{V-b}\,\frac{1}{\frac{RT}{(V-b)^2}\left[1-\frac{(V-b)^2}{V^3}\frac{2a}{RT}\right]} - V$$

$$= (V-b)\left[1+\frac{(V-b)^2}{V^3}\frac{2a}{RT}\right] - V$$

$\because (1-x)^{-1} \approx 1+x$, when x is very small.

$\left[\text{Here } x = \frac{(V-b)^2}{V^3}\frac{2a}{RT}\right]$

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

$\approx \frac{2a}{RT} - b\ [\because\ (V-b)^2 = V^2,$
as b is small compared to V

Eq. (8.9) gives us the value of Joule-Thomson coefficient for a van der Waals' gas whose initial temperature is T. Since the sign of ΔT is opposite to that of μ, adiabatic throttling of a van der Waals' gas produces

i) cooling ($\mu > 0$) if $\frac{2a}{Rb} > T$ or $\frac{RT}{2} < \frac{a}{b}$,

ii) heating ($\mu < 0$) for $\frac{2a}{Rb} < T$ or $\frac{RT}{2} > \frac{a}{b}$,

iii) neither heating nor cooling ($\mu = 0$), when

$$\frac{2a}{Rb} = T \quad \text{or} \quad \frac{RT}{2} = \frac{a}{b}$$

iv) defines inversion temperature in terms of van der Waals' parameters a and b:

$$T_i = \frac{2a}{Rb} \qquad (8.10)$$

You can now explain: (i) the existence of inversion temperature, and (ii) the observation of cooling/heating effect when temperature of the gas is below/above inversion temperature as an interplay of van der Waals' constants. Combining Eqs. (8.9) and (8.10), we have

$$\mu = \frac{b}{C_p}\left(\frac{T_i - T}{T}\right)$$

It shows that magnitude of Joule-Thomson coefficient depends upon the value of initial temperature (T) and its difference from the inversion temperature. Physically, we can say that a rarefied but strongly interacting gas will show cooling and vice versa.

To illustrate these ideas, we now work out a numerical example on Joule-Thomson effect.

Example 1

Helium gas at initial pressure of 31 atm and temperature of 77.3 K is forced through a porous plug at constant pressure into a region of 1 atm. Calculate the change in its temperature assuming it to be a van der Waals' gas with $a = 3.4\times10^{-8}$ atm m^6 mol^{-2} and $b = 23.7\times10^{-6}$ m^3 mol^{-1}. Also comment on the result obtained in the light of the value of inversion temperature determined from the given data ($C_p = \frac{5R}{2}$, R $= 8.2\times10^{-5}$ m^3 atm^{-1}).

Solution

From Eqn. (8.9), we have

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_p}\left(\frac{2a}{RT}-b\right)$$

Therefore,

$$\Delta T = \frac{1}{C_p}\left(\frac{2a}{RT}-b\right)\Delta p = \frac{2}{5R}\left(\frac{2a}{RT}-b\right)\Delta p$$

Here, $T = 77.3$ K and $\Delta p = (1 - 31)\ \text{atm} = -30\ \text{atm}$. Substituting these values, we get

$$\Delta T = \frac{2}{(5 \times 8.2 \times 10^{-5}\ \text{m}^3\ \text{atm}\ \text{mol}^{-1}\ \text{K}^{-1})}$$

$$\left[\left(\frac{2 \times 3.4 \times 10^{-8}\ \text{atm}\ \text{m}^6\ \text{mol}^{-2}}{(8.2 \times 10^{-5}\ \text{m}^3\ \text{atm}\ \text{mol}^{-1}\ \text{K}^{-1}) \times 77.3\ \text{K}} \right) - (23.7 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1}) \times (30\ \text{atm}) \right]$$

$$= +1.9\ \text{K}.$$

Thus, the gas is heated up by 1.9 K.

We know that inversion temperature of a van der Waals' gas is given by

$$T_i = \frac{2a}{Rb}$$

For helium

$$T_i = \frac{2 \times 3.4 \times 10^{-8}\ \text{atm}\ \text{m}^6\ \text{mol}^{-2}}{(8.2 \times 10^{-5}\ \text{m}^3\ \text{atm}\ \text{mol}^{-1}\ \text{K}^{-1}) \times (23.7 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1})}$$

$$= 35\ \text{K}$$

Since initial temperature of the gas is 77.3 K, which is higher than its inversion temperature, adiabatic throttling of the gas will warm it up.

You should now answer a simple SAQ.

SAQ 2

Choose appropriate words from the bracket to fill in the blanks in the following comparing quasistatic adiabatic expansion and Joule-Thomson expansion (constant, cooling, higher, inversion, irreversible, lower, perfect, real, reversible, variable).

Quasistatic adiabatic expansion	Joule-Thomson expansion
i) Gas expands against a .... pressure	i) Gas expands against a........ pressure.
ii) The process is	ii) The process is ....
iii) It always produces .... effect.	iii) Cooling or heating is produced depending upon whether the initial temperature is .... or ...... than the ...... temperature.
iv) Cooling is produced whether the gas is .... or	iv) Joule-Thomson effect is observed only in ..... gases.

We close this section by making the following remarks about Joule-Thomson effect.

i) This experiment played an important role in the study of real gases.

ii) Cooling produced in this experiment provided a means of liquefying gases.

iii) The successful theoretical explanation of this effect encouraged physicists to develop thermodynamic concepts related to the distinguishing features of ideal and real gases.

You will now study another method which can be used for production of low temperatures.

8.4 ADIABATIC DEMAGNETISATION

In 1926, Debye and Giauque independently suggested that very low temperatures can be produced by adiabatic demagnetisation of a paramagnetic salt. Do you know what a paramagnetic salt is ? From your previous knowledge, you would recall that it is a salt of transition metals or rare earths like chrome alum. Now we may ask: How does paramagnetism arise? When a paramagnetic salt is placed in a magnetic field, it experiences a weak attraction. From the microscopic view-point, you can trace its origin to the orbital motion and spin of electrons. These electrons behave like a current loop which is equivalent to a magnetic moment. (The direction of the moment is normal to the plane of the orbit.) The atoms of rare earths have permanent magnetic moment. Let us consider a solid containing N atoms each of which has a magnetic moment **m**. The interactions between these moments is very weak and you can regard them to be independent of each other. When there is no magnetic field, these moments are oriented randomly. (This is because of thermal energy of atoms at a finite temperature.) In the presence of magnetic field, the magnetic moments tend to orient along the field. (This is, however, opposed by the thermal motion of atoms.) At a given temperature, more and more moments orient themselves along the field as field strength is gradually increased. The relation between magnetisation M, which is defined as the total magnetic moment per unit volume, field and temperature is given by Curie's law:

$$\mathbf{M} = k\,\frac{\mathbf{B}}{T}$$

Thus, for a solid to be paramagnetic, it is necessary for some of its constituent atoms to possess a magnetic moment.

The susceptibility, χ of a paramagnetic substance varies inversely with temperature. Mathematically

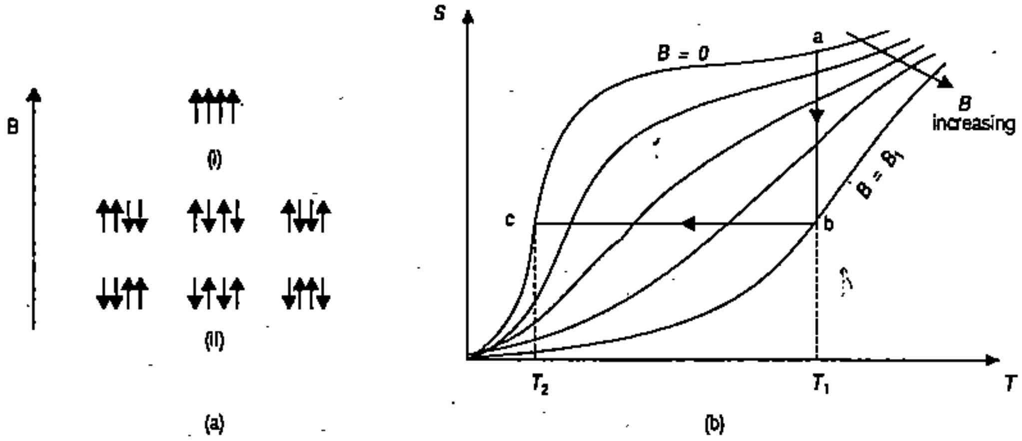
$$\chi = \frac{C}{T},$$

where C is called the Curie constant. At $T = T_c$ (Curie temperature), a transition takes place from para to ferromagnetism. So below T_c the atomic magnets have a greater tendency to get aligned along the applied magnetic field. Alignment occurs even in zero field due to spontaneous magnetisation.

Thermodynamically, we can consider it in two ways:

i) The internal energy of the paramagnetic salt is made to do work at its expense. As a result, the temperature will fall.

ii) At any temperature, the spins of atoms in a paramagnetic substance are randomly oriented. When these magnets are aligned parallel to one another [Fig. 8.5a(i)], their positional order is more than when they are randomly oriented [Fig. 8.5a(ii)]. This means that entropy in case (i) is less than that in case (ii). That is, when a paramagnetic substance is placed in a magnetic field, it is accompanied by decrease in entropy.



(a) (b)

Fig.8.5(a): A schematic representation of order and disorder among the atomic magnets of a paramagnetic salt. (i) All the four magnets are aligned in the direction of the applied magnetic field B. (ii) Six different arrangements having two atomic magnets pointing up and two pointing down. (b) The variation of entropy of a paramagnetic salt with temperature and magnetic field.

Refer to Fig. 8.5b. It shows the variation of entropy with temperature and magnetic field for a typical paramagnetic salt. When there is no field, the fall in entropy at the Curie temperature T_c corresponds to the onset of spontaneous ordering. (At higher temperatures, the entropy may always be reduced by applying a magnetic field.) The salt is first magnetised by applying a field B_1 at an initial temperature T_1. (Usually this temperature is attained by evaporating liquid ^{4}He or liquid ^{3}He under reduced pressure.) The heat evolved during magnetisation is conducted away to a helium bath, and the entropy falls. The salt then goes from state a to state b. The specimen is then isolated thermally and demagnetised. In other words, the field is switched off so that it is demagnetised adiabatically and its temperature falls. This is known as the **magneto–caloric effect**. If the field is reduced to zero, the final state of the salt will be at c, with temperature T_2. The lowest temperature to which the salt can be cooled by demagnetisation is effectively the Curie temperature.

You may now work out an SAQ on the principle of adiabatic demagnetisation.

SAQ 3

Write down the $T\,dS$-equation for the processes $a \rightarrow b$ and $b \rightarrow c$. Explain why heat is evolved during $a \rightarrow b$ and temperature falls during $b \rightarrow c$.

[Hint: Use the result of TQ 1(b) of Unit 6. You may consider $C_B = 0$ during $a \rightarrow b$]

Now that you have worked out SAQ 3, you must have understood very clearly the process of cooling by adiabatic demagnetisation. We may now obtain an expression for drop in temperature. While solving SAQ 3, you have derived that

$$dT = -\frac{T}{C_B}\left(\frac{\partial m'}{\partial T}\right)_p dB$$

Using Curie's law, you can write

$$m' = \frac{kB}{T}$$

where k is a constant

$$\therefore \left(\frac{\partial m'}{\partial T}\right)_B = \frac{kB}{T^2}.$$

$$\chi = \frac{M}{H} = \frac{C}{T},$$
$$M = \frac{m'}{V} \text{ and } H = \frac{B}{\mu_0}$$
$$\therefore \frac{m'}{V}\frac{\mu_0}{B} = \frac{C}{T}$$
$$\text{or } m' = \frac{CV}{\mu_0}\frac{B}{T}$$
$$= \frac{kB}{T}$$
$$\text{where } k = \frac{CV}{\mu_0}$$

If C_B is given by

$$C_B = DT^3$$

where D is a constant, we can write

$$dT = \frac{kB\,dB}{DT^4}$$

or $$T^4 dT = \frac{k}{D}\,B\,dB$$

so that

$$\int_{T_1}^{T_2} T^4 dT = \frac{k}{D}\int_{B_1}^{0} B\,dB$$

$$\therefore T_2^5 - T_1^5 = -\frac{5k}{2D}B_1^2$$

or $$T_2 = (T_1^5 - \frac{5k}{2D}B_1^2)^{1/5} \tag{8.14}$$

According to Debye's T^3 - law, we have in the vicinity of $T \to 0$, $C_B \propto T^3$

Knowing k, D, B_1 and T_1, you can easily compute T_2 using Eq. (8.14).

It has been observed that temperatures upto 10^{-3} K can be obtained using adiabatic demagnetisation, provided the following conditions are satisfied.

i) The paramagnetic salt used has large Curie constant and small heat capacity at constant magnetic flux density.

ii) The applied flux density **B** is high (>1 tesla).

iii) The intial temperature of the sample is as low as possible.

We shall now give a brief description of the arrangement used to perform adiabatic demagnetization.

The experimental set-up

Refer to Fig. 8.6. It depicts schematically the arrangement used for adiabatic demagnetization. C is a glass or metal cylinder surrounded by a bath of liquid He. This, in turn, is placed in a bath containing liquid H_2 or N_2. We place the complete assembly between the poles of a strong electromagnet. The liquid helium bath is connected to a diffusion pump so that it can be boiled under low pressure to produce an initial temperature of about 1 K.

A paramagnetic material (such as copper potassium sulphate, titanium cesium alum, iron ammonium alum, gadolinium sulphate, etc) in the form of a sphere or a spheroid is suspended by a silk or nylon thread in cylinder C. It is then evacuated and filled with He gas at low pressure. Next, we switch on the electromagnet so that the sample is magnetised. The heat of magnetisation is conducted by He gas to the surrounding liquid He bath and, thus, we cool the sample to about 1 K. (In view of conduction of heat by He gas, we call it exchange gas.) Now, we connect C to a vacuum pump to create vacuum of high order so that the sample is

8.5.1 Consequences of the Third Law

i) **Behaviour of thermodynamic potentials**

We know that $G = H - TS$ and $F = U - TS$. Now, as $T \rightarrow 0, S \rightarrow 0$ so that the product $TS \rightarrow 0$. That is, as temperature is close to absolute zero, Gibbs potential becomes equal to enthalpy and Helmholtz potential equals internal energy. Physically, it means that there is perfect order and all energy is available for work.

ii) **Isothermal volume and pressure expansion coefficient**

The entropy change of a system due to small changes of pressure during a process near 0 K may be expressed as

$$\Delta S = \int \left(\frac{\partial S}{\partial p} \right)_T dT$$

But as $T \rightarrow 0$, $\Delta S \rightarrow 0$. So we can say that

$$\underset{T \rightarrow 0}{\text{Lt}} \left(\frac{\partial S}{\partial p} \right)_T \rightarrow 0$$

But from Eq. (6.14d), $\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p$

$$\therefore \quad \underset{T \rightarrow 0}{\text{Lt}} \left(\frac{\partial V}{\partial T} \right)_p = 0 \tag{8.17}$$

But $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T} \right)_p$. So we have

$$\underset{T \rightarrow 0}{\text{Lt}} \ \beta = 0 \tag{8.18}$$

Similarly, you may show that

$$\underset{T \rightarrow 0}{\text{Lt}} \left(\frac{\partial p}{\partial T} \right)_V = 0 \tag{8.19}$$

iii) **Heat capacities near 0 K**

You know that,

$$C_p = T\left(\frac{\partial S}{\partial T} \right)_p$$

Hence, at constant pressure

$$dS = \frac{C_p\, dT}{T}$$

On integrating, we get

$$S(T_1) - S(T) = \int_T^{T_1} \frac{C_p\, dT}{T} \tag{8.20}$$

In the limit $T \rightarrow 0$, the third law implies that the integral on the right hand side of Eq. (8.20) must be finite. That is, it should not diverge as $T \rightarrow 0$. Thus, we have

$$\underset{T \rightarrow 0}{\text{Lt}} \ C_p = 0 \tag{8.21}$$

Similarly, it can be shown that

$$\underset{T \rightarrow 0}{\text{Lt}} \ C_V = 0 \tag{8.22}$$

It shows that $C_p - C_V \rightarrow 0$ in the limit $T \rightarrow 0$. This prediction is borne out by experiments.

You may now work out an SAQ on the consequences of the third law.

SAQ 5

a) Prove Eq. (8.19)

b) Using Eq. (6.17a), show that $C_p \rightarrow C_V$ as $T \rightarrow 0$.

Before rounding off this section, we touch upon the aspect of unattainability of absolute zero

8.5.2 Non-attainability of Absolute Zero

To show that absolute zero cannot be attained by a finite series of mechanical steps, we frame the following hypothesis. We consider a Carnot engine operating between two reservoirs; one of which is maintained at absolute zero and the other at some finite temperature T. Is this hypothesis wrong? To prove so, we represent the Carnot cycle in a $T-S$ diagram (Fig. 8.8). For a cyclic process, you know that

$$\Delta S = \oint \frac{\delta Q}{T} = 0$$

We know that

$$\Delta S = \Delta S_{12} + \Delta S_{23} + \Delta S_{34} + \Delta S_{41}$$

And $\Delta S_{12} = \frac{\delta Q}{T}$ where Q is the heat absorbed at temperature T. Since $2 \rightarrow 3$ and $4 \rightarrow 1$ are adiabats, $\Delta S_{23} = \Delta S_{41} = 0$ and by the third law, we have $\Delta S_{34} = 0$. Hence

$$\Delta S = \oint \frac{\delta Q}{T} = \Delta S_{12} \neq 0$$

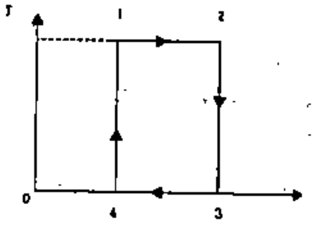


Fig. 8.8: T–S diagram of a Carnot cycle

But this contradicts the second law of thermodynamics. So our hypothesis must be wrong. In other words, we cannot have a Carnot engine operating between reservoirs one of which is at a finite temperature and the other at absolute zero. The temperatures of these reservoirs have to be non-zero. This means that absolute zero is unattainable.

Let us now summarise what we have learnt in this unit.

8.6 SUMMARY

- Joule-Thomson effect signifies the change in temperature of a gas on being throttled through a porous plug from a region of constant high pressure to that of constant low pressure under adiabatic conditions. This process does not involve any change in enthalpy of the system.

- Joule-Thomson coefficient is the change in temperature per unit change in pressure across the porous plug. It is given by $\mu = \left(\frac{\partial T}{\partial p}\right)_H$

- Sign of μ is opposite to that of the change in temperature.

- The locus of the maxima of isenthalps on the $T-p$ diagram of a real gas is called the inversion curve. The point where this curve meets the T - axis is known as the inversion temperature.

- On being subjected to adiabatic throttling, a gas is warmed or cooled depending upon whether its initial temperature is higher or lower than the inversion temperature.

- Adiabatic demagnetisation of a paramagnetic substance produces cooling much below 1 K. The effect is large if the sample has large Curie constant, small heat capacity and is subjected to high magnetic flux density at a low temperature.

- By no finite series of process is the absolute zero attainable.

- The equilibrium entropies of all systems and the entropy changes in all reversible isothermal processes tend to zero as temperature approaches absolute zero.

NOTES

Utter Pradesh
Rajarshi Tandon Open University

UGPHS-06
THERMODYNAMICS AND STATISTICAL MECHANICS

Block

3

ELEMENTARY KINETIC THEORY

UNIT 9
Ideal Gases 5

UNIT 10
Transport Phenomena 18

UNIT 11
Brownian Motion 36

UNIT 12
Real Gases 53

BLOCK 3 ELEMENTARY KINETIC THEORY

In Block 1 and 2 you have studied the subject of thermodynamics, which is essentially an empirical science. You learnt to relate thermic properties of materials such as heat capacities, compressibilities etc without any reference to the nature of the substance. Though thermodynamics is a very powerful tool, it has some limitations. For instance, from thermodynamic considerations alone, it is not possible even to derive the equation of state of a substance (Unit 1). We can, however, overcome this and some other limitations by making hypotheses regarding the nature of matter.

The most fruitful, and one of the oldest, hypotheses is that matter is made up of molecules. This idea was first conceived by an Indian Philosopher and saint, Kanada, in BC 600. He named these **parmanu.** (About a century later, a Greek philosopher Democritus visualised atoms as the minutest invisible particles of matter.) The credit for providing kinetic view point the modern outlook goes to Daniel Bernoulli. In 1738 he proposed the mechanical picture of gaseous state and studied variations in pressure and volume at constant temperature. However, there was little progress for several decades. Towards the end of 18th century, Dalton established the law of partial pressures and explained the laws of chemical combination. This work provided a much needed impetus. In 1811 came Avogadro's hypothesis. But it was not until 1859, when Maxwell showed that this result can be derived from kinetic theory, that physicists placed their confidence in this theory. Subsequent growth is due to pioneers like Joule, Clausius, Jeans and van der waals.

Molecules can exist in free state and possess all the basic properties of a substance. That is, matter is not continuous in structure. And whether a given state is a solid, a liquid or a gas is determined by the interplay of thermal energy and intermolecular forces. This gave birth to the **molecular theory**, which when supplemented by the laws of mechanics for **individual** molecules leads to **kinetic theory.** This is the subject matter of this block. You will learn that macroscopic properties of gases,such as pressure and temperature can be related to its microscopic properties such as speed and mass of its constituent atoms/ molecules.

In Unit 9 we have reviewed the basic concepts of the kinetic theory of gases with particular reference to ideal gases. You will learn to derive an expression for pressure exerted by the molecules on the walls of the container, and predict various gas laws from it. You may be familiar with some of these expressions but we have included them yet again to make the block self-contained. As a consequence of random motion of molecules, non-equilibrium conditions make gaseous substance to undergo transport processes. You will learn to derive expressions for mean free path, coefficient of viscosity, thermal conductivity and diffusion coefficient in Unit 10.

Although the kinetic theory of gases received an impetus because of its successful predictions about the vertical particle density gradient in our atmosphere, direct experimental evidence of molecular motion, which provided this theory a sound pedestal, came in the form of Brownian motion. Einstein analysed it from physical considerations and gave a satisfactory theoretical analysis. You will learn the theory of Brownian motion, and its connection with random motion in Unit 11. Physical examples of Brownian motion are also discussed. In Unit 12 we have discussed imperfect behaviour of real gases. van der waals' equation of state is discussed in detail.

After going through this block you will realise that kinetic theory has great aesthetic appeal. Very elegant laws governing the gaseous behaviour emerge out of chaotic motion of a large number of molecules. Recently, it has found application in the domain of cold-neutrons which holds great technological promise. This means that even today this theory finds applications in the frontier areas of physics. We, therefore, urge upon you to read the block carefully and work out SAQ's as well as TQ's. Only then you will enjoy it.

We wish you success.

Acknowledgments

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UNIT 9 IDEAL GASES

Structure

9.1 Introduction

Objectives

9.2 Assumptions of Kinetic Theory

9.3 Pressure Exerted by a Gas

Kinetic Interpretation of Temperature

Molecular Speeds

Deduction of Gas Laws

Equipartition of Energy

9.4 Heat Capacities of Gases

9.5 Summary

9.6 Terminal Questions

9.7 Solutions and Answers

9.1 INTRODUCTION

From your school science curriculum you would recall that matter is made up of molecules, which can exist in a free state and retain all the characteristic properties of the substance whose part they are. This hypothesis supplemented by the laws of mechanics for individual molecules gave birth to a new area of knowledge—the kinetic theory of matter. It has been used successfully to explain physical phenomena like different states of matter, compressibilities and evaporation. You are all familiar with H_2O. It can exist as ice (solid), water (liquid) and vapour (gas). The question logically arises : What determines the state of a substance? From Unit 7 of Block 2 you can identify temperature and pressure as two factors for determining the state of a substance. You may now ask: Is there any other factor also? Of course, yes. We know that the molecules of a substance are held together by intermolecular forces. In fact, the interplay of thermal agitation and intermolecular forces determines the state of a substance. In solids, cohesive forces (intermolecular forces) are much stronger than the effect of thermal agitation. This explains why solids have a definite shape even at considerably high temperatures. On the other hand, in gases, thermal agitation outplays the effect of intermolecular forces; gas molecules fly apart randomly and tend to occupy maximum space available.

Another hypothesis that triggered off sustained and coherent development of kinetic theory is based on the work of Joule. He conclusively established that heat is intimately connected with motion. We may therefore conclude that kinetic theory of gases is based on two postulates: (i) matter is made up of molecules and (ii) heat can be identified with molecular motion.

Based on these postulates, nineteenth century physicists, particularly Maxwell and Clausius, proposed a set of assumptions about the nature of molecules and their movement. (These assumptions are supplemented by the laws of mechanics.) From these follow the elegant laws governing the behaviour of ideal gases in equilibrium. In this unit you will learn the molecular interpretation of bulk properties of ideal gases, deduce gas laws and the law of equipartition of energy.

Objectives

After studying this unit you will be able to

- state the assumptions of kinetic theory of gases

- derive expressions for macroscopic quantities like pressure and temperature in terms of microscopic properties of constituent molecules
- derive gas laws from the equation $pV = \frac{1}{3} mN\overline{v^2}$, and
- apply the law of equipartition of energy to obtain expressions for heat capacities.

9.2 ASSUMPTIONS OF KINETIC THEORY

To avoid mathematcal complications, some simplifying assumptions were made by the early contributors to kinetic theory. We now state these with particular reference to ideal gases.

1. A gas consists of a very large number of identical molecules. This assumption is justified by experimental evidences. For instance, 1 mm^3 of a gas at STP contains 3×10^{16} molecules. (This number is almost a *million* times bigger than the population of the world today.)
2. The gas molecules can be regarded as point masses. Experiments reveal that the diameter of a molecule is about 2 Å or 2×10^{-10}m whereas the distance between them in a gas is nearly ten times larger. This means that their size is much less than the average distance between them.
3. The molecules are in a state of constant random motion. (It bears analogy with the motion of honeybees disturbed from their hive). That is, all directions and positions are equally probable (Fig. 9.1). The justification for this assumption came from the work of Robert Brown.

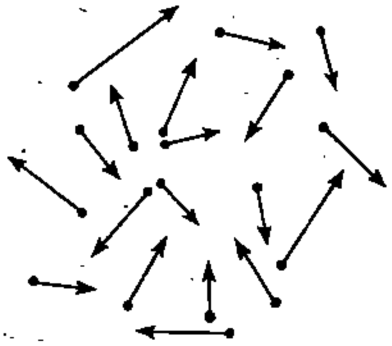


Fig. 9.1 : The motion of the molecules of a gas

4. The molecules of a gas do not experience any force except during collisions. This means that the intermolecular forces (of mutual attraction) or between the molecules and the walls of the container are negligible. The molecules of a gas can be thought of as moving about relatively freely and their energy is wholly kinetic, i.e., potential energy is zero.
5. The gas molecules are considered perfectly hard elastic spheres. This means that molecules do not deform when they collide. (You can imagine the mechanical equivalence as collisions between glass marbles, popularly known as Kanchas.) Moreever the time taken in a collision is negligible compared with the time between succesive collisions. This assumption implies that energy and momentum before and after a collision are the same.
6. In the absence of an external force (field), the directios of molecular velocities are distributed uniformly, i.e. are isotropic. In practice, there is always some randomness in the direction of the velocities because of the irregularities in the walls.
7. All molecules do not move with the same speed, i.e. there is a spread of speeds between some lower and upper bounds. Fig 9.2 shows the distribution of molecules in velocity space. The justification of this assumption lies in finite width of spectral lines.

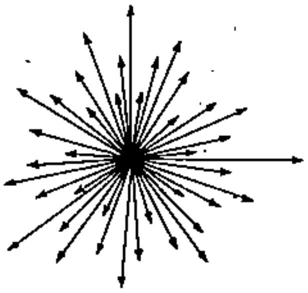
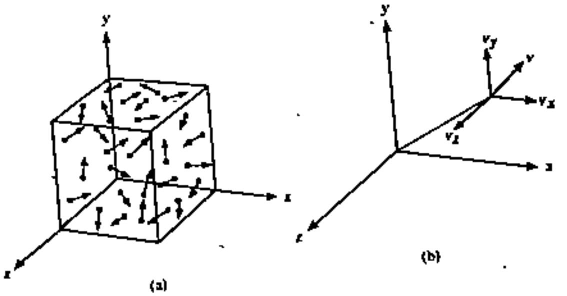


Fig. 9.2 : Distribution of velocities at a given temperature

These assumptions ensure that kinetic theory model will be applicable to all gases. But you must realise that some of these assumptions may not be true always. You will get an opportunity to discuss these limitations as soon as the theory is applied to real systems like liquefied gases or its domain is extended to observed phenomena.

9.3 PRESSURE EXERTED BY A GAS

Consider one mole of a gas in a cubical container of side L. Suppose there are N molecules, each of mass m. The molecules are in random motion and possess different velocities, as shown in Fig. 9.3(a). In the absence of an external field, these molecules exhibit complete chaos and collide with the walls of the container. Let us consider a molecule moving with velocity v. We can resolve it into three mutually orthogonal components v_x, v_y and v_z along the x-, y- and z- axes, as shown in Fig 9.3(b). Then you can write



(a)

(b)

Fig. 9.3 : (a) Schematics of a gas in a container (b) Resolution of velocity of a molecule into its components

$$v^2 = v_x{}^2 + v_y{}^2 + v_z^2 \tag{9.1}$$

Since all three directions are equally probable, Assumptions 3 and 6 suggest that it should be sufficient to consider motion along any one direction. Let us first consider the motion of the molecule along the x- axis. We know that x -axis is normal to the faces A_1 and A_2 of the cube. Before colliding with A_1, it will have momentum $m\,v_x$ normal to this face. After it collides elastically with the face A_1 at $x = L$, Assumption 5 implies that the molecule rebounds with the momentum $-m\,v_x$. Therefore, for each collision the change in the momentum of the molecule at $x = L$ is $m\,v_x - (-m\,v_x) = 2mv_x$. You may ask: How much momentum is imparted to the face A_1 in this collision? Since total momentum has to be conserved, the momentum imparted to A_1 will be $2mv_x$. After rebounding, this molecule will travel a distance $2\,L$ across the cube before it strikes A_1. This means that the molecule has to travel a distance $2\,L$ before it strikes the same face of the cube and the time interval between any two collisions with A_1 will be $\Delta t = 2L/v_x$. That is, a molecule makes $v_x/2L$ collisions per second. The question may logically arise: What will be the momentum imparted to the wall A_1 in unit time interval? The momentum imparted to the face A_1 per second by the molecule is $2mv_x/\Delta t = mv_x{}^2/L$.

According to Newton's second law of motion, the rate of change of momentum is force. So we find that the force exerted by one molecule on the face A_1 while moving along x- axis will be

$$f_{1x} = \frac{mv_x^2}{L}$$

Let us now pause for a minute and ask: What have we achieved so far? If you recall that force per unit area defines pressure, then you will realise that we have almost achieved the goal we set for ourselves. Since the molecule under consideration exerts the force mv_x^2/L over a surface area L^2, we can write

$$p_{1x} = \frac{f_{1x}}{L^2} = \frac{mv_x^2}{L^3}$$

If the total number of molecules in the cube is N, Assumption 7 tells us that there will be a spread in velocities (or speeds). That is, different molecules move with different velocities. And the total pressure is the sum of pressures due to each molecule striking the face. Therefore, the pressure exerted by all the molecules on the face A_1 will be

$$p_x = \frac{m}{L^3}\left(v_{1x}^2 + v_{2x}^2 + v_{3x}^2 + \ldots + v_{Nx}^2 \right)$$

To write it in a more compact form, we introduce the summation notation :

$$p_x = \frac{m}{L^3}\sum_{i=1}^{N} v_{ix}^2$$

$$= \frac{m}{V} N\overline{v_x^2} \qquad (9.2)$$

where $V = L^3$ signifies the volume of the container and $\overline{v_x^2}$ is the average value of v_x^2 for all the N molecules:

$$\overline{v_x^2} = \frac{\sum\limits_{i=1}^{N} v_{ix}^2}{N} \qquad (9.3)$$

From Eq. (9.1) we know that $v^2 = v_x^2 + v_y^2 + v_z^2$. On averaging over all the molecules, we can show that

$$\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = \overline{v^2}$$

Since the molecules move entirely at random, when the gas is in equilibrium, all directions of velocity will be equally probable.

That is, since the velocities are distributed isotropically, their properties must not vary with direction. Physically it means that the gas molecules do not have any preference for any face of the cube. So we can write

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$$

It readily follows that each one of these is one third of the averaged square velocity:

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}\overline{v^2}$$

Using this result in Eq. (9.2), we get

$$p_x = \frac{1}{3}\frac{m}{V}N\overline{v^2}$$

Since pressure exerted by a gas is same in all the directions, the average pressure exerted by it in any direction is same and we can write

$$p = \frac{1}{3} m\, n\, \overline{v^2} \qquad (9.4)$$

where $n = N/V$ is the number density. This is an important result. You will note that it relates macroscopic properties (p and V) with the microscopic properties (m and v) of individual molecules making up the system.

You will note that we have derived this result by considering a cubical box. Since only V occurs in Eq. (9.4), the shape of the container plays no role in determining the magnitude of pressure exerted on its sides. That is, Eq. (9.4) is valid for any general shape of the container.

Before we proceed to obtain deductions from Eq.(9.4), we wish that you should go through the following example.

Example 1

One mole of oxygen is contained in a hollow cube of side 10 cm. If the translational speed of the molecules, each of mass 5×10^{-26} kg, is 500 ms^{-1}, calculate the pressure exerted by the gas on the sides of the cube.

Solution

The change in the momentum of a gas molecule

$$= 2\,m\,v_x = 2 \times (5 \times 10^{-26}\,\text{kg}) \times (500\text{ms}^{-1})$$

$$= 5 \times 10^{-23}\,\text{kg ms}^{-1}$$

$$= 5 \times 10^{-23}\text{Ns}$$

The time interval between sucessive collisions on the same face

$$= \frac{2L}{v_x} = \frac{2 \times 0.1\text{m}}{500\ \text{ms}^{-1}} = 4 \times 10^{-4}\,\text{s}$$

Hence the rate of change of momentum of one molecule

$$= \frac{5 \times 10^{-23}\,\text{Ns}}{4 \times 10^{-4}\,\text{s}} = 1.25 \times 10^{-19}\,\text{N}$$

∴ The total force experienced due to all molecules

$$= (1.25 \times 10^{-19}\,\text{N}) \times (6 \times 10^{23})$$

$$= 7.50 \times 10^{4}\,\text{N}$$

Average pressure communicated to the walls of the container

$$= \frac{7.50 \times 10^{4}\,\text{N}}{3 \times 10^{-2}\,\text{m}} = 2.5 \times 10^{6}\,\text{Nm}^{-1}$$

You would recall that one atmospheric pressure is $1 \times 10^{5}\,\text{Nm}^{-1}$. So one mole of oxygen contained in a cube of side 0.1 m exerts pressure nearly 25 atmosphere on its sides

---

You may now like to answer following SAQ

SAQ 1

a) We ignored the intermolecular collisions in the above derivation. Will their inclusion affect Eq. (9.4)?

b) Rewrite Eq. (9.4) in terms of the density of the gas.

You will agree that we started from a purely mechanical picture of gas as a collection of randomly moving molecules. And we have been able to derive an expression for pressure in terms of the microscopic properties of individual molecules. It is therefore instuctive to know the kinetic interpretation of pressure and its predictions about gas laws. Now we will discuss these aspects.

9.3.1 Kinetic Interpretation of Temperature

To seek kinetic interpretation of temperature we first rewrite Eq. (9.4) as

$$pV = \frac{2}{3}N\left(\frac{1}{2}m\overline{v^2}\right)$$

$$= \frac{2}{3}N\,\varepsilon \tag{9.5}$$

where $\varepsilon = \frac{1}{2}m\overline{v^2}$ is the average translational kinetic energy of a molecule. We expect the motion of gas molecules to become more lively as temperature increases. So if we connect the average kinetic energy of a molecule to temperature so that

$$\varepsilon = \frac{3}{2} k_B T \tag{9.6}$$

Eq. (9.5) becomes

$$pV = N k_B T \tag{9.7}$$

where k_B is Boltzmann constant. Its value is 1.38×10^{-23} JK^{-1}. By definition, the number of molecules N is the product of the Avogadro number N_A and the mole fraction μ, i.e. $N = \mu N_A$. Then you can write

$$pV = \mu \, (N_A \, k_B) \, T$$

If we identify the product $N_A \, k_B$ with R, the gas constant, we find that

$$pV = \mu RT \tag{9.8}$$

Do you recognise this result? It is the **equation of state** for a perfect gas. You must have learnt it in your school science curriculum . Before we discuss the implications of this result, we may mention that from experiments the gas constant is known to be 8314 kJmol^{-1} K^{-1} and the Avogadro number is 6.02×10^{26} kmol^{-1} so that the Boltzmann constant k_B is 1.38×10^{-23} JK^{-1}. You must have realised that in arriving at the ideal gas equation we have connected a purely mechanical quantity – the average kinetic energy of a molecule – to temperature. This is a big step as it relates the molecular (microscopic) and macroscopic viewpoints through Boltzmann constant. (In Unit 13 you will learn that Boltzmann constant bridges the statistical and thermodynamic viewpoints as well.) This assigns a completely new and deeper meaning to temperature; it is linearly proportional to the average kinetic energy of molecules. It implies that at a given temperature, the kinetic energy of molecules of all gases, irrespective of the differences in their masses, will be the same. And for a given gas, higher the temperature, more will be its kinetic energy. In particular, at $T = 0$, $\varepsilon = 0$. That is, at absolute zero of temperature, the gas molecules will be devoid of all motion. Or molecular theory predicts that at absolute zero, there is no chaos; all molecules will be frozen in space and perfect order should prevail. For actual systems this is not true indicating that ideal behaviour should not be expected under all conditions.

To understand the use of Eq. (9.5) you should solve the following SAQ.

SAQ 2

Calculate the average kinetic energy of air molecules at 300 K. Given $k_B = 1.38 \times 10^{-23}$ JK^{-1}.

We have now developed a detailed reliable model of gaseous state. As a first check of this model we have learnt how it leads us to experimentally verifiable result like ideal gas equation. Let us now use this model to calculate some numbers of physical interest. One such quantity is molecular speed. Let us learn about it now.

9.3.2 Molecular Speeds

To know how fast the molecules in a gas move, we use the relation

$$k_B = \frac{R}{N_A}$$

in Eq. (9.6). This gives

$$\frac{1}{2} m\overline{v^2} = \frac{3}{2} k_B T = \frac{3}{2} \frac{R}{N_A} T$$

or

$$\overline{v^2} = \frac{3 k_B T}{m} = \frac{3RT}{M}$$

where $M = mN_A$ is the molecular weight. The square root of average mean square speed, called **root mean square speed**, is given by

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3RT}{M}} \tag{9.9}$$

That is, v_{rms} is inversely proportional to the molecular weight of a gas. So at a given temperature, lighter gas molecules move faster. For a few gases of interest, the values of v_{rms} at STP are given in Table 9.1. The fact that lighter molecules move faster has an interesting consequence for existence of life on the earth. From your elementary mechanics course you will recall that an object having radially outward velocity more than 11.2 km s^{-1} can escape from the influence of gravity of the earth.

Table 9.1: Values of v_{rms} for Different Gas Molecules at STP

Gas	v_{rms} (ms^{-1})
H_2	1838
O_2	461
N_2	493
CO_2	393
Air	485
H_2O	615

($v_e = \sqrt{2gR}$, where R is radius of the earth.) This means that gas molecules with speed greater than v_e have a chance of escaping from the earth. In fact, it is for this reason that gases like hydrogen, helium, carbon dioxide and water vapour are found in upper parts of earth's atmosphere, whereas oxygen is available near earth's surface (and sustains life on our planet). This also explains why the moon, which has a much lighter pull, has no atmosphere. This correct prediction of vertical density distribution of gases in our atmosphere proved an indirect evidence in favour of kinetic theory and boosted the confidence of earlier workers in it.

You will recall the assumption that not all molecules move with the same speed. So you may now logically ask: What is the distribution of molecular speeds? The answer to this interesting question was provided by Maxwell. We will quote his result without going into details. He showed that the number of particles having speeds between v and $v + dv$ is given by

$$dN_v = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 \exp \left(-\frac{mv^2}{2 k_B T} \right) dv \qquad (9.10)$$

You will get an opportunity to discuss this in detail in the next block.

The plot of Eq. (9.10) for three different temperatures is given in Fig. 9.4. You will note that as temperature increases, the curve becomes broader and flattened. Physically it implies that the fraction of molecules having higher energy increases with temperature.

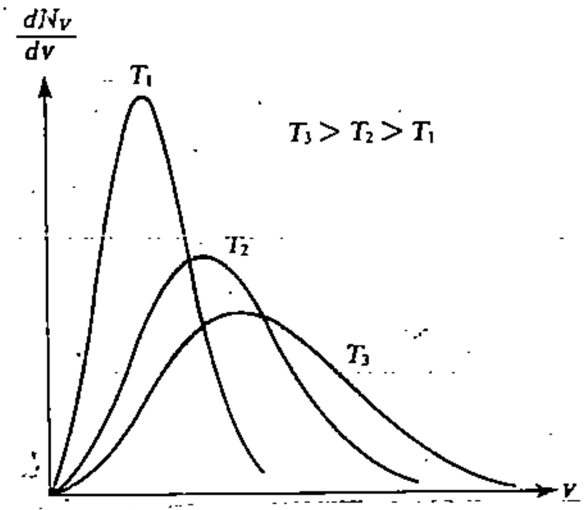


Fig. 9.4 : A plot of Maxwellian distribution at three different temperatures

Let us now learn to deduce gas laws.

9.3.3 Deduction of Gas Laws

All gas laws can be deduced from Eq. (9.5). Let us begin with Boyle's law.

Boyle's law : From Eq. (9.5) we note that for a given mass of a gas

$$pV = \frac{2}{3} N \varepsilon$$

Since kinetic energy remains constant at a fixed temperature, we note that

$$pV = \text{constant.}$$

It means that the pressure exerted by a given mass of a gas varies inversely with its volume, when temperature remains constant. This is Boyle's law, as you will recall from your earlier knowledge.

Charles' Law : When pressure remains constant, Eq. (9.5) implies that the volume of a given mass of a gas increases linearly with kinetic energy, i.e. temperature. This is Charle's law.

Avogadro's Law : This law states that at constant temperature and pressure, equal volume of all gases contains the same number of molecules. To obtain it from kinetic theory arguments, let us consider two different gases at the same temperature and pressure. Then, equality of pressure implies that

$$p = \frac{1}{3} m_1 n_1 \overline{v_1^2} = \frac{1}{3} m_2 n_2 \overline{v_2^2} \qquad (9.11)$$

where v_1 and v_2 are respectively the mean squared velocities of molecules of two gases.

If the temperature is constant, their mean kinetic energies should be equal. So we can write

$$\frac{1}{2} m_1 \overline{v_1^2} = \frac{1}{2} m_2 \overline{v_2^2} \qquad (9.12)$$

Dividing Eq. (9.11) by Eq. (9.12) we get

$$n_1 = n_2 \qquad (9.13)$$

This is mathematical statement of Avogadro's law. From your school science curriculum you would recall that Avogadro put forward this hypothesis while studying weights and proportions. That is, it had nothing to do with the motion of molecules. But the fact that the same result has been obtained from the theory of molecular motion, you will agree, is a significant success for kinetic theory.

To get a feel of these results you should go through the following example.

Example 2

Calculate the number density of oxygen at 1 atm $= 1.013 \times 10^5 \text{ Nm}^{-2}$ and $T = 300$ K.

Solution

From Eq. (9.4) we recall that

$$p = \frac{1}{3} mn \overline{v^2}$$

$$= n k_B T$$

so that

$$n = p/k_B T$$

On inserting the numerical values, we find that

$$n = \frac{1.013 \times 10^5 \text{ Nm}^{-2}}{(1.38 \times 10^{-23} \text{ JK}^{-1}) \times (300\text{K})}$$

$$= \frac{1.013 \times 10^{26}}{4.14} \text{m}^{-3} = 2.447 \times 10^{25} \text{ m}^{-3}$$

You may now like to solve an SAQ to check your progress.

SAQ 3

Prove Dalton's law of partial pressures for an ideal gas.

The remarkable elegance in accounting for the perfect gas laws brings out the aesthetic appeal of molecular theory. This is because chaotic motions of extremely large molecules obey elegant laws which can be confirmed by experiments upto a fairly reasonable degree of correctness. This success proved an important milestone in the growth of the molecular theory. As the next check, this theory was put to an acid test when its predictions about heat capacities were to be verified experimentally. In fact, it proved a highly contentious issue. And before we go into its details, it is worthwhile to reflect on what is called the equipartition of energy.

9.3.4 Equipartition of Energy

In Sec. 9.3.1 we have shown that the translational kinetic energy of a molecule is

$$\varepsilon = \frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T$$

But we know that

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

and since all three directions are equivalent, we can write

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}\overline{v^2}$$

The mean kinetic energy of a molecule associated with any one component of velocity, say v_x is therefore

$$\frac{1}{2} m \overline{v_x^2} = \frac{1}{6} m \overline{v^2} = \frac{k_B T}{2} \tag{9.14}$$

This means that the translational kinetic energy associated with each component of velocity is equal to $k_B T/2$; just one third of the total translational kinetic energy. In other words, we can say that in this case energy is equally partitioned among the three components of velocity. This is the **principle of equipartition of energy** for a monatomic gas. This is an important result of classical physics. And to discuss it in detail, we introduce the concept of degree of freedom (d.f.)

Degree of Freedom

The degree of freedom of a molecule is defined as the number of independent coordinates required to specify its position. A house fly moving on a stretched string has only one d.f. Do you know why? This is because we require only one coordinate to specify its position. However, when it moves on the floor, it has 2 d.f. whereas when it flies, it has 3 d.f. How many d.f. a randomly moving molecule of a monatomic gas (like helium, argon, or krypton) has? It has only three translational d.f. Before we generalise this discussion, we wish that you should answer the following SAQ.

The number of d.f. can also be defined as the total number of independent squared terms appearing in the expression of energy of a system.

SAQ 4

A point moving along a curved path has only one d.f. Comment.

In addition to translational d.f., a di–or poly–atomic molecule has a tendency to rotate (about fixed axes) because of intermolecular collisions as well as the collision with the walls of the container. From PHE-01 course you would recall that we can resolve the angular velocity of a rotating molecule along three mutually perpendicular coordinate axes. So you may expect that a rigid diatomic molecule will have three rotational d.f. But there cannot be any rotation about the line joining the atoms and, in general, a linear diatomic molecule has 2 d.f., of rotation. That is, there are in all five d.f. for a linear (diatomic) molecule. (A non–linear molecule like H_2O has 3 rotational d.f.) Further, since these molecules do not have a perfectly rigid structure, they may vibrate as a result of intermolecular collisions. The number of d.f. (f) of a system can be determined from the general result

$$f = 3p - c$$

where p is the number of particles constituting the system and c is the total number of constraints.

You can verify that for a single atom, $p = 1$ and $c = 0$ (since the motion is random) so that $f = 3$. Similarly, for a diatomic molecule, $p = 2$ and $c = 1$ because the distance between the atoms is a fixed quantity. So $f = 5$.

In the case of translational energy we have seen that the energy associated with each degree of freedom is a quadratic function of the variable specifying it and the mean value of the corresponding energy is equal to $k_BT/2$. For rotation, kinetic energy is $I\omega^2/2$ and we expect that the mean rotational energy will be $k_BT/2$. From PHE-02 course you may recall that for a harmonic oscillator, the potential energy is $kx^2/2$, where k is spring constant and mean potential energy is $k_BT/2$. We may conclude that every active d.f. for which the energy is a quardratic function of a variable has mean energy $k_BT/2$.(The total energy of the system is $fk_BT/2$.) This is the general statement of the principle of **equipartition of energy.**

Let us now discuss the classical theory of heat capacities of gases.

9.4 Heat Capacities of Gases

Consider one mole of a gas. Its total kinetic energy is given by

$$u = N_A \varepsilon$$

If the number of degrees of freedom of a system is f, we can write

$$u = \frac{fN_A}{2}k_BT = \frac{f}{2}RT \tag{9.15}$$

This equation implies that molar heat capacity, defined as the energy required to raise the temperature of one mole of an ideal gas by one kelvin, at constant volume is

$$c_V = \frac{f}{2}R \tag{9.16}$$

From Block 1 of this course, you know that $c_p = c_V + R$ so that we can write molar heat capacity at constant pressure as

$$c_p = \left(\frac{f+2}{2}\right)R \tag{9.17}$$

and the ratio of heat capacities

$$\gamma = \frac{c_p}{c_V} = \frac{f+2}{f} \tag{9.18}$$

You will recall that we could only get an expression for the difference $c_p - c_V$ between the heat capacities from thermodynamic considerations. But molecular theory predicts their absolute values as well as their ratio in terms of d.f. and the gas constant.

For monatomic gases, $f = 3$ so that

$$c_V = \frac{3}{2}R,\ c_p = \frac{5}{2}R \text{ and } \gamma = \frac{5}{3} = 1.67$$

That is, the value of c_V (or c_p) is same for all monatomic gases. This is fairly well borne out by experiments. Is it true even for diatomic molecules? To discover the answer this question, we note that for these molecules, $f = 5$ so that

$$c_V = \frac{5}{2}R,\ c_p = \frac{7}{2}R \text{ and } \gamma = \frac{7}{5} = 1.4$$

This shows that the ratio of heat capacities decreases with increasing atomicity of gases. This is in general conformity with experiments. So we may conclude that for all ideal gases, heat capacities and their ratio are independent of temperature. This result of molecular theory is fairly borne out by experiments. However, if we insert the measured values of γ in Eq. (9.18) and solve for f, the result is not, in general, exactly an integer. This is physically meaningless and raises serious doubts about equipartition of energy as well as kinetic theory.

Table 9.2: Molar Heat Capacities at Room Temperature

Gas	c_p^*/R	c_V/R	$\frac{c_p - c_V}{R}$	γ
He	2.50	1.51	0.99	1.66
Ne	2.50	1.52	0.98	1.64
A	2.51	1.51	1.00	1.67
H_2	3.47	2.47	1.00	1.40
O_2	3.53	2.52	1.01	1.40
Cl_2	4.07	3.00	1.07	1.36
CO_2	4.47	3.47	1.00	1.29
NH_3	4.41	3.32	1.10	1.33
CH_4	4.30	3.30	1.00	1.30
Air	3.50	2.50	1.00	1.40

* measured values

The disagreement between theory and experiment becomes apparent when we examine the temperature variation of heat capacities of diatomic gases. For hydrogen we find that at a temperature of 20K, c_V decreases to $\frac{3}{2}R$, whereas at 1000K, it increases to $\frac{7}{2}R$. This means that at higher temperatures rotational as well as vibrational modes contribute to the energy of hydrogen molecules. But at lower temperatures these modes seem to disappear. The correct explanation of temperature variation of heat capacities came from quantum statistics. You will learn it in Block 4.

Let us now sum up what you have learnt in this block.

9.5 SUMMARY

- Kinetic theory is based on two postulates: matter is made up of molecules which are in a state of constant random motion and heat can be identified with molecular motion.
- The pressure exerted by the gas molecules on the walls of a container is given by $p = \frac{1}{3} mn\overline{v^2}$.
- At absolute zero of temperature, gas molecules are devoid of all motion, i.e., average kinetic energy of a gas reduces to zero.
- Energy is equally divided amongst various active degrees of freedom of a molecule and its magnitude is $k_B T/2$.
- Kinetic theory enables determination of heat capacities of a gas in terms of degrees of freedom. It predicts that these are independent of temperature and are same for all gases.

9.6 TERMINAL QUESTIONS

1. Calculate v_{rms} for helium atoms at 300K. At what temperature will oxygen molecules have the same value of v_{rms}? Take $m_{He} = 6.67 \times 10^{-27}$ kg.
2. A cubical box of side 0.1 m contains 3×10^{22} molecules of oxygen at 300K. Compute the average pressure exerted by it on the walls of the cube.

UNIT 10 TRANSPORT PHENOMENA

Structure

10.1 Introduction
  Objectives
10.2 Mean Free Path
  Elementary Derivation
  Distribution of Free Paths
  Experimental Determination
10.3 Transport Phenomena
  Viscosity: Transport of Momentum
  Thermal Conductivity: Transport of Energy
  Diffusion: Transport of Matter
10.4 Summary
10.5 Terminal Questions
10.6 Solutions and Answers

10.1 INTRODUCTION

We have seen that ideal gases can be considered as consisting of point molecules which move randomly. Even at room temperature, the molecules of a gas, say oxygen, move with very large speeds; $v_{rms} = 480 \text{ ms}^{-1}$. We should expect that when molecules are moving with such enormous speeds, the gaseous mass contained in a vessel should disappear in no time. But this does not happen leading to an apparent paradox. A simple way out was suggested by Clausius. According to him, the gas molecules have finite size, and as they move, they collide with one another. As a result, it takes them much larger time to diffuse. You may now like to ask: What is the average distance travelled by a molecule between succesive collisions? What is the mechanism of these collisions? To answer these questions we introduce the concept of **mean free path.** We will derive an expression for mean free path in Section 10.2. The distribution of free paths and the experimental determination of mean free path is also discussed in this section.

When a gas is endowed with mass motion and has a velocity, temperature or density gradient, thermal motion of molecules leads to transport of momentum, energy, or mass, respectively. We can characterise these by the coefficients of viscosity, thermal conductivity and diffusion. These processes, collectively referred to as **transport phenomena**, are discussed in Sec. 10.3.

In the next unit you will learn the theory of Brownian Motion, which provided direct evidence in favour of molecular theory.

Objectives

After studying this unit, you should be able to

- derive an expression for mean free path
- describe the law of free paths and apply it to determine mean free path experimentally
- derive expressions for the coefficients of viscosity, thermal conductivity and self-diffusion, and
- solve numerical problems.

10.2 MEAN FREE PATH

In deriving an expression for the pressure exerted by the molecules of a perfect gas, we regarded gas molecules as point masses and ignored intermolecular collisions. But Clausius pointed out that every gas molecule necessarily collides with every other molecule and undergoes frequent changes in direction. This results in a series of zig-zag paths of unequal length for each molecule. These are called **free paths.** The trajectory of a molecule moving with average speed $\bar{v}$ is shown in Fig. 10.1.

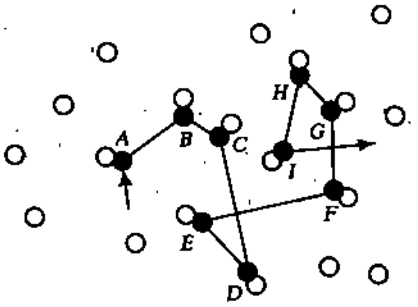


Fig. 10.1: The trajectory of a molecule moving in a gas

To visualise it, consider the following situation: You go to see a football match. During the play, team A (East Bengal) scores a goal, which is contested by team B (JCT). JCT supporters start throwing chairs, and bottles on the ground. To restore order, the police decides to burst tear gas shells. Everybody runs for safety. In the course of retreat, you are bound to collide with others and change your direction randomly. A trace of your motion will resemble the motion of a gas molecule.

If you closely examine Fig. 10.1, you will note that some of the free paths are short while others are long. The average lengths of these free paths are referred to as mean free path. Thus, **mean free path is the mean distance travelled by a molecule between two successive collisions.** We denote it by the symbol λ.

If $\lambda_1, \lambda_2, \lambda_3, ..., \lambda_N$ are the succesive free paths traversed in time t and N is the total number of collisions, then

$$\lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \ldots + \lambda_N}{N}$$

$$= \frac{\text{total distance travelled}}{\text{total number of collisions}}$$

If $\bar{v}$ is the average speed of a molecule, then you can write

$$\lambda = \frac{\bar{v}\, t}{N} \tag{10.1}$$

If τ ($= t/N$) denotes the mean time between two successive collisions, then you can write

$$\lambda = \bar{v}\tau = \frac{\bar{v}}{P_c} \tag{10.2}$$

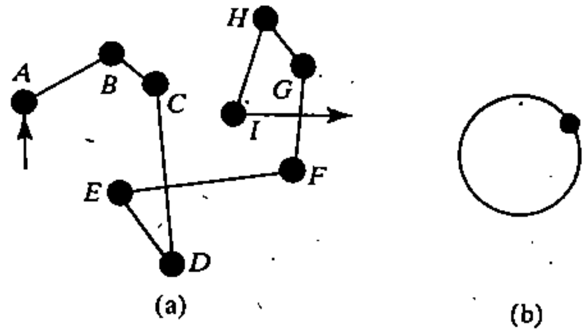
where $P_c = (\tau^{-1})$ denotes the collision frequency, which is a measure of the average number of collisions per second.

You may now ask : How is λ related to microscopic properties of a gas ? To discover the answer to this question, we shall make an elementary calculation.

10.2.1 Elementary Derivation

Consider a gas consisting of a large number of molecules, each of mass m and diameter d. We assume that the collisions are taking place at random. Mathematically speaking, the probability that a molecule undergoes a collision in a small interval of time dt is independent of the history of past collisions. This has a simple analogy in that if you throw a dice, the probability of getting a six does not depend on the preceding throw where a six may or may not have appeared.

To derive an expression for λ, we note from Eq. (10.2) that we must know to calculate P_c. We shall make this calculation for two cases. First we consider a hypothetical case and assume that one molecule, labelled as 1, moves in a sea of other molecules that can be treated as though they are at rest. It will collide with a stationary molecule when the centre to centre distance is equal to d, the diameter of gas molecules. The trajectory of this molecule will appear like that shown in Fig. 10.1. The centre to centre distance will also be d if the stationary molecules were shrunk to geometrical points and the moving molecules to be taken of radius d. This is illustrated in Fig. 10.2. It is as if the moving molecule carries with it a circular disc of radius d. Therefore, the moving molecule can be thought of sweeping out a cylinder of cross-sectional area πd^2 and length $\bar{v}\,t$ in time t. This is illustrated in Fig. 10.3. During this time, it will collide with all other molecules whose centres lies within this volume (= $\pi d^2 \bar{v}\,t$). If the number of molecules is n, the number of molecules contained in this volume is equal to $\pi d^2 \bar{v}\,t\,n$. This is also equal to the number of collisions suffered by the moving molecule in time t. The collision frequency,



(a) (b)

Fig. 10.2 : (a) Collision between a moving molecule and a stationary molecule
(b) Equivalent representation of collision between two molecules

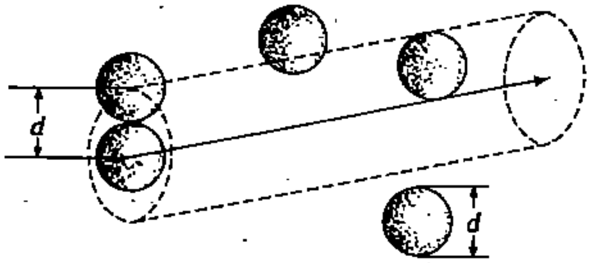


Fig. 10.3 : Cylindrical area mapped by a moving molecule

which is defined as the number of collisions per second, is given by

$$P_c = \pi d^2 n \bar{v} \tag{10.3}$$

Substituting this result in Eq. (10.2) we get

$$\lambda = \frac{\bar{v}}{P_c} = \frac{1}{\pi d^2 n} = \frac{1}{\sigma n} \tag{10.4}$$

where $\sigma = \pi d^2$ is known as **collision cross section.** It plays a very important role in scattering theory, which is a lively research area today.

Let us pause for a moment and ask: What is good about the relation contained in Eq. (10.4)? What are its implications? To answer these questions, we note that our analysis is over simplified and predicts that mean free path is inversely proportional to number density as well as collision cross section. Therefore, the mean free path will be less for a denser and/or a heavier gas. This is in perfect agreement with our observations and lends support to the basic tenets of kinetic theory.

You may now logically ask: What is the typical magnitude of the mean free path? You will discover the answer to this question in the following example.

Example 1

The mean speed of hydrogen molecules is 1690 $\mathrm{ms^{-1}}$. The radius of a hydrogen molecule is 1.37×10^{-10} m. Calculate (i) the total collision cross section, (ii) collision frequency, (iii) mean free path and (iv) mean free time. Take $n = 3 \times 10^{25}\ \mathrm{m^{-3}}$.

Solution

Since $n = 3 \times 10^{25}\ \mathrm{m^{-3}}$ we find that

(i) $\sigma = \pi d^2 = 4\pi(1.37)^2 \times 10^{-20}\ \mathrm{m^2} = 23.6 \times 10^{-20}\ \mathrm{m^2}$

(ii) $P_c = \pi d^2 n\bar{v} = n\bar{v}\sigma = (3 \times 10^{25}\ \mathrm{m^{-3}}) \times (1.69 \times 10^3\ \mathrm{ms^{-1}}) \times (23.6 \times 10^{-20}\ \mathrm{m^2})$

$= 1.2 \times 10^{10}\ \mathrm{s^{-1}}$

(iii) $\lambda = \dfrac{1}{(3 \times 10^{25}\ \mathrm{m^{-3}}) \times (23.6 \times 10^{-20}\ \mathrm{m^2})} = 14 \times 10^{-8}\ \mathrm{m} \approx 1400$ Å

(iv) $\tau = P_c^{-1} = 8.3 \times 10^{-11}$ s

The number of collisions per second is of the order of 10^{10}, which is a very large number. The path of molecule is thus made up of so many kinks and zig–zags that we can never follow its trajectory even speaking classically.

You will also note that λ is large compared to intermolecular distances, which are about a few Angstroms.

For an ideal gas, the pressure p is given by

$$p = n k_B T \tag{10.5}$$

On substituting for n from this equation, Eq. (10.4) takes the form

$$\lambda = \frac{k_B T}{\sigma p} \tag{10.6}$$

This tells us that the mean free path is inversely proportional to pressure. This raises a very interesting question. Suppose we reduce p to a very small value using a vacuum pump. What value will λ take ? Will the value approach ∞? It cannot increase indefinitely. At the most the value of the mean free path becomes equal to the dimensions of the container. This finds an interesting application in getting well directed molecular beams for research purposes.

To check your progress, we give you an SAQ.

SAQ 1

The mean speed of oxygen molecules is 450 $\mathrm{ms^{-1}}$. If the radius of an oxygen molecule is 1.8 Å, calculate σ, P_c, λ, and τ. Take $n = 3 \times 10^{25}\ \mathrm{m^{-3}}$.

You will agree that in deriving Eq. (10.5), we have made a rather artificial assumption that only one molecule moves while other molecules are at rest. In actual practice, all molecules move about randomly with all possible velocities. For simplicity we assume that all molecules have the same average speed $\bar{v}$. Then, collision frequency is given by

$$P_c = n\bar{v}_r \sigma \tag{10.7}$$

where $\bar{v}_r$ denotes the mean relative velocity of one molecule with respect to all others. Let us consider any two molecules and label them 1 and 2. The relative velocity of molecule 1 with respect to molecule 2 is given by (Fig. 10.4)

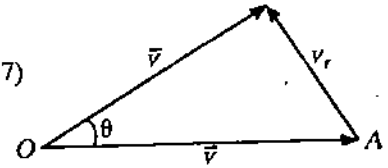


Fig. 10.4 : Relative velocity of molecule 1 moving along *OA* with respect to another molecule moving along *OB*. The velocity vectors are inclined at an angle θ.

$$\begin{aligned} v_r &= \sqrt{(\bar{v})^2 + (\bar{v})^2 - 2(\bar{v})^2 (\cos\theta)} \\ &= \sqrt{2}\,\bar{v}\,(1 - \cos\theta)^{1/2} = 2\bar{v}\sin\frac{\theta}{2} \end{aligned} \tag{10.8}$$

where θ is the angle between the two velocity vectors.

Since all directions for *OB* are equally probable, we can easily show (TQ 1) that the fraction of molecules moving in directions lying between θ and θ + $d\theta$ with respect to *OA* is (1/2) sinθ $d\theta$. Hence,

$$\overline{v_r} = \frac{1}{2}\int_0^{\pi} v_r \sin\theta \, d\theta = \overline{v}\int_0^{\pi} \sin\theta \sin\frac{\theta}{2} d\theta = 2\overline{v}\int_0^{\pi} \sin^2\frac{\theta}{2}\cos\frac{\theta}{2} d\theta$$

To evaluate this integral, we intoduce a change of variable and write $\frac{\theta}{2} = x$ so that $d\theta = 2\,dx$ and the limits of integration change to 0 to $\pi/2$. Then above expression takes the form

$$\overline{v_r} = 4\overline{v}\int_0^{\pi/2} \sin^2 x \cos x \, dx$$

This integral can be easily evaluated to yield

$$\overline{v_r} = \frac{4}{3}\overline{v} \tag{10.9}$$

The general integral $\int_0^{\pi/2} \sin^m x \cos^n x \, dx$ has the value

$$\frac{(m-1)(m-3)\ldots(n-1)(n-3)\ldots}{(m+n)(m+n-2)(m+n-4)\ldots}$$

If both m and n are even, this result is multiplied by $\pi/2$.

On inserting this result in Eq. (10.7), we get

$$P_c = \frac{4}{3} n \sigma \overline{v} \tag{10.10}$$

and

$$\lambda_{Cl} = \frac{3}{4n\sigma} = \frac{0.75}{n\sigma} \tag{10.11}$$

This result is due to Clausius (1857). You will note that the collision frequency increases when all the molecules are in motion. This, of course, is expected physically since a molecule is more likely to suffer collision when all of them are in motion than in a collection of molecules at rest in their respective positions.

If we take the Maxwellian distribution of velocities into account, the expression for mean free paths gets modified to

$$\lambda_M = \frac{1}{\sqrt{2}\, n\sigma} = (0.707)\,\frac{1}{n\sigma} \tag{10.12}$$

so that $\frac{\lambda_M}{\lambda_{Cl}} = 0.94$. That is, the correction is only 6%. Thus in most cases, replacing the Maxwell's distribution by a uniform speed model is a fairly good approximation. You will also note that for point molecules ($d \to 0$), $\sigma \to 0$ and $\lambda \to \infty$.

To test your understanding you may like to attempt the following SAQ.

SAQ 2

The mean free path of the molecules of a gas at a temperature of 15°C is 6.28×10^{-8}m. If the radius of the molecule is 1.88 Å, calculate the pressure exerted by the gas. Also calculate the number of collisions suffered by a molecule in traversing a distance of one metre. Take $k_B = 1.38 \times 10^{-23}\ \text{JK}^{-1}$.

You now know that molecules suffer collisions very frequently. We therefore expect that the mean free paths can have all values from zero to infinity. (In the language of probability theory, the free path is a random variable with mean equal to λ.) It is therefore instructive to know the distribution of free paths. This we propose to do in the following sub-section.

10.2.2 Distribution of Free Paths

Consider a man shooting aimlessely in a thick forest. Every bullet will eventually hit a tree, but some will travel farther than others. This situation is analogus to the flights of the gas molecules. We now wish to know: By what equation can we describe the free paths? To discover the answer, let us consider a molecule at the start of its journey at the point O. We

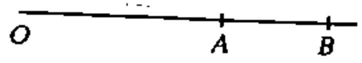


Fig 10.5 : A molecule travels from O to A without a collision and traverses the distance AB in time dt

assume that the past history of the molecule does not influence its subsequent motion. Suppose that moving with average speed $\overline{v}$, it travels a distance $OA = x$ without suffering any collision. The probability of this event will be a function of x. Let us denote it by $f(x)$. The probability that this molecule will make a collision in going from A to B in time $dt = P_c\,dt$ where P_c is the collision frequency. Since $dx = \overline{v}\,dt$, we can rewrite using Eq. (10.2) as

$$P_c\,dt = P_c \frac{dx}{\overline{v}} = \frac{dx}{\lambda}$$

where λ is the mean free path. Hence, the probability that the molecule traverses a distance dx without a collision is $1 - \frac{dx}{\lambda}$.

Since the passage from O to A and from A to B are independent events, we can say that the probability of this molecule completing its journey from O to B without making any collision is equal to $f(x)\left(1 - \frac{dx}{\lambda}\right)$. Hence, we must have

$$f(x + dx) = f(x)\left(1 - \frac{dx}{\lambda}\right) \tag{10.13}$$

Using Taylor series expansion we can write

$$f(x + dx) = f(x) + \frac{df(x)}{dx} + \ldots = f(x)\left(1 - \frac{dx}{\lambda}\right)$$

where we have ignored second and higher order terms in the expansion. On simplification, we can write

$$\frac{df(x)}{dx} = -\frac{f(x)}{\lambda}$$

You can easily integrate it to obtain

$$f(x) = A \exp\left(-x/\lambda\right) \tag{10.14}$$

The constant of integration A can be easily evaluated using the fact that $f(0) = 1$. This gives $A = 1$. Hence, Eq. (10.14) becomes

$$f(x) = \exp\left(-x/\lambda\right) \tag{10.15}$$

This is the law of **distribution of free paths**. In probability theory, it is known as the exponential distribution. It suggests that the probability of a molecule describing very large free paths is vanishingly small.

If we have a sample of N_0 molecules to start with, only $N_0 \exp(-x/\lambda)$ of these will survive a collision in traversing a distance x. Let this number be denoted by N. Then we have

$$N = N_0 \exp\left(-\frac{x}{\lambda}\right) \tag{10.16}$$

This is known as the **survival equation.** Similar equations arise in other areas of physics. For example, radioactive decay obeys the equation $N = N_0 \exp(-\lambda t)$, where N is the number of atoms which survive after time t and λ is the disintegration constant. (You should not confuse it with mean free path.) Similarly in optics, Biot's law describing the intensity of an incident beam after it has traversed a distance x in a medium exhibits exponential character. Eq. (10.16) is plotted in Fig. 10.6.

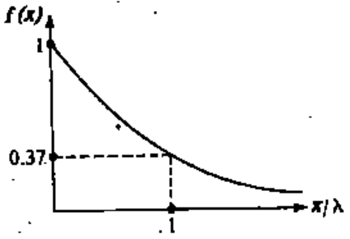


Fig. 10.6 : The plot of the survival equation

The fraction of molecules with free paths larger than λ is only $e^{-1} \simeq 0.37$.

$f(x)$ is not a probability density in the sense that the area under the curve $y = f(x)$, i.e., $\int f(x)\,dx$ has not been normalised to unity.

If we take the Maxwellian distribution of speeds into account, the calculations become slightly more involved. We just quote the result which is due to Jeans:

$$f(x) = \exp\left(-1.04\,x/\lambda\right) \tag{10.17}$$

We now solve an example to enable you to fix up your ideas.

Example 2

In a sample of 10^4 molecules, each molecule is moving with the same velocity. What is the number of molecules that will travel undeflected after traversing distances of 0.4, 0.5, 1, 2, and 10 times the mean free path?

Solution

For $\frac{x}{\lambda} = 0.4$, we have

$$N = 10^4 e^{-0.4} = 6703$$

For other values of x/λ, we have tabulated the values of N below :

$\frac{x}{\lambda}$	0.5	1	2	10
N	6065	3680	1353	0.4540

You will note that for $x/\lambda = 10$, essentially no molecule will be spared of a collision.

You may now like to solve an SAQ to assess your understanding.

SAQ 3

The mean free path of molecules of a gas at (p, T) is 5.2×10^{-8} m. Calculate the probabilities that under the conditions (i) $(p, 2T)$, (ii) $(2p, 2T)$, (iii) $(3p, T)$ a molecule can travel a distance 10.4×10^{-8} m without making a collision.

You may now be tempted to know as to how we can check the accuracy of the survival equation. Born put the law of free paths to test when he suggested a method for the experimental determination of mean free path. Let us now know about it.

10.2.3 Experimental Determination

The method described here for the experimental determination of the mean free path is due to Born (1920). His appratus is sketched in Fig 10.7.

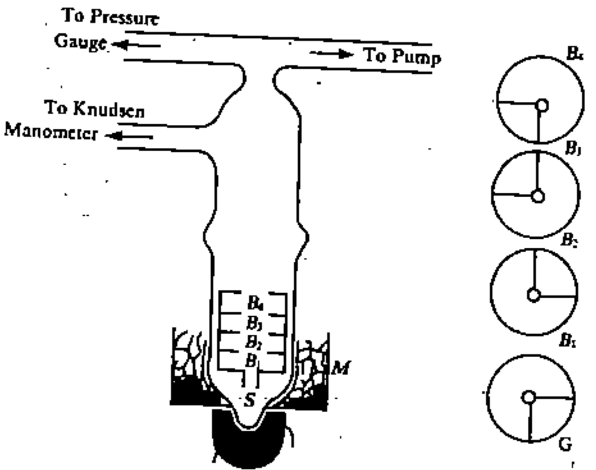


Fig. 10.7 : Born's apparatus for the determination of λ.

The idea is to make silver atoms move through air. When the pressure is low, the collision rate also decreases and these atoms can travel reasonably large distances without making a collision. Silver is heated at the lower end of the quartz tube. On evaporation, the silver vapour passes through the narrow slit S. B_1, B_2, B_3, B_4 are four brass discs, each having a circular hole and carrying a glass quadrant G such that the apex of each quadrant lies at the centre of the hole. They are separated through a distance of 1 cm. The evaporated silver continues its onward journey through these holes. Each quadrant is oriented in such a way that it is displaced through 90° relative to the preceding one. This arrangement ensures that each quadrant receives one-fourth of the incident beam. The pressure can be changed to any desired value using a vacuum pump.

The experiment is started by cooling the discs using a cooling mixture (M). All the gas is pumped out using a vacuum pump. Then mean free path equals the length of the chamber. The amount of silver deposited on a given quadrant is determined by photometric methods. Let the density of the deposit be denoted by d_{10}. Next we introduce the gas and determine the density on the same quadrant. Let it be d_1. Then, using the law of free paths, we can write

$$d_1 = d_{10} \exp\left(-\frac{x_1}{\lambda}\right) \tag{10.18}$$

where x_1 is the distance of the quadrant from S. Similarly, for any other quadrant

$$d_2 = d_{20} \exp\left(-\frac{x_2}{\lambda}\right) \tag{10.19}$$

Eqs. (10.18) and (10.19) may be combined to give

$$\lambda = \frac{(x_2 - x_1)}{\ln\left(\frac{d_1}{d_2}\frac{d_{20}}{d_{10}}\right)} \tag{10.20}$$

In the present arrangement $(x_2 - x_1) = 1$ cm. So once we know the density of the deposits, we can easily determine the value of mean free path at a given temperature and pressure. Born's results are given below :

p (mm)	λ(cm)
5.8×10^{-3}	1.7
4.5×10^{-3}	2.4
atmospheric pressure	1.3×10^{-5}

You will note that the product $p\,\lambda$ turns out to be constant, as predicted by theory. This also serves to verify the law of distribution of free paths.

10.3 TRANSPORT PHENOMENA

We now know that each gas molecule has a finite mass and is characterised by random molecular velocity. Therefore, it possesses momentum and energy. So while moving from one part of the container to another, it is a carrier of these physical quantities. You may now ask: When a gas is in equilibrium, why is there no net transport of matter, momentum or energy? This is because the rate of transport across a given plane is exactly balanced by an equal amount in the opposite direction. However, when a gas, in addition, is endowed with macroscopic velocity, i.e., the entire gas or a part of it is moving as a whole in a particular direction, the following three cases may occur singly or jointly:

1. The different parts of the gas may be moving with different velocities resulting in relative motion between adjacent layers of the gas. In such a case, the faster moving layers will lose momentum to the slower moving layers. Therefore, across an imaginary plane there will be a net transport of momentum in the preferential direction of motion. This gives rise to frictional force which can be characterized by the coefficient of viscosity. It is important to realise that the viscosity in gases arises due to the random thermal motion of molecules rather than any frictional force between the layers, as in the case of liquids. You can visualise it with the following analogy:

   Imagine two trains running on parallel tracks at slightly different speeds, and passengers are jumping from one train to the other. As a result, the faster train may lose momentum and the slower train may gain momentum. On the other hand, in case of liquids, we may imagine that the passengers find themselves caught by the coat tail. They make a determined effort to detach themselves but fail to do so.

2. If the different parts of the gas are at different temperatures, the molecules of the gas will carry thermal energy from regions of higher temperature to regions of lower temperature (and tend to attain equilibrium). This gives rise to the phenomenon of thermal conduction.

3. If the different parts of gas have different concentrations, the molecules from regions of higher concentration will migrate to the regions of lower concentration. This results in the transport of mass (matter) giving rise to the phenomenon of diffusion.

$$= \frac{(1/3)\,\lambda^2}{(1/2)\,\lambda}$$

$$= \frac{2\lambda}{3} \tag{10.24}$$

That is, on an average each molecule would make its last collision at the height equal to two thirds of the mean free path above or below the surface xx' before crossing it. At a height $(2/3)\lambda$ above the plane xx', the flow velocity of the gas molecules will be $u + (2/3)\,\lambda\,\frac{du}{dy}$, where u is flow velocity at the plane xx'. The momentum transported by a molecule moving with this velocity is

$$m\left(u + \frac{2}{3}\lambda\frac{du}{dy}\right)$$

So, the total momentum in the direction of the flow carried across the surface per unit area per unit time by all the molecules crossing the surface xx' from above is

$$P^{+} = \frac{1}{4}n\,\bar{v}\,m\left(u + \frac{2}{3}\lambda\frac{du}{dy}\right)$$

Similarly, the total momentum carried across the surface xx' per unit area per unit time by the molecules crossing it in the upward direction from below is

$$P^{-} = \frac{1}{4}n\,\bar{v}\,m\left(u - \frac{2}{3}\lambda\frac{du}{dy}\right)$$

Hence, the net rate of transport of momentum across xx' in the direction of mass motion per unit area per unit time, which is equal to the viscous force per unit area, is given by

$$P = P^{-} - P^{+} = -\frac{1}{3}mn\bar{v}\lambda\,\frac{du}{dy} \tag{10.25}$$

On comparing Eqs. (10.21) and (10.25) we find that the coefficient of viscosity of a gas is given by

$$\eta = \frac{1}{3}m\,n\,\bar{v}\,\lambda = \frac{1}{3}\rho\,\bar{v}\,\lambda \tag{10.26}$$

On substituting the expression for λ from Eq. (10.12), we get

$$\eta = \frac{1}{3\sqrt{2}}\,\frac{m\bar{v}}{\sigma} \tag{10.27}$$

This is a remarkable result based on elementary kinetic theory. It enables us to estimate the molecular diameter since η is a directly measurable quantity. From Eq. (10.27) we note that the viscosity of the gas is directly proportional to $\bar{v}$. That is $\eta \alpha T^{1/2}$ and is independent of n (or pressure). Both these conclusions are in conformity with experiments. For instance, for pressures from a few mm of mercury upto several atmospheres, the coefficient of viscosity of a gas is found to be independent of pressure. However, at very low or very high pressures, this does not hold. At very low pressure, the intermolecular collisions are rare and mean free path becomes comparable with the dimensions of the apparatus. But the number density decreases continuously as pressure is lowered. Consequently, the coefficient of viscosity decreases as pressue decreases. This fact was experimentally verified by Crookes.

Warburg and von Babo showed that at very high pressures, the coefficient of viscosity increases as pressure increases. This is due to the fact that at such high pressures, mean free path becomes comparable with the molecular size.

Example 3

The coefficients of viscosity of argon and helium are 22×10^{-6} Pl and 19×10^{-6} Pl, respectively. Calculate the mean free paths for these gases if they are kept under identical conditions.

Solution

We have from Eq. (10.26)

$$\frac{\eta\,(\text{A})}{\eta\,(\text{He})} = \frac{m\,(\text{A})}{m\,(\text{He})}\,\frac{\bar{v}\,(\text{A})}{\bar{v}\,(\text{He})}\,\frac{\lambda\,(\text{A})}{\lambda(\text{He})}$$

$$= \sqrt{\frac{m\,(\text{A})}{m\,(\text{He})}}\;\frac{\lambda\,(\text{A})}{\lambda\,(\text{He})}$$

In writing the last step we have made use of the fact that at constant temperature,

$$E = \frac{1}{2} m\,(\text{He})\,\overline{v^2}\,(\text{He}) = \frac{1}{2} m\,(\text{A})\,\overline{v^2}\,(\text{A})$$

Hence, on re-arrangement we find that

$$\frac{\lambda\,(\text{A})}{\lambda\,(\text{He})} = \sqrt{\frac{m\,(\text{He})}{m\,(\text{A})}}\;\frac{\eta\,(\text{A})}{\eta\,(\text{He})}$$

$$= \left(\frac{22 \times 10^{-6}\ \text{Pl}}{19 \times 10^{-6}\ \text{Pl}}\right)\left(\frac{4}{39.9}\right)^{1/2}$$

$$= 0.368$$

Example 4

The molecules of helium move with an average speed of 1200 ms^{-1}. If $\eta = 19 \times 10^{-6}$ Pl, calculate λ for helium.

Solution

We know that in terms of η, we can express mean-free path as

$$\lambda = \frac{3\eta}{m\,n\,\overline{v}} = \frac{3\eta V}{M\,\overline{v}}$$

where M is molecular weight and V is volume occupied by one mole. On inserting the given numerical values, we get

$$\lambda = \frac{3 \times (19 \times 10^{-6}\ \text{Pl}) \times (22.4\ \text{lit})}{4 \times (1200\ \text{ms}^{-1})} = 2521\ \text{Å}$$

You should now attempt the following SAQ.

SAQ 4

Calculate the radius of an oxygen molecule, if its coefficient of viscosity is 19.6×10^{-6} Pl at 15°C and $\overline{v} = 436\ \text{ms}^{-1}$.

As mentioned earlier, Eq. (10.27) implies that

$$\eta \propto T^{0.5}$$

In actual practice, the increase is faster than $\sqrt{T}$. The departure from the value 0.5 provides us an opportunity to get an insight into the nature of intermolecular forces. In fact, σ is independent of T only for rigid hard spheres. The long range attractive part of the force increases the scattering probability of a molecule. At lower temperatures, the molecules have lower velocities and can easily be scattered. If we denote the repulsive part of the potential by $V(r) = \frac{A}{r^s}$, it turns out that $\eta \propto T^n$ with

$$n = \frac{1}{2} + \frac{2}{s-1}$$

For rigid hard spheres, $s = \infty$, so that $n = 0.5$. From experimental observations made on η at different temperatures, we can deduce the value of s. Some representative values are given below:

Gas	s
H_2	11.3
He	14.6
Cl_2	5.0
HCl	4.97

You may recall from your earlier classes that for liquids η decreases with T. Can you reason out why?

10.3.2 Thermal Conductivity: Transport of Energy

When a temperature gradient exists between different layers of a gas, net transport of energy takes place from regions of higher temperature to regions of lower temperature. The net rate of energy (heat) transported across any surface per unit area is given by

$$Q = -K\frac{dT}{dy} \tag{10.29}$$

where K is thermal conductivity. (You should not confuse it with the symbol for kelvin, the unit of temperature.)

To obtain an expression for thermal conductivity, we require, as before, the expressions for the average number of molecules crossing any layer and the average height at which a molecule makes its last collision before crossing it. These are exactly the same as in the case of coefficient of viscosity. However, you have to keep in mind that the average energy possessed by a gas molecule is $\frac{f}{2}k_BT$, where f is the number of degrees of freedom. You can readily show that

$$K = \frac{f}{6}n\bar{v}\lambda k_B \tag{10.30}$$

We, therefore find that like viscosity, thermal conductivity is also independent of pressure. This is fairly well borne out by experiments down to very low pressures. Further, $K \alpha T^{1/2}$. In actual practice, K increases somewhat more rapidly suggesting that intermolecular forces do influence energy transport.

When we closely examine expressions for η and K, we expect some connection between them. It is instructive to discover it as both these quantities are physically measurable. Therefore, we dividve Eq. (10.30) by Eq. (10.26) to get

$$\frac{K}{\eta} = \frac{f}{2}\frac{k_B}{m}$$

$$= \frac{f}{2}\frac{k_B N_A}{M} = \frac{f}{2}\frac{R}{M}$$

since $m = \frac{M}{N_A}$, where M is molecular weight of the substance.

From Unit 9 you will recall that molar heat capacity

$$C_V = \frac{f}{2}R$$

so that

$$\frac{K}{\eta} = \frac{C_V}{M}$$

or

$$\frac{KM}{\eta C_V} = 1 \tag{10.31}$$

That is, our elementary theory predicts that the ratio $KM/\eta\, C_V$ is equal to one for all gases. But experiments show that this ratio is greater than one. There can be several reasons for this discrepancy. The most obvious seems that we have not taken the distribution of velocities into account. The faster molecules will cross a given plane more frequently and result in increased energy transport, enhancing the ratio $KM/\eta\, C_V$.

A more rigorous calculation due to Chapman and Enskog showed that the rate of energy transport is 1.5 to 2.5 times faster than that given by our elementary treatment. This suggests that the hard sphere model of a molecule is not adequate.

We will now like you to work out an SAQ.

SAQ 5

Calculate the thermal conductivity of helium at STP using the following data:

$$\eta = 19 \times 10^{-6}\,\mathrm{Nsm^{-2}},\ C_V = 12.5 \times 10^{3}\,\mathrm{J\,kmol^{-1}\,K^{-1}}\ \text{and}\ M = 4\,\mathrm{kg\,mol^{-1}}.$$

10.3.3 Diffusion: Transport of Matter

Consider two gases, say hydrogen and oxygen, contained in the glass jars. The hydrogen jar is inverted over the oxygen jar and the lids are removed. As such, in either direction there will be no large scale movement of these gases, which are at the same temperature and pressure. But after some time one finds that the two gases mix with one another. (Oxygen molecules have moved against gravity.) This gradual inter-mixing of gases is called diffusion. It is responsible for the smell of flowers reaching us. Similarly, due to diffusion process only sitting in your study room you can find what is being cooked in the kitchen . It is a direct consequence of random molecular motion when there are inequalities in concentration. Molecules diffuse from regions of higher concentration towards regions of lower concentration Fig. 10.10(a) schematically shows the diffusion of like molecules. Diffusion of unlike molecules is shown in Fig. 11.10(b).

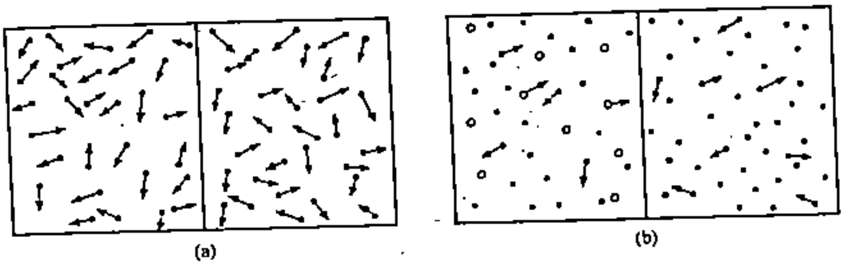


Fig 10.10a : Self-diffusion: Two identical samples of a gas in a container are separated by a barrier. As soon as the barrier is removed, they diffuse into one another.(b)Diffusion of unlike molecules.

We can describe intermixing of gases in terms of the coefficient of diffusion, *D*. If the molecular concentration along a horizontal plane xx' is n and there is positive concentration gradient dn/dy in the vertical plane, the number of particles crossing the given surface per unit area per unit time is given by

$$\Gamma = -D\frac{dn}{dy} \tag{10.32}$$

For the general case, the calculation of the diffusion coefficient is complicated due to the fact that the rates of the two gases may not be the same. We can simplify this problem and still bring out the essential ideas by considering the diffusion of like molecules, i.e., **self-diffusion**. The diffusion of the isotopes of the same element (say ${}^{235}U$ and ${}^{238}U$) is an example of this type.

Self diffusion finds very important use in nuclear power generation via uranium enrichment. For this we convert uranium into uranium hexaflouride (UF_6) gas and make it to diffuse through a porous barrier. Normally it is a ceramic material ,which consists of fine capillary pores. Since ${}^{235}U$ has slightly smaller mass than ${}^{238}U$, its rate of diffusion is more. As a result, the outcoming gas is richer in ${}^{235}U$ content. Repetition of this process several hundred times results in the desired level of enrichment. In India we have nuclear power plants at Tarapur, Maharashtra where enriched (2 – 3 %)uranium is made to fission by thermal neutrons. (If this process goes uncontrolled, it can lead to untold destruction.) Unfortunately such an innocent process has been misused for destruction of humanity. You must have read that during the second World War, atom bombs were dropped at Hiroshima and Nagasaki by Allied forces led by the U.S. Uranium enriched upto 90% in ${}^{235}U$ was used in these bombs.

Natural uranium has two isotopes ${}^{238}U$ and ${}^{235}U$ whose concentrations are 99.21% and 0.71% respectively. Of these, ${}^{235}U$ isotope is more important as it is it fissile. From physical arguments is desirable to increase its amount above its natural concentration. In that case we say that the uranium has been enriched.

To proceed with the calculation of *D*, we note that, as before each molecule makes its last collision before crossing the reference plane at a perpendicular distance of (2/3) λ . If n_0 is the concentration of gas molecules at the reference plane, the number density at a distance (2/3)λ above or below xx' will be $n^{\mp} = n_0 \pm \frac{2}{3}\lambda\frac{dn}{dy}$.

From Eq. (10.23) you will recall that the number of molecules crossing the given surface per unit area per second is equal to (1/4) $n\,\bar{v}$. Hence, you can easily show that the net number of molecules transferred upward across the given surface per unit area per second is given by

$$\Gamma = -\frac{1}{3}\bar{v}\frac{dn}{dy}\lambda \tag{10.33}$$

On comparing Eqs. (10.32) and (10.33), we get

$$D = \frac{1}{3}\overline{v}\lambda \tag{10.34}$$

For air at STP, $\lambda = 100$ nm, and $\overline{v} = 450\ \mathrm{ms}^{-1}$ so that coefficient of diffusion is of the order of $10^{-5}\ \mathrm{m}^{-2}\ \mathrm{s}^{-2}$. Since $\lambda \alpha (T/p)$ and $\overline{v} \alpha T^{1/2}$, Eq. (10.34) implies that the diffusion coefficient will vary inversely as p and directly as $T^{3/2}$. The predicted variation with pressure is in agreement with the observed results but the power of T lies between 1.75 and 2. The reason for the more rapid increase with temperature can be assigned to the presence of intermolecular forces in actual gases. To be precise, it is due to the attractive part of the intermolecular potential. If we combine Eqs. (10.26) and (10.34), we get

$$\frac{D}{\eta\rho} \equiv \xi = 1$$

The observed value of ξ varies between 1.3 and 1.5. A rigorous theoretical analysis by Chapman and Enskog yields $\xi = 1.2$ for hard spheres and $\xi = 1.543$ for the intermolecular potential $V(r) = \frac{A}{r^5}$.

So far we have been talking about self-diffusion. In actual measurements of D for this process, there must be some way to follow the diffusing molecules. In other words, molecules must be labelled or tagged somehow. For instance, we can induce radioactivity on the nuclei of some molecules and their diffusion may be followed by a Geiger counter. However the sizes of the radioactive and the non-radioactive molecules may not be identical. Moreover, in practice we are interested in the diffusion of one gas (labelled 1, concentration n_1, average molecular velocity $\overline{v}_1$) through another (labelled 2, concentration n_2, average molecular velocity $\overline{v}_2$). For this general case of diffusion, we can show that the diffusion coefficient is given by

$$D = \frac{1}{3}\frac{\lambda_1\overline{v_1}\,n_1 + \lambda_2\,\overline{v_2}\,n_2}{n_1 + n_2} \tag{10.35}$$

where λ_1, and λ_2 denote the mean free paths, of gas 1 and gas 2, respectively. A study of variation of D with the composition of the mixture is quite interesting. We denote D as D_{12} when $n_1 << n_2$ and as D_{21} when $n_2 << n_1$. D_{12} will be proportional to $\sqrt{m_2/m_1}$ and D_{21} will be proportional to $\sqrt{m_1/m_2}$.

Experimental investigations show variations amongst the observed values as well as the departure from theoretical predictions. This brings out the limitations of such an elementary treatment. A rigorous analysis, however, shows a fairly good agreement. But its discussion is beyond the scope of your study.

Now you may like to solve an SAQ.

SAQ 6

Consider a cylindrical vessel of cross-sectional area A containing a small quantity of the liquid at the bottom. The vessel is full of air and diffusing vapour. The top end of the vessel is open and is a cold surface on which the vapour condenses. Derive an expression for D_{12}, the diffusion coefficient of vapour through air.

Let us now summarise what you have learnt in this unit.

10.4 SUMMARY

- The mean free path is the average distance travelled by a molecule between successive collisions. The exact expressions for λ is given by

  $$\lambda_M = \frac{1}{\sqrt{2}\,n\sigma}$$

  where n is the molecular number density and σ is the collision cross-section. For a sphere of diametre d, $\sigma = \pi d^2$

- When we have a sample of N_0 molecules, the number of molecules which travel a distance x, without making any collision is given by the survival equation:

  $$N = N_0 \exp(-x/\lambda)$$

- When a gas is endowed with mass motion, random molecular motion may result in transport of energy, momentum or mass depending on the physical conditions.

- The coefficient of viscosity, η, for gases is given by

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

  where m is the molecular mass and $\bar{v}$ is the average speed of a molecule.

  At a given temperature, η is independent of pressure. This result is valid so long as $d << \lambda << L$, where L is a measure of the linear dimensions of the container.

- The coefficient of thermal conductivity, K is given by

  $$K = \frac{f}{3} n\, \bar{v}\, \lambda\, k_B$$

  where f is the number of degrees of freedom.

- K and η are connected by the relation

  $$\frac{KM}{\eta C_V} = 1$$

- The coefficient of diffusion D is given by

  $$D = \frac{\bar{v}}{3}\lambda = \frac{0.376}{\sigma}\,\frac{(k_B T)^{3/2}}{p\sqrt{m}}$$

- D and η are related through the relation

  $$\frac{D\rho}{\eta} = 1$$

10.5 TERMINAL QUESTIONS

1. Molecules of a gas move randomly. Show that the fractions of molecules moving in directions lying between θ and $\theta + d\theta$ is given by $\frac{1}{2}\sin\theta\, d\theta$.

2. Calculate the radius of the nitrogen molecule using the following data :

   $$K = 23.7 \times 10^{-3}\ \mathrm{Wm^{-1}\,K^{-1}},\ C_V = 20.9 \times 10^{3}\ \mathrm{J\,mol^{-1}\,K^{-1}}\ \text{at}\ 0^\circ C$$

3. Calculate the mean free path for hydrogen molecules at STP. The diameter of a hydrogen molecule = 2.9 Å.

10.6 SOLUTIONS AND ANSWERS

SAQs

1. We have

   $$\sigma = 4\pi a^2 = 4\pi(1.8 \times 10^{-10}\ \mathrm{m})^2 = 40.7 \times 10^{-20}\ \mathrm{m}^2$$

   $$P_c = \sigma\, n\, \bar{v} = (40.7 \times 10^{-20}\ \mathrm{m}^2) \times (3 \times 10^{25}\ \mathrm{m}^{-3}) \times (450\ \mathrm{ms}^{-1})$$

   $$= 5.49 \times 10^{9}\ \mathrm{s}^{-1}$$

   $$\tau = P_c^{-1} = 1.8 \times 10^{-10}\ \mathrm{s}$$

   and

   $$\lambda = \frac{1}{(3 \times 10^{25}\ \mathrm{m}^{-3}) \times (40.7 \times 10^{-20}\ \mathrm{m}^2)} = 819\ \text{Å}$$

2. $\sigma = 4\pi a^2 = 4\,(1.88 \times 10^{-10}\ \mathrm{m})^2 = 44.4 \times 10^{-20}\ \mathrm{m}^2$

   We know that

$$\lambda = \frac{1}{\sqrt{2}\,\sigma}\,\frac{k_B T}{p}$$

so that

$$p = \frac{k_B T}{\sqrt{2}\,\lambda\,\sigma} = \frac{(1.38 \times 10^{-23}\,\mathrm{JK^{-1}}) \times (288\,\mathrm{K})}{(44.4 \times 10^{-20}\,\mathrm{m^2}) \times \sqrt{2} \times (6.28 \times 10^{-8}\,\mathrm{m})}$$

$$= 1.01 \times 10^5\,\mathrm{N\,m^{-2}}$$

Number of molecules suffered by a molecule per metre of the path

$$= \frac{1}{6.28 \times 10^{-8}\,\mathrm{m}} = 16 \times 10^6\,\mathrm{m^{-1}}$$

3. $$\lambda = \frac{1}{\sqrt{2}\sigma}\,\frac{k_B T}{p}$$

$$\lambda(p, T) = 5.2 \times 10^{-8}\,\mathrm{m}$$

(i) $\lambda(p, 2T) = 2\lambda(p, T) = 10.4 \times 10^{-8}\,\mathrm{m}$

Required probability $e^{-1} = 0.37$

(ii) $\lambda(2p, 2T) = \lambda(p, T) = 5.2 \times 10^{-8}\,\mathrm{m}$

Required probability $= e^{-2} = 0.14$

(iii) $\lambda(3p, T) = \frac{1}{3}\lambda(p, T) = \frac{5.2}{3} \times 10^{-8}\mathrm{m} = 1.7 \times 10^{-8}\,\mathrm{m}$

Required probability $= e^{-6} = 2.5 \times 10^{-3}$

4. $$m = \frac{32}{6 \times 10^{26}} = 5.33 \times 10^{-26}\,\mathrm{kg}$$

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

or

$$\eta = \frac{1}{3} mn\,\bar{v}\,\frac{1}{\sqrt{2}\,n\,\sigma} = \frac{1}{3\sqrt{2}}\,\frac{m\,\bar{v}}{\pi d^2}$$

On re-arrangement, we can write

$$d^2 = \frac{m\bar{v}}{3\pi\sqrt{2}\,\eta} = \frac{(5.33 \times 10^{-26}\,\mathrm{kg}) \times (436\,\mathrm{ms^{-1}})}{3\pi\sqrt{2} \times (19.6 \times 10^{-6}\,\mathrm{Nsm^{-2}})} \times 10^{-20}\,\text{Å}^2$$

Hence,

$$d = \left(\frac{5.33 \times 436}{3\pi\sqrt{2} \times 19.6}\right)^{1/2}\,\text{Å} = 2.98\,\text{Å}$$

and $r = 1.49\,\text{Å}$

5. From Eq. (10.31) we know that

$$K = \frac{\eta C_V}{M}$$

On inserting the given values, we get

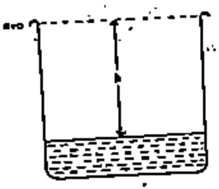
$$K = \frac{(18.6 \times 10^{-6}\,\mathrm{N\,sm^{-2}}) \times (12.5 \times 10^3\,\mathrm{J\,kmol^{-1}\,K^{-1}})}{4\,\mathrm{kg\,mol^{-1}}}$$

$$= 58.1 \times 10^{-3}\,\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}$$

6. Just above the liquid surface, the vapour is at its saturation vapour pressure. At the cold surface, the vapour condenses so that n is very nearly zero. In the steady state, there can be no accumalation of vapour molecules in any section. In other words,

$$\frac{dn}{dy} = \frac{n}{h}$$

The mass of vapour transferred and condensed on the cold surface per unit time is given by



$$m' = D_{12} A \frac{dn}{dy} m = D_{12} A \frac{n}{h} m$$

or

$$D_{12} = \frac{m'h}{Amn} = \frac{m'h}{A\rho}$$

where ρ is the mass density of the saturated vapour.

TQs

1. The fraction of molecules which are moving in a direction lying within an element $d\Omega$ of the solid angle $= \dfrac{d\Omega}{4\pi}$

$$= \frac{\sin\theta \, d\theta \, d\phi}{4\pi}$$

Hence the required fraction is given by

$$\frac{1}{4\pi} \sin\theta \, d\theta \int_0^{2\pi} d\phi = \frac{1}{2} \sin\theta \, d\theta$$

2. We have from Eq. (10.31)

$$K = \frac{\eta C_V}{M} = 0.376 \frac{\sqrt{m}}{\sigma} (k_B T) \frac{C_V}{M}$$

$$= \frac{0.376}{\sigma} (k_B T) \frac{C_V}{\sqrt{NM}}$$

Hence,

$$\sigma = 4\pi r^2 = \frac{(0.376)(k_B T) C_V}{K\sqrt{NM}}$$

or

$$r^2 = \frac{(0.376)(k_B T) C_V}{4\pi K \sqrt{NM}} \times 10^{20} \text{ Å}$$

$$= \frac{(0.376)(1.38 \times 10^{-23}\ \text{JK}^{-1}) \times (273\text{K}) \times (20.9 \times 10^{3}\ \text{J mol}^{-1}\ \text{K}^{-1}) \times 10^{20}\ \text{Å}}{4\pi \times (23.7 \times 10^{-3}\ \text{J m}^{-1}\ \text{s}^{-1}\ \text{K}^{-1}) \times (6 \times 10^{26}) \times (28.02\ \text{kg})}$$

$$= 1.2 \text{ Å}$$

3. $$\lambda = \frac{1}{\sqrt{2}\, n\sigma}$$

And

$$\sigma = \pi d^2 = \pi (2.9 \times 10^{-10})^2 \text{ m}^2 = 26.42 \times 10^{-20} \text{ m}^2$$

$$n = 3 \times 10^{25} \text{ m}^{-3}$$

Hence,

$$\lambda = \frac{1}{\sqrt{2} \times (3 \times 10^{25}\ \text{m}^{-3}) \times (26.42 \times 10^{-20}\ \text{m}^2)}$$

$$= 8.92 \times 10^{-8} \text{ m}$$

$$= 892 \text{ Å}$$

UNIT 11 BROWNIAN MOTION

11.1 Introduction
Objectives
11.2 Brownian Motion Revisited
11.3 One-dimensional Random Walk
11.4 Theoretical Analysis of Brownian Motion
Einstein's Derivation
Langevin's Analysis
11.5 Examples of Brownian Motion
11.6 Determination of Avogadro's Number
11.7 Summary
11.8 Terminal Questions
11.9 Solutions and Answers

11.1 INTRODUCTION

In the preceding units you have seen how kinetic theory successfully explains many observed properties of gases. The theory is based on the fundamental observation that matter is not continuous; it is made of molecules, which are in continuous random motion. You will agree that in a sense, kinetic theory has a great aesthetic appeal; well defined laws can be used to describe chaotic motion. Introduction of the concept of intermolecular collisions further enrich this theory. Apart from overcoming apparent contradictions, it enables us to derive quantitative expressions for coefficients characterising transport phenomena. Although the agreement of theoretically predicted behavior with experiments furnishes indirect evidence in favour of molecular theory, it is desirable for a sound basis to establish the existence of molecules and their motion by experimentation. It is instructive to point out that in the initial stages of the development of molecular theory, even prominent scientists were reluctant to accept the realities of the atoms and molecules. The German physicist Wilhelm Ostwald regarded the atoms as a merely hypothetical conception that affords a very convenient picture of matter. Similarly, Ernst Mach maintained that atoms and molecules must be treated as convenient fictions.

The first experimental evidence for the existence of molecules and their motion was provided by Robert Brown while he was observing the random course of a particle suspended in a fluid. This remarkable phenomenon is called the **Brownian motion**. In view of its importance, in Sec. 11.2 we review what led to Brownian motion.

The random motion of the suspended particles is due to their incessant bombardment by the molecules of the fluid. The suspended particles can be likened to a fleet of buoys charting their course through a turbulent sea of molecules. The course of a suspended particle is similar to the groggy steps of drunken man who starts walking from a lamp post on a city square. This analogy between Brownian motion and random walk turns out to be very fruitful and is discussed in Sec 11.3.

You will be surprised to know that Albert Einstein predicted this phenomenon on theoretical grounds in 1905, although he was unaware of its observation by Brown as early as 1828. He related the mean square displacement of suspended particles and the diffusion coefficient. This made experimental determination of Avogadro's number and the mass of a molecule possible. Sec. 11.4 deals with the theoretical analysis of Brownian motion.

Several efforts have been made to give a mathematically more satisfying theory of Brownian motion. This has given birth to many new mathematical techniques for handling random phenomena. Here we shall confine ourselves to a discussion of Einstein's and Langevin's theories. Examples of Brownian motion are described in Sec. 11.5.

We have discussed the experimental determination of Avogadro's number in Sec. 11.6. It is due to Perrin, who made a detailed study of Brownian motion.

Objectives

After studying this unit you should be able to

- explain the significance of random walk
- derive an expression for the mean squared displacement using Einstein's and Langevin's theories
- state examples of Brownian motion, and
- describe the importance of Perrin's experiments.

11.2 BROWNIAN MOTION REVISITED

Brownian motion has been holding unending charm for mathematicians as well as scientists ever since its discovery. It was discovered by Robert Brown, a botanist, while making observations on pollen grains suspended in water using a high power microscope. He observed an irregular dancing motion that never ceased. This irregular motion is exhibited by any small particle suspended in a viscous medium.

The first dynamical theory of the Brownian motion proposed that the particles were alive. It was argued that vitality is retained by the molecules of a plant for long after its death. However experiments by Brown and others proved conclusively that the motion is not due to any biological or chemical factors. In fact, Brown made observations on a drop of water trapped in a chunk of igneous rock as the rock cools from its melt. By focusing a microscope on the drop he saw scores of tiny particles suspended in the drop executing a random dance. Careful experiments by Guy Williams and others supported the kinetic theory. It was found that :

(i) Smaller particles are more agitated than the bigger ones.

(ii) The motion is more in a less viscous fluid.

(iii) It becomes more pronounced as the temperature is increased.

Boltzmann and Gibbs had made great progress in applying statistical laws to physical systems. But it required the genius of Einstein to work out a detailed theory of Brownian motion in terms of the effect of collisions between molecules. He realized that this could provide evidence in favour of the kinetic theory. Einstein's predictions were found to be precisely correct by the beautiful experiments of Perrin. This also paved the way for accurate determination of molecular masses. This work convinced everyone, including the sceptics, of the reality of the molecular nature of matter and launched the subject to attain wider horizons.

Brownian motion has now become a paradigm for a large class of random phenomena. It opened very fertile channels of research. As a result, very sophisticated mathematical techniques have been developed to describe the motion of a Brownian particle. However, these details, though beyond the scope of your present study, have been included in a simplified manner to convince you regarding the significance of Brownian motion, particularly in reference to kinetic theory.

11.3 ONE-DIMENSIONAL RANDOM WALK

From your school science curriculum you are familiar with the process of diffusion. In the preceding unit we derived an expression for diffusion coefficient when one gas mixes with the other. You now know that it signifies transport of mass if a gas is endowed with mass motion. And random molecular motion acts as the carrier. In probability theory, it can be characterised as the evolution of a system in time and space through random discrete steps, each of which is independent of the preceding or succeeding steps. The study of such a motion is referred to as random walk problem.

You can realise a simple random walk problem by coin tossing at regular intervals. We move a step to the right if head appears and to the left if tail shows up. Our position at any time will depend on the sequence of heads or tails. Another very simple example of random walk problem is the motion of drunks who begin their stroll from a single lightpost, but are so intoxicated that each step may be in random direction and of a range of different lengths.

In addition to diffusion, random walk provides models for numerous applications in physics. These include (i) Brownian motion, (ii) turbulence in fluids, (iii) neutron diffusion,

$$f(x,t) = \frac{\sqrt{\tau}}{\sqrt{2\pi t r^2}} \exp\left(-\frac{r^2}{2tr^2}\tau\right)$$

$$= \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \tag{11.7}$$

where $D = r^2/2\tau$ is known as diffusion coefficient. This equation gives the probability that the particle is at a distance x at time t. It represents a gaussian distribution curve (Fog. 11.2).

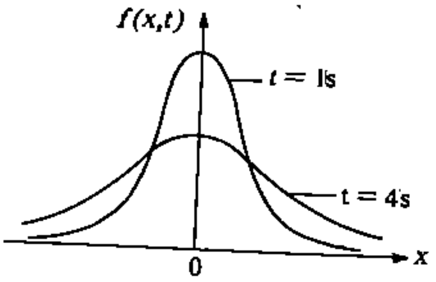


Fig. 11.2 : Plot of Eq. (11.7)

Let us now calculate the mean square displacement of a Brownian particle defined as

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 f(x,t)\, dx$$

If you substitute for $f(x,t)$ from Eq. (11.7), you will get

$$\langle x^2 \rangle = \frac{1}{2\sqrt{\pi Dt}} \int_{-\infty}^{\infty} \exp\left(-\frac{x^2}{4Dt}\right) dx$$

You will note that if we replace x by $-x$, the value of the integral remains unchanged. Such an integral is said to be symmetric and we can rewrite the above expression for mean square displacement as

$$\langle x^2 \rangle = \frac{1}{\sqrt{\pi Dt}} \int_{0}^{\infty} x^2 \exp\left(-\frac{x^2}{4Dt}\right) dx \tag{11.8}$$

To evaluate this integral, we introduce a new variable by defining

$$\frac{x^2}{4Dt} = y$$

so that

$$x^2 dx = 4(Dt)^{3/2} y^{1/2} dy$$

$$\int_0^{\infty} x^n \exp(-x)\, dx \quad (n > -1)$$

is, by definition, gamma function of order (n+1). And

$\Gamma(n+1) = n\Gamma(n)$

with

$\Gamma(1) = 1$

$\Gamma(1/2) = \sqrt{\pi}$

On substituting this result in Eq. (11.8) we find that

$$\langle x^2 \rangle = \frac{4Dt}{\sqrt{\pi}} \int_0^{\infty} y^{1/2} \exp(-y)\, dy$$

$$= \frac{4Dt}{\sqrt{\pi}} \Gamma(3/2)$$

where $\Gamma(x)$ is gamma function. Since $\Gamma(3/2) = \sqrt{\pi}/2$, we get

$$\langle x^2 \rangle = 2Dt \tag{11.9}$$

You will learn in the next section that this result is the same as derived by Einstein from considerations of the molecular concentration gradient. You can also obtain it by integrling the diffusion equation. This has been posed as SAQ.

SAQ 1

Obtain Eq. (11.9) by integrating the diffusion equation

$$\frac{\partial n(x;t)}{\partial t} = D\frac{\partial^2 n(x,t)}{\partial x^2}$$

On solving this SAQ you may be tempted to conclude that the diffusion process can be modelled by random walk problem. If you think so, you are not wrong. In fact, essentially this line of argument was used by Einstein to work out theoretical analysis of this phenomenon. You will learn about it in the following section.

11.4 THEORETICAL ANALYSIS OF BROWNIAN MOTION

In 1905, Einstein gave a systematic mathematical theory of Brownian motion. His arguments were based on physical processes that take place inside a colloidal solution. In 1908, Langevin rederived Einstein's formula by considering the equation of motion of suspended particles. Let us first discuss Einstein's derivation.

11.4.1 Einstein's Derivation

Einstein gave an exact description of Brownian motion in terms of the effects of random collisions between the molecules of the liquid and the suspended particles. He was the first person to recognise that the existence of atoms/molecules can be revealed through the motion of suspended particles in a fluid. He quantified this problem by relating the diffusion of suspended particles to the properties of the molecules responsible for collisions. That is, he calculated the diffusion coefficient from the erratic motion of particles arising from molecular bombardment.

Osmotic pressure of a solution is the pressure required to prevent osmosis when the solution is separated from pure solvent by a semi-permeable membrane.

We also know that the molecules of a solute dissolved in a dilute solution exert osmotic pressure between different parts of the solution. This causes the suspended particles to diffuse. Einstein used van't Hoff's law to calculate D by considering the motion of the suspended particles under the influence of the osmotic pressure difference. He then equated these expressions to calculate mean squared displacement of a Brownian particle. We now give a simple derivation of D based on random molecular motion.

Calculation of D from random molecular motion

We know that random molecular motion causes Brownian partcles to diffuse and their motion is totally erratic. For simplicity, we confine ourselves to one-dimensional Brownian motion and assume that, on an average, each particle is displaced through a distance s in time τ. Let us imagine a cylinder of cross-sectional area A and length s with its axis parallel to the x-axis. Its end faces are denoted by Q_1 and Q_2 in Fig. 11.3. Let the molecular concentration of Brownian particles at Q_1 be n_1 and that at Q_2 be n_2 such that $n_1 > n_2$ That is, there exists a molecular concentration gradient dn/dx, where n is mean concentration along the cylinder. This makes the suspended particles to diffuse. Then the number of particles crossing Q_1 to the right in time τ is equal to $\frac{n_1}{2} s A$. The factor (1/2) arises because only half of the particles contained in a cylinder of volume sA situated to the left of Q_1 will cross it in this time. Similarly, the number of particles entering Q_2 and moving in the negative x- direction in time τ is equal to $\frac{n_2}{2} sA$. So the excess number of particles crossing the vertical plane R at the centre of the cylinder in the positive x- direction in time τ is given by

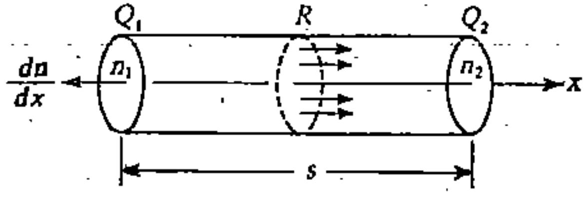


Fig. 11.3 : Calculation of diffusion coefficient for one-dimensional Brownian motion

terms of x^2 To do so, we multiply Eq. (11.14) throughout by x. This gives

$$m x \ddot{x} = -C x \dot{x} + x F_x \tag{11.15}$$

Proceeding further we note that

$$\frac{d}{dt}(x^2) = 2x\dot{x} \Rightarrow x\dot{x} = \frac{1}{2}\frac{d}{dt}(x^2)$$

and

$$\frac{d^2}{dt^2}(x^2) = 2x\ddot{x} + 2(\dot{x})^2$$

or

$$x\ddot{x} = \frac{1}{2}\frac{d^2}{dt^2}(x^2) - (\dot{x})^2$$

On substituting these results in Eq. (11.15), we find that

$$\frac{m}{2}\frac{d^2}{dt^2}(x^2) - m(\dot{x})^2 = -\frac{C}{2}\frac{d}{dt}(x^2) + x F_x$$

This equation is valid for each suspended particle. If we average it over a large number of particles, we get

$$\frac{m}{2}\langle \frac{d^2}{dt^2}(x^2)\rangle - m\langle(\dot{x})^2\rangle = -\frac{C}{2}\langle\frac{d}{dt}(x^2)\rangle + \langle x F_x\rangle \tag{11.16}$$

where $\langle ... \rangle$ denotes the average over all suspended particles.

Since both x and F_x vary randomly, the product $\langle x F_x \rangle$ appearing in Eq. (11.16) will be zero. Further, Brownian particles are in thermal equilibrium with fluid molecules and it follows from the equipartition theorem that their mean kinetic energy (associated with each degree of freedom) is $k_B\, T/2$. That is,

$$m\langle(\dot{x})^2\rangle = k_B\, T$$

Using these results in Eq. (11.16), we finally obtain

$$\frac{m}{2}\langle\frac{d^2}{dt^2}(x^2)\rangle + \frac{C}{2}\langle\frac{d}{dt}(x^2)\rangle = k_B\, T$$

or

$$\langle\frac{d^2}{dt^2}(x^2)\rangle + \alpha^2\langle\frac{d}{dt}(x^2)\rangle = \frac{2k_B\, T}{m} \tag{11.17}$$

where $\alpha^2 = C/m$.

To solve this equation we make use of the fact that the operations of averaging and differentiation are commutative, i.e., these can be performed in any order. Then, we can write

$$\langle\frac{d}{dt}(x^2)\rangle = \frac{d}{dt}\langle(x^2)\rangle = u$$

and

$$\langle\frac{d^2}{dt^2}(x^2)\rangle = \frac{d^2}{dt^2}\langle(x^2)\rangle = \dot{u}$$

Then, Eq. (11.17) becomes

$$\dot{u} + \alpha^2 u = \frac{2\, k_B\, T}{m} \tag{11.18}$$

This is a first order inhomogeneous ordinary differential equation (ODE). You have learnt to solve such equations in Block 1 of PHE-05 course. Its most general solution is

$$u = \frac{2k_B T}{C} + A\ \exp(-\alpha^2 t) \tag{11.19}$$

The general solution of an inhomogeneous ODE consists of the particular and complementary solutions. The particular solution is obtained by noting that

$$u = \frac{1}{\left(\frac{d}{dt} - \alpha^2\right)}\frac{2k_B T}{m} = \frac{1}{\left(\frac{d}{dt} + \alpha^2\right)\frac{m}{2k_B T}} = \frac{2k_B T}{m\alpha^2}$$

$$= \frac{2k_B T}{C}$$

On the other hand, the complementary solution is obtained by equating the RHS of Eq. (11.18) equal to zero. The resulting equation can readily be integrated to get

$$u = A\ \exp(-\alpha^2 t)$$

where A is constant of integration.

At $t = 0, x = 0 \Rightarrow u = 0$ so that $A = -2\,k_B\,T/C$. Inserting this result in Eq. (11.19), we can write

$$u = \frac{d}{dt}\langle (x^2)\rangle = \frac{2\,k_B\,T}{C}\left[1 - \exp(-\alpha^2 t)\right]$$

Integrating again, we have

$$\langle x^2\rangle\Big|_0^\tau = \frac{2k_B\,T}{C}\left[t + \frac{1}{\alpha^2}\,e^{-\alpha^2 t}\right]_0^\tau$$

or

$$\langle x_\tau^2\rangle - \langle x_0^2\rangle = \frac{2k_B\,T}{C}\left[\tau - \frac{1}{\alpha^2}(1 - e^{\alpha^2\tau})\right] \tag{11.20}$$

There are two special cases of interest:

(i) When $\tau << \alpha^{-2}$ or $\alpha^2\tau << 1$, $\exp(-\alpha^2\tau) = 1 - \alpha^2\tau + \frac{1}{2}(\alpha^2\tau)^2 - \ldots$, and Eq (11.20) becomes

$$\langle x_\tau^2\rangle - \langle x_0^2\rangle = \frac{2k_B\,T}{C}\left[\tau - \frac{1}{\alpha^2}\left\{1 - (1 - \alpha^2\tau + \frac{1}{2}\alpha^4\tau^2 - \ldots)\right\}\right]$$

$$= \frac{k_B\,T\,\alpha^2\tau^2}{C} \approx \frac{k_B\,T}{m}\tau^2 \tag{11.21}$$

That is, the suspended particle behaves like a free particle moving with constant thermal speed $\sqrt{\frac{k_B\,T}{m}}$.

(ii) When $\tau >> \alpha^{-2}$ or $\alpha^2\tau >> 1$, $\exp(-\alpha^2\tau) \to 0$, and Eq. (11.20) takes a compact form :

$$\langle x_\tau^2\rangle - \langle x_0^2\rangle = \frac{2k_B\,T}{C}\left(\frac{\alpha^2\tau - 1}{\alpha^2}\right)$$

$$\approx \frac{2k_B\,T}{C}\tau \tag{11.22}$$

On substituting for C, we find that the mean of the squares of the projections of actual displacements on the x-axis is given by

$$\langle x_\tau^2\rangle - \langle x_0^2\rangle = \frac{k_B\,T}{3\,\pi\,\eta\,r_0}\tau = \frac{RT}{N_A}\,\frac{1}{3\,\pi\,\eta\,r_0}\tau \tag{11.23}$$

This result is same as given by Eq. (11.12).

You should realise that $\Delta\langle (x^2)\rangle$ is in no sense the actual displacement of Brownian particles. It tells us that we must take a snapshot of the suspension at time $t = 0$ and again at time $t = \tau$. Then we should measure the component of displacement along any arbitrarily chosen direction, say x-axis and determine $\Delta(x^2)$ for each particle. A sum over all the $\Delta(x^2)$ and division by the number of particles gives $\Delta\langle (x^2)\rangle$. In his experiments, Perrin worked with 100 different particles of known size. And, if we closely re-examine Fig. 11.3 we find that the motion is so complex that an experimentalist may find it inconvenient to work with such a large number. However, we can make use of the fact that if one particle is followed for N successive intervals of time (when N is a large number,), the motion is almost equivalent to the motion of N particles during a single time interval. (This corresponds to the assumption that differentiation and averaging are commutative.)

11.5 EXAMPLES OF BROWNIAN MOTION

We have just now seen that colloidal suspensions in a fluid exhibit Brownian motion. We come across many other interesting examples of Brownian motion. These include sedimentation, diffusion of pollutants in our atmosphere or smoke particles in air, motion of a galvanometer mirror and Johnson noise in amplifiers (electrical appliances). We will discuss these now.

1. Sedimentation

We know that if we take sandy water in a beaker, the sand settles down at the bottom. This process is known as sedimentation. It is responsible for clearing rain water stored in ponds and lakes. In sedimentation, the distribution of particles is determined by the influence of gravity and diffusion. Whereas gravity tends to settle them, diffusion brings about homogenisation. (The same is true of pollutants in our atmosphere.) To calculate the number of particles at a given height, we consider a shallow box of thickness Δz enclosing layers of particles bounded at heights z and $z + \Delta z$. Let p be the pressure on the lower face and $p + \Delta p$ be the pressure at the upper face, as shown in Fig. 11.4.

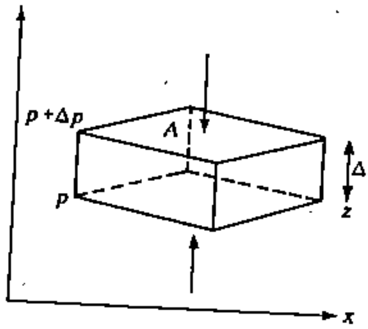


Fig. 11.4 : A shallow box of depth Δz and cross-sectional area A. The pressures on the upper and lower faces are $p + \Delta p$ and p, respectively.

We consider the equilibrium of unit area. If ρ and g respectively denote the density of particles and acceleration, then for equilibrium we must have

$$\Delta p = -g \rho \Delta z$$

where negative sign denotes that pressure decreases as height increases. If m is the mass of a single particle and n is the number density, $\rho = nm$. Then we can rewrite the above expression as

$$\Delta p = -mng \Delta z$$

$$= -\frac{mgN}{V} \Delta z$$

If we assume that Brownian particles obey gas laws, then on replacing V by $\mu RT/p$, we find that

$$\frac{\Delta p}{p} = -\frac{mgN}{\mu RT} \Delta z$$

where μ denotes the number of moles.

This may be integrated to obtain

$$p = p_0 \exp\left(-\frac{mgN}{\mu RT} z\right) \qquad (11.24a)$$

where $p = p_0$ at $z = 0$.

We know that $p = \frac{1}{3} mn \overline{v^2}$ so that we can rewrite Eq. (11.24a)

$$n = n_0 \exp\left(-\frac{mgN}{\mu RT} z\right) \qquad (11.24b)$$

This suggests that during sedimentation, the particle concentration decreases exponentially with height. In practice, the supended particles experience upward bouyant force due to difference in the densities of the solute ρ and the solvent ρ'. As a result, the effective mass of the suspended particles is reduced to

$$m_{eff} = \frac{4\pi}{3} (\rho - \rho') r_0^3 \qquad (11.24c)$$

where r_0 is the radius of a particle. If $\rho \simeq \rho'$, m_{eff} would be substantially small.

Eq. (11.24) suggests that if we study the variation of n with height for fine suspensions, we can conveniently determine Avogadro's number. Perrin worked with emulsions of gamboge and mastic and obtained a value very close to the presently accepted value obtained by other sophisticated methods. This suggests that fine particles in thermal equilibrium behave like gas molecules.

We will discuss Perrin's work in detail a little later.

Example 1

In his experiment on water suspension of gamboge at 20°C, Perrin observed an average of 49 particles per cm^2 in a layer at one level and 14 particles per cm^2 in a layer 60 microns higher (1 micron = 10^{-6} m). If the density of gamboge is 1.194 g cm^{-3} and radius of each particle is 0.212 micron, calculate Avogadro's number.

Solution

From Eq (11.24), we have

$$N_A = \frac{3\,RT}{4\,\pi\, r_0^3\,(\rho - \rho')\,gz}\ \ln\left(\frac{n_0}{n}\right)$$

On substituting the values of various quantities, we get

$$N_A = \frac{3 \times (8.31\ \mathrm{J\ mol^{-1}\ K^{-1}})}{4 \times 3.14 \times (0.212 \times 10^{-6}\ \mathrm{m})^3 \times (1.194 - 1.0) \times 10^3\ \mathrm{kgm^{-3}})} \times \frac{(293\ \mathrm{K})}{(9.8\ \mathrm{ms^{-2}} \times (60 \times 10^{-6}\ \mathrm{m})}\ \ln\left(\frac{49}{14}\right)$$

$$= \frac{3 \times 8.31 \times 293 \times 1.25}{4 \times 3.14 \times (0.212)^3 \times 0.194 \times 9.8 \times 60} \times 10^{21}\ \mathrm{mol^{-1}}$$

$$= 6.7 \times 10^{23}\ \mathrm{mol^{-1}}$$

---

2. Galvanometer mirror

In Block 1 of PHE-02 course, you have learnt that a suspended type galvanometer carries a mirror which focuses light from a source on a scale. When some current is made to pass through it in an electric circuit, we find that it jiggles all the time, i.e., it undergoes small random oscillations. The net result is that the galvanometer reading fluctuates, and the system shows an unsteady position. Do you know why it happens? It arises due to collisions of air molecules with the suspended system.

The Brownian fluctuations of the galvanometer mirror are expressed in terms of root mean square angular deflection, θ_{rms}. To calculate this, we note that the mirror has a single degree of oscillation about its axis so that the thermal energy associated with root mean square angular deflection $<\theta^2>$ is $k_B\,T/2$, i.e.,

$$\frac{1}{2} C < \theta^2 > = \frac{k_B\,T}{2}$$

so that

$$\theta_{rms} = \sqrt{\frac{k_B\,T}{C}} = \sqrt{\frac{k_B\,T}{I\,\omega_0^2}} \qquad (11.25)$$

where C is couple per unit twist or torsional rigidity of the galvanometer suspension, I is the moment of inertia and ω_0 is the angular velocity.

This implies that smaller the value of C, larger will be θ_{rms}. That is, fluctuations will be more in a more sensitive galvanometer. For a fine quartz fibre, $C \sim 10^{-13}$ Nm rad^{-1} so that at 300K

$$\theta_{rms} = 2 \times 10^{-2}\mathrm{rad}$$

If the lamp and scale arrangement is at a distance of 1m from the galvanometer mirror, fluctuation of 2×10^{-4} rad corresponds to an rms fluctuation of the light spot of 4×10^{-4} m (0.4 mm). This is shown in Fig.11.5.

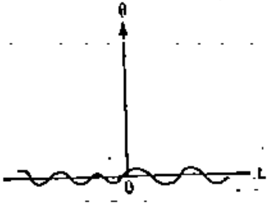


Fig.11.5: Brownian motion of a galvanometer mirror

SAQ 2

Suppose that the temperature and pressure of air are reduced below normal. Can we eliminate random fluctuations in θ completely?

3. Johnson Noise

You are familiar with thermal noise (heating) in electrical circuits. The conduction electrons in a metal may be regarded as a gas. We expect that these may give rise to fluctuating voltage across a resistor. This indeed was observed by Johnson and is known as **Johnson noise or electrical noise**. The *rms* potential fluctuation across a resistor of resistance R in thermal equilibrium at temperature T is given by

$$V_{rms} = \left[4 R k_B T (f_2 - f_1) \right]^{1/2} \tag{11.26}$$

where $(f_2 - f_1)$ is the frequency bandwidth over which the measurements are made. Eq. (11.26) shows that there is a limit to useful amplification. If the original signal is too feeble compared to the random electrical noise, reception will not improve with amplification.

In the domain of economics, the variation in stock prices under certain conditions, can be modelled to follow the Brownian equation of motion.

SAQ 3

Consider an RL series ac circuit. The equation of motion of charge q is

$$L \frac{d^2 q}{dt^2} + R \frac{dq}{dt} = E(t)$$

where $E(t)$ is impressed e.m.f.Draw an analogy with Langevin's equation and compute $< q^2 >$.

Having discussed examples of Brownian motion, it is now desirable to experimentally illustrate various concepts developed here. In particular, we will discuss Perrin's experiments on colloidal suspensions and determination of Avogadro's number. This work signifies a great triumph of molecular theory. For these investigations Perrin was awarded the Nobel Prize for Physics in 1926. In his famous book **Les Atomes** (Atoms), he wrote, "The atomic theory has triumphed. Until recently, still numerous, its adversaries, at last overcome, now renounce one after another their misgivings, which were, for so long, both legitimate and undeniably useful."

Let us now know in brief about Perrin's experiments.

11.6 DETERMINATION OF AVOGADRO'S NUMBER

To determine Avogadro's number, we have to measure $< x^2 >$, the mean square displacement of a Brownian particle. Perrin observed the motion of a single gamboge grain suspended in water at intervals of thirty seconds with the help of a microscope using the camera lucida. To locate the particles, the microscope had in its field of view a series of

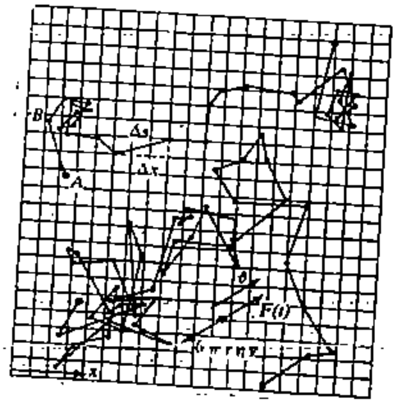


Fig. 11.6 : Calculation of $< x^2 >$ for a Brownian particle

mutually perpendicular lines, as shown on a graph paper in Fig. 11.6, with 16 divisions being equal to 5×10^{-3} cm. The projections of the succesive displacements along the x- axis give a set of values of x from which x^2 can be calculated. You may ask: How could Perrin make such wonderful observations with a simple arrangement? The physical basis of his work is very sound. Perrin derived his argument from the fact that $v_{rms} = 2 \times 10^{-2}\ \mathrm{ms^{-1}}$ at 300K for a 2×10^{-7}m radius grain of gamboge having a mass of about 3×10^{-17}kg (which is

10^9 times the mass of the H_2O molecule). This combination of slow speeds and large size was exploited by Perrin to observe the motion of suspended particles. It justifies the popular belief that Nature likes simplicity. And all natural laws have been unfolded using very simple arguments. Our own Sir C.V.Raman explained the scattering of light using a very modest apparatus.

It should be realised that the straight line segments in Fig. 11.6 are in no way a representation of the actual path of the particle. The particle is hit millions of times in a second,and hence, its trajectory has a jagged and irregular structure. For example, if we magnify the part *AB* of the trajectory say 100 times, it will appear as shown in Fig. 11.7.

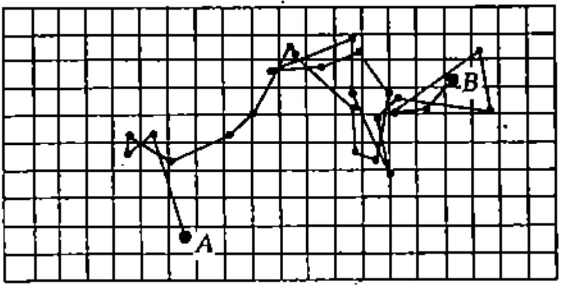


Fig.11.7 : The path *AB* after magnification

From his measurements, Perrin obtained N_A equal to 6.85×10^{26} molecules kmol^{-1}. Westgren obtained the value 6.05×10^{26} which differs from the standard value by just 1%. From this value of Avogadro's number, you can estimate the mass of a molecule. For example, one kilo mole of nitogen gas has a mass of 14 kg. Hence,mass of a nitrogen molecule

$$m_{N_2} = \frac{14\ \text{kg}}{6.05 \times 10^{26}} = 2.31 \times 10^{-26}\ \text{kg}.$$

Perrin is, therefore, said to be the first person to have weighed the atom and kinetic theory is the tool.

Other features of Eq. (11.24) have been brilliantly confirmed by the work of Perrin, Westgren, Svedberg and others.

The motion of a galvanometer mirror can also be used to determine N_A. This was first shown by Keppler in 1931. With $I = 4.552 \times 10^{-4}\text{g cm}^2\ \text{rad}^{-1}$ and $\nu_0 = 1379\ \text{s}^{-1}$ we find that

$$C = \frac{4\pi^2 I}{\nu_0^2} = 9.443 \times 10^{-9}\ \text{g cm}^2\ \text{s}^{-2}\ \text{rad}^{-1}$$

The observed value of $< \theta^2 >$ was $4.178 \times 10^{-6}\ \text{rad}^2$ at $T = 287.1$ K. Using Eq. (11.25), we find that

$$k_B = 1.374 \times 10^{-16}\ \text{erg K}^{-1}$$

and

$$N_A = \frac{R}{k_B} = \frac{8.31 \times 10^7\ \text{erg mol}^{-1}\ \text{K}^{-1}}{1.374 \times 10^{-16}\ \text{erg K}^{-1}} = 6.06 \times 10^{23}\ \text{mol}^{-1}$$

which is almost identical with the value obtained by Westgren.

Let us now sum up what you have learnt in this unit.

11.7 SUMMARY

- The probability of finding the particle at $x = m$ after N steps is given by

$$W(m, N) = \frac{N!}{\left(\frac{N+m}{2}\right)!\left(\frac{N-m}{2}\right)!}\left(\frac{1}{2}\right)^{N}$$

For large N,

$$W(m,N) = \sqrt{\frac{2}{\pi N}}\, \exp\left(-\frac{m^2}{2N}\right)$$

- The probability that after N steps, the particle is between x and $x + dx$ is given by

$$f(x,N) = \frac{1}{\sqrt{2\pi}\,\sigma} \exp\left(-\frac{x^2}{2\sigma^2}\right)$$

with $\sigma^2 = Nr^2$

Interms of the diffusion coefficient D,

$$\langle x^2 \rangle = 2Dt$$

- The **Einsteins relation** for mean square displacement of a Brownian particle is

$$\langle x^2 \rangle = \frac{RT}{N_A} \frac{1}{3\pi\eta r_0} \tau$$

11.8 TERMINAL QUESTIONS

1. W. Pospisil observed the motion of soot particles of radius 0.4×10^{-4}cm in a water-glycerine solution with $\eta = 0.0278$ poise at $T = 292$K The observed value of $\langle x^2 \rangle$ was $3.3 \times 10^{-8}\,\text{cm}^2$ for $t = 10$ s. Use this information to calculate N_A

2. The following table gives the results of an actual observation made on the Brownian motion of a spherical particle of radius 0.4 μ The 403 values of x, observed after succesive intervals of 2 s each, were distributed as follows:

Displacement x (in μ)	Frequency of occurrence
$x < -5.5$	0
$-5.5 < x < -4.5$	1
$-4.5 < x < -3.5$	2
$-3.5 < x < -2.5$	15
$-2.5 < x < -1.5$	32
$-1.5 < x < -0.5$	95
$-0.5 < x < 0.5$	111
$0.5 < x < 1.5$	87
$1.5 < x < 2.5$	47
$2.5 < x < 3.5$	8
$3.5 < x < 4.5$	5
$4.5 < x < 5.5$	0
$x > 5.5$	0

The viscosity of the fluid medium, water, was 10^{-3} Pl at $T = 300$ K.

Calculate $\langle x^2 \rangle$, D, and k_B

11.9 SOLUTIONS AND ANSWERS

SAQs

1. We have

$$\frac{\partial n(x,t)}{\partial t} = D \frac{\partial^2 n(x,t)}{\partial x^2}$$

Multiplying both sides by x^2 and integrating with respect to x from $-\infty$ to ∞, we obtain

$$\int_{-\infty}^{\infty} x^2 \frac{\partial n(x,t)}{\partial t} = D\int_{-\infty}^{\infty} \frac{\partial^2 n(x,t)}{\partial x^2} x^2\, dx$$

The left hand side $= \dfrac{\partial}{\partial t}\displaystyle\int_{-\infty}^{\infty} x^2\, n(x,t)\, dx = N\frac{\partial}{\partial t}\langle x^2\rangle$ (i)

The right hand side

$$= -D\left\{\left[x^2\frac{\partial n}{\partial x}\right]_{-\infty}^{\infty} - 2\int_{-\infty}^{\infty} x\,\frac{\partial n}{\partial x}\,dx\right\}$$

Using the condition

$$\frac{\partial n}{\partial x} \to 0 \text{ as } x \to \pm\infty$$

we find that the first term drops out. Hence

$$\text{RHS} = -2D\int_{-\infty}^{\infty} x\,\frac{\partial n}{\partial x}\,dx$$

Integrating again by parts, we find that

$$\text{RHS} = -2D\,[x\,n(x)]_{-\infty}^{\infty} + 2D\int_{-\infty}^{\infty} n(x)\,dx = 2DN \quad \text{(ii)}$$

since $n(x) \to 0$, as $x \to \pm\infty$.

Therefore, from (i) and (ii), we get

$$\frac{\partial}{\partial t}\langle x^2\rangle = 2D$$

or

$$\langle x^2\rangle = 2Dt$$

where we have assumed that $\langle x^2\rangle_{t=0} = 0$.

2. Even at the lowest pressure possible in the laboratory, there are a very large number of air molecules present. When the pressure is high, the number of collisions is very large and hence the natural oscillation of the system is heavily damped. At smaller values of p, damping becomes smaller and the rms amplitude remains the same.

3. By comparing the given equation with the Langevin equation, we fix can the following correspondence:

$$L \leftrightarrow m,\ x \leftrightarrow q,\ F(t) \leftrightarrow E(t), \text{ and } C \leftrightarrow R$$

Making these substitution in Eq. (11.22) we find that

$$\Delta\langle q^2\rangle = \frac{2k_B T}{R}\tau$$

It has been assumed that $\langle q\,E(t)\rangle = 0$ and the mean magnetic energy $\frac{1}{2}L\langle I^2\rangle = \frac{1}{2}k_B T$.

The result is independent of L for $t >> \dfrac{L}{R}$

TQs

1. We have

$$\langle x^2\rangle = \frac{k_B T}{3\pi\eta r_0}\tau$$

On rearrangement, we can write.

$$k_B = \frac{3\pi\eta r_0}{T\tau}\langle x^2 \rangle$$

$$= \frac{3\pi \times (0.0278 \text{ poise}) \times (0.4 \times 10^{-4} \text{ cm}) \times 3.3 \times 10^{-8}}{(292 \text{ K}) \times (10 \text{ s})}$$

$$= 1.18 \times 10^{-16} \text{ erg K}^{-1}$$

This yields

$$N_A = \frac{R}{k_B} = \frac{8.31 \times 10^{7} \text{ erg mol}^{-1} \text{ K}^{-1}}{1.18 \times 10^{-16} \text{ ergK}^{-1}} = 7.04 \times 10^{23} \text{ mol}^{-1}$$

2. We have

$$\langle x \rangle = \frac{(-5 \times 1) + (-4 \times 2) + (-3 \times 15) + (-2 \times 32) + (-1 \times 95) + (87 \times 1) + (47 \times 2) + (8 \times 3) + (5 \times 4)}{403}$$

$$= \frac{8}{403} = 0.02 \approx 0$$

$$\langle x^2 \rangle = \frac{(5^2 \times 1) + (4^2 \times 2) + (3^2 \times 15) + (2^2 \times 32) + (1^2 \times 95)}{403} + \frac{(1^2 \times 87) + (2^2 \times 47) + (3^2 \times 8) + (4^2 \times 5)}{403}$$

$$= \frac{842}{403} = 2.09 \times 10^{-8} \text{ cm}^2$$

$$D = \frac{\langle x^2 \rangle}{2\tau} = \frac{2.09 \times 10^{-8} \text{ cm}^2}{4 \text{ s}} = 5.22 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$$

$$k_B = \frac{3\pi \times (10^{-3} \text{ Pl}) \times (0.4 \times 10^{-6} \text{ m})}{(300 \text{ K}) \times 2} \times 2.09 \times 10^{-12} \text{ m}^2$$

$$= 1.31 \times 10^{-23} \text{ J K}^{-1}$$

It is instructive to plot the frequency distribution and see that it fits a normal distribution fairly well.

UNIT 12 REAL GASES

12.1 Introduction

Objectives

12.2 Deviations from Ideal Gas Behaviour

12.3 van der Waals' Equation of State

Comparison with Experimental Results

Limitations

12.4 Other Equations of State

12.5 Summary

12.6 Terminal Questions

12.7 Solutions and Answers

12.1 INTRODUCTION

In this block so far you have studied the behaviour of ideal gases, which obey the equation of state : $pV = \mu RT$. This equation is remarkably simple. It relates the quantity of gas, its temperature, pressure and volume. It implies that at a given temperature, the product pV will be constant. So a plot of pV as a function of p should be a straight line parallel to the pressure axis. Similarly,if we vary pressure as a function of volume, the curve, called an isotherm, is part of a rectangular hyperbola. For a set of temperatures, these isotherms form a family of parallel curves. You may now ask : Do all gases obey this equation of state or show any deviation from this behaviour under any condition ? Certainly gases show deviation. Experimental investigations of Boyle, Regnault, Andrews, Amagat, Onnes and several others revealed that in actual practice, the behaviour of a gas may not resemble the perfect gas behaviour even at room temperature. In fact, you should have expected such a behaviour as some of our assumptions leading to ideal gas laws are not very realistic. Then the question arises : How to describe the behaviour of a real gas ? This posed a great challenge to nineteenth century physicists. Many equations were proposed to describe the behaviour of real gases. Some of these were purely empirical. However, the best explanation came from van der Waals. He made allowance for the finite size of gas molecules as well as intermolecular forces. In this unit you will learn the behaviour of real gases and see how van-der Waals explained it.

Objectives

After studying this unit you should be able to

- discuss the nature of isotherms of CO_2
- establish van der Waals' equation of state for a real gas
- discuss determination of van der Waals' constants and relate them to critical constants
- obtain reduced equation of state and discuss the law of corresponding states
- discuss limitations of van der Waals' equation of state, and
- write other equations of state.

12.2 DEVIATIONS FROM IDEAL GAS BEHAVIOUR

You now know that ideal gas model is simple but widely applicable. Yet it does not hold universally. As pointed out in the introduction to this unit, the concept of ideal gas breaks down for common gases at high pressures and low temperatures. That is, the ideal gas equation does not apply in such situations. Two other major drawbacks of ideal gas model have been discovered. These include its inability to predict processes such as liquefaction and adsorption, which are technologically important. You will now definitely like to know about the reasons responsible for these limitations. The following paragraphs will serve this purpose.

1. **van Marum's Experiments** : At the end of the eighteenth century, van Marum designed experiments to test the validity of Boyle's law for real gases. Working with ammonia (chemical symbol NH_3), he observed that as the gas is compressed, pressure increases. Though the nature of variation was similar to that predicted by Boyle's law, there were differences in detail (Fig. 12.1).

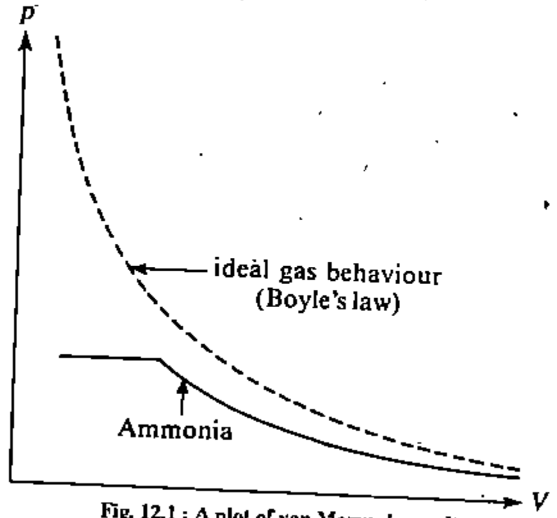


Fig. 12.1 : A plot of van Marum's results on ammonia

At a pressure of about seven atmospheres, he observed that volume decreases even as pressure remains constant. This was due to the formation of liquid ammonia–a phenomenon unknown to the contemporaries of van Marum. This puzzled physicists as no satisfactory explanation was available. Nevertheless, this opened a fertile channel of active research and motivated further experimentation. In the following years, efforts made by Regnault, Andrews, Amagat and others to liquefy other common gases by varying both pressure and temperature proved fairly successful. We shall now discuss these.

2. **Regnault's Experiments** :Regnault carried out very careful investigations on hydrogen, oxygen, nitrogen and carbon dioxide. He applied pressures upto about 30 atm and temperature was varied in the range 0-100° C. His main results are shown in Fig. 12.2,

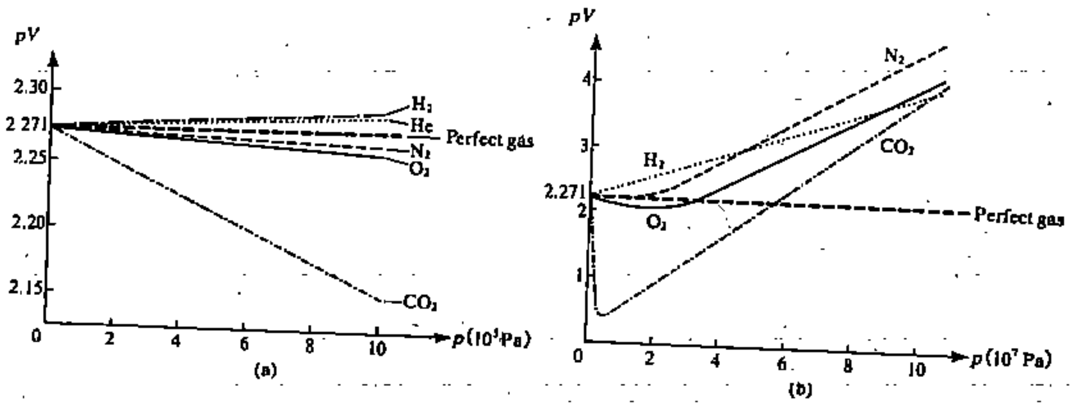


Fig. 12.2 : Variation of pV versus p for hydrogen, oxygen, nitrogen and carbon dioxide at low pressures (0 – 1 atm) and high pressure (0 – 1000 atm). The dotted horizontal lines indicate the values for an ideal gas.

where we have plotted pV as a function of p. On closely examining these graphs, you will note that :

(i) For hydrogen (H_2), the product pV increases with p but in case of nitrogen (N_2), oxygen (O_2), and carbon dioxide (CO_2), it first decreases and then increases.

(ii) The curves are straight lines inclined to p-axis.

You will agree that these observations are a pointer to the imperfect nature of real gases.

3. **Andrews' Experiments** : Andrews carried out detailed experiments on the compressibility of gases while trying to liquefy them. In a sense, he repeated van Marum's work at different but constant temperatures. For carbon dioxide his results are shown on an indicator diagram in Fig. 12.3. You can draw the following conclusions:

(i) Above 323 K, the behaviour of CO_2 resembles that of a perfect gas.

(ii) As the temperature is lowered, isotherms are distorted.

(iii) At 304 K, a kink appears in the isotherm. It signifies that CO_2 gas has begun to condense.

(iv) At about 294.5 K, the kink spreads into a horizontal line. It represents liquid- gas coexistence. Physically, it signifies a discontinuous change in the density of the material for a certain range of values of pressure and temperature. (Experimentally, it implies a meta-stable state.)

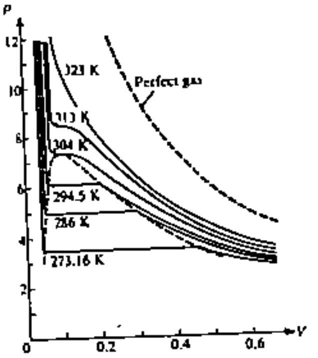


Fig.12.3 : Andrews' curves for CO_2

The set of values of temperature (T_c) and pressure (p_c) at which a gas just begins to condense constitutes the critical point. You may enquire : Are the gaseous and liquid phases identical at this point? To quote Andrews : 'If anyone asks whether the system is now in the gaseous or in the liquid state, the question does not, I believe, admit of a positive reply'. The values of T_c and p_c for some common gases are given in Table 12.1 You will note that each gas has its characteristic critical values of T_c and p_c. Furthermore, the pressure required for liquefaction is less for a gas having lower value of critical temperature.

Table 12.1 Critical temperature and pressure for some common gases

Gas	T_c (K)	p_c (10^5Pa)
He	5.2	2.3
A	151	49
H_2	33	13
O_2	155	51
NH_3	405	113
CO_2	304	74

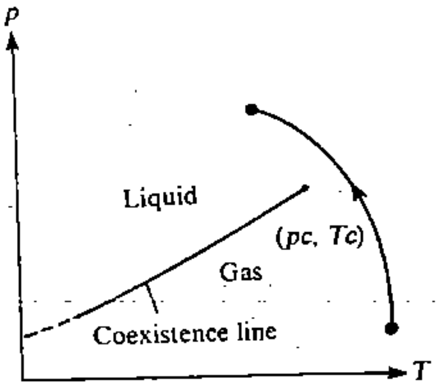


Fig. 12.4 : Liquid-gas coexistence graph for a typical substance

It is important to emphasize here that :

(i) A gas can be liquefied only if it is cooled upto or below its characteristic critical temperature. It is therefore clear that the upward rise in pV for hydrogen observed by Regnault (Fig. 12.2) arises because its critical temperature is much below the room temperature.

(ii) There exists a continuity of liquid and gaseous states. That is, these are two distinct stages of a continuous physical phenomenon. To understand this, refer to Fig. 12.4, which depicts liquid-gas coexistence for a typical substance. The coexistence line marks the pressure and temperature conditions at which density of a substance exhibits discontinuous change. You will note that the difference in densities decreases as we move to higher temperatures and pressure until at the critical point it disappears completely. (In terms of $p - V$ graph (Fig. 12.3), it amounts to moving to other isotherms.) This means that the boundary is incomplete and we can bypass the coexistence line. That is, it is possible to move from the gas to the liquid phase without passing through any point at which we can distinguish two phases.

You may now pose the question : Is it necessary to refer to two distinct phases? Yes it is, because we do see two phases along the coexistence line for many natural systems.

You may now answer the following SAQ.

SAQ 1

In Table 12.1 we have given values of T_c and p_c for some common gases. Which of these gases can not be liquefied by compression at room temperature ?

4. **Amagat's Experiments** : Amagat investigated the behaviour of several gases at various temperatures and upto very high pressures (300 atmospheres). This work lent support to the findings of Regnault and Andrews. His results for CO_2 are shown in Fig. 12.5.

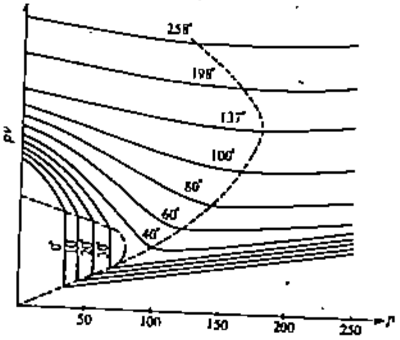


Fig. 12.5 : Amagat's isotherms for CO_2

We summarise the main conclusions:

(i) For $T < T_c$ isotherms have a straight line portion which is parallel to the pV-axis. That is, below the critical temperature, volume increases even though pressure remains constant. This corresponds to the condensation of the gas (as in the horizontal part in Fig. 12.3).

(ii) The curvature of the isotherms decreases as temperature increases. At the critical temperature, the straight line part collapses to a point.

(iii) As temperature increases, the minimum of an isotherm gradually shifts away from the origin towards the right. After a particular temperature, it shifts towards the left. The locus of the minima, shown by the dashed curve, is almost parabolic.

(iv) The parabola cuts the $p = 0$ axis at some temperature, called the Boyle's temperature, T_B. For $T > T_B$, the value of pV steadily increases.

We may now conclude that

A. The compression promotes liquefaction.
B. Lower the temperature, easier it is to liquefy a gas.
C. No liquefaction can occur above critical temperature, how high the pressure may be.

SAQ 2

A fixed mass of CO_2 is compressed to 70 atm at 25°C. It is suddenly released to atmospheric pressure. What is the physical state of CO_2 before and after being released ?

12.3 VAN DER WAALS' EQUATION OF STATE

You will now agree that the perfect gas equation fails to explain the observed results on CO_2 and other gases. This is particularly true when pressure is high ($p > p_c$) and temperature is low ($T < T_c$). A satisfactory explanation of these results posed a real challange to theoretical physicists. You may now like to know : How reasonable are the assumptions of the ideal gas model? And how can we modify these? Several scientists put forward equations of state to describe the behaviour of real gases. But the most elegant effort in this direction was made by van der Waals. In fact, his work provided a silver lining in an otherwise ambiguous horizon at that time. You must now be anxious to know: How did van der Waals modify the ideal gas equation? He made some reasonable assumptions regarding the size of gas molecules and intermolecular forces. By so doing, he obtained a remarkable equation of state, which is still in use. It is therefore now pertinent to know the assumptions made by him.

Assumptions

1. Gas molecules have finite size. They cannot be regarded as point masses.
2. Gas molecules attract one another with a weak force which depends on the distance between them. (This implies that molecules of a real gas have both kinetic and potential energies.)
3. Only nearest neighbour interactions are important.
4. The number of collisons with the walls of the container remain the same for point and finite size molecules.

Derivation

A) **Correction for finite size** : Consider one mole of a gas contained in a vessel of volume V. If we think of the gas molecules as point masses, all the space will be available to them for free mtion. But if molecular size is finite and gas molecules behave as incompressible rigid spheres, some volume will be lost as far as their free motion is concerned. Let us denote this loss by b. Then, the total volume available for free movement to molecules will be $V-b$. Therefore, for one mole of the gas, we can write

$$p(V-b) = RT \qquad (12.1)$$

You may now ask: What is the magnitude of b? For one mole of a gas, b is equal to four times the total volume of all its molecules put together. Let us discover this result now.

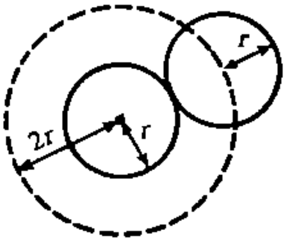


Fig. 12.6 : Collision of two molecules of radius r

Suppose that the radius of each molecule is r. If we consider any two molecules at the instant of collision, their centre-to-centre distance will be $d = 2r$, as shown in Fig. 12.6. This means that around any molecule, spherical volume $V_s = \frac{4\pi}{3} d^3$ will be denied to other molecules.(This volume is called the **sphere of exclusion** and is eight times the volume of a molecule, $V_m = \frac{4\pi}{3} r^3$. That is, $V_s = 8V_m$.)

Let us now imagine that the container is filled with molecules one at a time, starting from the perfect vacuum condition. Then you can readily imagine that

(i) The volume accessible to the first molecule for free movement = V

(ii) The volume accessible to the second molecule for free movement
$$= V - V_s = V-(2-1)V_s$$

(iii) The volume accessible to the third molecule = $V-(3-1)V_s$ and so on.

Since one mole of each gas contains N_A molecules, where N_A denotes Avogadro's number, we can write by induction.

The volume available to N_Ath molecule = $V-(N_A-1)V_s$

The average volume available to each molecule is obtained by taking the arithmetic mean. Hence

The sum of a finite series, containing N terms is equal to $\frac{N(N+1)}{2}$.

$$\overline{V} = \frac{V+(V-V_s)+(V-2V_s)+....[V-(N_A-1)V_s]}{N_A}$$

$$= V - \frac{V_s}{N_A}[1+2+3+....+(N_A-1)]$$

Since the sum within the square brackets is equal to $\frac{N_A(N_A-1)}{2}$, we can write

$$\overline{V} = V - \frac{(N_A-1)}{2} V_s$$

Since $N_A >> 1$, this expression takes a compact form:

$$\overline{V} = V - \frac{N_A}{2} V_s$$

$$= V - 4 N_A V_m$$

where we have used the fact that volume of sphere of exclusion is eight times the volume of a molecule. If we now put $b = 4 N_A V_m$, we find that average volume available to any molecule for free movement is given by

$$\overline{V} = V - b \tag{12.2}$$

You will agree that b signifies the loss in accessible volume due to finite molecular size. This is shared by all molecules and is called **co-volume**. It depends on the nature of the gas.

You can now argue: What is the implication of this result vis-a-vis the equation of state for a perfect gas? It tells us that the perfect gas behaviour can be reproduced if we use corrected volume, i.e., replace V by $V-b$ in the equation of state.

You can now logically enquire: Will there be a pressure correction also? Following van der Waals, we may argue that correction in pressure arises due to intermolecular attraction. Let us now consider it in detail.

B) **Correlation between pressure correction and Intermolecular attraction** : Refer to Fig. 12.7 which depicts the physical picture of a gas. You will note that the local environment of a molecule changes as it moves towards the wall and leaves other molecules behind.

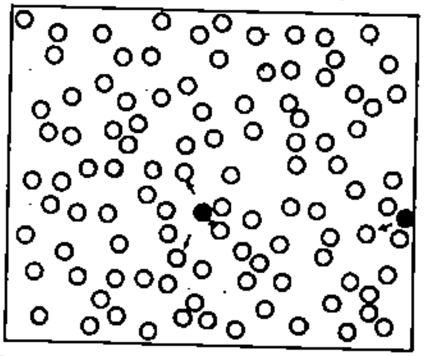


Fig. 12.7 : Physical picture of a gas in a container : Correlation between pressure and intermolecular attraction

Physically, a molecule in the interior of the gas is, on an average, attracted equally in all directions. Therefore, it will not experience any net force. That is, a gas molecule in the body of a gas may behave as if intermolecular interactions were absent. However, this is not true for a molecule near a wall. In fact, as a molecule approaches the wall, it has neighbours only on the side away from the wall. It experiences a pull back into the body of gas. For simplicity, we ignore adhesive forces between the molecules of the gas and the wall. Then you can resolve the force on the gas molecule along the wall and in a direction normal to it. Then, you will find that a molecule experiences net inward force away from the wall. As a result, intermolecular attractions slow down the molecule as it approaches the wall. Consequently, the pressure communicated to the walls of the container will be different from that in the body of the gas.

We know that majority of molecules are in the body of gas rather than near the walls. Therefore, the pressure term in the equation of state should correspond to the bulk of gas, though it is measured at the walls. For the equation of state to be written in terms of measured pressure and to describe the bulk of the gas, it is necessary to modify the pressure term. Obviously, this correction arises because of intermolecular attraction. From the viewpoint of physics, this correction results in decrease in pressure. The drop is known as **cohesive pressure.**

To calculate the cohesive pressure we note that the retarding force experienced by any molecule is proportional to the number of moleculers pulling it backward and hence the number density (N_A/V) of the gas. This is true for all molecules striking the wall. If the number of molecules striking unit area of the wall per second is N, the decrease in pressure due to intermolecular forces is

$$\Delta p \,\alpha\, N\left(\frac{N_A}{V}\right)$$

Since N is also proportional to the number density, we can write

$$\Delta p \,\alpha \left(\frac{N_A}{V}\right)^2$$

$$= \frac{a'N_A}{V^2} = \frac{a}{V^2} \tag{12.3}$$

where $a = a'N_A^2$; a' being constant of proportionality.

You may think that this is a qualitative, in fact, heuristic argument and lacks sound theoretical basis. Its justification arises only from the success of van der Waals' equation in explaining observed results. Inserting $p_{per} = p_{obs} + \frac{a}{V^2}$ and $V_{per} = (V - b)$ in the perfect gas equation $p_{per}\ V_{per} = RT$, we find that

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \tag{12.4}$$

where we have dropped the subscript *obs* appearing with p.

This remarkable equation is known as **van der Waals' equation of state**. The constants a and b are known as van der Waals' constants. Their values are assumed to depend only on the nature of the gas. For some common gases; we have listed values of van der Waals' constants in Table 12.2.

Table 12.2: van der Waals' Constants for Some Common Gases

Gas	$a \times 10^6$ (atm m^6 mol^{-2})	$b \times 10^6$ (m^3 mol^{-1})
H_2	0.244	26.6
He	0.034	23.7
N_2	1.39	39.1
O_2	1.36	31.8
A	1.35	32.2
NH_3	4.17	37.1
CO_2	3.59	42.7
CH_4	2.25	42.8

SAQ 3

Write down van der Waals' equation for μ moles of a gas.

For a rarefied gas, $p >> \frac{a}{V^2}$ and $V >> b$. Then, van der Waals' equation reduces to the equation of state for an ideal gas. For a given temperature, plot of Eq. (12.4) on the indicator diagram is shown in Fig. 12.8. The contribution of self-attracting term is also shown.

To enable you to get an idea about the magnitude of these terms, we have given a solved example. You should go through it carefully.

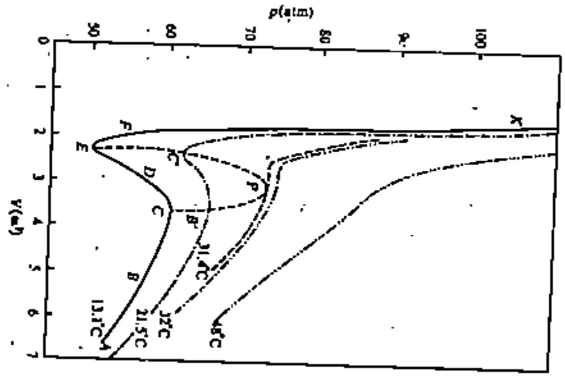


Fig. 12.9 : Theoretical isotherms for CO_2

simultaneously. This corresponds to a collapsible state, which is unnatural and can never be realised in practice. We thus find that a proper interpretation of van der Waals' curves goes a long way in resolving the apparent discrepancy with observed results.

The equation of the locus of the maxima and minima, shown by the dotted curve in Fig. 12.9 can be obtained by putting $(\partial p/\partial V)_T$ equal to zero. Hence, on differentiating Eq. (12.6) with respect to V, we get

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} - \frac{2a}{V^3}$$

On equating it to zero and solving for T, we find that

$$T = \frac{2a\,(V-b)^2}{RV^3} \tag{12.11}$$

Eliminating T between Eqs. (12.5) and (12.11), we get

$$p = \frac{a\,(V-2b)}{V^3} \tag{12.12}$$

It signifies the equation for the curve passing throught the maxima and minima points. We now know that below T_c, a gas can be liquefied by changing pressure alone. For the critical isotherm, these two points coalesce into one. Similarly, from Fig. 12.9 we note that below P all isotherms have maxima and minima but above P no isotherm exhibits wave-like pattern. For this reason, the point P is referred to as the **critical point**. The isotherm passing through P is the **critical isotherm**.

For P to be the point of inflexion, we differentiate Eq. (12.12) with respect to V and equate the resultant expression to zero. This gives

$$\frac{a}{V^3} - \frac{3a\,(V-2b)}{V^4} = 0$$

or

$$V_c = 3b \tag{12.13}$$

Using this result in Eqs. (12.11) and (12.12), we have

$$T_c = \frac{8a}{27\,Rb} \tag{12.14}$$

and

$$p_c = \frac{a}{27\,b^2} \tag{12.15}$$

On combining these results, you can write

$$\frac{RT_c}{p_c V_c} = C_c = \frac{8}{3} \tag{12.16}$$

That is, van der Waals' equation predicts that the critical coefficient is equal to 8/3 and is the same for all gases, irrespective of their nature. (For an ideal gas, $C_c = 1$.) The observed values of the critical coefficient for common gases vary between 3.28 and 3.48. Therefore, we find that van der Waals' equation predicts a lower value of the critical coefficient. Moreover, it varies from gas to gas and appears to depend upon the molecular structure of a gas.

SAQ 4

At the critical point, all three roots of van der Waals' equation are equal. Use this result with Eq. (12.6) and verify expressions for critical constants.

Example 2

Calculate the critical temperature of helium if the critical pressure is 2.26 atm and critical density is 0.069 g cm^{-3}.

Solution

From Eq. (12.16) we note that the critical coefficient is given by

$$\frac{RT_c}{p_c V_c} = \frac{8}{3}$$

so that

$$T_c = \frac{8}{3}\,\frac{p_c V_c}{R}$$

Here, $p_c = 2.26 \text{ atm} = 2.26 \times 1.013 \times 10^5 \text{ Nm}^{-2}$ and $\rho_c = 69 \text{ kg m}^{-3}$ so that the critical volume for 1 kg of the gas is $(1/69)\text{ m}^3$. Hence, the critical volume per kmol of the gas is $(4/69)\text{ m}^3$, i.e. $V_c = (4/69)\text{ m}^3$ kmol.

On substituting the values of various physical quantities, we get

$$T_c = \frac{8}{3}\,\frac{\times(2.26 \times 1.013 \times 10^5 \text{ N m}^{-2}) \times (4/69)\text{ m}^3 \text{ kmol}^{-1}}{8.31 \times 10^3 \text{ J kmol}^{-1} \text{ K}^{-1}}$$

$$= 4.26 \text{ K}$$

This explain why it is so difficult to liquefy helium gas.

Example 3

Calculate van der Waals' constants for helium using the data $T_c = 5.3\text{K}$, $p_c = 2.25$ atm and $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$.

Solution

To calculate a, we combine Eqs. (12.14) and (12.15). This gives

$$a = \frac{27R^2}{64}\,\frac{T_c}{p_c}$$

On substituting the values of various quantities, we get

$$a = \frac{27 \times (8.31 \text{ J mol}^{-1} \text{ K}^{-1})^2 \times (5.3\text{K})^2}{64 \times (2.25 \times 1.013 \times 10^5 \text{ Nm}^{-2})}$$

$$= 3.59 \times 10^{-3} \text{ Nm}^4 \text{ mol}^{-2}$$

To calculate the second van der Waals' constant, we use the expression for critical coefficient and write

$$b = \frac{RT_c}{8p_c}$$

since $b = \frac{V_c}{3}$. Hence,

$$b = \frac{(8.31\ \text{J mol}^{-1}\ \text{K}^{-1}) \times (5.3\text{K})}{8 \times (2.25 \times 1.013 \times 10^5\ \text{Nm}^{-2})}$$

$$= 2.42 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}$$

SAQ 5

Assume that van der Waals' equation is valid for neon. Calculate the diameter of neon atom. Given, $T_c = 44.75\text{K}, p_c = 26.86$ atm and $k_B = 1.36 \times 10^{-28}$ atm m^3 K^{-1}.

12.3.2 Limitations

You may be convinced now that van der Waals' equation satisfactorily explains the general features of the behaviour of real gases. However, it fails to explain the quantitative details. Some of its limitations are listed below:

1) **van der Waals' isotherms** : A part of van der Waals' isotherms consists of wave like pattern, which cannot be observed experimentally.

2) **Values of a and b** : van der Waals assumed that for any gas, a and b are constant. However, experiments reveal that they depend on temperature. This is because we can make any isotherm agree closely with the equation by suitably choosing the values of a and b. But the same values do not give good agreement with other isotherms.

3) **Critical volume** : From Eq. (12.13) we note that the critical volume $V_c = 3b$ for all gases, independent of their nature. However, experiments show that V_c varies from 1.4 b for argon to 2.8 b for hydrogen. This implies that van der Waals' equation is not followed exactly by any gas near its critical point.

4) **Critical coefficient** : Theory predicts that the critical coefficient $RT_c/p_c V_c = 8/3$ for all gases. In practice, it is different for different gases with values ranging from 3.28 for hydrogen to 3.48 for CO_2.

In spite of these defects, van der Waals' equation is commonly used even today because of its inherent simplicity.

12.4 OTHER EQUATIONS OF STATE

To overcome the shortcomings of van der Waals' equation, a number of other equations have been proposed. Some of these are based on rigorous theoretical considerations while others consist of adding more empirical constants which can be suitably chosen. We will first mention some of the latter type.

1. **Onnes' equation** : Onnes proposed an empirical equation of the form

$$pV = A + Bp + Cp^2 + \ldots \tag{12.17}$$

where A, B, C, are called virial coefficients. These are characteristic of a gas at a fixed temperature and may vary with temperature in a complex manner.

Eq. (12.17) reduces to that for a perfect gas for $p \rightarrow 0$. That is, the first virial coefficient is equal to RT for one mole of the gas. The second virial coefficient is of special interest because it determines departure from ideal gas behaviour. At very low temperatures it has a negative value. As temperature increases, it shows a gradual rise through zero and becomes positive. At room temperature, $B < 0$ for oxygen, nitorgen and carbon dioxide, whereas $B > 0$ for hydrogen and helium. For all gases, $B = 0$ at the Boyle temperature, T_B. At moderate pressures, Eq.(12.17) implies that at $T = T_B$

$$pV = A$$

and

$$\frac{\partial(pV)}{\partial p} = B = 0 \tag{12.18}$$

The constant C is always positive but very small.

In his studies, Onnes had to use twenty five constants for best representation of experimental results. Later, Holborn and Otto found that it is sufficient ot retain only four virial coefficients. The empirical equation of Onnes lacked physical basis. Moreover its mathematical form as a series expansion is not very convenient for handling rapid variations in gaseous behaviour.

Let us now express B in terms of van der Waals' constants. At not too high pressures, we find that Eq. (12.4) can be written as

$$pV = RT - \left(\frac{a - RTb}{V}\right) + \frac{ab}{V^2}$$

In terms of p, we can express it as

$$pV = RT + \left(b - \frac{a}{RT}\right)p + \frac{ab}{(RT)^2}\,p^2$$

Comparing it with Eq. (12.17) we find that

$$A = RT$$

$$B = b - \frac{a}{RT}$$

$$C = \frac{ab}{(RT)^2} \qquad (12.19)$$

At the Boyle temperature, $B = 0$. Hence,

$$b - \frac{a}{RT_B} = 0$$

or

$$T_B = \frac{a}{Rb} \qquad (12.20)$$

You can readily correlate T_B to critical temperature and show that

$$T_B = 3.375\, T_c \qquad (12.21)$$

2. **Berthelot's equation** : Berthelot also proposed an empirical equation of the form

$$\left(p + \frac{a'}{TV^2}\right)(V - b) = RT \qquad (12.22)$$

where van der Waals' constant a has been modified to a'/T.

It gives better agreement with experiments than van der Waals' equation over a wider range of pressures. However, near the critical point, it fails as badly as van der Waals' equation.

3. **Dieterici's equation** : By assuming that the number density near the walls of the container is smaller than that in the interior, Dieterici deduced the following equation for pressure exerted by a gas :

$$p = \frac{RT}{V - b}\exp\left(-\frac{a}{RTV}\right) \qquad (12.23)$$

It is instructive to note that at low pressures, this equation reduces to van der Waals' equation, if $b < < V$.

How do we interpret the changes in the ideal gas equation introduced by Dieterici? You will note that the correction in the volume term is the same as in the van der Waals' equation. But the exponential factor is reminiscent of the pressure variation with height in earth's atmosphere. It signifies that the potential energy of moving molecules changes continuously in going from the body of the gas to the walls.

In general, this equation is more accurate than van der Waals' equation. It gives

$$T_c = \frac{a}{4Rb},\ V_c = 2b,\ p_c = \frac{a}{4b^2 e^2}$$

and

$$RT_c/p_c V_c = 3.695$$

4. **Saha and Bose's equation** : From thermodynamic considerations and the theory of probability, Saha and Bose derived the following equation of state:

$$p = -\frac{RT}{2b} \exp\left(-\frac{a}{RTV}\right) \ln\left(\frac{V-2b}{V}\right) \tag{12.24}$$

This equation predicts that the critical coefficient $RT_c/p_c V_c = 3.53$, which is in much better agreement with observed values for common gases.

Various other equations have been proposed but none of them explains the behaviour of all gases for all temperatures and pressures. For this reason, one generally evaluates the virial coefficients from theoretical considerations and compares them with the observed values.

Let us now sum up what you have learnt in this unit.

12.5 SUMMARY

- Liquefaction is promoted by compression and cooling. A gas cannot be liquefied by pressure alone for $T > T_c$.
- Critical temperature (T_c) of a gas is the temperature above which it cannot be liquefied by applying pressure. The minimum pressure which just liquefies a gas at T_c is called critical pressure and the volume corresponding to critical values of p and T is known as critical volume (V_c). The quantity $RT_c/p_c V_c$ is referred to as critical coefficient of the gas.
- van der Waals' equation of state for one mole of a real gas is

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

  Here a/V^2 arises from the intermolecular interaction and is called cohesive pressure. b is known as co-volume and arises from the finite size of the gas molecules.
- Critical constants of a van der Waals' gas are given by

  $$V_c = 3b,\ p_c = a/27b^2 \text{ and } T_c = 8a/27Rb.$$

12.6 TERMINAL QUESTIONS

1. 210 g of N_2 gas at 8 atm occupies 24×10^{-3} m^3 of volume. Assuming that the gas obeys van der Waals' equation of state ($a = 1.39 \times 10^{-6}$ atm m^6 mol^{-2}, $b = 39.1 \times 10^{-6}$ m^3 mol^{-1}), calculate its temperature.
2. Using the values of critical constants for NH_3 from Table 12.1, calculate van der Waals' constants.
3. Using the values of a and b listed in Table 12.2 determine the temperature to which each of the following gases must be cooled for liquefaction by applying pressure alone:

   (i) He (ii) H_2 (iii) A and (iv) Cl_2

   Also determine the corresponding critical pressures.
4. The van der Waals' constants depend on the nature of gas. Eliminate these and write the equation in a form which applies to all gases.

12.7 SOLUTIONS AND ANSWERS

SAQs

1. We know that a gas can be liquefied by compression when its temperature is below its critical temperature. So we cannot liquefy helium, argon, hydrogen and oxygen at room temperature.

2. When the gas is suddenly released from 70 atm to 1 atm, it undergoes adiabatic expansion. Therefore, its final temperature can be computed using the relation

$$T_f = \left(\frac{p_i}{p_f}\right)^{\frac{1-\gamma}{\gamma}} T_i$$

On inserting the given data, we get

$$T_f = \left(\frac{70\text{ atm}}{1\text{ atm}}\right)^{-\frac{0.3}{1.3}} \times 298\text{ K}$$

$$= 112\text{ K}$$

3. When we have μ moles of a real gas in a container of volume V, the average volume available to a molecule is $\mu(v_1 - b) = V - \mu b$ where v_1 is the volume occupied by one mole of gas. Similarly, $\Delta p = \frac{a}{v_1^2} = \frac{a}{(V/\mu)^2} + a\mu^2/V^2$. Hence, van der Waals equation for μ moles has the form

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

4. At the critical point, three roots are equal. i.e., $V_1 = V_2 = V_3 = V_c$. This means that

$$(V - V_c)^3 = 0$$

or

$$V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0 \qquad \text{(i)}$$

Let us now consider Eq. (12.6):

$$pV^3 - (pb + RT)V^2 + a(V - b) = 0$$

Dividing through out by p, we can rewrite it as

$$V^3 - \left(b + \frac{RT}{p}\right)V^2 + \frac{a}{p}V - \frac{ab}{p} = 0$$

Since $T = T_c$ and $V = V_c$ at the critical point, we find that for a critical isotherm

$$V^3 - \left(b + \frac{RT_c}{p_c}\right)V^2 + \frac{a}{p_c}V - \frac{ab}{p_c} = 0 \qquad \text{(ii)}$$

On comparing the coefficient of each power of V, we find that

$$3V_c = b + \frac{RT_c}{p_c}$$

$$3V_c^2 = \frac{a}{p_c}$$

and

$$V_c^3 = \frac{ab}{p_c}$$

You can readily solve these to obtain the required result.

5. We know that for a van der Waals' gas, the co-volume is given by

$$b = 4N_A V_m = 4N_A \frac{4}{3}\pi\left(\frac{\sigma}{2}\right)^3 = \frac{2}{3}N_A \pi \sigma^3$$

where σ is diameter of the atom. Therefore,

$$\sigma = \left(\frac{3}{2\pi}\frac{b}{N_A}\right)^{1/3}$$

But from Example 3, we recall that

$$b = \frac{RT_c}{8p_c} = \frac{N_A k_B T_c}{8p_c}$$

where k_B is Boltzmann constant. Thus,

$$\sigma = \left(\frac{3}{16\pi}\,\frac{k_B T_c}{p_c}\right)^{1/3}$$

$$= \left(\frac{3 \times 1.36 \times 10^{-28}\ \text{atm m}^3\,\text{K}^{-1} \times 44.75\ \text{K}}{16 \times 3.14 \times 26.86\ \text{atm}}\right)^{1/3}$$

$$= 0.238 \times 10^{-9}\ \text{m} = 0.24\ \text{nm}$$

TQs

1. Since mass of the gas taken is 210 g and its molecular weight is 28, number of moles is $\frac{210\ \text{g}}{28\ \text{g}} = 7.5$

Volume of the gas $V = 24 \times 10^{-3}\ \text{m}^3$

External pressure $p = 8$ atm

Now, van der Waals' equation of state for n moles reads

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

Substituting various values, we get

$$T = \frac{1}{nR}\left(p + \frac{n^2 a}{V^2}\right)(V - nb)$$

$$= \frac{1}{7.5 \times (8.21 \times 10^{-5}\ \text{atm m}^3\,\text{mol}^{-1}\,\text{K}^{-1})}\left(8\ \text{atm} + \frac{(7.5)^2 \times (1.39 \times 10^{-6}\ \text{atm m}^6\,\text{mol}^{-2})}{(24 \times 10^{-3}\ \text{m}^3)^2}\right)$$
$$(24 \times 10^{-3}\ \text{m}^3 - 7.5 \times 39.1\ \text{m}^3 \times 10^{-6}\ \text{m}^3\,\text{mol}^{-1})$$

$$= 313.2\ \text{K}$$

2. Critical constants for NH_3 are

$$T_c = 405.5\text{K},\ p_c = 112.2\ \text{atm},\ V_c = 72.02 \times 10^{-6}\ \text{m}^3\,\text{mol}^{-1}$$

Therefore,

$$a = \frac{27}{64}\,\frac{R^2 T_c}{p_c} = \frac{27 \times (8.21 \times 10^{-5}\ \text{atm m}^3\,\text{mol}^{-1}\,\text{K}^{-1})^2 \times (405.5\ \text{K})^2}{(64 \times 112.2\ \text{atm})}$$

$$= 4.17 \times 10^{-6}\ \text{atm m}^6\,\text{mol}^2$$

and

$$b = \frac{RT_c}{8p_c} = \frac{(8.21 \times 10^{-5}\ \text{atm m}^3\,\text{mol}^{-1}\,\text{K}^{-1}) \times (405.5\ \text{K})}{8 \times (112.2\ \text{atm})}$$

$$= 37.1 \times 10^{-6}\ \text{m}^3\,\text{mol}^{-1}$$

3. We know that a gas can be liquefied by applying pressure alone if its temperature is less than or equal to its critical temperature T_c. For a van der Waals' gas

$$T_c = 8a/27Rb$$

and critical pressure is given by

$$p_c = a/27b^2$$

(i) For He, $a = 3.4 \times 10^{-8}\ \text{atm m}^6\,\text{mol}^{-2}$

and $b = 23.7 \times 10^{-6}\ \text{m}^3\,\text{mol}^{-1}$

Therefore,

$$T_c = \frac{8 \times 3.4 \times 10^{-8}\ \text{atm m}^6\ \text{mol}^{-2}}{27 \times (8.21 \times 10^{-5}\ \text{atm m}^3\ \text{mol}^{-1}\ \text{K}^{-1}) \times (23.7 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1})} = 5.2\ \text{K}$$

and

$$p_c = \frac{3.4 \times 10^{-8}\ \text{atm m}^6\ \text{mol}^{-2}}{27 \times (23.7 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1})^2} = 2.24\ \text{atm}$$

(ii) For H_2

$$a = 2.44 \times 10^{-7}\ \text{atm m}^6\ \text{mol}^{-2}$$

$$b = 26.6 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1}$$

Therefore,

$$T_c = \frac{8 \times 2.44 \times 10^{-7}\ \text{atm m}^6\ \text{mol}^{-2}}{27 \times (8.21 \times 10^{-5}\ \text{atm m}^3\ \text{mol}^{-1}\ \text{K}^{-1}) \times (26.6 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1})} = 33.1\ \text{K}$$

and

$$p_c = \frac{2.44 \times 10^{-7}\ \text{atm m}^6\ \text{mol}^{-2}}{27 \times (26.6 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1})^2} = 12.8\ \text{atm}$$

(iii) For argon

$$a = 1.35 \times 10^{-6}\ \text{atm m}^6\ \text{mol}^{-2}$$

$$b = 32.2 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1}$$

Therefore,

$$T_c = \frac{8 \times 1.35\ 10^{-6}\ \text{atm m}^6\ \text{mol}^{-2}}{27 \times (8.21 \times 10^{-5}\ \text{atm m}^3\ \text{mol}^{-1}\ \text{K}^{-1}) \times (32.2 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1})} = 151.3\ \text{K}$$

and

$$p_c = \frac{1.35 \times 10^{-6}\ \text{atm m}^6\ \text{mol}^{-2}}{27 \times (32.2 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1})^2} = 48.2\ \text{atm}$$

(iv) For Cl_2

$$a = 6.49 \times 10^{-6}\ \text{atm m}^6\ \text{mol}^{-2}$$

and

$$b = 56.2 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1}$$

Therefore,

$$T_c = \frac{8 \times 6.49 \times 10^{-6}\ \text{atm m}^6\ \text{mol}^{-2}}{27 \times (8.21 \times 10^{-5}\ \text{atm m}^3\ \text{mol}^{-1}\ \text{K}^{-1}) \times (56.2 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1})} = 416.8\ \text{K}$$

and

$$p_c = \frac{6.49 \times 10^{-6}\ \text{atm m}^6\ \text{mol}^{-2}}{27 \times (56.2 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1})^2} = 76.1\ \text{atm}$$

4) We introduce dimensionless variables

$$p_r = \frac{p}{p_c},\ T_r = \frac{T}{T_c} \text{ and } V_r = \frac{V}{V_c}$$

where p, V and T are the actual pressure, volume and temperature of a gas. On introducing these in the equation

NOTES

Utter Pradesh
Rajarshi Tandon Open University

UGPHS-06
THERMODYNAMICS AND STATISTICAL MECHANICS

Block

4

ELEMENTS OF STATISTICAL MECHANICS

UNIT 13

Basic Concepts of Statistical Mechanics 5

UNIT 14

The Partition Function 25

UNIT 15

Quantum Statistics 43

BLOCK INTRODUCTION

So far you have learnt to describe the properties of matter on the basis of thermodynamics and kinetic theory of gases. You must have realised that thermodynamics is essentially an empirical science based on everyday experiences. You will agree that these laws give us no information about the processes at work at the microscopic level. But the kinetic theory of gases, discussed in the preceding block, was the first attempt to understand the properties of macroscopic systems from the microscopic view point. Very elegant laws stem out of the molecular chaos.

Statistical mechanics is a more profound and realistic approach to understand the observed behaviour of matter (or radiation). The laws of mechanics are coupled with statistical methods. So to enable you to master the techniques of statistical mechanics, we have discussed key probabilistic concepts in Unit 13. The concept of phase space, the Boltzman relation, expression for classical distribution function and the concept of partition function have also been introduced here. A serious drawback of classical statistics is that it regards all particles as distinguishable. This leads to Gibbs paradox. The Sackur-Tetrode equation discussed in Unit 14 is a way out of it. You will learn to evaluate rotational and vibrational partition functions with particular reference to heat capacity of hydrogen. You will realise that partition function is a very convenient mathematical device; there is nothing physical about it. The classical statistics fails to explain the behaviour of an assembly of photons, liquid helium and conduction electrons in metals. In particular, the existence of zero point energy and Bose-Einstein condensation—two remarkable phenomena—are completely unknown in the tenets of classical physics. These are quantum effects and to satisfactorily explain these, we require quantum statistics. Geniuses like Bose, Einstein, Fermi, Dirac, Fowler and Planck have immensely contributed to its growth. You will learn these details in Unit 15.

The units in this block are not of equal length. To enable you to plan your study, we are suggesting estimates for the study time for each unit:

Unit 13	7 h
Unit 14	6 h
Unit 15	9 h

We hope that you will enjoy studying this block.
We wish you success.

Acknowledgements

We are thankful to Shri Sunder Singh and Shri Gopal Krishan for word-processing and secretarial assistance.

UNIT 13 BASIC CONCEPTS OF STATISTICAL MECHANICS

Structure

13.1 Introduction

Objectives

13.2 Elementary Probability Theory

Basic Terminology

Elementary Combinatorics

Random Variables

13.3 Description of a System in Equilibrium

Basic Concepts

Bridging Microscopic and Macroscopic View-points

13.4 The Distribution Function

13.5 Summary

13.6 Terminal Questions

13.7 Solutions and Answers

13.1 INTRODUCTION

In the previous block, you have learnt to describe the properties of matter on the basis of kinetic theory of gases. The kinetic theory of gases was the first attempt to understand the properties of macroscopic systems from the microscopic view point. Statistical mechanics aims to derive the observed (bulk) properties of matter (or radiation) from the laws of mechanics applied to its constituent parts. For example, suppose we have a gas in a container, occupying a volume V at a temperature T. Given the nature of intermolecular forces, statistical mechanics enables us to derive a relation between the pressure and the volume — the so-called equation of state. However, the observed/predicted properties are essentially average values. The deviations (fluctuations), which are always present in every system, provide us insight about many phenomena. In this study, we have to use the methods of statistics. So, we would like you to master the key probabilistic concepts. It is possible that you may be familiar with some or all of these concepts from your school curriculum. Or you may have opted for the Mathematical Methods in Physics Course (PHE-04). However, we have discussed these in Sec. 13.2 for completeness and to make the unit self-contained.

The basic concepts of **phase space**, micro- and macro- states, the thermodynamic probabilities, etc., are introduced in Sec. 13.3. These help us to describe the behaviour of a system of large number of particles elegantly. In this section, you will also learn to establish the Boltzmann relation which bridges the thermodynamic and statistical view-points. We know that the equilibrium state of a system is a state of maximum entropy. Statistically speaking, it is the most probable state of an isolated system. To describe the equilibrium state, we use the Boltzmann relation to derive an expression for classical distribution function, which contains two unknown constants. When we determine these constants, we perform sum over all states. This introduces what we call the **partition function**, Z. There is nothing physical about partition function; it is a useful mathematical device because we can express all thermodynamic functions in terms of Z. You will learn to evaluate the partition function for some simple systems in the next unit.

Objectives

After studying this unit, you should be able to:

- understand the significance of the terms sample space, event and probability of an event
- compute the average of a random variable
- derive the connection between entropy and thermodynamic probability
- derive the distribution function for a system obeying classical statistics.

13.2 ELEMENTARY PROBABILITY THEORY

In statistical mechanics, we invariably compute the averages of physical quantities of interest. We then establish connection between these values and the experimentally observed values. So, it is essential to know the basic concepts of probability theory.

13.2.1 Basic Terminology

Suppose we toss two coins. The possible outcomes can be listed as follows:

Coin 1	H	H	T	T
Coin 2	H	T	H	T

That is, there are four outcomes of this statistical experiment, which may be listed as:

$$\Omega = \{(H,H),(H,T),(T,H),(T,T)\} \tag{13.1a}$$

This set of outcomes is called the **sample space** of the experiment. For a single coin

$$\Omega = \{H,T\} \tag{13.1b}$$

The elements of Ω are known as **sample points**. Thus in Eq. (13.1a), we have four sample points and in Eq. (13.1b), we have only two. This number is called the **cardinality** of Ω and is denoted by $n(\Omega)$.

Thus for (13.1a) and (13.1b), we have

$$n(\Omega) = 4 \qquad \text{and } n(\Omega) = 2$$

Next we introduce the concept of an event. **An event is a subset of Ω.** Let us consider the sample space of (13.1a). The event

$$E_1 = \text{'two heads appear'}$$

is given by the subset

$$E_1 = \{(H, H)\}$$

while $E_2 = \{(H, T), (T, H), (T, T)\}$ describes the event 'at least one tail appears'. Similarly,

$$E_3 = \{(T, T)\},\ E_4 = \{(H, T)\}, \text{ and } E_5 = \{(T, H)\}$$

signify other events. Can you name these ?

The complement of an event with respect to Ω also denotes an event. For example,

$$E_3^c = \text{'two tails do not appear'}$$
$$= \{(H, H),\ (H, T),\ (T, H)\},$$
$$E_2^c = \{(H,H)\}$$

An event which contains only one sample point is called a simple event; e.g., E_1, E_2^c, E_3 are simple events.

The total number of subsets of a set of cardinality n is 2^n. For Eq. (13.1b), the possible number of events are

$$E_1 = \{H\}, E_2 = \{T\}, E_3 = \{H,T\} = \Omega,\ E_4 = \phi$$

E_3 is the event that a head or a tail appears. This is called the **sure event** and is equal to Ω itself. E_4 is called the **impossible** or **null event**, denoted by ϕ. It is the complement of Ω : $\phi = \Omega^c$. The certain event contains all the simple events and the null event contains ***none***.

You may now like to solve an SAQ.

SAQ 1

i) An unbiased die is rolled. Write down the sample space for the experiment.

ii) n coins are tossed. What is the sample space?

iii) List all possible events for the sample space Ω given by (13.1a).

We introduce the basic operations of union and intersection, which can be used to define new events:

$E_1 \cup E_2 \rightarrow$ Either E_1 or E_2 occurs, or both occur (at least one of E_1 or E_2 occurs)

$E_1 \cap E_2 \rightarrow$ *Both* E_1 and E_2 occur

If there are no sample points common to E_1 and E_2, then $E_1 \cap E_2 = \phi$ and the events are said to be ***disjoint*** or ***mutually exclusive***. Diagramatically, we have shown these in Fig. 13.1.

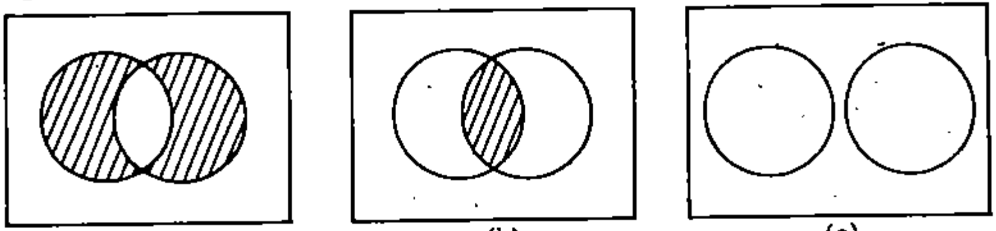


Fig. 13.1: (a) The shaded portion represents $E_1 \cup E_2$, (b) The shaded portion represents $E_1 \cap E_2$ and (c) There is no overlap between E_1 and E_2.

For (13.1b), we have

$$\Omega = E_1 \cup E_2$$

and for (13.1a)

$$\Omega = E_1 \cup E_3 \cup E_4 \cup E_5$$

In general, if the distinct simple events are E_1 , ..., E_n, we have

$$\Omega = E_1 \cup E_2 \cdots \cup E_n = \bigcup_{i=1}^{n} E_i \tag{13.2}$$

Having introduced the concept of a sample space, we now turn to define the probability of an event. It is sufficient for our purpose to consider the simple case in which Ω has a finite number of points and all the outcomes are equally likely. Let A be any subset of Ω. Then we define the probability of the event A to be

$$P(A) = \frac{n(A)}{n(\Omega)} \tag{13.3}$$

To fix your ideas, we wish that you should go through the following example carefully.

Example 1

Two coins are tossed. What is the probability that (a) two heads appear, (b) at least one tail appears ?

Solution

We have $n(\Omega) = 4$. $n(E_3) = 1$, $n(E_2) = 3$. Hence, (a) $P(E_3) = 1/4$, (b) $P(E_2) = 3/4$. It is easy to verify that :

i) $0 \leq P(A) \leq 1$ *ii*) $P(\Omega) = 1, P(\phi) = 0,$

E_1 and E_2 are called **independent events** if

$$P(E_1 \cap E_2) = P(E_1)P(E_2) \tag{13.4}$$

In words, if the probability of the simultaneous occurrence of two events is the product of their individual probabilities, then they are independent events.

Example 2

Suppose three coins are tossed. Let E_1 be the event that a head appears on the first coin and E_2 the event that a tail appears on the third throw. Are E_1 and E_2 independent?

Solution

We have here

$$\Omega = \{HHH, HHT, HTH, THH, HTT, THT, TTH, TTT\}$$

$$E_1 = \{HHH, HHT, HTH, HTT\} \; n(E_1) = 4; \; P(E_1) = 1/2.$$

$$E_2 = \{HHT, HTT, THT, TTT\} \; n(E_2) = 4; \; P(E_2) = 1/2$$

Clearly, (13.4) is satisfied. Hence, E_1 and E_2 are independent.

In solving problems in probability theory, we frequently need to use simple results from combinatorial analysis. We shall summarise these for ready reference.

13.2.2 Elementary Combinatorics

We begin by stating the multiplication rule.

Multiplication rule

If there are m ways in which an event U can take place, and n ways in which an **independent** event V can occur, then there are mn ways in which the two events can occur jointly. An alternative formulation of this result is that if an operation can be performed in m ways and, after it is performed in any one of these ways, a second independent operation can be performed in n ways, then the two operations can be performed jointly in mn ways.

Example 3

Four coins are flipped in succession. Find the total number of possible outcomes.

Solution

These are two possible outcomes, head (H) or tail (T) for each case. Hence, the total number of possible outcomes

$$= 2 \times 2 \times 2 \times 2 = 16$$

When we are dealing with a large collection of objects, it is often necessary to compute the number of permutations and combinations of the objects.

Permutations

A **permutation** is any arrangement of a set of objects in a **definite** order. The number of permutations of n elements taken r at a time is $\frac{n!}{(n-r)!}$. It is denoted by the symbol $^n p_r$.

Combinations

A **combination** is a selection of n distinct objects without regard to order. The number combinations of n element taken r at a time is $\frac{n!}{(n-r)!\,r!}$. It is denoted by ^nC_r or simply $\binom{n}{r}$. These are just the binomial coefficients because they appear in Newton's binomial expansion

$$(x_1 + x_2)^n = x_1 + n\,x_1^{n-1}\,x_2 + \cdots + x_2^n$$

$$= \sum_{r=0}^{n} \binom{n}{r} x_1^{n-r} x_2^r$$

where n is a positive integer.

Example 4

Seven physicists assembled for a meeting shake hands with one another. How many handshakes take place?

Solution

This is equal to the number of ways of choosing two physicists from a set of seven, which is

$$\binom{7}{2} = \frac{7!}{2!\,5!} = 21$$

Having discussed the basic notions of sample space, events and probability of an event, we will conclude this section by introducing the concept of a random variable.

13.2.3 Random Variables

Stated in simple language, a random variable (r.v) is a variable which can be associated with the outcomes of a statistical experiment. Recall the experiment of tossing two coins. Let X be the number of heads which appear. Then X is a random variable with possible values 0, 1, 2. Also

$$P(0) = \frac{1}{4}\ ,\ P(1) = \frac{1}{2}\ ,\ P(2) = \frac{1}{4}$$

The total probability = 1/4 + 1/2 + 1/4 = 1, as it should be. In general, let X take values $x_1, x_2, \ldots, x_n$ with probabilities $f(x_2), f(x_2), \ldots$, i.e.,

$$P(X = x_i) = f(x_i),\ i = 1, 2, \ldots, n$$

$f(x_i)$ is called the **Probability distribution** of x. It satisfies the obvious property $f(x_i) \geq 0$, and the normalisation condition $\sum_{i=1}^{n} f(x_i) = 1$.

The **mean value** or **expectation value** of X is defined as

$$\bar{X} = \langle X \rangle = \sum_{i=1}^{n} x_i f(x_i) \tag{13.5}$$

The **variance** or **dispersion** of X is given by

$$\mathrm{Var}(X) = \langle (X - \langle X \rangle)^2 \rangle = \langle X^2 \rangle - |\langle X \rangle|^2 \tag{13.6}$$

The square root of Var (X) is called the standard deviation (S.D) of X. The standard deviation is important because it gives us an estimate of the width of the distribution $f(x_i)$. Physically, it gives us some idea about fluctuations around (average) observed values. This finds direct use in stochastic processes like random walk problem, reactor power fluctuations, regulated power supply and enables us to relate variance to some thermic properties of the system.

It is instructive to interpret a probability distribution $f(x_i)$ as a distribution of a unit mass along the x – axis in a discrete manner, so that $f(x_i)$ is the fraction of mass located at the point x_i (Fig. 13.2).

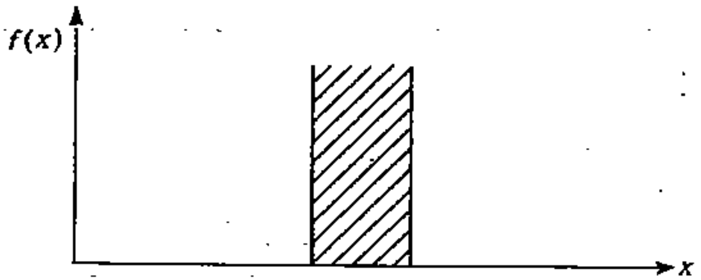


Fig. 13.2: Discrete probability density $f(x)$

According to this picture, the average of X, given y (13.3), is the centre of mass this system.

Continuous distribution

The probability distribution described above is called a discrete probability distribution and the associated random variable X is called a discrete random variable (discrete r.v). In some cases, X can assume a continuum of values. Then, it is called a continuous r.v. $f(x)$ is called a continuous probability distribution.

Consider a unit mass to be distributed continuously along the x–axis (Fig. 13.3). We define linear mass density $f(x)$ by $dm = f(x)\,dx$ where dm is the fraction of the mass lying between x and $x + dx$.

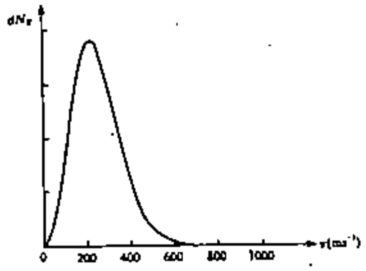


Fig. 13.3: Continuous probability density $f(x)$

By analogy, we define the probability that the r.v.X will have a value lying between x and $x + dx$, to be equal to $f(x)dx$. Hence,

$$P(x \le X \le x + dx) = f(x)dx$$

The probability that X lies in the interval $[a, b]$ is given by

$$P(a \le X \le b) = \int_a^b f(x)\; dx \tag{13.7}$$

This is represented by the shaded area of Fig. 13.3. It represents the fraction of mass contained in the interval $[a, b]$. The normalisation condition becomes

$$\int_{-\infty}^{\infty} f(x)dx = 1 \tag{13.8}$$

The equations corresponding to (13.5) and (13.6) are

$$< X >= \int_{-\infty}^{\infty} x f(x)dx \tag{13.9}$$

$$\text{Var}\;(X) = \sigma_X^2 = \int_{-\infty}^{\infty} (X - < X >)^2\; f(x)dx \tag{13.10}$$

Example 5

The simplest example of a continuous distribution is the **uniform distribution**. The density function is given by

$$\left.\begin{aligned} f(x) &= A \\ &= 0 \end{aligned}\right\} \begin{aligned} &a \le x \le b \\ &\text{otherwise} \end{aligned}$$

where A is a constant. It is plotted in Fig. 13.4.

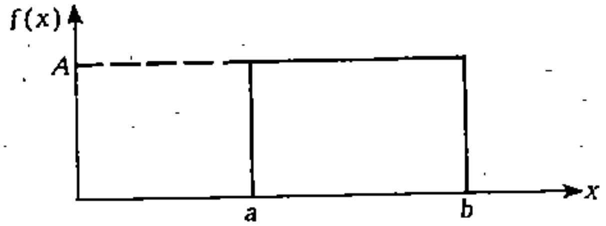


Fig. 13.4: A uniform distribution

The normalisation condition gives $A = \dfrac{1}{b-a}$

SAQ 2

Calculate the variance of a r.v. obeying the uniform distribution.

Having introduced the basic concepts of probability theory, we shall now discuss how a system in equilibrium can be described mathematically.

13.3 DESCRIPTION OF A SYSTEM IN EQUILIBRIUM

You now know that thermodynamic description of physical systems is at the macroscopic level without reference to the microscopic details. The kinetic theory of gases is a step forward in our quest for understanding the properties of systems in terms of their constituents. But, we have to make many assumptions to achieve any progress. This invariably restricts the scope of the theory severely. A major advance in this direction was made by Gibbs (1839-1903). He coined the name ***statistical mechanics*** for that branch of physics which deals statistically with systems consisting of a large number of particles.

Let us consider a thirty-five years old man. It is impossible for us to predict his exact life-span. However, if we consider a large number of such individuals, it is possible to make some predictions about their average life-expectancy. Have you ever thought how life insurance companies fix the premia to be paid by the policy-holders ? They collect data on the average life expectancy of different age-groups and fix the premia accordingly.

Consider now a gas of N molecules occupying a volume V at a temperature T. Suppose that, at a given instant of time, we know the positions and velocities of all the particles. Then by solving Newton's equations of motion, it should be possible to determine how the system evolves. But N is a very large number $(\sim 10^{26}$ for a kilomole). Hence, the calculations, though possible in principle, will be extremely cumbersome. Even the present day computing machines will take very long time to solve them. It is in such difficult situations that the methods of statistical mechanics come to our rescue. Instead of looking at each individual molecule, we treat the collection as a whole and try to compute average properties.

We begin by discussing how this system can be described mathematically.

13.3.1 Basic Concepts

You know that the position of an object in a plane, for example, an ant on a table, can be specified completely by giving its coordinates (x, y) with respect to a set of Cartesian axes. It is like specifying the latitude and longitude of a place on a map. Similarly, the position of an object in space, like a bird flying in a garden can be described by the coordinate triple (x, y, z).

Let us now consider the motion of a single particle along a line. Its position at any given time can be completely described by specifying its position (q) and momentum(p). By solving the equations of motion, we can determine the values of these quantities at any time t. We can represent the situation geometrically by drawing a set of Cartesian axes, labelled q and p, as shown in Fig. 13.5. The state of the particle is then given by a point $A(q,p)$ in this two-dimensional space. This space is called the ***phase space*** of the system and A is called a **phase point**. Can you draw any analogy of phase space with sample space Ω? Certainly we can. The phase space and phase point correspond to sample space and sample point, respectively.

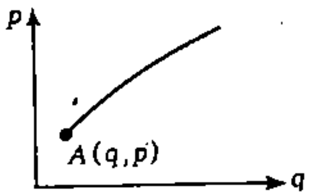


Fig. 13.5: Phase-space for a particle in one dimension.

You should not confuse p with pressure.

These considerations can be easily extended to an N-particle system, like the molecules of a gas, with the particle moving in space. For a single particle, the state at any instant t is described by the phase point $(q_1, q_2, q_3, p_1, p_2, p_3)$ in a six-dimensional phase space. You will realise that this space is just a mathematical construction and does not correspond to anything real. If we now consider a collection of N particles, a state of the system is given by a point $(q_1, q_2, \cdots, q_{3N}, p_1, p_2, \cdots p_{3N})$ in a $6N$–dimensional phase space (Fig. 13.6).

SAQ 3

Suppose the particles have two rotational degrees of freedom also. What will be the dimension of the phase space ?

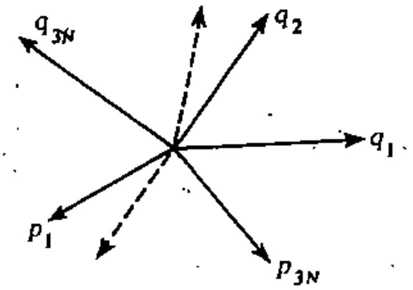


Fig. 13.6: Phase space for an N particle system

Suppose that this N-particle system is confined to a volume V and let the total internal energy of the system be U. By describing the system in terms of the macroscopic quantities N, V, U, we are giving what is known as a ***coarse-grained*** description of the system. In other words, the triple (N, V, U) defines a macrostate of the system. But in statistical mechanics, we intend to derive the ***macroscopic*** properties from a knowledge of the constituents of the system. To achieve this end, we proceed as follows :

Let us divide the phase space into small elements or 'cells' of volume

$$d\Gamma = dq_1 dq_2 \cdots dq_{3N} dp_1 dp_2 \cdots dp_{3N} = \prod_{i=1}^{3N} dq_i dp_i \tag{13.11}$$

where the symbol Π signifies product of all terms from $i = 1$ to $i = 3N$.

Since the product $dq\ dp$ has dimensions of angular momentum, $d\Gamma = h^{3N}$, where the constant h has the dimensions of angular momentum, and can be chosen as small as we like. However, because of Heisenberg's uncertainty principle, h cannot be smaller than Planck's constant (6.62×10^{-34} Js) in quantum description. We will come back to this point in Unit 15 and discuss its implications in detail.

For the simple case of a single particle moving in a plane, we have $d\Gamma = dq\ dp$. This is shown diagramatically in Fig. 13.7

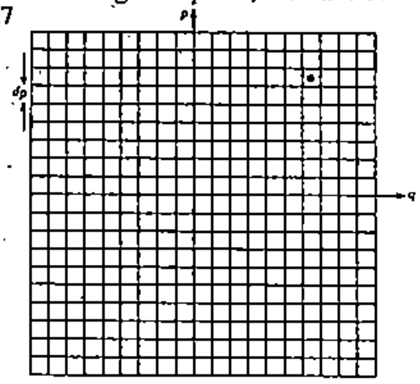


Fig. 13.7: Two-dimensional phase space divided into cells of 'volume' dq dp. ● is the phase point representing a particle.

Imagine the cells to be numbered 1, 2, ... and let n_1, n_2, ... denote the populations of the various cells. In other words, there are n_1 phase points occupying cell 1, n_2 occupy cell 2, and so on. Any phase point will lie in one of the cells. If we specify the ***number*** of phase points in each cell, we define a ***macrostate*** of the system. But specification of exactly ***which*** particles are in the various cells, defines a ***microstate***. Obviously, many different microstates can correspond to the same macrostate. We illustrate this by a simple example.

Example 6

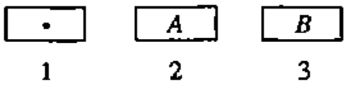
Suppose there are just three cells in phase space labelled 1, 2, 3, and two particles, A and B. Enumerate the different macrostates and the microstates corresponding to each of them.

Solution

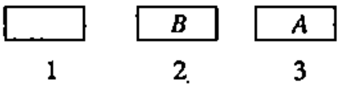
The possible macrostates are

	(i)	(ii)	(iii)	(iv)	(v)	(vi)
n_1	2	0	0	0	1	1
n_2	0	2	0	1	0	1
n_3	0	0	2	1	1	0

For macrostate (i), there is only one possible microstate, viz, $\boxed{AB}\ \boxed{}\ \boxed{}$ Similar remarks apply to (ii) and (iii). Corresponding to (iv), we have the microstates



and



Similarly, two microstates correspond to each of (v) and (vi).

SAQ 4

Suppose there are two cells and four particles. Enumerate the possible macrostates and the corresponding microstates.

In statistical mechanics, we always seek the number of microstates corresponding to a given macrostate (N, V, U). It is called the ***thermodynamic probability*** or the ***statistical weight*** of the macrostate and is denoted by $W(N, V, U)$. You will agree that W can assume a very large value; the minimum value being one. The question now arises: Is it related to any thermodynamic variable ? In fact, yes and the variable is entropy. You will observe that the relation between the entropy S and the thermodynamic probability W forms the basis of entire statistical analysis. We now intend to introduce this relation.

13.3.2 Bridging Microscopic and Macroscopic View-points

From Unit 5, you will recall that the second law of thermodynamics introduces a very important state function, the entropy S. We also know that the state of equilibrium of a thermally isolated system corresponds to the maximum entropy. We can say that a system in equilibrium is equally likely to be in any of its accessible states. That is, the equilibrium state is the most probable one in the sense that it has the largest thermodynamic probability W. The larger the choice of microstates, the greater will be the degree of unpredictability or disorder in the system. This suggest that S and W are closely connected. We can explore this connection in a very simple manner as follows :

Consider two systems 1 and 2 under similar external conditions of temperature and pressure. Let S_1 and S_2 be their entropies. Suppose that these systems are put in thermal contact. Then, the total entropy of the combined system is given by

$$S = S_1 + S_2$$

This relation is a statement of the fact that the entropy is an extensive variable.

Let the statistical weights of the states in 1 and 2 be W_1 and W_2, respectively. Then the statistical weight W of the combined system is

$$W = W_1 W_2 \tag{13.13}$$

We express functional relation between entropy and thermodynamic probability as

$$S = f(W) \tag{13.14}$$

Eqs. (13.12) and (13.13) impose the following condition on $f(W)$:

$$f(W_1) + f(W_2) = f(W_1 W_2)$$

Differentiating it with respect to W_2, we obtain

$$\frac{df(W_2)}{dW_2} = \frac{df(W_1 W_2)}{dW_2} = \frac{df(W_1 W_2)}{dW} \; W_1$$

Since it readily follows from Eq. (13.13) that

$$\frac{d}{dW_2} = W_1 \frac{d}{dW}$$

Next, we differentiate it with respect to W_1. This gives

$$\begin{aligned} 0 &= \frac{df(W)}{dW} + W_1 \frac{d}{dW_1}\left(\frac{df}{dW}\right) \\ &= \frac{df(W)}{dW} + W_1 \, W_2 \frac{d^2 f}{dW^2} \end{aligned}$$

or

$$\frac{f''(W)}{f'(W)} = -\frac{1}{W} \qquad (13.15)$$

where prime(s) denotes differentiation with respect to W. On integration, we get

$$\ln f'(W) = -\ln W + \ln k$$

where k is a constant. We can rewrite it as

$$f'(W) = \frac{k}{W} \qquad (13.14)$$

Integrating again, with respect to W, we obtain

$$f(W) = k \ln W + W_0$$

Using Eq. (13.14), we can write

$$S = k \ln W + W_0 \qquad (13.17)$$

From the third law of thermodynamics, we know that the entropy of a completely ordered state ($W = 1$) is zero. This implies that we can write the relation between entropy and thermodynamic probability as

$$S = k \ln W \qquad (13.18)$$

This is the famous Boltzmann relation connecting entropy and probability. The constant k is identified with the Boltzmann constant, $k_B (= 1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}})$.

Eq. (13.18) provides a link between the macroscopic and microscopic view-points. It opens the way for a more direct and elegant application of the techniques of probability theory to study widely diverse systems.

It is known that Boltzmann never got the recognition in his lifetime for this work. This frustration sadly forced him to commit suicide in 1906. This relation is engraved on his resting place in the central cemetery of Vienna.

13.4 THE DISTRIBUTION FUNCTION

Consider an ideal monatomic gas made up of N particles enclosed in a volume V and having total internal energy U. The state of the system at any time t is represented by a point in a $6N$-dimensional phase space. This means that every particle is associated with six dimensional phase space, also called the μ space. μ stands for the first letter of molecule). The particles are moving independently of each other and the contributions of individual particles remain separate.

To give a microscopic description of the system, we divide the μ-space into cells of volume h^3. Recall that in classical statistics, we can choose h as small as we like. Each particle will be found to occupy a cell in this network. Suppose the cells are numbered 1, 2, ... Let the energy of a particle in the ith cell be denoted by ε_i · Then, we have

$$N = \sum_i n_i \qquad (13.19a)$$

and

$$U = \sum_i n_i \varepsilon_i \qquad (13.19b)$$

The macrostate (N, V, U) can be realised in a number of different ways. In order to proceed with our argument, we advance the hypothesis that all microstates are equally probable. In other words, equal phase elements in phase space are associated with equal probabilities. It corresponds to the assumption that the faces of a die are equally probable. This hypothesis is known as the ***postulate of equal a priori probabilities***.

The thermodynamic probability W is simply the number of ways of placing N distinguishable objects in cells such that there are n_1 objects in the first cell, n_2 in the second and so on. This number is given by

$$W = \frac{n!}{n_1!\,n_2!\cdots} = \frac{N!}{\prod_{i=1} n_i!} \tag{13.20}$$

We can easily prove this result by noting that there are $\binom{n}{n_1}$ number of ways of choosing n_1 objects that are to be placed in the first cell. Then we will be left with $(N - n_1)$ objects. Out of these $(N - n_1)$ objects, there are $\binom{n - n_1}{n_2}$ ways of choosing n_2 objects to be placed in the second cell. We can continue in this fashion till all objects are placed in given cells. Then the total number of ways

$$W = \binom{N}{n_1}\binom{N - n_1}{n_2}\binom{N - n_1 - n_2}{n_3}\cdots 1$$

$$= \frac{N!}{(N - n_1)!\,n_1!}\cdot\frac{(N - n_1)!}{(N - n_1 - n_2)n_2!}\cdot\frac{(N - n_1 - n_2)!}{(N - n_1 - n_2 - n_3)!\,n_3!}\cdots = \frac{N!}{n_1!\,n_2!\cdots}$$

Symbolically, we write this as $\binom{N}{n_1, n_2 \cdots}$ and call it a **multinomial coefficient**.

we know that equilibrium corresponds to maximum of the thermodynamic probability W. Since $S = k_B \ln W$, it is more appropriate to look at $\ln W$ rather than W itself. (Since $\ln W$ is a monotonically increasing function of W, its extreme points will coincide with those of W). Then, Eq. (13.20) gives

$$\ln W = \ln N! - \sum_i \ln n_i! \tag{13.21}$$

For most systems of practical interest, N is a very large number. By the same reasoning, most of the n_i's will be sufficiently large so that we can simplify this relation using Stirling's formula (Appendix *A*) :

$$\ln x! = x\,(\ln x - 1)$$

For small n_i, $\ln n_i!$ will be small and hence not of any consequence. Proceeding further, we insert Stirling's formula in Eq. (13.21). The result is

$$\ln W = (N \ln N - N) - \sum_i (n_i \ln n_i - n_i)$$

$$= N \ln N - \sum_i n_i \ln n_i$$

since $\sum_i n_i = N$.

You would recall that we set our goal to determine the set $\{n_i\}$ which maximizes $\ln W$. The condition for maximum probability is

$$\delta \ln W = 0$$

We now calculate a small change in $\ln W$ and equate it to zero. This gives

$$\delta \ln W = -\sum_i n_i \delta \ln n_i - \sum_i (\ln n_i)\delta n_i = 0 \tag{13.22}$$

This expression has been derived by assuming that N and U are constant :

$$\delta N = \sum_i \delta n_i = 0 \tag{13.23a}$$

$$\delta U = \sum_i \varepsilon_i \delta n_i = 0 \tag{13.23b}$$

The first term on the R.H.S. of Eq. (13.22) is, therefore, equal to zero :

$$\sum_i n_i \delta(\ln n_i) = \sum_i n_i (1/n_i)\delta n_i = \sum_i \delta n_i = 0$$

Then Eq. (13.22) reduces to

$$\sum_i \ln n_i \delta n_i = 0 \tag{13.24}$$

To accommodate the conditions embodied in Eqs. (13.23a, b), we employ the method of Lagrange multipliers (Appendix B). We multiply Eq. (13.23a) by α, and Eq. (13.23b) by β. The result so obtained is added to Eq. (13.24). This leads to

$$\sum_i (\ln n_i + \alpha + \beta\,\varepsilon_i)\delta n_i = 0 \tag{13.25}$$

Since the variations δn_i are arbitrary, this relation will hold only if the coefficient of each term vanishes. Hence, we must have

$$\ln n_i + \alpha + \beta\,\varepsilon_i = 0$$

or

$$n_i = e^{-\alpha-\beta\varepsilon_i} = \frac{1}{A}e^{-\beta\varepsilon_i} \tag{13.26}$$

where we have put $A = e^{\alpha}$. (13.27)

Eq (13.26) constitutes what is called the **Maxwell-Boltzmann distribution**. You will note that we wished to know the set (n_i) which characterises the equilibrium state. But we find that Eq. (13.26) contains two unknown Lagrange multipliers α and β. We must now evaluate them in terms of known quantities.

Evaluation of Lagrange Multipliers: The Partition Function

The constant A (or α) is determined using the normalisation condition. The probability that the state with energy ε_i is occupied is given by Eq. (13.26) with A defined by Eq. (13.27). Since $\sum_i n_i = N$, we can write

$$\sum_i n_i = N = \frac{1}{A}\sum_i e^{-\beta\varepsilon_i}$$

or

$$\frac{1}{NA}\sum_i e^{-\beta\varepsilon_i} = 1$$

If we now define

$$Z = \sum_i e^{-\beta\,\varepsilon_i} \tag{13.28}$$

we can write the degeneracy parameter A as

$$A = \frac{Z}{N} \tag{13.29}$$

The sum $\sum_i \exp(-\beta\varepsilon_i)$, denoted by Z, is called the single-particle partition function.

It is also called the **phase integral**. The name partition function is due to Darwin and Fowler (1922). It arises from the observation that when systems 1 and 2 are in thermal contact, the partitioning of energy between them is determined by the corresponding partition functions Z_1 and Z_2. Planck (1921) called $\sum_i e^{-\beta\varepsilon_i}$ Zustandssumme (sum over states) and denoted it by Z. We shall follow Planck's notation here. It is important to remark that partition function occupies a pivotal position in statistical mechanics because all thermodynamic functions can be written in terms of Z. But before we do so, it is important to remark that the partition function characterises a sum over discrete states. This is characteristic of a discrete spectrum. But in classical physics, the energy is taken to be continuous. However, if the levels are very closely spaced, even the discrete sum becomes a continuum and it is possible to replace the summation by integration. This is illustrated in the following example.

Example 7

Starting from the distribution given by Eq. (13.26) with $A = \frac{Z}{N}$, obtain Maxwell's law of distribution of velocities.

Solution

We note from Eqs. (13.26) and (13.29) that

$$\frac{n_i}{N} = \frac{\exp(-\beta\,\varepsilon_i)}{Z}$$

In the next unit, we will show that for an ideal monoatomic gas

$$Z = \frac{V}{h^3}(2\pi m k_B T)^{3/2}$$

Hence, using the normalisation condition

$$\sum_i n_i / N = 1,$$

we get

$$\frac{1}{Z}\sum_i e^{-\beta \varepsilon_i} = 1$$

If the energy states are very closely spaced, we can replace summation by integration:

$$\sum_i e^{-\beta \varepsilon_i} \cong \iiint_V \iiint_p e^{-\beta \varepsilon} dx\,dy\,dz\,dp_x\,dp_y\,dp_z$$

$$= \frac{V}{h^3} \iiint_p e^{-\beta \varepsilon} dp_x\, dp_y\, dp_z$$

where we have replaced $\iiint dx dy dz$ by the ratio of volume in the Cartesian space to the volume of one cell ($= h^3$). Moreover, if we assume azimuthal symmetry, we can write

$$\iiint dp_x\, dp_y\, dp_z = \int 4\pi p^2\, dp$$

Hence,

$$\frac{1}{Z}\left(\frac{V}{h^3}\right) 4\pi \int e^{-\beta \varepsilon} p^2\, dp = 1$$

On substituting for Z, we get

$$\frac{4\pi}{(2\pi m k_B T)^{3/2}} I = 1 \qquad \text{(i)}$$

where

$$I = \int_0^\infty \exp(-\beta\varepsilon) p^2\, dp$$

To evaluate this integral, we write $p = mv$ so that $dp = m\, dv$. Also we know that $\varepsilon = (1/2)\, mv^2$. Hence

$$I = m^3 \int_0^\infty \exp\left(-\frac{mv^2}{2k_B T}\right) v^2\, dv$$

Inserting this in (i), we get

$$4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^\infty \exp\left(-\frac{mv^2}{2k_B T}\right) v^2\, dv = 1$$

Hence, the number of molecules having speeds between v and $v + dv$ is given by

$$dN_v = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right) v^2\, dv \qquad \text{(ii)}$$

This is Maxwell's law for distribution of speeds.

We now proceed to express thermodynamic variables in terms of partition function. To this end, we substitute for n_i from Eq. (13.26) into Eq. (13.21). This gives

$$\ln W = N \ln N - \sum_i n_i (\ln N - \ln Z - \beta \varepsilon_i)$$

$$= N \ln Z + \beta U$$

Now use of Boltzmann relation gives

$$S = N k_B \ln Z + \beta k_B U \qquad (13.30)$$

We can use this relation to introduce the concept of temperature by relating entropy and internal energy of a system :

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V = \frac{N k_B}{Z}\left(\frac{\partial Z}{\partial \beta}\right)_V \left(\frac{\partial \beta}{\partial U}\right)_V + k_B \beta + k_B U \left(\frac{\partial \beta}{\partial U}\right)_V \qquad (13.31)$$

From Eq. (13.28), we note that

$$\left(\frac{\partial Z}{\partial \beta}\right)_V = -\sum_i \varepsilon_i \exp(-\beta\varepsilon_i) \tag{13.32}$$

On combining Eqs. (13.23b) and (13.26), we get

$$U = \sum_i n_i\varepsilon_i = \frac{N}{Z}\sum_i \varepsilon_i \exp(-\beta\,\varepsilon_i)$$

Using this result in Eq. (13.32), we get

$$\left(\frac{\partial Z}{\partial \beta}\right)_V = -\frac{ZU}{N} \tag{13.33}$$

Combining it with Eq. (13.31), we get

$$\left(\frac{\partial S}{\partial U}\right)_V = k_B\,\beta \tag{13.34}$$

so that $\beta = (k_B\,T)^{-1}$ (13.35)

You may now ask: Is this value of β unique? This is the subject of one of the terminal questions.

From Eq. (13.33), we have

$$\left(\frac{\partial Z}{\partial T}\right)_V = \left(\frac{\partial Z}{\partial \beta}\right)_V \left(\frac{\partial \beta}{\partial T}\right)_V = -\frac{1}{k_B T^2}\left(\frac{\partial Z}{\partial \beta}\right)_V = \frac{U}{k_B T^2}\,\frac{Z}{N}$$

Hence,

$$U = Nk_B T^2 \frac{1}{Z}\left(\frac{\partial Z}{\partial T}\right)_V = Nk_B T^2 \frac{\partial}{\partial T}(\ln Z) \tag{13.36}$$

The Helmholtz free energy, F, defined as

$$F = U - TS$$

is given by

$$F = -N\,k_B T\,\ln Z \tag{13.37}$$

since

$$S = Nk_B \ln Z + \frac{U}{T} \tag{13.38}$$

The pressure exerted by a classical gas is related to Helmholtz free energy through the relation

$$p = -\left(\frac{\partial F}{\partial V}\right)_T$$

so that

$$p = \frac{k_B T N}{Z}\left(\frac{\partial Z}{\partial V}\right)_T \tag{13.39}$$

We have now seen that all the thermodynamic functions can be related to the partition function Z. It means that once we evaluate Z, which, of course, may not always be easy, we can readily determine a thermodynamic function of interest. This is the subject of discussion of the next unit.

13.5 SUMMARY

- The entropy and thermodynamic probability are connected through the relation

  $$S = k_B \ln W$$

  This relation bridges the gap between thermodynamic and statistical view-points.
- The termodynamic probability of distributing N particles into various energy states

(cells) so that n_1 are in first, n_2 are in second and so on is given by

$$W=\binom{N}{n_1 n_2 n_3\ldots}=\frac{N!}{n_1!\,n_2!\ldots n_i!}$$

$$=\frac{N}{\prod\limits_i n_i!}$$

- The classical (Maxwell-Boltzmann) distribution is given by

  $$n_i = e^{-\alpha-\beta\varepsilon_i}=\frac{1}{A}e^{-\beta\varepsilon_i}$$

  with $A = e^{\alpha}$.
- The degeneracy parameter $A=\frac{Z}{N}$ and $\beta=(k_B T)^{-1}$
- For discrete energy states, the single particle partition function is given by

  $$Z=\sum_i e^{-\beta\varepsilon_i}$$
- For a continuous spectrum, Z takes the form

  $$Z=\frac{1}{h^{3N}}\int e^{-\beta\varepsilon(q,p)}\,d\Gamma$$
- The various thermodynamic functions are related to Z:

  $$U = Nk_B T^2\frac{\partial}{\partial T}(\ln Z)$$

  $$S = Nk_B \ln Z+\frac{U}{T}$$

  $$F = -Nk_B T\ln Z$$

and

$$p=\frac{k_B T}{Z}\left(\frac{\partial Z}{\partial V}\right)_T$$

13.6 TERMINAL QUESTIONS

1. Draw the phase space for a linear harmonic oscillator. What will happen if we consider the same problem from the point of view of quantum theory?
2. Draw the phase space for a particle having energy E, constrained to move in one dimension.
3. Consider two systems having N and N' particles, respectively. Let them be brought in thermal contact. Show that β is the same for the two assemblies.
4. For a system in equilibrium with a heat bath at temperature T, the probability for being in the state E_i is proportional to exp $(-\beta E_i)$. Calculate Var (E) and the relative root mean-square fluctuation of E.
5. Consider a system of N particles and a phase space consisting of only two cells with energies 0 and ϵ $(\epsilon > 0)$, respectively. Calculate the partition function and the internal energy.

13.7 SOLUTIONS AND ANSWERS

SAQs

1. (i) The sample space is

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

   (ii) The sample space is

   $$S = \{\underbrace{(H,H,\ldots,H)}_{n\text{ entries}}\ \underbrace{(H,H,\ldots,T)}_{n\text{ entries}}\cdots\underbrace{(T,T,\ldots,T)}_{n\text{ entries}}\}$$

the total number of sample points being 2^n.

iii) The possible events are

$$\phi,\ \{(H,H)\},\ \{(H,T)\},\ \{(T,H)\},\ \{(T,T)\},\ \{(H,H),\ (H,T)\},$$
$$\{(H,H),\ (T,H)\},\ \{(H,H),\ (T,T)\},\ \{(H,T),\ (T,H)\},\ \{(H,T),\ (T,T)\},$$
$$\{(T,H),\ (T,T)\},\ \{(H,H),\ (H,T),(T,H)\},\ \{(H,H),\ (H,T),\ (T,T)\}$$
$$\{(H,T),\ (T,H),\ (T,T)\},\ \{(H,H),\ (T,H),\ (T,T)\},\ \Omega.$$

2. We have

$$\text{Var}(X) = < X^2 > - < X >^2$$

$$< X > = \int x f(x) dx = A \int_a^b x\, dx \frac{1}{(b-a)} \frac{b^2-a^2}{2}$$
$$= \frac{1}{2}(a+b)$$
$$< X^2 > = \int x^2 f(x) dx = A \int_a^b x^2\, dx = \frac{1}{(b-a)} \frac{b^3-a^3}{3}$$
$$= \frac{a^2+ab+b^2}{3}$$

Hence,

$$Var\ (X) = \frac{a^2+ab+b^2}{3} - \frac{1}{4}(a+b)^2 = \frac{4(a^2+ab+b^2)-3(a+b)^2}{12}$$
$$= \frac{1}{12}[a^2-2ab+b^2] = \frac{(b-a)^2}{12}$$

3. The total number of degrees of freedom for each particle is (3 + 2) = 5. Hence the phase space will be $10N$-dimensional

4. i) The possible macrostates are

(i) 4–0, (ii) 3–1, (iii) 2–2, (iv) 1–3, (v) 0–4.

The value of W for both (i) and (v) is one.

For (ii), $W = 4$, viz., $\boxed{abc}\ \boxed{d}$, $\boxed{abd}\ \boxed{c}$, $\boxed{acd}\ \boxed{b}$ and $\boxed{bcd}\ \boxed{a}$. Similarly, $W_3 = 6$ and $W_4 = 4$.

ii) The possible macrostates are

	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	(ix)	(x)
n_1	2	0	0	0	1	1	0	1	0	0
n_2	0	2	0	0	1	0	0	0	1	1
n_3	0	0	2	0	0	1	1	0	1	0
n_4	0	0	0	2	0	0	1	1	0	1

For (i) to (iv), $W = 1$. For (v), we have $W = 2$, viz.,

$\boxed{a}\ \boxed{b}$ and $\boxed{b}\ \boxed{a}$

Terminal Questions

1. The equation of motion of a linear harmonic oscillator is

$$\frac{d^2q}{dt^2} = -kq$$

where k is the spring constant. The solutions of this equation are of the form

$$q = A\cos(\omega t + \phi), \qquad \text{(i)}$$

where A is the amplitude, $\omega = \sqrt{\frac{k}{m}}$, m being the mass and ϕ is the phase. The total energy $E = \frac{1}{2}m\omega^2A^2$

Also

$$p = m\dot{q} = -mA\omega\sin(\omega t + \phi) \qquad \text{(ii)}$$

where dot over q signifies its time derivative.

From (i) and (ii), we have

$$\frac{q^2}{A^2} + \frac{p^2}{m^2\omega^2A^2} = 1 \qquad \text{(iii)}$$

Using (iii), we obtain

$$\frac{q^2}{\left(\frac{2E}{m\omega^2}\right)} + \frac{p^2}{2mE} = 1.$$

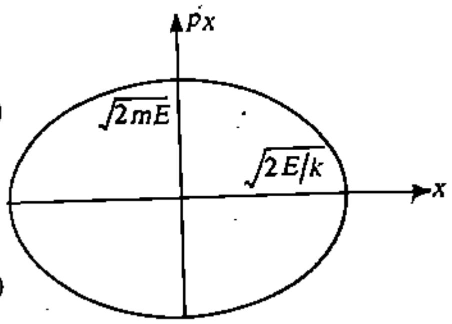


Fig. 13.8: Phase space of a linear harmonic oscillator

Hence, the phase space is an ellipse with area $= \pi\sqrt{\frac{2E}{m^2}}\ \sqrt{2mE} = \frac{2\pi E}{\omega}$. This is shown in Fig. 13.8. In the quantum theory, the energy is quantized and the phase space consists of equally spaced ellipses.

2. Let us consider a particle moving in one dimension within a box of length L. Hence, q is confined to the interval $[0, L]$. The energy

$$E = \frac{p^2}{2m}$$

where p is the momentum. If E is fixed, p can have values $\sqrt{2mE}$ and $-\sqrt{2mE}$. In practice, a system is never completely isolated. Hence, the energy may lie between E and $E + dE$. Thus, p must lie in a small range around $\pm\sqrt{2mE}$.

3. The states of the two systems will adjust themselves so that they have a common temperature T. Let the set of occupation numbers and energies be $\{n_i\}$, $\{\varepsilon_i\}$, $\{n'_i\}$, and $\{\varepsilon'_i\}$, respectively, for the two systems. Then we have

$$W = \frac{N!}{\prod_i n_i!}\ \frac{N'!}{\prod_i n'_j!} \qquad \text{(i)}$$

and

$$\ln W = N\ln N - \sum_i n_i \ln n_i + N'\ln N' - \sum_i n'_j \ln n'_j \qquad \text{(ii)}$$

The constraints are

$$\sum_i n_i = N,\ \sum_j n'_j = N',\ \sum_i\sum_j (n_i\varepsilon_i + n'_j\varepsilon'_j) = U \qquad \text{(iii)}$$

Multiplying with Lagrange multipliers α, α' and β, and adding to (ii), we get

$$\sum_i(\ln n_i + \alpha + \beta\varepsilon_i)\delta n_i + \sum_j(\ln n'_j + \alpha' + \beta\varepsilon'_j)\delta n'_j = 0$$

Since δn_i, $\delta n'_j$ are arbitrary and independent, we obtain

$$n_i = e^{-\alpha-\beta\varepsilon_i},\ \ n'_j = e^{-\alpha'-\beta\varepsilon'_j}$$

Thus, β has the same value for two systems which are in thermal equilibrium with each other. Hence, β must be a function of T.

4. The mean value of energy is

$$\langle E\rangle = \bar{E} = \frac{\sum_i E_i e^{-\beta E_i}}{\sum e^{-\beta E_i}} = -\frac{\partial}{\partial\beta}(\ln Z_N)$$

Appendix B: A Brief Note on the Method of Lagrange Multipliers

You are familiar with the problem of finding the maxima and minima of functions. Sometimes, however, we are required to find these extreme values subject to certain conditions or constraints. We have already come across this problem in Sec 13.2, where we had to maximise W, the thermodynamic probability, subject to the conditions that N and U are fixed. There is an elegant technique to solve such problems. It is called the **method of undetermined multipliers** and is due to the French analyst Lagrange.

Suppose we want to find the extrema of the function $f(x, y)$. We solve the two equations

$$\frac{\partial f}{\partial x} = 0 \text{ and } \frac{\partial f}{\partial y} = 0 \tag{B.1}$$

simultaneously. The resulting pair (or pairs) of values of x and y specify the point (or points) at which f has a maximum, minimum, or point of inflection. Now suppose that there is an auxiliary condition

$$g(x, y) = 0 \tag{B.2}$$

In principle, we can eliminate one of the variables. However, in practice, this may not always be possible. So we proceed as follows:

Eqs. (B.1) gives us

$$\left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = 0 \tag{B.3}$$

From Eq. (B.2), we have

$$dg = \left(\frac{\partial g}{\partial x}\right)_y dx + \left(\frac{\partial g}{\partial y}\right)_x dy = 0 \tag{B.4}$$

Multiplying Eq. (B.4) by λ and adding to Eq. (B.3) yields

$$\left(\frac{\partial f}{\partial x} + \lambda \frac{\partial g}{\partial x}\right) dx + \left(\frac{\partial f}{\partial y} + \lambda \frac{\partial g}{\partial y}\right) dy = 0$$

where we have dropped subscripts x and y.

Since x and y are independent, we have

$$\left(\frac{\partial f}{\partial x}\right) + \lambda \left(\frac{\partial g}{\partial x}\right) = 0$$

and

$$\left(\frac{\partial f}{\partial y}\right) + \lambda \left(\frac{\partial g}{\partial y}\right) = 0 \tag{B.5}$$

These equations have to be solved simultaneously to determine the values of x, y, and λ.

UNIT 14 THE PARTITION FUNCTION

Structure

14.1 Introduction

Objectives

14.2 The Partition Function of an Ideal Monatomic Gas

Thermodynamic Functions

Gibbs Paradox

14.3 The Sackur-Tetrode Formula

14.4 Diatomic Gases

Rotational and Vibrational Partition Functions

Heat Capacity of Hydrogen

14.5 Summary

14.6 Terminal Questions

14.7 Solutions and Answers

14.1 INTRODUCTION

In the previous unit, we obtained the distribution function for a classical Maxwell-Boltzmann ideal monatomic gas. Then we introduced the concept of partition function and learnt to express various thermodynamic functions in terms of the partition function. It is, therefore, important to know to compute the partition function for a thermodynamic system of interest. In Sec. 14.2, you will learn to compute the partition function of an ideal monatomic gas. The expressions for thermodynamic functions will also be derived. Gibbs showed that the expression for entropy so derived suffers from a serious flaw; entropy fails to exhibit its extensive character. You will learn to resolve this so-called Gibbs paradox in Sec. 14.3. This leads us to the Sackur-Tetrode equation. From Unit 9 of Block 3, you would recall that unlike a monatomic gas, diatomic gases have rotational and vibrational degrees of freedom. These contribute to their total energy and hence heat capacities. You will learn to evaluate rotational and vibrational partition functions with particular reference to hydrogen.

Objectives

After studying this unit, you should be able to :

- compute the partition function of an ideal monatomic gas and work out all the thermodynamic functions
- point out the flaw in the expression for entropy
- derive the Sackur-Tetrode formula and resolve the Gibbs paradox
- calculate rotational and vibrational contributions to heat capacities of diatomic gases
- explain the observed temperature variation of heat capacity of hydrogen.

14.2 THE PARTITION FUNCTION OF AN IDEAL MONATOMIC GAS

Consider an ideal monatomic gas consisting of N particles, each of mass m and occupying a volume V. This means that the energy of the system is wholly translational. That is, the potential energy is zero since intermolecular forces are absent.

explanation of molecular chaos lies in statistical arguments, which are more profound.

The Helmholtz free energy expressed in terms of Z is

$$F = -Nk_B T \ln Z$$

$$= -Nk_B\, T \ln\left[\frac{V}{h^3}(2\pi m k_B\, T)^{3/2}\right] \tag{14.14}$$

From the previous unit, you would recall that entropy and partition function are connected by the relation

$$S = Nk_B \ln Z + \frac{U}{T}$$

On substituting for ln Z and U from Eqs. (14.8) and (14.11), we get

$$S = Nk_B[\ln V - 3\ln h + \frac{3}{2}\ln(2\pi m k_B) + \frac{3}{2}\ln T] + \frac{3}{2}Nk_B$$

$$= Nk_B \ln\left\{\frac{V(2\pi m k_B T)^{3/2}}{h^3}e^{3/2}\right\} \tag{14.15}$$

This is the classical expression for the entropy of an ideal monatomic gas. We will consider it in detail a little later. To get a little practice, you should solve the following SAQ.

SAQ 1

Obtain the entropy and pressure from Helmholtz energy

The degeneracy parameter A is given by

$$A = \frac{Z}{N} = \frac{(2\pi m k_B T)^{3/2}}{nh^3} \tag{14.16}$$

You will note that at high temperatures and/or low densities, A will be large. We can relate it to the deBroglie wavelength λ_{dB} and inter-particle distance by noting that

$$\lambda_{dB} = \frac{h}{p}$$

with $\dfrac{p^2}{2m} = k_B T$. Hence,

$$\lambda_{dB} = \frac{h}{\sqrt{2mk_B T}} \tag{14.17}$$

Also, the mean inter-particle distance r_0 is given by

$$r_0 = \left(\frac{V}{N}\right)^{1/3}$$

Hence,

$$A = \left(\frac{r_0}{\lambda_{dB}}\right)^3 \tag{14.18}$$

When $A >> 1$, we have $\lambda_{dB} << r_0$. That is, the thermal wavelength is very small compared to the inter-particle distance and classical results hold good at high temperatures and/or low densities.

The chemical potential μ is given by

$$\mu = k_B T \ln A = k_B T \ln\left[\frac{(2\pi m k_B T)^{3/2}}{nh^3}\right] \tag{14.19}$$

Let us now re-examine the expression for entropy closely.

14.2.2 Gibbs Paradox

From Eq. (14.15), we note that entropy of an ideal gas depends on V, T and N. Moreover, the functional dependence on volume and temperature is the same as obtained from thermodynamic considerations. But we note that as $T \to 0\text{K}$, $S \to -\infty$. This is not physically meaningful and contradicts the third law of thermodynamics (which states that $S \to 0$ as $T \to 0$).However, you should not be unduely concerned. In fact, you should have expected this result because classical statistics is a good description only at high temperatures. The explanation has genesis in quantum mechanics. You will learn this in detail in the next unit.

A more serious objection against Eq. (14.15) is its implication that entropy does not behave as an extensive quantity. Let us increase both V and N by a factor α. Eq. (14.15) contains a term $N \ln V$. Hence, S will not increase in the same proportion. This can be clearly understood by considering intermixing of two ideal gases.

You would recall that in thermodynamics we characterize variables as intensive and extensive. Intensive variables do not depend on the number of particles or the size of the system. On the other hand, extensive parameters depend on the size of the system, i.e. get multiplied by the factor the size of the system under consideration increases.

The entropy of a system of N particles occupying a volume V is given by

$$S = Nk_B[\ln V - 3\ln h + \frac{3}{2}\ln(2\pi m k_B) + \frac{3}{2}\ln T] + \frac{3}{2}Nk_B$$

$$= Nk_B[\ln V + \frac{3}{2}\ln T + \sigma] \qquad (14.20)$$

with

$$\sigma = \frac{3}{2}\ln(2\pi m k_B) - \ln h^3 + \frac{3}{2}$$

$$= \ln\left[\left(\frac{2\pi m k_B}{h^2}\right)^{3/2} e^{3/2}\right]$$

Let us now consider two ideal gases contained in two chambers of volumes V_1 and V_2 and separated by a rigid partition as shown in Fig. 14.1. Suppose that these gases are in equilibrium at Temperature T. Then the entropy of each gas is given by

$$S_1 = N_1 k_B[\ln V_1 + \frac{3}{2}\ln T + \sigma_1]$$

and

$$S_2 = N_2 k_B[\ln V_2 + \frac{3}{2}\ln T + \sigma_2]$$

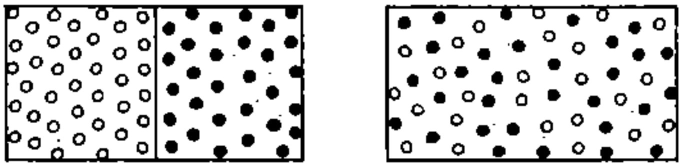


Fig. 14.1: a) The system divided by a partition into 1 and 2.
b) A system of N-particles in a volume V.

So, the total initial entropy of these gases is

$$S_i = S_1 + S_2 = N_1 k_B[\ln V_1 + \frac{3}{2}\ln T + \sigma_1]$$
$$+ N_2 k_B[\ln V_2 + \frac{3}{2}\ln T + \sigma_2]$$

Now we remove the partition and these gases mix by diffusing into one another. We can regard it as free expansion of each gas to volume $V = V_1 + V_2$. Then final entropy of the system is

$$S_f = N_1 k_B[\ln V + \frac{3}{2}\ln T + \sigma_1]$$
$$+ N_2 k_B[\ln V + \frac{3}{2}\ln T + \sigma_2]$$

two axes at right-angles to the line connecting m_1 and m_2 and passing through the centre of gravity C, is given by

$$I_y = I_z = I = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2$$

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

is the reduced mass of the molecule. The moment of inertia about the line joining the molecules is taken to be equal to zero. The kinetic energy of the molecule is

$$E = \frac{1}{2} I_y \, \omega_y^2 + \frac{1}{2} I_z \, \omega_z^2$$

$$= \frac{1}{2} I(\omega_y^2 + \omega_z^2) \tag{14.26}$$

If the bonding is not perfectly rigid, these atoms can vibrate about their respective equilibrium positions. The simplest assumption is that each atom executes simple harmonic motion. From Unit 1, Block 1 of PHE-02 course, you may recall that the motion of these atoms can be reduced to the harmonic vibration of a single point mass μ about an equilibrium position. Thus, for a diatomic molecule, we can have two vibrational degrees of freedom, apart from translational and rotational degrees of freedom. The total number of degrees of freedom

$$f = f_{tran} + f_{rot} + f_{vib}$$

$$= 3 + 2 + 2 = 7 \tag{14.27}$$

Since each degree of freedom in classical physics is associated with energy ($k_B T/2$), we find that

$$\bar{\varepsilon} = \frac{7}{2} k_B \, T$$

so that heat capacity for the gas made of N-particles is $C_V = \frac{7}{2} R$ and the ratio of heat capacities

$$\gamma = \frac{9}{7} = 1.29 \tag{14.28}$$

It shows that heat capacity of a gas is constant; independent of temperature and same for all gases. And γ for a diatomic gas is less than the value for a monoatomic gas. In Table 14.1, we have listed the values of γ, obtained by measurements of the velocity of sound at room temperature for some diatomic gases of interest.

Table 14.1: Values of γ from velocity of sound measurements for diatomic gases

Gas	γ
H_2	1.410
O_2	1.401
N_2	1.404
CO	1.404
NO	1.400

You will note that γ is close to 1.4 and agreement with theoretical value is not very good. However, if we take $f = 5$, we find that

$$\gamma = \frac{7}{5} = 1.4$$

This suggests that around room temperature, either rotational or vibrational degrees of freedom, not both, contribute to mean energy. It is as if some degrees of freedom are 'frozen' and hence do not show up in experiments. This led Sommerfield to remark that **'Degrees of freedom should be weighted not counted.'**

SAQ 4

Calculate γ for a polyatomic gas having f degrees of freedom.

As the number of atoms increases, f also increases and γ decreases. This is well borne out by experiments. In fact, γ is found to satisfy the inequality

$$1 < \gamma < 1.67 \tag{14.29}$$

It may be remarked here that qualitative features of heat capacity of diatomic gases predicted by theory are borne out by experiments. However, if we look at its temperature variation, we find that the agreement is very poor. In most cases, heat capacity increases as temperature is raised and decreases as temperature is lowered. For example, the heat capacity of hydrogen at 20K is just $\frac{3}{2}R$. That is, it behaves like a monoatomic gas and rotational as well as vibrational degrees of freedom are effectively 'frozen'. A correct explanation is provided by quantum statistics. The basic argument is very simple and can be introduced without a detailed discussion of the basic features of quantum statistics.

In the quantum description of a system, we have a set of allowed discrete energy levels. Let the separation of the levels around the mean energy be denoted by ΔE. If

$$\Delta E << k_B T \tag{14.30}$$

the discrete nature of the sepctrum is not important and the equipartition theorem should be a good approximation. This is certainly true at sufficiently high temperatures. But, if

$$\Delta E = k_B T \tag{14.31}$$

the discrete nature of the spectrum becomes important. If we introduce a characteristic temperature, θ, defined by

$$\theta = \frac{\Delta E}{k_B} \tag{14.32}$$

Eqs. (14.30) and (14.31) respectively take the form

$$T >> \theta \quad \text{and}\ T = \theta \tag{14.33}$$

We now turn to a calculation of rotational and vibrational partition functions.

14.4.1 Rotational and Vibrational Partition Functions

The rotational energy levels of a diatomic molecule are given by

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1), \qquad J = 0, 1, 2, .. \tag{14.34}$$

and each energy level is $(2J+1)$-fold degenerate.

The partition function for rotational motion of a hetero-nuclear molecule — a molecule consisting of two different kinds of atoms such as HCl — is given by

$$Z_{rot} = \sum_{J=0}^{\infty} (2J+1) \exp\left(-\frac{J(J+1)\theta_{rot}}{T}\right) \tag{14.35a}$$

$$= 1 + 3\exp\left(-\frac{2\theta_{rot}}{T}\right) + 5\exp\left(-\frac{6\theta_{rot}}{T}\right) + \cdots \tag{14.35b}$$

where

$$\theta_{rot} = \frac{h^2}{8\pi^2 I k_B}$$

defines the characteristic rotational temperature. You will note that θ_{rot} is low for heavier molecules. For example, $\theta_{rot} = 15.2$ K for HCl, 2.1K for O_2 and 0.3K for Cl_2. On the other hand, $\theta_{rot} = 85.5$K for hydrogen. When $T << \theta_{rot}$, the thermal energy of the system ($\sim k_B T$) is not suffficient to take the molecule to higher rotational levels. So it is very likely that the hetero-nuclear diatomic molecule is in its ground state of rotational motion. When $T >> \theta_{rot}$, the significant number of rotational states are excited and the spacing between consecutive levels is much smaller compared to $k_B T$. Then, energy can be treated as continuous and we can replace the summation in Eq. (14.35a) by integration:

$$Z_{rot} = \int_0^{\infty} (2J+1) \exp\left[-J(J+1)\frac{\theta_{rot}}{T}\right] dJ \tag{14.36}$$

To evaluate this integral, we introduce a change of variable by defining

$$x = J(J+1)\frac{\theta_{rot}}{T}$$

so that

$$dx = \frac{\theta_{rot}}{T}(2J+1)dJ$$

Subsituting these in the above expression, we get

$$Z_{rot} = \left(\frac{T}{\theta_{rot}}\right) \int_0^{\infty} e^{-y} dy = \frac{T}{\theta_{rot}} = \frac{8\pi I k_B T}{h^2} \tag{14.37}$$

Hence,

$$\ln Z_{rot} = \ln\left(\frac{8\pi I k_B}{h^2}\right) + \ln T$$

For $T >> \theta_{rot}$, the mean energy for rotational motion of a molecule is given by

$$U_{rot} = Nk_B T^2 \left(\frac{\partial \ln Z_{rot}}{\partial T}\right)_{V,N} = \frac{Nk_B T^2}{T} = Nk_B T \tag{14.38}$$

and

$$\frac{(C_V)_{rot}}{R} = \frac{d}{dT} U_{rot} = 1 \tag{14.39a}$$

A somewhat more accurate expression for rotational contribution to heat capacity is obtained by using Euler-Maclaurin formula in evaluating the integral contained in Eq. (14.37). We will just quote the result:

$$\frac{(C_V)_{rot}}{R} = 1 + \frac{1}{45}\left(\frac{\theta_{rot}}{T}\right)^2 + \cdots \tag{14.39b}$$

You will note that as $T \to \infty, (C_V)_{rot} \to R$.

Since $(C_V)_{rot}$ must approach zero as $T \to 0$, Eq. (14.39b) suggests that $(C_V)_{rot}$ versus T curve should show a maximum.

Low Temperature Limit

For low temperatures, the series in Eq. (14.35b) can be used directly to calculate $(C_V)_{rot}$. To do so, we note that

$$\frac{d Z_{rot}}{dT} = \left(\frac{d Z_{rot}}{T^2}\right)\left[6 \exp\left(-\frac{2\theta_{rot}}{T}\right) + 30 \exp\left(-\frac{6\theta_{rot}}{T}\right) + \cdots\right]$$

so that

$$\frac{1}{Z_{rot}} \frac{d Z_{rot}}{dT} = \frac{d}{dT} \ln Z_{rot} = \frac{\theta_{rot}}{T^2} \left[\frac{6 \exp\left(-\frac{2\theta_{rot}}{T}\right) + 30 \exp\left(-\frac{6\theta_{rot}}{T}\right) + \cdots}{1 + 3 \exp\left(-\frac{2\theta_{rot}}{T}\right) + 5 \exp\left(-\frac{6\theta_{rot}}{T}\right) + \cdots}\right]$$

Hence, mean rotational energy at low temperatures is

$$U_{rot} = Nk_B T^2 \left(\frac{1}{Z_{rot}} \frac{d Z_{rot}}{dT} \right)$$

$$= \frac{6Nk_B \theta_{rot} \left[e^{-\frac{2\theta_{rot}}{T}} + 5e^{-\frac{2\theta_{rot}}{T}} + \cdots \right]}{1 + 3e^{-\frac{2\theta_{rot}}{T}} + 5e^{-\frac{2\theta_{rot}}{T}} + \cdots}$$

$$= 6Nk_B \theta_{rot} e^{-\frac{2\theta_{rot}}{T}} \qquad (14.40)$$

Hence,

$$\frac{(C_V)_{rot}}{R} = 12 \left(\frac{\theta_{rot}}{T} \right)^2 e^{-\frac{2\theta_{rot}}{T}} \qquad (14.41)$$

Vibrational Partition Function

The vibrational partition function can be written as

$$Z_{vib} = \sum_n e^{-\beta \epsilon_n} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})}$$

$$= e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}$$

Since

$$\sum_{n=0}^{\infty} e^{-nx} = 1 + e^{-x} + e^{-2x} + \cdots\cdots = \frac{1}{1 - e^{-x}}$$

we find that

$$Z_{vib} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} = e^{-\frac{\theta_{vib}}{2T}} \left(1 - e^{-\frac{\theta_{vib}}{T}} \right)^{-1} \qquad (14.42)$$

where $\theta_{vib} = \frac{\hbar\omega}{k_B}$ defines the characteristic vibrational temperature. For an HCL molecule, $\theta_{vib} = 4130$K, whereas for H_2, $\theta_{vib} = 6140$K. This show that vibrational states of diatomic molecules are not excited around room temperature.

We now extend this discussion for the particular case of hydrogen.

14.4.2 Heat Capacity of Hydrogen Gas

The heat capacity of hydrogen is found to be less than $\frac{5R}{2}$ even at room temperature. Eucken investigated temperature dependence of C_V at low temperatures. He found that its value gradually falls down to $\frac{3R}{2}$ at about 60K. The observed variation of specific heat of hydrogen with temperature is shown in Fig. 14.3. This suggests a departure from the theoretical predictions.

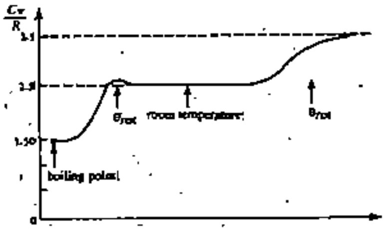


Fig. 14.3: Temperature variation of C_V for hydrogen

Ehrenfest attempted a general explanation of these curves by including the contribution of rotational motion. But he failed to explain the observed behaviour. Then, Hori carried out a complete rotational analysis of Lyman band of hydrogen. He found that when he substituted $I = 0.467 \times 10^{-40}$ g cm^{-2} in the expression for rotational partition function, he was unable to explain the observed curves. This anomaly was successfully resolved by Denison. He pointed out that the contribution of nuclear spin to the partition function should also be taken into account. We know that hydrogen nuclei have spin 1/2. So in the hydrogen molecule, the two nuclei may have their spins either parallel or anti-parallel. And the resultant spin is either one or zero. Thus, the hydrogen gas should be regarded as consisting of two varieties of hydrogen: (i) an **ortho-form** for which $J = 1$ and (ii) a **para-form** for which $J = 0$. The statistical weights of ortho–, and para–forms of hydrogen are 3 and 1, respectively. That is, the hydrogen gas is a mixture of two distinct gases in metastable equilibrium and their relative proportions do not alter during experimentation.

It can be shown from Pauli's exclusion principle that the ortho-molecules can exist only in the odd-valued ($J = 1, 3, 5, \ldots$) quantum states while the para-molecules can exist only in the even-valued ($J = 0, 2, 4, \ldots$.) quantum states. So we have to consider two different rotational partition functions (for ortho– and para–hydrogens). These are given by

$$(Z_{rot})_{ortho} = \sum_{J=1,3,5\cdots}(2J+1)\, e^{-J(J+1)\frac{\theta_{rot}}{T}}$$

$$= 3e^{-2\frac{\theta_{rot}}{T}} + 7e^{-12\frac{\theta_{rot}}{T}} + 11e^{-30\frac{\theta_{rot}}{T}} + \cdots$$

and

$$(Z_{rot})_{para} = \sum_{J=0,2,4\cdots}(2J+1)\, e^{-J(J+1)\frac{\theta_{rot}}{T}}$$

$$= 1 + 5e^{-6\frac{\theta_{rot}}{T}} + 9e^{-20\frac{\theta_{rot}}{T}} + \cdots \qquad (14.44)$$

We know that at room temperature, the proportion of ortho-molecules to para-molecules is 3:1. But as temperature decreases, the equilibrium proportion of para-molecules increases gradually. It becomes nearly 100% at 20K. And even at lower temperatures, one generally has a non-equilibrium mixture of ortho – and para – molecules in the ratio 3:1. Thus, we must define

$$(C_V)_{rot} = \frac{3}{4}(C_V)_{ortho} + \frac{1}{4}(C_V)_{para}$$

We know that

$$<E> = Nk_B T^2\left(\frac{\partial \ln Z}{\partial T}\right)_{V,N}$$

and

$$C_V = \frac{\partial <E>}{\partial T} = \frac{\partial}{\partial T}\left(Nk_B T^2 \frac{\partial \ln Z}{\partial T}\right)$$

Thus,

$$(C_V)_{para} = \frac{\partial}{\partial T}\left[Nk_B T^2 \frac{\partial(\ln Z_{rot})_{para}}{\partial T}\right] \qquad (14.45)$$

and

$$(C_V)_{ortho} = \frac{\partial}{\partial T}\left[Nk_B T^2 \frac{\partial(\ln Z_{rot})_{ortho}}{\partial T}\right] \qquad (14.46)$$

The calculated values of $(C_V)_{para}$, $(C_V)_{ortho}$ and $(C_V)_{rot}$ are shown in Fig. 14.4 by curves (a), (b) and (c) respectively. The curve for $(C_V)_{rot}$ agrees favourably with the experimental observations.

Finally, we look at the contribution from the vibrational degrees of freedom. From Eq. (14.42), we have

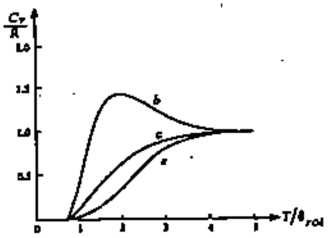


Fig. 14.4: Temperature variation of $(C_V)_{para}$, $(C_V)_{ortho}$ and $(C_V)_{rot}$

$$U_{vib} = N_A k_B T^2 \frac{\partial}{\partial T}(\ln Z_{vib})$$

$$= R\,\theta_{vib}\left[\frac{1}{2} + \frac{1}{\exp\left(\frac{\theta_{vib}}{T}\right) - 1}\right]$$

Hence,

$$(C_V)_{vib} = \left(\frac{\partial U}{\partial T}\right)_V = R\left(\frac{\theta_{vib}}{T}\right)^2 \frac{\exp\left(\frac{\theta_{vib}}{T}\right)}{\left[e^{\frac{\theta_{vib}}{T}} - 1\right]^2}$$

$$= R\, f\left(\frac{\theta_{vib}}{T}\right) \tag{14.47a}$$

where

$$f\left(\frac{\theta_{vib}}{T}\right) = \left(\frac{\theta_{vib}}{T}\right)^2 \frac{\exp\left(\frac{\theta_{vib}}{T}\right)}{\left[\exp\left(\frac{\theta_{vib}}{T}\right) - 1\right]^2} \tag{14.47b}$$

For $T >> \frac{\theta_{vib}}{T}$, $f\left(\frac{\theta_{vib}}{T}\right) \longrightarrow 1$ and we recover the classical result. Similar considerations apply to polyatomic gases but the discussion is more involved. We will not go into these details.

14.5 SUMMARY

- The partition function of an ideal monoatomic gas is given by

$$Z_N = \frac{V^N}{h^{3N}}(2\pi m k_B T)^{3N/2}$$

The internal energy $U = \frac{3}{2}RT$ and

heat capacity $C_V = \frac{3}{2}R$

- The classical expression for the entropy of an ideal monoatomic gas is

$$S = Nk_B \ \ln\left[\frac{V(2\pi m k_B T)^{3/2}}{h^3}\ e^{3/2}\right]$$

- The **Sackur-tetrode formula** accounts for indistinguishability of molecules and is given by

$$S = Nk_B \ln\left[\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} e^{5/2}\right]$$

- The rotational partition function

$$Z_{rot} = \frac{T}{\theta_{rot}} \qquad T >> \theta_{rot}$$

$$= 1 + 3e^{-2\left(\frac{\theta_{rot}}{T}\right)} + 5e^{-6\left(\frac{\theta_{rot}}{T}\right)} + \cdots \qquad T << \theta_{rot}$$

where $\theta_{rot} = \dfrac{h^2}{8\pi k_B I}$

- The vibrational partition function

$$Z_{vib} = \frac{1}{2\sinh\left(\frac{\theta_{vib}}{2T}\right)}$$

where $\theta_{vib} = \dfrac{\hbar\omega}{k_B}$.

- For hydrogen, the rotational heat capacity at constant volume

$$(C_V)_{rot} = \frac{3}{4}(C_V)_{ortho} + \frac{1}{4}(C_V)_{para}$$

where ortho refers to the state with parallel nuclear spins and para refers to the state with anti-parallel nuclear-spins.

14.6 TERMINAL QUESTIONS

1. Consider a system of N classical linear harmonic oscillators. Calculate (i) the partition function, (ii) the free energy, (iii) entropy, (iv) C_V and Cp.
2. Consider a classical ideal gas consisting of N particles. The energy ε of a particles is given by $\varepsilon = cp$, where c is a constant and p is the magnitude of the momentum. Calculate (i) the partition function of the system, (ii) internal energy, and (iii) C_V.
3. Consider a classical linear oscillator with

$$\varepsilon = \frac{p^2}{2m} + bx^4,$$

where b is a constant. Assuming that the oscillator is in thermal equilibrium with a heat reservoir at temperature T, calculate (i) the mean kinetic energy, (ii) the mean potential energy, and (iii) C_V for an assembly of N such oscillators.

4. Prove Eq. (14.39b).

14.7 SOLUTIONS AND ANSWERS

SAQs

1. We have

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$= Nk_B \ln\left[\frac{V}{h^3}(2\pi m k_B T)^{3/2}\right] + Nk_B T\left(\frac{3}{2T}\right)$$

$$= Nk_B \ln\left[\frac{V}{h^3}(2\pi m k_B T)^{3/2} e^{3/2}\right]$$

Similarly,

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_B T}{V}$$

2. $$\ln W = -\sum_i \ln n_i! = -\sum_i (n_i \ln n_i - n_i)$$

$$= N - \sum_i n_i \ln n_i \qquad \text{(i)}$$

From Eqs. (13.26) and (13.29), we have

$$n_i = \frac{N}{Z} e^{-\beta\varepsilon_i} \qquad \text{(ii)}$$

Substitution into (ii) yield

$$\ln W = N - \frac{N}{Z}\sum_i e^{-\beta\varepsilon_i}[\ln N - \ln Z - \beta\varepsilon_i)$$

$$= N - N\ln N + N\ln Z + \beta U$$

Therefore,

$$S = k_B \ln W = Nk_B \ln Z + k_B \beta U + N(1 - \ln N)k_B \qquad \text{(iii)}$$

It differs from Eq. (14.20) by the factor $N(1 - \ln N)\, k_B$. In other words,

$$(Z_N)_{corrected} = \frac{Z_N}{N!} \qquad \text{(iv)}$$

3. We have

$$S_1 = N_1 k_B \left[\ln\left(\frac{V_1}{N_1}\right) + \frac{3}{2}\ln T + \sigma_0\right]$$

$$S_2 = N_2 k_B \left[\ln\left(\frac{V_2}{N_2}\right) + \frac{3}{2}\ln T + \sigma_0\right]$$

$$\therefore\ S_1 + S_2 = S_i = N_1 k_B \ln\left(\frac{V_1}{N_1}\right) + N_2 k_B \ln\left(\frac{V_2}{N_2}\right) + \frac{3}{2}Nk_B \ln T + Nk_B\sigma_0$$

On removing the partition, there will be N particles in space V. So final entropy of the system is

$$S_f = Nk_B \left[\ln\left(\frac{V}{N}\right) + \sigma_0\right]$$

Hence, change in entropy $S_f - S_i$ is

$$\Delta S = k_B(N_1 + N_2)\ln\left(\frac{V_1 + V_2}{N_1 + N_2}\right) - N_1 k_B \ln\left(\frac{V_1}{N_1}\right) - N_2 k_B \ln\left(\frac{V_2}{N_2}\right)$$

The densities of the two samples must be equal if the gases are at the same temperature and pressure:

$$\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N}{V} = \rho$$

Thus, we have

$$\Delta S = k_B\left[N\ln\left(\frac{1}{\rho}\right) - N_1\ln\left(\frac{1}{\rho}\right) - N_2\ln\left(\frac{1}{\rho}\right)\right]$$

$$= 0$$

Thus, indistinguishability of particles of an ideal monoatomic gas is the key to the resolution of Gibbs paradox.

4. For a system with f degrees of freedom

$$U = \frac{f}{2} N k_B T = \frac{f}{2} RT$$

$$\therefore \; C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{f}{2} R, \text{ and } C_p = C_V + R = \frac{f+2}{2} R$$

Hence,

$$\gamma = \frac{C_p}{C_V} = \frac{f+2}{f} = 1 + \frac{2}{f}$$

Clearly γ decreases as f increases.

TQs

1. The partition function is given by

$$Z = \frac{1}{\beta \hbar \omega}$$

Assuming the oscillators to be indistinguishable, we have

$$Z_N = (\beta \hbar \omega)^{-N}$$

The free energy $F = -N k_B T \ln Z = N k_B T \ln \left(\frac{\hbar \omega}{k_B T}\right)$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = N k_B \left[-\ln\left(\frac{\hbar\omega}{k_B T}\right) + 1 \right] = N k_B \left[\ln\left(\frac{k_B T}{\hbar\omega}\right) + 1 \right]$$

$$U = F + TS = N k_B T$$

$$C_V = N k_B, \qquad p = -\left(\frac{\partial F}{\partial V}\right)_T = 0$$

$$H = U + pV = N k_B T, \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p = N k_B$$

2. We have

$$Z = \frac{V}{h^3} \iiint e^{-\beta c p} \, dp_x \, dp_y \, dp_z$$

In terms of spherical polar coordinates, we can rewrite the volume element as

$$Z = \frac{V}{h^3} 4\pi \int_0^\infty e^{-\beta c p} p^2 \, dp = \frac{8\pi V (k_B T)^3}{(ch)^3}$$

Hence,

$$Z_N = \left[\frac{8\pi V (k_B T)^3}{(ch)^3} \right]^N$$

$$\therefore \; U = N k_B T^2 \frac{\partial}{\partial T} (\ln Z) = N k_B T^2 \frac{\partial}{\partial T} \left[\ln\left(\frac{8\pi V k_B^3}{(ch)^3}\right) + 3 \ln T \right]$$

$$= 3 N k_B T$$

and

$$C_V = 3 N k_B$$

3. We have

i) Mean kinetic energy

$$\bar{E} = \frac{\int e^{-\beta p^2/2m}\left(\frac{p^2}{2m}\right)dp}{\int e^{-\beta p^2/2m}\,dp} = -\frac{\partial}{\partial\beta}\ln\left(\int e^{-\beta p^2/2m}\,dp\right)$$

We have

$$I = \int_{-\infty}^{\infty} e^{-\beta p^2/2m}\,dp$$

By putting $\frac{\beta p^2}{2m} = x$, we find that

$$dp = \sqrt{\frac{m}{2\beta}}\,\frac{1}{\sqrt{x}}\,dx$$

so that

$$I = 2\int_0^{\infty} e^{-x}\frac{1}{\sqrt{x}}\sqrt{\frac{m}{2\beta}}\,dx$$

or

$$I = \sqrt{\frac{2m\pi}{\beta}}$$

Hence,

$$\text{mean kinetic energy} = -\frac{1}{2}\frac{\partial}{\partial\beta}\,[\ln\,2m\pi - \ln\beta] = \frac{1}{2\beta} = \frac{k_B T}{2}$$

$$\overline{PE} = \frac{\int e^{-\beta bx^4}(bx^4)\,dx}{\int e^{-\beta bx^4}\,dx} = -\frac{\partial}{\partial\beta}\ln\left(\int e^{-\beta bx^4}\,dx\right)$$

$$= \frac{k_B T}{4}$$

Total mean energy for N oscillators

$$U = \left(\frac{1}{2}k_B T + \frac{1}{4}k_B T\right)N = \frac{3}{4}Nk_B T$$

and $C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{4}Nk_B$

4. We have

$$f(x) = (2x+1)\exp\left(-\frac{x(x+1)\theta_{rot}}{T}\right)$$

so that

$$\frac{1}{2}f(0) = \frac{1}{2}$$

Similarly,

$$f'(x) = 2\exp\left(-\frac{x(x+1)\theta_{rot}}{T}\right) + (2x+1)\exp\left(-\frac{x(x+1)\theta_{rot}}{T}\right)\times \left(-\frac{\theta_{rot}}{T}\right)(2x+1)$$

- point out the inadequacies of the classical theory
- derive expressions for the Bose-Einstein and Fermi-Dirac distribution functions
- apply Bose-Einstein statistics to an assembly of photons
- explain the behaviour of liquid helium at low temperatures
- explain the concept of zero point energy
- explain temperature dependence of heat capacity of electrons, and
- predict thermodynamic functions of degenerate B.E. and F.D. gases.

15.2 TOWARDS QUANTUM STATISTICS

In classical physics we postulate that it is possible to determine the position and momentum coordinates of a gaseous molecule/atom simultaneously as precisely as we like. All that we have to do is to follow its trajectory as it moves in space. This means that these particles are distinguishable and can be labelled. But this is not true. You will recall that Heisenberg's uncertainty principle forbids determination of the position (q) and the momentum (p) of a particle simultaneously with infinite precision. If the uncertainties in the measurements of q and p are Δq and Δp, respectively, we have

$$\Delta q \, \Delta p \geq \frac{h}{4\pi} \tag{15.1}$$

where h (= 6.63×10^{-34} Js) is Planck's constant. That is, the product $\Delta q \Delta p$ cannot be made less than $h/4\pi$. So it does not make much sense to talk about the trajectory of a particle. Moreover, the task of labelling particles is just impossible and when we study the behaviour of an assembly of identical particles statistically, we should treat it as a collection of **indistinguishable** particles. It is important to remark here that though Heisenberg enunciated this famous principle in 1924, the rumblings about the health of the classical theory became too loud to be ignored by 1900 itself. Lord Kelvin spoke about two dark clouds on the horizon of classical physics; the heat capacity of solids and the black-body radiation. This shook the edifice of classical physics to its very foundations. You may now like to know about these in some detail. The paragraphs that follow are devoted to these two aspects.

Heat Capacity of Solids

You would recall from your school physics curriculum that solids behave as a collection of independent harmonic oscillators, and energy associated with them is equal to $3N_A k_B T$, where N_A is Avogadro's number. Hence, heat capacity at constant volume is constant, equal to $3R$ regardless of the substance:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3R = 24.9\,\mathrm{J\,mol^{-1}\,K^{-1}} \tag{15.2}$$

This now famous **Dulong and Petit's law** does not exhibit what experiments reveal about temperature variation of heat capacity. The deviations from this law, particularly in the low temperature region are striking, as shown in Fig. 15.1. As T decreases below room temperature, C_V also decreases and becomes zero at absolute zero.

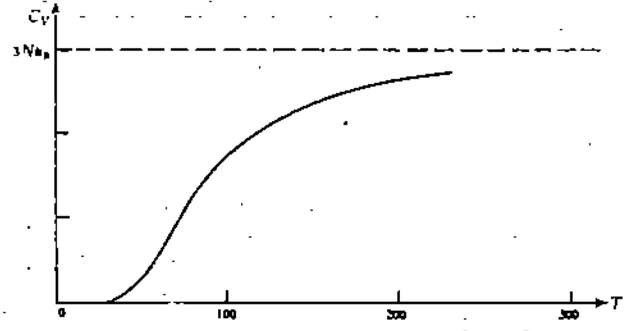


Fig. 15.1: Temperature variation of constant volume heat capacity of a solid

A qualitative theoretical explanation was provided by Einstein, using Planck's ideas on quantisation of energy. You will learn these details in your PHE-11 course on Modern Physics. The key to Einstein's success was that he discarded the law of equipartition of energy. The mean energy of a classical oscillator is given by $\overline{\varepsilon} = k_B T$. In the quantum theory, we have

$$\overline{\varepsilon} = \left[\frac{1}{2} + \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} \right] \hbar\omega \tag{15.3}$$

where $\hbar = h / 2\pi$.

For a system of N_A oscillators vibrating with Einstein frequency ω_E, this gives

$$U = 3 N_A \hbar \omega_E \left[\frac{1}{2} + \frac{1}{\exp(\hbar\omega_E / k_B T) - 1} \right] \tag{15.4}$$

so that

$$C_V = \frac{3N_A\, \hbar\omega_E e^{\hbar\omega_E/k_B T}}{\left[\exp(\hbar\omega_E / k_B T) - 1\right]^2} \left(\frac{\hbar\omega_E}{k_B T^2} \right)$$

$$= 3R \left(\frac{\hbar\omega_E}{k_B T} \right)^2 \frac{e^{\hbar\omega_E/k_B T}}{\left[e^{\hbar\omega_E/k_B T} - 1\right]^2}$$

$$= 3R \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{\left[e^{\theta_E/T} - 1\right]^2} \tag{15.5}$$

where we have introduced Einstein temperature $\theta_E = \hbar\omega_E / k_B$. For copper, a plot of this equation is shown in Fig. 15.2. You will note that this relation reproduces all the general features of the observed curve at least qualitatively. However, there are disagreements in details, particularly near absolute zero.

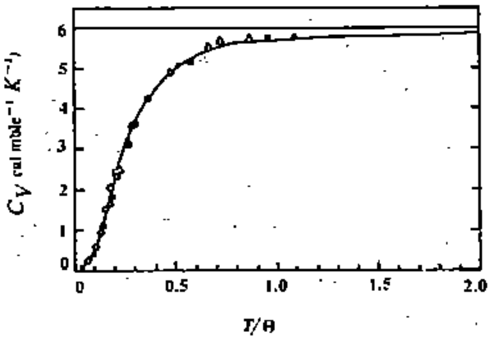


Fig. 15.2: Plot of Eq. (15.5) for copper

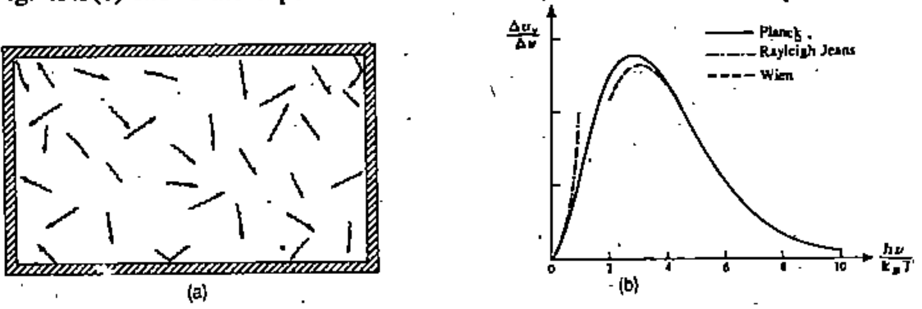
Debye (1912) subsequently refined Einstein's theory and obtained an excellent agreement with experiments.

The heat capacity of metals also posed an interesting puzzle, in fact a challenge, to the classical physicists. You know that every metal contains free electrons. If we assume that these electrons constitute a monoatomic gas, they should contribute an amount $\frac{3}{2}R$ to C_V. Hence, the heat capacity of a metal should be $3R + \frac{3}{2}R = \frac{9}{2}R$. However we experimentally find that metals obey the Dulong-Petit's law as good as do insulators. This raises the question: Why do electrons not contribute to thermal processes? The fact is that we should not analyse this problem on classical arguments — electrons obey Fermi-Dirac statistics. A satisfactory explanation was given by the German physicist Sommerfeld in 1928 on the basis of quantum statistics.

The problem of black-body radiation

We now consider the commonplace phenomenon of black-body radiation. It deserves a unique place in physics because it gave birth to the quantum theory. You know that when a body is heated, it emits electromagnetic waves (from its surface) in all directions over a broad range of frequencies. The spectrum of radiated frequencies from 0 to ω peaks at a frequency which is proportional to the absolute temperature of the body. Suppose that such thermal radiation is contained inside a hollow cavity whose walls are opaque to radiation and maintained at a constant temperature. The radiation in the interior must, therefore, have exactly the same spectral distribution as that of black-body radiation. In other words, the energy distribution over various wavelengths becomes a function of temperature, independent of the shape and size of the cavity (Fig. 15.3a). A small opening in one of the walls enables us to study experimentally the emerging radiation. Such experiments were carried out by a large number of investigators in the period 1895-1900. We may make particular mention of Rubens and Kurlbaum. The results of these experiments established beyond doubt the inability of classical theories to reproduce experimental curves.

Let $u_\nu\, d\nu$ denote the energy density (energy per unit volume) between ν and $\nu + d\nu$. Fig. 15.3(b) shows the experimental curves for u_ν at two different temperatures.



(a) (b)

Fig. 15.3: (a) The electromagnetic radiation inside an oven is treated as a photon gas in equilibrium with the oven walls (b) Spectral distribution of energy in black-body radiation.

Lord Rayleigh studied the problem using ideas of classical physics and obtained an expression for $u_\nu\, d\nu$. Jeans discovered a numerical error in his formula and subsequently corrected it. This so-called **Rayleigh-Jeans** law is of the form

$$u_\nu\, d\nu == \frac{8\pi\nu^2}{c^3} d\nu \bar{\varepsilon} \tag{15.6a}$$

where $\bar{\varepsilon}$ is the mean energy of an oscillator. Lord Rayleigh and Sir James Jeans used the law of equipartition of energy and used $\bar{\varepsilon} = k_B T$. Using this result in the above equation, we obtain

$$u_\nu\, d\nu = \frac{8\pi\nu^2}{c^3} k_B\, T\, d\nu \tag{15.6b}$$

For small values of ν, it reproduces the experimental curve very well. However, for $\nu \to \infty$, Eq. (15.6b) has a serious flaw; it predicts that the total energy density will be infinite:

$$u = \int_0^\infty u_\nu\, d\nu = \infty \tag{15.7}$$

This unphysical situation was termed the **ultraviolet catastrophe** by P. Ehrenfest. Wien carried out thermodynamic analysis of black body radiation spectrum and showed that u_ν is of the form

$$u_\nu\, d\nu = \nu^3 F\left(\frac{\nu}{T}\right) \tag{15.8}$$

You can easily verify that this result gives a finite u which varies as T^4, in accordance with Stefan's law. Moreover, the frequency at which u_ν is maximum is directly proportional to T.

SAQ 1

Using $F\left(\frac{\nu}{T}\right) = e^{-c_2\nu/T}$, where c_2 is a constant, calculate u from Eq. (15.8).

However, Wien's law fails at small value of ν. It means that something is really wrong with classical theory. A look at Fig. 15.3 will convince you that the classical theories fall between two stools and the two ends of the spectrum remain disjoint.

It was at this stage that Max Planck proposed a remarkable idea. He argued that energy is not a continuous variable; it is discrete, in fact **quantized**. That is, emission and absorption of energy takes place in integral multiples of $h\nu$, called **quanta**. It means that each oscillator can possess only discrete energies; $0, h\nu, 2h\nu \cdots$ so that

$$\varepsilon_n = nh\nu \qquad (n = 0,1,2,3,\ldots) \tag{15.9a}$$

To calculate the number of oscillators of energy ε_n at a temperature T, Planck assumed that Boltzmann statistics holds good. Then, it readily follows that

$$N_n \alpha\, e^{-\varepsilon_n/k_B T} \tag{15.9b}$$

Hence, the mean energy of an oscillator is given by

$$\bar{\varepsilon} = \frac{\sum N_n \bar{\varepsilon}_n}{\sum N_n} = \frac{\sum\limits_{n=0}^{\infty} nh\nu\, e^{-nh\nu/k_B T}}{\sum\limits_{n=0}^{\infty} e^{-nh\nu/k_B T}} \tag{15.10}$$

You can easily perform these sums to obtain

$$\bar{\varepsilon} = \frac{h\nu}{\exp\left(\dfrac{h\nu}{k_B T}\right) - 1} \tag{15.11}$$

SAQ 2

Verify Eq. (15.11).

On combining Eqs. (15.6a) and (15.11) we obtain

$$u_\nu\, d\nu = \frac{8\pi h\nu^3}{c^3} \frac{d\nu}{\exp\left(\dfrac{h\nu}{k_B T}\right) - 1} \tag{15.12}$$

This is Planck's law of radiation. He announced it to the German Physical Society on 14th December, 1900. It reproduces the experimental curves of Fig. 15.3 beautifully. We will discuss important aspects of this law in Sec. 15.3.

Notwithstanding the enormous success of his new law of radiation, Planck was quite uneasy about his quantum hypothesis. He himself took quite some time to appreciate the significance of his work, which had no counterpart in classical physics. It is interesting to know what Jeans remarked while comparing his theory with that of Planck:

> "The methods of both are in effect the methods of statistical mechanics and the theorem of equipartition of energy but I carry the method further than Planck, since Planck stops short of the step of putting $h = 0$. Of course, I am aware that Planck's law is in good agreement with experiment if h is given a value other than zero...."

The resolution of Gibbs paradox led us to conclude that identical particles have to be treated as indistinguishable. Heisenberg's uncertainty principle tells us that the concept of the trajectory of a particle is meaningless. Hence, particles cannot be labelled. The detailed consequences of this concept can be understood fully only after a thorough understanding of the principles of quantum mechanics. You will know these in PHE-11 course on Modern Physics. For the present it is sufficient to note that:

a) A simultaneous determination of a position and momentum cannot be accomplished to infinite precision. Instead, uncertainities Δp and Δq in these quantities are subject to $\Delta q\ \Delta p \sim h$. that is, **the volume of a cell in phase space cannot be arbitrarily small.** In fact, the smallest volume of a cell must now be taken as h^3. A still finer subdivision of the phase space is not allowed.

b) According to Planck's hypothesis, energy is quantized, it is not a continuous variable and can take only discrete values. This has an important consequence in that **all integrals appearing in the theory have to be replaced by sums.** This is called the **diffraction effect.** Nevertheless in many situations we calculate the sums by replacing them by suitable integrals. Some examples of this technique will appear later in this unit.

c) The basic feature of quantum statistics is the **indistinguishability of identical particles.** In other words, permutation of particles does not lead to a different state and should not be counted as such. This has profound consequences. All known elementary particles can be classified into two categories on the basis of their spin. You will recall from your school science curriculum that spin is the intrinsic angular momentum of an elementary particle, quantized in units of $\hbar$. Particles having integral spin ($0, \hbar, \hbar 2, \ldots\ldots$) obey the Bose-Einstein statistics and are termed **bosons.** This applies to photons, pions, ^{4}He, etc. The number of bosons that can occupy a given quantum-state has no restriction. Bosons love company; they are gregarious!

Particles with half-integral spin $\frac{\hbar}{2}, \frac{3\hbar}{2}, \ldots.$ are termed **fermions** and obey the Fermi-Dirac statistics. Particles like electrons, protons, neutrons, muons, etc. belong to this category. The number of fermions in a quantum-state is determined by Pauli's exclusion principle. For example, there cannot be more than two electrons in the same quantum state. You are familiar with the implications of this principle in electronic configuration of elements in the Periodic Table. Fermions tend to avoid one another! In general, the number of fermions in a quantum state is limited to $(2S + 1)$, where $S\hbar$ is the spin of the fermion.

Pauli's exclusion principle states that two particles having all the four identical quantum numbers cannot occupy the same state.

These features constitute the **symmetry effects.** You will learn in your third level courses that bosons and fermions are characterized respectively by symmetric wave-functions (which do not change even if the particles are permuted) and antisymmetric wave-functions (which change sign on a permutation). (The limit $h \rightarrow 0$ is usually called the classical limit.)

You should now test your understanding by solving the following SAQ.

SAQ 3

Helium has two isotopes, viz., ^{3}He and ^{4}He. Classify these as fermions and bosons. Justify your conclusion.

To illustrate the consequences of indistinguishability, let us consider the following simple example.

Suppose we have a system consisting of only two particles A and B and three quantum states, $i = 1, 2, 3$. According to classical statistics, these can be distributed in nine ways. These are tabulated below:

States → Distribution ↓	1	2	3
1	AB	–	–
2	–	AB	-
3	–	–	AB
4	A	B	–
5	B	A	–
6	A	–	B
7	B	–	A
8	–	A	B
9	–	B	A

That is, we have 3^2 possibilities. It is straightforward to show that if we have N_i particles to be distributed among g_i states, the total number of ways is $g_i^{N_i}$.

In the case of quantum statistics, we cannot distinguish A from B. However, in B.E distribution, there is no restriction on the number of particles that can occupy a given state. So there are only six possibilities:

States → Distribution ↓	1	2	3
1	AA	–	–
2	–	AA	–
3	–	–	AA
4	A	A	–
5	A	–	A
6	–	A	A

In general, the result is $\binom{N_i + g_i - 1}{N_i}$. This can be proved in several ways. We shall do it using a simple, yet interesting method. (Another way to arrive at the same result is the subject of TQ1.)

Suppose we want to distribute N_i indistinguishable particles among g_i cells. Imagine the N_i - particles, denoted by stars and arranged in a line, as shown in Fig. 15.4a. The cell boundaries may be represented by $(g_i + 1)$ vertical bars. For example, when $g_i = 5$ and $N_i = 10$, a typical distribution is shown in Fig. 15. 4b.

...* * * * * * * * * *.... |*|* * *||* * * *|* *|

(a)   (b)

Fig. 15.4: (a) N_i particles arranged along a line. (b) A possible distribution for $N_i = 10$ and $g_i = 5$.

There is one particle in the first cell, three in the second, none in the third, four in the fourth, and two in the fifth. The total number of stars and bars is $(g_i + 1 + N_i)$. Since the two end positions in such a diagram would always be occupied by bars, the required number of distributions Ω is equal to the number of ways of choosing N_i positions for the particles from $(N_i + g_i + 1\text{-}2)$, i.e. $(N_i + g_i - 1)$ positions. Hence

$$\Omega = \binom{N_i + g_i - 1}{N_i} \tag{15.13}$$

If we now put $N_i = 2$ and $g_i = 3$, we get $\Omega = \binom{4}{2} = 6$, which reproduces the earlier result.

In the case of Fermi-Dirac statistics, there can, at best, be only one particle per cell and we necessarily have $n_i < g_i$. Of course, for particles of spin $s\hbar$, the number of possibilities have to be multiplied by the factor $(2s + 1)$. For the above-said system, we have just three possibilities as shown below:

States → Distribution ↓	1	2	3
1	A	A	–
2	A	–	A
3	–	A	A

If we now define a parameter r as

$$r = \frac{\text{Probability that two particles are found in the same state}}{\text{Probability that the particles are found in different states}}$$

we have

$$r_{\mathrm{MB}} = \frac{3}{9} = \frac{1}{3},\ r_{\mathrm{BE}} = \frac{3}{6} = \frac{1}{2}, \text{and } r_{\mathrm{FD}} = 0$$

These values of r illustrate a striking difference between these three statistics. You should note that $r_{\mathrm{FD}} = 0$ because of the Pauli's principle. On the other hand, r_{BE} is greater than r_{MB}. That is, bosons have a greater tendency to bunch together like classical particles. This explains why the condition for realising a laser in actual practice is statistically favourable.

We may now conclude that a remarkable feature of quantum statistics is the presence of correlations even in a non-interacting system. We are now equipped with the necessary tools for a detailed discussion of quantum statistics. We begin by discussing an ideal Bose-Einstein gas.

15.3 IDEAL BOSE-EINSTEIN GAS

We shall first derive the Bose-Einstein distribution law. As we show, this paves the way for Bose's derivation of Planck's law. In fact, when Planck was not convinced of the physical basis of his derivation, Bose proposed the correct method for treating a system on the basis of quantum statistics. Einstein extended his ideas to the case of material particles obeying Bose statistics. During his investigations, Einstein came to the remarkable conclusion that Bose-Einstein gas can tend to a highly ordered state. This phenomenon, known as **Bose-Einstein condensation**, was invoked by F. London to explain the superfluidity exhibited by liquid ^{4}He.

15.3.1 Bose-Einstein Distribution Function

Consider a system of N non-interacting bosons occupying a volume V and sharing a given energy U. In the limit of large V, the energy levels of the system are very closely spaced. Hence, we can bracket the energy levels into groups, which may be called the energy cells. This is known schematically in Fig. 15.5.

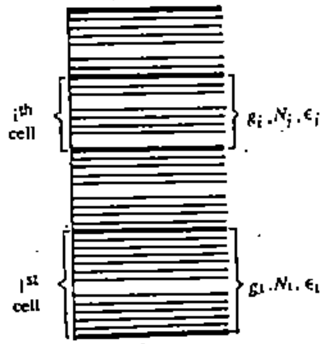


Fig.15.5: Energy levels of a system bracketed into cells

We assume, without any loss of generality, that the number of levels in the ith cell, g_i, is very much greater than one ($g_i >> 1$). It is still reasonable to talk about the energy of the levels in the ith cell as ε_i, since they are lying very close to each other.

Let Ω_i denote the number of ways in which N_i particles can be distributed amongst the g_i levels of the ith cell. This number is already available to us from Eq. (15.13). We have

$$\Omega_i = \binom{N_i + g_i - 1}{N_i} = \frac{(g_i + N_i - 1)!}{N_i!\,(g_i - 1)!} \tag{15.14}$$

Denoting by $W(N_1, N_2, ..., N_i, ...) = W(\{N_i\})$, the number of ways in which we can put N_1 particles in group g_1, N_2 particles in group g_2, ..., N_i particles in group g_i, we have

$$W(\{N_i\}) = \prod_i \Omega_i = \prod_i \frac{(g_i + N_i - 1)!}{N_i!\,(g_i - 1)!} \tag{15.15}$$

We maximize W subject to the conditions

$$\sum_i N_i = N \tag{15.16a}$$

and

$$\sum_i N_i\ \varepsilon_i = U \tag{15.16b}$$

Then, Eq. (15.15) gives

$$\ln W = \sum_i [\ln\ (g_i + N_i - 1)! - \ln\ (g_i - 1)! - \ln\ N_i!]$$

Using Stirling's formula, we have

$$\begin{aligned}\ln\ W &= \sum_i [(g_i + N_i - 1)\ \ln\ (g_i + N_i - 1) - (g_i + N_i - 1)\\ &\qquad -(g_i - 1)\ \ln\ (g_i - 1) + (g_i - 1) - N_i\ \ln\ N_i + N_i]\\ &= \sum_i [(g_i + N_i - 1)\ \ln\ (g_i + N_i - 1) - (g_i - 1)\ \ln\ (g_i - 1) - N_i\ \ln\ N_i]\\ &= \sum_i [g_i + N_i)\ \ln\ (g_i + N_i) - g_i\ \ln\ g_i - N_i\ \ln\ N_i]\\ &= \sum_i [g_i + N_i)\ \ln\ (g_i + N_i) - g_i\ \ln\ g_i - N_i\ \ln\ N_i]\end{aligned} \tag{15.17}$$

since N_i and $g_i >> 1$.

The condition for maximum probability is

$$\delta \ln W = 0$$

On combining this with Eq. (15.17), we get

$$\begin{aligned}\delta \ln W = \sum_i [(g_i + N_i)\frac{1}{(g_i + N_i)}\delta N_i + \ln(g_i + N_i)\delta N_i\\ -\delta N_i - \delta N_i \ln N_i] = 0\end{aligned}$$

or

$$\sum_i [\ln(g_i + N_i) - \ln N_i]\delta N_i = 0 \tag{15.18}$$

Since N and U are fixed, we have from Eqs. (15.16a) and (15.16b)

$$\delta N = \sum_i \delta N_i = 0 \tag{15.19a}$$

and

$$\delta U = \sum_i \varepsilon_i\ \delta N_i = 0 \tag{15.19b}$$

Multiplying Eqs. (15.19a) and (15.19b) by α and $-\beta$, respectively, and adding to Eq. (15.18), we obtain

$$\sum_i [\ln\ (g_i + N_i) - \ln\ N_i + \alpha - \beta\varepsilon_i]\ \delta N_i = 0 \tag{15.20}$$

Since the variations δN_i are arbitrary, the coefficient of each term in Eq. (15.20) must vanish. Hence, we have

$$\ln\left(\frac{g_i + N_i}{N_i}\right) = -\alpha + \beta\varepsilon_i$$

or

$$\frac{N_i}{g_i} = \frac{1}{e^{-\alpha+\beta\varepsilon_i} - 1} \tag{15.21}$$

As before, we put e^{α} equal to A. Then, Eq. (15.21) takes the form

$$\frac{N_i}{g_i} = \frac{1}{A^{-1}e^{\beta\varepsilon_i} - 1} \tag{15.22}$$

Yet another way of rewriting Eq. (15.21) is to define a parameter called the **fugacity** as

$$z = e^{-\alpha} = e^{-\beta\mu}, \tag{15.23}$$

where μ is the chemical potential. Eq. (15.22) becomes

$$\frac{N_i}{g_i} = \frac{1}{e^{\beta(\varepsilon_i-\mu)} - 1} \tag{15.24}$$

It we treat energy as a continuous variable, the number of particles with energy ε is given by

$$\frac{N(\varepsilon)}{g(\varepsilon)} = \frac{1}{e^{\beta(\varepsilon-\mu)} - 1} = \frac{1}{A^{-1}e^{\beta\varepsilon} - 1} \tag{15.25}$$

This relation is known as the **Bose-Einstein distribution**. How it differs from the Maxwell-Boltzmann or a Fermi-Dirac distribution ? To discover this you should solve the following SAQ.

SAQ 4

a) In classical statistics, the number of ways in which N_i particles can be distributed among g_i states is $g_i^{N_i}$ Divide this by $N_i!$ and obtain the Maxwell-Boltzmann distribution.

b) Calculate the number of ways in which N_i fermions can be accommodated in g_i cells if $N_i < g_i$.

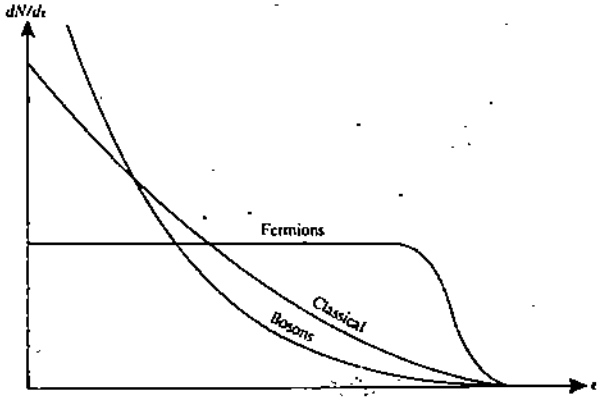


Fig. 15.6: Comparison of BE, FD and MB distributions. Every system is taken at the same temperature and has the same number of particles

A plot of Eq. (15.25) is shown in Fig. 15.6. For comparison, MB and FD distribution functions are also shown. You will note that the distribution of bosons is skewed towards lower energy states. That is, there is larger probability of finding bosons in low level multiply occupied states. On the other hand, fermions are skewed towards higher energy states. We will now illustrate the statistical method of arriving at Planck's law of radiation.

15.3.2 Bose's Derivation of Planck's Law

Indian physicist S.N. Bose gave a very elegant derivation of Planck's law in 1924. He communicated his work to Einstein, who immediately recognised its significance. He translated it into German and got it published. In a sense, this paper marked the birth of quantum statistics.

We consider the equilibrium properties of electromagnetic radiation enclosed in a cavity of volume V at temperature T. From your school physics course, you may recall that the distribution of energy among the various frequencies is independent of the nature of the walls of the container; it is a function of T and V only. We now wish to determine the form of this function. From a quantum mechanical point of view, the radiation in the cavity can be considered as a collection of photons of different frequencies moving with speed of light completely randomly. The photons of the same frequency are indistinguishable. This is a perfect example of a system of non-interacting, indistinguishable particles.

The energy of a photon of frequency ν is taken to be $h\nu$. We should also remember that photons are particles with zero rest mass and spin $\hbar$. Each photon can have two kinds of polarization. These are the two transverse modes; their being no longitudinal photons. In other words, the propagation vector and the polarization vector (giving the direction of polarization of the electric field associated with the photon) are normal to each other. (This is a consequence of the transversality of the electric field, i.e., $\vec{\nabla}.\vec{E} = 0$.)

You would also appreciate the fact that atoms can emit or absorb photons and the total number of photons is not constant. In other words, we have only one constraint, namely U = constant. This essentially means that in Eq. (15.25), we need only one Lagrange multiplier β and $\alpha = 0$ or $A = 1$. Then Eq. (15.25) reduces to

$$\frac{N_\nu}{g_\nu} = \frac{1}{e^{\beta h\nu} - 1} \tag{15.26}$$

Let $g_\nu\, d\nu$ denote the number of quantum states between ν and $\nu + d\nu$. We can derive an expression for this using the principles of quantum mechanics. However, a simple argument can be used to get the result. Let us first calculate $g_\mathbf{p}\, d\mathbf{p}$, the number of quantum states between $\mathbf{p}$ and $\mathbf{p} + d\mathbf{p}$. The volume of phase space occupied by a particle in a box of volume V and with momentum between $\mathbf{p}$ and $\mathbf{p} + d\mathbf{p}$ is $V\, d^3p$. Since $d^3p = p^2 dp\, \sin\theta\, d\theta\, d\phi$, integration over θ and ϕ gives 4π. Since each cell has volume h^3, we have

$$g_\mathbf{p}\, d\mathbf{p} = \frac{4\pi p^2 dp}{h^3} V \tag{15.27}$$

From de Broglie's relation

$$p = \frac{h}{\lambda} = \frac{h\nu}{c}$$

and

$$p^2\, dp = \left(\frac{h}{c}\right)^3 \nu^2\, d\nu$$

Inserting this result in Eq. (15.27), we get

$$g_\nu\, d\nu = \frac{4\pi V}{c^3} \nu^2\, d\nu$$

Since photons can have two kinds of polarization, we have

$$g_\nu\, d\nu = \frac{8\pi V}{c^3} \nu^2\, d\nu$$

so that

$$N_\nu = \frac{8\pi V}{c^3} \frac{\nu^2\, d\nu}{e^{\beta h\nu} - 1} \tag{15.28}$$

Let $E_\nu d\nu$ denote the energy lying in the frequency range ν and $\nu + d\nu$. Combining Eqs. (15.26) and (15.28), we obtain

$$E_\nu\, d\nu = N_\nu\, h\nu\, d\nu = \frac{8\pi h V}{c^3} \frac{\nu^3\, d\nu}{e^{\beta h\nu} - 1}$$

We prefer to speak of energy density rather than total energy. Why? This is because the total energy of photons depends on the size of the oven but the energy density does not. If we let u_ν represent energy density, we have

$$u_\nu \, d\nu = \frac{E_\nu \, d\nu}{V} = \frac{8\pi h}{c^3} \frac{\nu^3 \, d\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} \tag{15.29}$$

It is important to note that Planck had derived the law by combining classical electromagnetic theory and the quantum hypothesis. On the other hand, Bose in a manuscript to Einstein in 1924 treated electromagnetic radiation as a system of indistinguishable particles which have the same properties as particles of light—what we now call **photons**. Subsequent investigations led Einstein to the concept of stimulated emission, which culminated in the development of masers and lasers—devices finding use in medicine, industry, energy production in fusion reactors, and military applications. Before we consider limiting cases of Planck's law you should learn to write it in other equivalent representations. For this you should solve the following SAQ.

SAQ 5

Rewrite Eq. (15.29) in terms of energy. Integrate the resulting expression to compute average number of photons in an enclosure.

Limiting Cases

Let us now discuss limiting cases of Planck's radiation law. At short frequencies (long wavelengths) we note that if $\frac{h\nu}{k_B T} << 1$, the exponential term

$$e^{h\nu/k_B T} \equiv 1 + \frac{h\nu}{k_B T}$$

so that

$$e^{h\nu/k_B T} - 1 = \frac{h\nu}{k_B T}$$

Hence, Eq. (15.29) reduces to

$$u_\nu \, d\nu = \left(\frac{8\pi}{c^3} k_B T\right) \nu^2 \, d\nu \tag{15.30}$$

This is the **Rayleigh-Jeans** law

For $\frac{h\nu}{k_B T} >> 1$, we can neglect 1 in comparison with the exponential term in the denominator. Then we find that

$$u_\nu \, d\nu = \frac{8\pi h\nu^3}{c^3} e^{-h\nu/k_B T} \, d\nu \tag{15.31}$$

This is **Wien's** law. It is straightforward to calculate the total area under the Planck or the Wien curve. These are given by $\frac{\pi^4}{15} (\cong 6.49)$ and 6, respectively. It is obvious that the area under the Rayleigh-Jeans curve, Eq.(15.30), will be infinite! This, you will recall, is Ehrenfest's ultraviolet catastrophe.

It is also possible to relate Stefan's constant σ and Wien's constant b to Planck's constant. To illustrate this we calculate the total energy density, u, in the cavity. From Eq. (15.29), we have

$$u = \int_0^\infty u_\nu \, d\nu = \frac{8\pi h}{c^3} \int_0^\infty \frac{\nu^3 \, d\nu}{e^{h\nu/k_B T} - 1} \tag{15.32}$$

To evalute this integral, we change the variable of integration by defining

$$\frac{h\nu}{k_B T} = x$$

so that $\nu^3 d\nu = \left(\frac{k_B T}{h}\right)^4 x^3 dx$. Substituting this result in Eq. (15.32), we get

$$u = \frac{8\pi (k_B T)^4}{(ch)^3} \int_0^\infty \frac{x^3}{e^x - 1} dx$$

The integral occurring in this expression can be calculated using the method outlined in Appendix 1. This has the value

$$\int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$$

so that

$$u = \frac{8\pi^5}{15(ch)^3} (k_B T)^4 = aT^4 \tag{15.33}$$

where

$$a = \frac{8\pi^5 k_B^4}{15 h^3 c^3} = 7.56 \times 10^{-16} \text{J m}^{-3}\text{K}^{-4}$$

If we consider the sun as black body whose interior consists of photon gas at constant temperature of 3×10^6K, we find that energy density

$$u = (7.56 \times 10^{-16} \text{J m}^{-3}\text{K}^{-4}) \times (3 \times 10^6 \text{K})^4$$
$$= 6.1 \times 10^{10} \text{J m}^{-3}$$

The total volume of the sun is nearly 1.4×10^{27} m^3 so that

$$U = uV = (6.1 \times 10^{10} \text{J m}^{-3}) \times (1.4 \times 10^{27} \text{m}^3) = 8.6 \times 10^{37} \text{J}$$

If we assume that photons effuse out of a small hole in the black body (sun), the net rate of flow of radiation per unit area

$$R = \frac{1}{4} uc = \frac{2\pi^5 k_B^4}{15 h^3 c^2} T^4$$

$$= \sigma T^4 \tag{15.34}$$

where

$$\sigma = \frac{2\pi^5 k_B^4}{15 h^3 c^2} = 5.67 \times 10^{-8} \text{J m}^{-2}\text{s}^{-1}\text{K}^{-4}$$

is Stefan-Boltzmann constant.

In your school physics curriculum you have studied Wien's displacement law $\lambda_m T = b$. You can obtain this expression starting from Planck's law. To convince yourself, you should solve the following SAQ.

SAQ 6

Express Eq. (15.29) in terms of λ. Suppose $u_\lambda \, d\lambda$ peaks at $\lambda = \lambda_m$ such that $\lambda_m T = b$. By differentiating the expression so obtained, obtain an expression for b.

You have now seen that Planck's law of radiation incorporates all the classical laws and is the only correct law. Moreover, it has been verified experimentally by several workers. In the quantum picture, we regard radiation in a cavity as a gas of non-interacting photons. You may, therefore, expect that all familiar results of the kinetic theory of gases should hold. Let us show it by deriving an expression for the pressure exerted by radiation on the walls of the enclosure.

15.3.3 Radiation Pressure and Entropy of Photons

We can write the partition function for photons as (Eq. (15.26))

$$Z_{ph} = \prod_{r} \frac{1}{1 - e^{-\beta\varepsilon_\nu}} \tag{15.35}$$

$$\therefore \quad \ln Z_{ph} = -\sum_{\nu} \ln\left[1 - \exp\left(-\beta\varepsilon_\nu\right)\right]$$

We replace the summation by integration. This gives

$$\ln Z_{ph} = -\left(\frac{8\pi}{c^3}\right) V \int_0^\infty \nu^2 \ln[1 - \exp(-\beta h\nu)]\, d\nu$$

Hence, Helmholtz free energy is given by

$$F = -k_B T \ln Z_{ph}$$

$$= \left(\frac{8\pi k_B T}{c^3}\right) V \int_0^\infty \nu^2 \ln\,[1 - \exp(-\beta h\nu)]\, d\nu$$

To simplify this expression, we introduce a change of variable by defining

$$x = \beta h\nu$$

so that $\nu^2 d\nu = \frac{x^2 dx}{\beta^3 h^3}$. On substituting it in the above integral, we obtain

$$F = \left(\frac{8\pi k_B^4 T^4}{h^3 c^3}\right) V \int_0^\infty x^2 dx\, \ln(1 - e^{-x})$$

On integrating by parts, we get

$$\int_0^\infty x^2 \ln(1 - e^{-x})\, dx = -\frac{1}{3}\int_0^\infty \frac{x^3 e^{-x}}{1 - e^{-x}}\, dx$$

$$= -\frac{1}{3}\int_0^\infty \frac{x^3}{e^x - 1}\, dx$$

$$= -\frac{1}{3}\Gamma(4)\zeta(4)$$

$$= -\pi^4 / 45$$

Hence, the expression for Helmholtz free energy reduces to

$$F = -\left(\frac{8\pi^5 k_B^4}{45 h^3 c^3}\right) V = \frac{1}{3} uV$$

The radiation pressure, defined as

$$p = -\left(\frac{\partial F}{\partial V}\right)_T$$

is given by

$$p = \frac{8\pi^5 k_B^4 T^4}{45 h^3 c^3} = \frac{u(T)}{3} \tag{15.36}$$

It is interesting to note that for a photon gas, $pV = \frac{U}{3}$. Can you recall the corresponding expression for pressure exerted by ideal gas ? It is equal to $\frac{2}{3}E$. So we can draw a useful analogy that radiation behaves like particles.

You can now easily show that entropy of an assembly of photons is given by

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$= \left(\frac{32\pi^5 k_B^4}{45 h^3 c^3} \right) VT^3 \qquad (15.37)$$

and

$$C_V = T\left(\frac{\partial S}{\partial T} \right)_V = 3S \qquad (15.38)$$

This shows that entropy of the system is proportional to VT^3.

If radiation undergoes an adiabatic change (S = constant), we find that

$$VT^3 = \text{Constant}$$

In terms of pressure and volume, the equation for the adiabate of the system takes the form

$$pV^{4/3} = \text{Constant} \qquad (15.39)$$

From this you may be tempted to conclude that the ratio of specific heats at constant pressure to that at constant volume for a photon gas is 4/3. Actually this ratio is infinite !

Bose statistics finds useful application in explaining the remarkable phenomena exhibited by liquid helium, particularly at low temperatures. We will now give its brief account.

15.3.4 Liquid ^{4}He and Bose-Einstein Condensation

The first element in the Periodic Table, hydrogen, has contributed in a large measure to the development of new concepts and theories in physics. We discussed the refinements with particular reference to temperature variation of heat capacity in Unit 14. The second element, helium, is still more remarkable. Do you know that its existence in the sun was discovered during a solar eclipse in India in 1868. (Ramsay could produce it in the laboratory almost thirty years later.) Helium derives its name from the Greek word helios, which means the sun. Among all the elements, helium has the unique distinction of not solidifying even at the lowest attainable temperatures. It is due to very weak forces between helium atoms. (Its solid phase can be obtained only under an external pressure of about 25 atmospheres.) The *p-T* diagram, shown in Fig. 15.7 indicates the absence of a triple-point. At atmospheric pressure, helium condenses into a normal liquid at 4.2K. As the temperature is lowered further, liquid helium exhibits another phase transition at 2.18K. You may expect helium to solidify. Instead, it changes into another liquid of very surprising, in fact, unique properties. The new phase is called **liquid He II** to distinguish it from the phase above 2.18K, which is termed **liquid He I**. You may recall from Unit 7 of Block 2 of this course that helium transition is a second order phase transition. The point at which the phase transition occurs is called the λ-point. This nomenclature is used because the shape of heat capacity curve resembles the Greek letter 'lambda'.

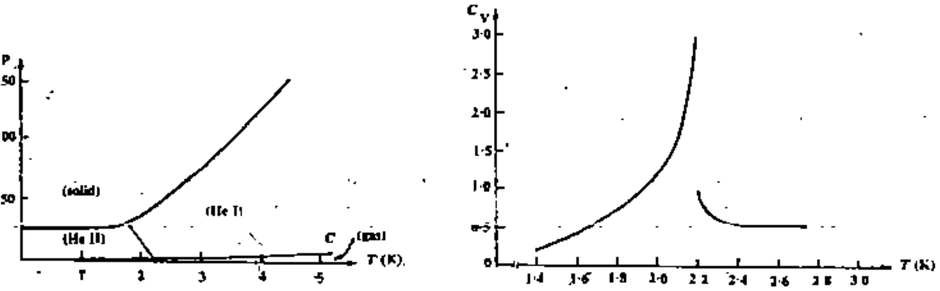


Fig. 15.7: (a) *p-T* diagram of ^{4}He, (b) temperature variation of heat capacity of helium near λ-point

A more dramatic manifestation of the unusual properties of liquid He II is its ability to flow through very narrow channels with zero viscosity. This property is known as **superfluidity.** A series of beautiful experiments have been designed to illustrate the consequences of this property. Here, we shall discuss only one of them, viz. the **fountain effect.**

We take a U-tube and immerse it in a bath of liquid He II, as shown in Fig. 15.8. The lower portion of the tube is filled with emery powder. On shining a beam of light on the powder, heat is absorbed and the superfluid tends to flow from the bath to the hotter region. The motion is so violent that a jet of helium is forced up through the vertical tube and emerges as a fountain, going as high as 30 cm.

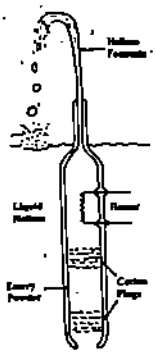


Fig.15.8: The fountain effect

F. London (1938) suggested that the λ-transition should be identified with **Bose-Einstein condensation.** Einstein proposed a simple model that allows us to apply BE statistics to liquid helium in order to gain insight into its peculiar behaviour. Following him, we assume that the distribution of excited states accessible to the atoms of liquid helium is that of a quantum gas and treat the ground state separately. If there are N atoms in all, let N_g be in the ground state and N_{ex} in the excited state. Then,

$$N = N_g + N_{ex} \tag{15.40a}$$

or

$$N - N_g = CV\int_0^\infty \frac{\varepsilon^{1/2}\,d\varepsilon}{\frac{1}{A}e^{\varepsilon/k_BT} - 1} \tag{15.40b}$$

where

$$N_g = \frac{1}{\frac{1}{A} - 1} = \frac{1}{e^{-\mu/k_B T} - 1}$$

and $C = \frac{2\pi}{h^3}\left(2mk_B\, T\right)^{3/2}$.

To evaluate this integral, we make the substitution $\varepsilon / k_B T = x$. Then, $\varepsilon^{1/2}d\varepsilon = (k_B T)^{3/2}x^{1/2}dx$ so that for a completely degenerate gas ($A = 1$), we get

$$N - N_g = CV(k_B T)^{3/2}\int_0^\infty \frac{x^{1/2}\,dx}{e^x - 1}$$

$$= CV(k_B T)^{3/2}\,\Gamma(3/2)\,\zeta(3/2) \tag{15.41}$$

where $\Gamma(3/2) = \frac{\sqrt{\pi}}{2}$ is gamma function and $\zeta(3/2) = 2.612$ is the Riemann - Zeta function of order (3/2).

It shows that number density of excited particles is a function of temperature. As $T \to 0$, $N_{ex} \to 0$ and $N \to N_g$ i.e., all particles condense into ground state. This phenomenon is referred to as **Bose-Einstein condensation.** However, as T increases N_{ex} also increases; it may become arbitrarily large. But N is finite and N_{ex} has to be necessarily less than (at best equal to) N. We therefore postulate that Eq. (15.41) holds only as along as $N_{ex} \le N$. If T_c is the maximum temperature which satisfies it, then

$$\begin{aligned} N_{ex} &= CV\zeta(3/2)\quad(3/2)(k_BT)^{3/2} && \text{for } T \le T_c \\ &= N && \text{for } T > T_c \end{aligned} \tag{15.42}$$

That is, at low temperatures, the number of atoms in excited states increases as $T^{3/2}$ until all atoms are in the excited states at temperature T_c. So we can write

$$N = CV\Gamma(3/2)\zeta(3/2)(k_B T_c)^{2/3}$$

or

$$T_c = \frac{1}{k_B}\left[\frac{N}{CV\Gamma(3/2)\zeta(3/2)}\right]^{2/3}$$

$$= \frac{h^2}{2\pi m k_B}\left[\frac{N}{2.612V}\right]^{2/3} \tag{15.43}$$

T_c is known as the **Bose-Einstein condensation temperature.**

In the framework of this model, we can write N_g and N_{ex} in terms of N. To do so, we note that

$$\frac{N_{ex}}{N} = \left(\frac{T}{T_c}\right)^{3/2}$$

or

$$N_{ex} = N\left(\frac{T}{T_c}\right)^{3/2} \qquad (15.44)$$

Hence,

$$\begin{aligned} N_g = N - N_{ex} &= N\left[1-\frac{N_{ex}}{N}\right] \\ &= N\left[1-\frac{T}{T_c}\right]^{3/2} \qquad (15.45) \end{aligned}$$

It shows that at $T = 0$, all particles condense into the lowest energy state. Fig. 15.9 shows how $\frac{N_{ex}}{N}$ and $\frac{N_g}{N}$ vary with temperature.

If you use $N / V = 2.2\times10^{28}\,\text{m}^{-3}$ and $m = 6.65\times10^{-27}\,\text{kg}$ in the expression for T_c, you will get

$$T_c = 3.13 \text{ K}$$

which is close to the observed value of 2.18K for the onset of condensation in liquid helium.

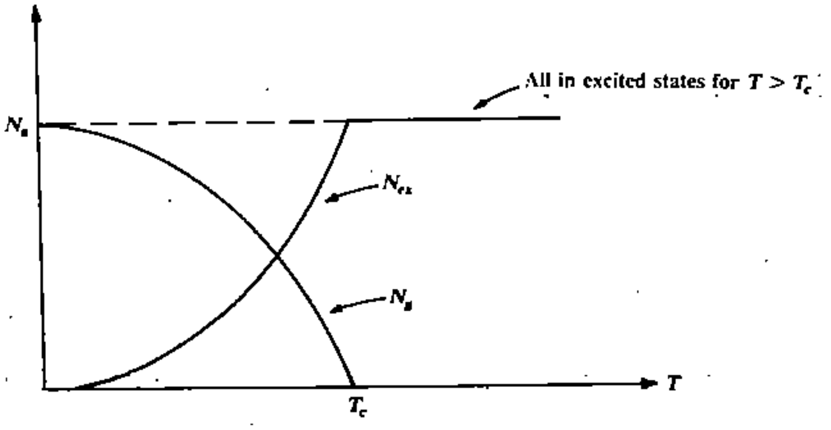


Fig. 15.9 : Plot of N_{ex} and N_g as a function of temperature according to Einstein model

We can now say that helium II consists of two components, a **normal fluid** component and a **superfluid component,** which is characterised by remarkable properties like apparently zero viscosity and infinite thermal conductivity. This means that irrespective of where you heat the liquid, it will evaporate from the top surface. (On the contrary, fluids such as water vaporise from wherever the heat input is.) The He I → He II phase transition is visually characterised by the disappearing of bubbles and boiling.

The 2.18K phase transition from He-I to He-II can be explained, atleast qualitatively, using Bose-Einstein statistics. It tells us that condensation into the ground state is a necessary condition for the occurrence of superfluid behaviour.

Having discussed the ideal B-E gas and some simple Boson systems, let us now consider an ideal Fermi-Dirac gas.

15.4 IDEAL FERMI-DIRAC GAS

We have seen that the wave function of a system of indistinguishable particles possesses definite symmetry properties. For bosons, the wave function is symmetric whereas for fermions, which are subject to restrictions imposed by the exclusion principle, the wave function is asymmetric. You may now ask: Can it be a combination of symmetric and antisymmetric wave functions? It can not be so. To determine the thermodynamic properties of an ideal Fermi-Dirac gas, let us first obtain the distribution function.

15.4.1 Fermi-Direc Distribution Function

In Sec. 15.3.1 we derived B.E. distribution function. In the present case, the whole exercise has to be repeated with appropriate changes. We know that fermions are subject to Pauli's principle and not more than one particle can occupy a state. Then, from SAQ 4(b) you would recall that the number of ways in which we can distribute N_i particles into g_i states (cells) of level i is given by $\binom{g_i}{N_i}$. The total number of ways whereby we can put N particles into the various levels are

$$W(\{N_i\}) = \prod_i \binom{g_i}{N_i} = \prod_i \frac{g_i}{(g_i - N_i)!\,N_i!} \tag{15.46}$$

This distribution is subject to the conditions that total number of particles in the system and the energy of the system remain constant. That is,

$$\delta N = \sum \delta N_i = 0 \tag{15.47a}$$

and

$$\delta U = \sum \delta N_i \,\varepsilon_i = 0 \tag{15.47b}$$

As before, we wish to know the most probable distribution by finding the set of numbers which maximise W. We do this by maximising the logarithm of W, rather than W itself, using the procedure followed for MB and BE distributions. Thus we set

$$\delta \ln W = 0$$

On taking logarithm of both sides of Eq. (15.46), we obtain

$$\sum_i [\ln g_i! - \ln(g_i - N_i)! - \ln N_i!] \tag{15.48}$$

Using Stirling's approximation, we get

$$\begin{aligned}\ln W &= \sum_i [g_i \ln g_i - g_i - (g_i - N_i)\ln(g_i - N_i) + (g_i - N_i) \\ &\qquad - N_i \ln N_i + N_i] \\ &= \sum_i [g_i \ln g_i - (g_i - N_i)\ln(g_i - N_i) - N_i \ln N_i]\end{aligned}$$

Hence,

$$\begin{aligned}\delta \ln W &= \sum_i \left[(N_i - g_i)\frac{1}{(g_i - N_i)}(-\delta N_i) + \delta N_i \ln(g_i - N_i)\right] \\ &\qquad - N_i \frac{1}{N_i}\delta N_i - \ln N_i \,\delta N_i] \\ &= \sum_i \left[\ln\left(\frac{g_i}{N_i} - 1\right)\right]\delta N_i\end{aligned}$$

Equating $\delta \ln W$ to zero, we obtain

$$\sum_i \ln\left(\frac{g_i}{N_i} - 1\right)\delta N_i = 0 \tag{15.49}$$

This expression is subject to the conditions given by Eqs. (15.47a) and (15.47b). To incorporate these and obtain a general expression we multiply Eq. (15.47a) by α, Eq. (15.47b) by $-\beta$ and add to Eq. (15.49). This gives

$$\sum_i \left[\ln\left(\frac{g_i}{N_i}-1\right)+\alpha-\beta\varepsilon_i \right]\delta N_i = 0$$

Since the δN_i are arbitrary and can be varied independently, we can set the coefficient of each δN_i equal to zero. This gives

$$\ln\left(\frac{g_i}{N_i}-1\right)+\alpha-\beta\,\varepsilon_i=0$$

or

$$\frac{N_i}{g_i}=\frac{1}{e^{-\alpha+\beta\varepsilon_i+1}}$$

Using the same notation as in Sec. 15.3.1, we can rewrite it as

$$\frac{N_i}{g_i}=\frac{1}{Ae^{\beta\varepsilon_i}+1}=\frac{1}{e^{\beta(\varepsilon_i-\mu)}+1} \tag{15.50}$$

This defines the **Fermi-Dirac distribution.** For continuous distribution, the Fermi function $f(\varepsilon)$ is defined by

$$f(\varepsilon)=\frac{1}{e^{\beta(\varepsilon-\mu)}+1} \tag{15.51}$$

Let us pause for a moment and compare it with expressions for BE and MB distribution functions:

$$\begin{aligned} f_{\mathrm{MB}} &= \frac{1}{e^{\beta(\varepsilon-\mu)}} \\ f_{\mathrm{BE}} &= \frac{1}{e^{\beta(\varepsilon-\mu)}-1} \\ f_{\mathrm{FD}} &= \frac{1}{e^{\beta(\varepsilon-\mu)}+1} \end{aligned}$$

A close examination of these expressions reveals that inspite of the great differences in the assumptions used to arrive at these expressions, they have a similar appearance. In fact, we can combine them into just one expression:

$$f = \frac{1}{e^{\beta(\varepsilon-\mu)}+\kappa}$$

where

$$\kappa = \begin{cases} 0 & \text{MB distribution} \\ 1 & \text{FD distribution} \\ -1 & \text{BE distribution} \end{cases}$$

This logically raises the question: What are its manifestations in describing the behaviour of a system? To discover the enormous consequences of κ, you should refer back to Fig. 15.6. You will note that whereas BE distribution is skewed towards highly occupied low energy states, FD distribution is skewed to high energy states compared with classical (MB) distribution. You will note that at $T = 0$ ($\beta = \infty$), the exponent becomes $-\infty$ for $\varepsilon < \mu$, whereas for $\varepsilon > \mu$, the exponent becomes infinite, so that

$$f(\varepsilon)=\begin{cases} 1 \text{ for } \varepsilon<\mu \\ 0 \text{ for } \varepsilon>\mu \end{cases} \tag{15.52}$$

Mathematically speaking, it defines a step-function. Physically, it implies that at absolute zero, upto certain energy all levels are occupied and higher energy states are empty. (You can compare it with a partly filled glass of water.) This energy is known as Fermi energy, ε_F You will know about it in the following section. This is shown in Fig. 15.10(a). Fig 15.10(b) shows the effect of raising the temperature. The curve develops a tail, which is symmetrical about $\varepsilon = \varepsilon_F$. Moreover, at this energy $f(\varepsilon) = \frac{1}{2}$.

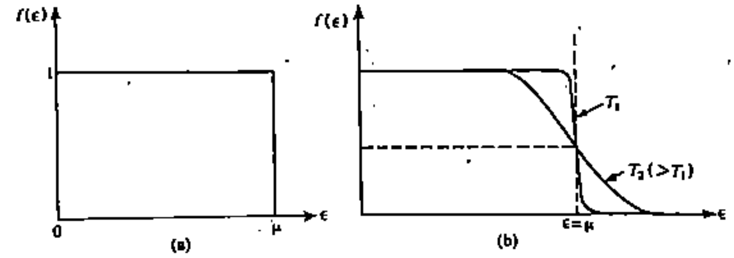


Fig. 15.10: (a) The Fermi function at $T = 0$: Complete Degeneracy (b) $T > 0$ $(\varepsilon - \mu >> 1)$: Strong Degeneracy

For $\varepsilon >> \mu$, $\beta(\varepsilon - \mu) >> 1$ and you can ignore one. Then $f(\varepsilon) = e^{-\beta(\varepsilon - \mu)}$ and the distribution behaves like a classical (MB) distribution.

If the temperature is finite, above absolute zero, the fermions in region I shift to region II, bringing about deviations in the step function. It means that as we increase temperature, fermions below the Fermi energy jump to energy states above Fermi energy. However, the width of this region is of the order of $k_B T$. Normally deviations from the step-function ($T = 0$) are important only for those values of ε for which $|\beta(\varepsilon - \mu)|$ is of the order of one. For larger values, the exponential term will either be zero or one. Thus a thermal reshuffling of the particles is confined to $k_B T$ around $\varepsilon = \varepsilon_F$. That is, the number of electrons which contribute to thermal processes is proportional to T. However, the major proportion of distribution is not influenced by the rise in temperature.

15.4.2 Fermi Energy

Consider a system of N fermions enclosed in a volume V. We know that because of Pauli's principle, only one fermion can be accommodated in a given state. You have already learnt that the highest energy possessed by a fermion at $T = 0$ is called the **Fermi energy**, ε_F. Let us now derive an expression for ε_F.

We know that the number of quantum states of a particle with momentum in the interval p and p + dp is $\frac{4\pi V}{h^3} p^2 \, dp$. We have to multiply this number by $(2S + 1)$.

For electrons, $S = \frac{1}{2}$ so that the required number of states is $\frac{8\pi V}{h^3} p^2 \, dp$. Denoting the highest momentum by p_F, we have

$$N = \frac{8\pi V}{h^3} \int_0^{p_F} p^2 \, dp = \frac{8\pi V}{h^3} \frac{p_F^3}{3} \tag{15.53}$$

This yields an expression for **Fermi momentum**, p_F:

$$p_F = \left(\frac{3N}{8\pi V}\right)^{1/3} h \tag{15.54}$$

and the Fermi energy

$$\varepsilon_F = \frac{p_F^2}{2m} = \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3} \tag{15.35}$$

If we draw a sphere with radius p_F, all the particles will be found inside the sphere. This is called the **Fermi surface**. In the case of the alkali and the noble atoms, the surface is a sphere. In other cases, the shape can be quite complicated.

We define what is known as **Fermi temperature**, T_F, through the relation

$$T_F = \frac{\varepsilon_F}{k_B} \tag{15.56}$$

The values of ε_F range from about 2 eV to 15 eV It is the lowest for Cs (1.58 eV) and highest for Be (14.14 eV). The corresponding Fermi temperatures are of order 10^4K–10^5K. To get exact ideas about these values, you should solve the following SAQ.

SAQ 6

Calculate ε_F for copper, given density = 9 g cm^{-3}, atomic weight = 63.5 and valency equal to one.

The ground state energy is given by

$$\begin{aligned} E_0 &= \frac{8\pi V}{h^3}\int_0^{p_F}\frac{p^2}{2m}p^2\,dp = \frac{8\pi V}{h^3}\frac{p_F^5}{10m} \\ &= \frac{8\pi V}{5h^3}p_F^3\varepsilon_F \end{aligned}$$

Using Eq. (15.54), we obtain

$$E_0 = \frac{3}{5}N\varepsilon_F \tag{15.57}$$

The mean energy per fermion for a completely degenerate electron gas is given by

$$\bar{\varepsilon} = \frac{E_0}{N} = \frac{3}{5}\varepsilon_F \tag{15.58}$$

For conduction electrons in copper

$$\begin{aligned} \bar{\varepsilon} &= \frac{3}{5}\times(7.0\,\text{eV} \\ &= 4.2\,\text{eV} \end{aligned}$$

This energy corresponds to several thousand kelvin of temperature to which an electron, if treated classically, would have to be raised. This shows that unlike a classical particle, a fermion has appreciable energy even at absolute zero ! That is, a fermion system is quite alive. This is a quantum effect arising out of the Pauli principle and brings out the inadequacy of classical statistics in describing the behaviour of systems at extremely low temperatures.

Since $C_V = \left(\frac{\partial E}{\partial T}\right)_V$, Eq. (15.56) implies that heat capacity of a fermion system drops to zero at absolute zero. Similarly, we can show that entropy of a F.D. system also vanishes at 0 K. This is consistent with the third law of thermodynamics. Now you may ask: Is it true for pressure also ? We know that $p = \frac{2}{3}\frac{E}{V}$. So we find that pressure exerted by a fermion system at 0 K is equal to $\frac{2}{5}\left(\frac{N}{V}\right)\varepsilon_F$. This shows that if electrons in a metal were neutral, they would exert a pressure of almost 10^6 atmospheres! Does it make we experience this enormous pressure? If not, why? Do electrons to evaporate spontaneously? Actually this pressure is counter-balanced by Coulomb attraction of electrons by ions.

The Fermi energy is the kinetic energy of electrons in the highest occupied state. We can relate it to the work function of a metal. Refer to Fig. 15.11. It shows a potential well in which the electrons reside and the filled states upto ε_F. If the well depth is $\varepsilon_F = W - \phi$. So once we know ϕ and W, we can get an estimate of ε_F.

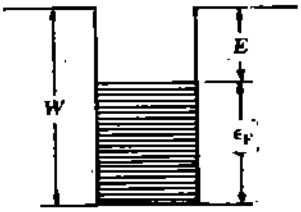


Fig.15.11: Relationship between well depth Fermi energy, and work function for electrons in a metal. Horizontal lines indicate filled energy levels.

We have so far considered a FD system at absolute zero. To know the behaviour of its heat capacity and entropy, we must extend this study to temperatures above absolute zero. In particular, we will confine ourselves to electrons. However, it is important to note that for $T \ll T_F$, the mean occupation number does not differ much from the value at 0K. Such a fermion system is said to be **strongly degenerate**. We know that for conduction electrons in metals, T_F is of the order of 10^4 to 10^5K. This means that conduction electrons are in extremely degenerate condition even under normal conditions. Very few of these are free. By far most of them are trapped in low lying states with nowhere to go.

We will not go into a detailed discussion of these properties. However, very simple arguments can be used to understand the heat capacity of metals. This is the subject of the following sub-section.

15.4.3 Electronic Heat Capacity

You will recall from Sec. 15.2 that correct explanation of heat capacity of metals remained a puzzle for a long time. Of course, it should be no surprise to you that classical statistics fails to give the right answer because an assembly of electrons (electron gas) obeys F.D. statistics. We can easily show, using F.D. statistics, that electronic heat capacity varies linearly with temperature. Moreover, heat capacity of a metal at low temperatures is the sum of an electronic contribution which is proportional to T, and the lattice contribution which is proportional to T^3.

Experiments reveal that the contribution of electronic heat capacity is about 1% of the total. To show this we assume that only those electrons which occupy energy states upto $k_B T$ of the Fermi level participate in thermal processes. Hence, the fraction of particles thermally excited is proportional to $k_B T / \varepsilon_F$. Since the thermal energy per excited particle is $k_B T$

$$U \sim (k_B T)\frac{k_B T}{\varepsilon_F} N = \frac{N k_B^2 T^2}{\varepsilon_F}$$

Hence,

$$(C_V)_{el} = \left(\frac{\partial U}{\partial T}\right)_V \frac{N k_B^2 T}{\varepsilon_F} = N k_B \left(\frac{T}{T_F}\right) \tag{15.59}$$

That is, for $T << T_F$, the electronic heat capacity of fermions varies linearly with temperature. At room temperature,

$$\frac{T}{T_F} = \frac{300}{10^4} \sim O(10^{-2})$$

A more exact, but somewhat difficult, calculation gives the following result:

$$(C_V)_{el} = \frac{N k_B \pi^2}{2T_F} T = aT \tag{15.60}$$

where

$$a = \frac{N k_B \pi^2}{2T_F} = \frac{N k_B^2 \pi^2}{2\varepsilon_F},$$

is known as the **Sommerfeld constant.**

The total heat capacity of a metal is made up of two parts. The electronic contribution dominates at low temperatures. But around room temperature, the electronic contribution is a small fraction of the total.

$$(C_V)_{Total} = aT + bT^3 \tag{15.61a}$$

or

$$\frac{(C_V)_{Total}}{T} = a + bT^2 \tag{15.61b}$$

A plot of Eq. (15.61b) is shown in Fig.15.12 as a function of T^2 for potassium. The agreement is seen to be excellent. The intercept gives the values of a. For potassium, sodium and copper the typical values are 2.08, 1.38 and 0.695, respectively.

There are a variety of other F.D. systems which are of great interest. Examples are the protons and neutrons in nuclear matter, electrons in white dwarf stars, ^{3}He, etc. A detailed discussion of these is beyond our scope. However, those of you who feel deeply interested should look up some other references available in your study centre.

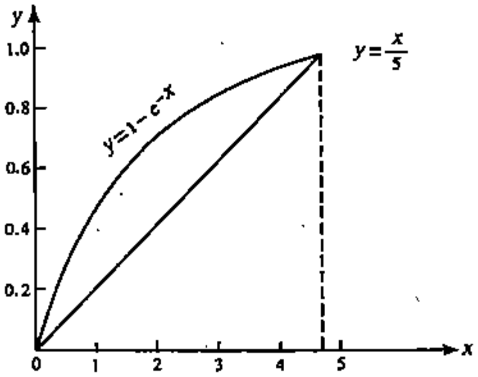


Fig.15.12: Plot of Eq. (15.61b) as a function of T^{2}

Let us now sum up what you have learnt in this unit.

15.5 SUMMARY

- The Bose-Einstein distribution function is given by

  $$\frac{N_i}{g_i} = \frac{1}{\exp[\beta(\varepsilon_i - \mu] - 1}$$

  For continuous distribution, we can write

  $$N(\varepsilon) = \frac{g(\varepsilon)}{\exp[\beta(\varepsilon - \mu)] - 1}$$

- Planck's law of black-body radiation tells us that the spectral energy density is given by

  $$u_\nu d\nu = \left(\frac{8\pi h}{c^3}\right)\frac{\nu^3}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}d\nu$$

  In the limit $h\nu << k_B T$, we obtain the Rayleigh-Jeans law:

  $$u_\nu d\nu = \frac{8\pi^{2}}{c^3}(k_B T)d\nu$$

  On the other hand, $h\nu >> k_B T$, we obtain Wien's law:

  $$u_\nu d\nu = \frac{8\pi h\nu^3}{c^3}\exp\left(-\frac{h\nu}{k_B T}\right)d\nu$$

  The total energy density

  $$U = \frac{8\pi^5}{15(ch)^3}(k_B T)^4$$

  and Stefan's constant $\sigma = \dfrac{2\pi^5 k_B^4}{15c^2h^3}$

- Radiation pressure

  $$p = \frac{8\pi^5}{45(ch)^3}(k_B T)^4 = \frac{u}{3}$$

- Liquid ^{4}He undergoes a phase-transition, the so-called λ-transition, at $T_c = 2.18$K. The phase below T_c, He II, exhibits superfluidity. Some of its properties can be explained on the basis of Bose-Einstein condensation

- The Fermi-Dirac distribution function is given by

$$\frac{N_i}{g_i} = \frac{1}{\exp[\beta(\varepsilon_i - \mu) + 1}$$

For continuous distribution, we can write

$$f(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon - \mu) + 1}$$

- The Fermi energy $\varepsilon_F = \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3}$
- The pressure exerted by a F.D. gas at T = 0 is

$$p_F = \frac{2}{5}\left(\frac{N}{V}\right)\varepsilon_F$$

- The electronic contribution to the heat capacity of a metal is given by

$$(C\ )_{el} = aT$$

where the Sommerfeld constant $a = \frac{Nk_B^2\pi^2}{2\varepsilon_F}$

15.6 TERMINAL QUESTIONS

1. Calculate the Fermi temperature for (i) liquid ^{3}He and (ii) electrons in a white dwarf star using the known experimental data on the two systems.
2. Calculate the exact expression for electronic contribution to heat capacity for a F.D. system at finite temperatures. You may make use of the fact that to first order in T, μ may be replaced by its value $\mu = \varepsilon_F$ at $T = 0$, in the expression for $f(\varepsilon)$.

15.7 SOLUTIONS AND ANSWERS

SAQs

1. $u = \int_0^\infty \nu^3 F\left(\frac{\nu}{T}\right) d\nu = \int_0^\infty \nu^3 \exp\left(\frac{-c_2\nu}{T}\right) d\nu$

Let $\frac{c_2\nu}{T} = x$ or $d\nu = \frac{T}{c_2}dx$

$$\therefore\ u = \int_0^\infty \left(\frac{T}{c_2}\right)^3 x^3 e^{-x}\left(\frac{T}{c_2}\right) dx$$

$$= \frac{T^4}{(c_2)^4}\int_0^\infty e^{-x}x^3\,dx = \frac{6}{(c_2)^4}T^4$$

2. We know from Eq. (15.8) that

$$\bar{\varepsilon} = \frac{\sum_{n=1}^{\infty} nh\nu\, e^{-nh\nu/k_B T}}{\sum_{n=0}^{\infty} \exp\left(-\frac{nh\nu}{k_B T}\right)}$$

Put $\dfrac{h\nu}{k_B T} = x$

Then we have

$$\bar{\varepsilon} = \frac{\sum_{n=1}^{\infty} n\, e^{-nx}(x k_B T)}{\sum_{n=0}^{\infty} e^{-nx}}$$

The denominator is

$$\sum_{n=0}^{\infty} \exp(-nx) = 1 + e^{-x} + e^{-2x} + \cdots = \frac{1}{1-e^{-x}}$$

Differentiating both sides with respect to x, we have

$$\sum_{n=0}^{\infty} \exp(-nx)(-n) = -\frac{e^{-x}}{(1-e^{-x})^2}$$

or

$$\sum_{n=0}^{\infty} n e^{-nx} = \frac{e^{-x}}{(1-e^{-x})^2}$$

Hence,

$$\bar{\varepsilon} = x k_B T \frac{e^{-x}}{(1-e^{-x})^2}(1-e^{-x}) = \frac{x k_B T}{e^{x}-1}$$

$$= \frac{h\nu}{\exp\left(\dfrac{h\nu}{k_B T}\right) - 1}$$

which is identical with Eq. (15.9).

3. Generally, a particle consisting of an odd number of Fermi particles is a fermion and a particle consisting of an even number of Fermi particles is a boson. A particle consisting of only bosons is a boson. ^{3}He consists of two protons, one neutron, and two electrons. Hence, it consists of five particles of spin 1/2, and is a fermion. ^{4}He, on the other hand, consists of two protons, two neutrons and two electrons. Hence, it consists of six fermions and is a boson.

4. a) We want to derive the Maxwell-Boltzmann distribution with the correct Boltzmann counting. We have

$$\Omega_i = \frac{g_i^{N_i}}{N_i!}$$

and $\quad W(\{N_i\}) = \prod_i \Omega_i = \prod_i \dfrac{g_i^{N_i}}{N_i!} \qquad$ (i)

We must maximise W subject to

$$\sum_i N_i = N, \quad \text{(ii)} \quad \text{and} \quad \sum_i N_i \varepsilon_i = U \qquad \text{(iii)}$$

From (i) we have, on using Stirling's approximation

$$\ln W = \sum_i [N_i \ln g_i - \ln N_i!] = \sum_i [N_i \ln g_i - N_i \ln N_i + N_i]$$

$$= \sum_i [N_i \ln g_i - N_i \ln N_i + N_i]$$

Hence,

$$\delta \ln W = \sum_i [\delta N_i \ln g_i - \delta N_i - \delta N_i \ln N_i + \delta N_i]$$

$$= \sum_i [\ln g_i - \ln N_i]\delta N_i = 0 \qquad \text{(iv)}$$

Since N and U are fixed, we can write

$$\sum_i \delta N_i = 0 \qquad \text{(v)}$$

and

$$\sum_i \varepsilon_i \delta N_i = 0 \qquad \text{(vi)}$$

Multiplying Eqs. (v) and (vi) by α and $-\beta$, respectively, and adding to (iv) we have

$$\sum_i [(\ln g_i - \ln N_i) + \alpha - \beta\varepsilon_i]\,\delta N_i = 0$$

Since the δN_i's are arbitrary, this relation should be true for every δN_i. Hence, we must have

$$\ln g_i - \ln N_i + \alpha - \beta\varepsilon_i = 0$$

or

$$\ln\left(\frac{N_i}{g_i}\right) = \alpha - \beta\varepsilon_i$$

which can be rewritten as

$$\frac{N_i}{g_i} = \frac{1}{\exp(-2 + \beta\varepsilon_i)} = \frac{1}{A\exp(\beta\varepsilon_i)} \qquad \text{(vii)}$$

The B.E. distribution, given by

$$\frac{N_i}{g_i} = \frac{1}{A\exp(\beta\varepsilon_i) - 1}$$

reduces to (vii) for $A >> 1$. This limit ($A >> 1$) occurs for high temperatures and low densities, where the quantum connections are known to be small.

b) In the case of fermions, no single level can accommodate more than one particle. Hence, $N_i << g_i$ and

The required number of ways = number of ways in which N_i objects can be chosen out of g_i

$$= \binom{g_i}{N_i} = \frac{g_i!}{(g_i - N_i)!\,N_i!}$$

It is equal to the number of ways in which g_i levels can be divided into two sub-groups, one consisting of N_i levels, occupied by one particle each and the other of (g_i - N_i) unoccupied levels.

5. We know that

$$u_\nu\, d\nu = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/k_B T-1}}\, d\nu$$

From $c = \nu\lambda$, we have $\nu = \frac{c}{\lambda}$ and

$$d\nu = -\frac{c}{\lambda^2}\, d\lambda$$

Also $|u_\nu\, d\nu| = |u_\lambda\, d\lambda|$, since $\int u_\nu\, d\nu = \int u_\lambda\, d\lambda$

Hence,

$$u_\lambda\, d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{\exp\left(\dfrac{hc}{\lambda k_B T}\right) - 1}$$

We note that u_λ is a maximum when $\lambda^5\left[\exp\left(\dfrac{ch}{\lambda k_B T}\right) - 1\right]$ is a minimum.

Hence, we put

$$\frac{d}{d\lambda}[\lambda^5(e^{hc/\lambda k_B T} - 1)] = 0$$

On simplification, we have

$$1 - e^{-x} = \frac{x}{5} \text{ with } x = \frac{hc}{\lambda k_B T}$$

You can solve this equation graphically and obtain $x = 4.96$. Hence,

$$\frac{hc}{\lambda_m k_B T} = 4.96$$

Putting $\lambda_m T = b$, we find that $b = \lambda_m T = \dfrac{hc}{4.96 k_B}$

$$= 0.290 \text{ Å K}$$

6. We have $\varepsilon_F = \dfrac{h^2}{2m}\left(\dfrac{3N}{8\pi V}\right)^{2/3}$

Number density of copper atoms = 9/63.5 = 0.14 mol cm^{-3}. Since valency of copper is one,

$$\frac{N}{V} = \frac{9}{63.5} \times 6.02 \times 10^{23} = 8.4 \times 10^{22} \text{ electrons cm}^{-3}$$

Using the standard values of h and m, we find that

$$\varepsilon_F = 11.3 \times 10^{-12} \text{erg} \simeq 7.0 \text{eV}$$

TQs

1. We have $T_F = \dfrac{\varepsilon_F}{k_B} = \dfrac{h^2}{2mk_B}\left(\dfrac{3N}{8\pi V}\right)^{2/3}$

   i) For liquid ^{3}He

   $$\frac{V}{N} = 63 \text{Å}^{-3} \text{ atom}^{-1} = 63 \times 10^{-24} \text{ cm}^{-3}\text{atom}^{-1}$$

   $$\therefore \frac{N}{V} = \frac{10^{24}}{63} \text{ atom cm}^{-3}$$

   $$m = 5.01 \times 10^{-24} \text{g}$$

   This yields, $T_F \simeq 4.9$K

   ii) For white dwarfs $\rho = 10^7$ g cm^{-3}

   $$n = \frac{N}{V} = 10^{30} \text{ electrons cm}^{-3}$$

   This yields,

   $$T_F = 10^{10}\text{K}$$

2. At $T = 0$, the levels upto $\varepsilon = \varepsilon_F$ are filled. As we raise the temperature, the following processes take place.

NOTES