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**Indira Gandhi National
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School of Sciences**

Block

2

THE ZEROTH AND THE FIRST LAWS OF THERMODYNAMICS

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CONTENTS

BLOCK 2: THE ZEROTH AND THE FIRST LAWS OF THERMODYNAMICS

In Block 1, you have learnt about elementary kinetic theory where we made simplifying assumptions about the motion of gas molecules. You must have realized that kinetic theory of gases explains various observed phenomena with aesthetic elegance. This block deals with the basic concepts of thermodynamics, the terminology used therein, the zeroth law of thermodynamics, the first law of thermodynamics and some of its applications. From your school physics course, you are familiar with some of these concepts. But to make the block self-contained, we have included these in brief.

In Unit 5, we have introduced the basic terminology of thermodynamics and explained the basic concepts to be used in this course. You will get familiar with the thermodynamic systems and processes and learn to classify the thermodynamic processes based on the behaviour of the thermodynamic parameters of the system.

This is followed by the discussion of the zeroth law of thermodynamics in Unit 6. You will also learn that the zeroth law introduces the concept of temperature, which, in turn, helps us in formulating the equation of state of a thermodynamic system.

We have discussed the thermodynamic concepts of heat and work in Unit 7. In this process you will learn about the concept of internal energy of a system. This helps us to develop mathematical formulation of the first law of thermodynamics, which is the principle of conservation of energy for thermodynamic systems. The applications of this law to diverse physical phenomena observed in nature like propagation of sound as well specific heat capacity measurement of a gas as performed in a laboratory are also given in this unit. An interesting phenomenon of adiabatic lapse rate, responsible for explaining the drop in the temperature as we move upwards in the atmosphere is explained in the Appendix of this unit. Please note that you will not be examined for the material provided in the Appendices of the course, but it will surely provide you an enriched learning experience.

You will appreciate that each law of thermodynamics introduces a new thermodynamic variable. Moreover, thermodynamics is phenomenological and powerful science. The mathematics used in these units is quite simple. Yet you should brush up your previous knowledge of +2 physics as well as differential calculus, with particular emphasis on partial differentiation.

We wish you the best for learning of this interesting topic of physics!

A thermodynamic system is usually characterized by its interaction with the surrounding, which is governed by the nature of its boundary. You will learn about the behaviour of familiar things like hot tea kept in an open cup and a thermos flask in this unit.

THERMODYNAMIC DESCRIPTION OF A SYSTEM

Structure

STUDY GUIDE

In the last block, you learnt basic concepts of kinetic theory of gases. You discovered that macroscopic properties of a gas could be related to its microscopic properties. You also learnt about Brownian motion and how it provided undisputed evidence in favour of kinetic theory. This unit deals with basic concepts of thermodynamics. We are sure that you are familiar with at least some of these concepts from your school physics course. Therefore, it provides perfect platform for starting our journey into the interesting field of thermodynamics.

The solved examples and SAQs given here should help you fix your ideas and check your progress. We expect you to answer TQs yourself. Even if you find them tough, do not look for answers at the first instance. We strongly recommend that you go through the particular section again. This will help you to develop better appreciation of the subject.

> *Classical thermodynamics ... is the only physical theory of universal content which I am convinced ... will never be overthrown.*

Albert Einstein

5.1 INTRODUCTION

There may have been some occasions for you to use a bicycle pump to inflate a tyre. Did you feel that the pump get hot? In winter, when we rub our palms together, we get a sensation of warmth. In these examples, the heating is not caused in the conventional way by a flame or something hot underneath the pump or the palm. The heat arises due to motion, i.e. the mechanical work done in compressing the gas inside the pump or forcing the palms to move against friction. These examples suggest a connection between mechanical and thermal effects. The study of the relationship between mechanical and thermal energies constitutes the subject of thermodynamics.

We begin our journey by discussing what we understand by a thermodynamic system enclosed by an arbitrary surface called boundary. Classification of systems and boundaries is also discussed in Sec. 5.2. This is followed by a discussion of thermodynamic state of a system, thermodynamic variables – intensive and extensive – and thermodynamic equilibrium in Sec. 5.3. A discussion of thermodynamic processes forms the subject matter of Sec. 5.4. We have introduced the concepts of reversible and quasi-static processes. This is followed by representation of a process – isothermal, isobaric, isochoric, cyclic and adiabatic – on an indicator diagram. This information will be used in the study of heat engines based on Carnot cycle.

Expected Learning Outcomes

After studying this unit, you should be able to:

❖   identify thermodynamic systems with their surroundings and boundaries;

❖   explain the term thermodynamic variable and identify the variables characterising different thermodynamic systems;

❖   explain thermodynamic equilibrium;

❖   distinguish between a reversible and an irreversible process;

❖   describe the character of a quasi-static process; and

❖   depict different types of thermodynamic processes diagrammatically.

5.2 BASIC TERMINOLOGY

While beginning our journey in the study of thermodynamics, we focus our attention on a certain quantity of matter or a definite region of space, which is considered to be distinct and separated from everything else that can influence it. We refer to it as a **thermodynamic system**. Every such system is enclosed by a surface, either real or imaginary, which is called its **boundary**. The boundary may be at rest or in motion and it may or may not change its shape. The region of space and everything else that lies outside the boundary constitute its **surroundings**. These are illustrated schematically in Fig. 5.1. In thermodynamics, we consider only that portion of the surroundings as effective, which can influence the system.
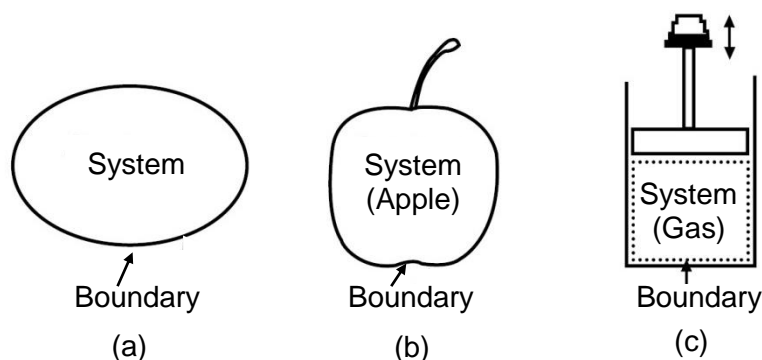
Fig. 5.1: a) General depiction of a system and boundaries; b) an apple as a system; c) compressed gas in a cylinder.

Any study of thermodynamics begins with the identification of a system, its boundary and surroundings (Fig. 5.1a). Let us consider some specific examples of systems with different kinds of boundaries.

If we consider apple as a thermodynamic system (Fig. 5.1b), the boundary is real and fixed. Everything outside the skin of the apple constitutes the surroundings. For the system of a compressed gas (Fig. 5.1c) in a cylinder fitted with a piston, the boundary is real but movable since the piston, which is a part of the boundary, can be moved in or out. Everything outside the boundary of the gas constitutes its surroundings.

A system may be simple, such as water in a vessel or complex, like a dry cell which has zinc and carbon electrodes, electrolyte etc. A system may be completely uniform with respect to its chemical composition and physical conditions. Then it is said to be **homogeneous.** However, an inhomogeneous system is called **heterogeneous.** Air in a cylinder or in a rubber balloon is a uniform mixture of gases like N_2, O_2 and CO_2. It, therefore, makes up a homogeneous system. On the other hand, ice and water in a beaker constitute a heterogeneous system.

Thermodynamic systems can also be classified from the point of view of their interactions with the surroundings. In fact, interacting systems are of greater interest in thermodynamics. Let us learn to classify systems according to the nature of interaction.

5.2.1   Classification of Thermodynamic Systems

Closed system: A system is said to be closed if it exchanges energy with the surroundings but the mass remains unchanged. In other words, no mass can cross the boundary of a closed system but its volume may change. For example, the gas in a conducting cylinder fitted with an air-tight piston is an example of a closed system (Fig. 5.1c). In this case, no mass crosses the boundary. However, the movement of piston can change the volume of the gas. You may note that the piston and cylinder walls are conducting and energy may cross the boundary. That is, *in a closed system, there is exchange of energy but not of matter (mass)*. Mathematically, we can write

$$\Delta E \neq 0, \Delta V \neq 0, \Delta m = 0$$

Open system: A system is said to be open if it exchanges mass as well as energy with the surroundings. However, an open system has a fixed volume, known as the **control volume.** An electrically operated water heater used in bathroom is a familiar example of an open system. The water in its tank is heated in order to get a steady supply of hot water. The hot water flowing out of the tank is replaced by cold water flowing in. In this case, it is not convenient to choose a given mass of water as our system. Instead we direct our attention on the volume formed by the inner surface of the tank. Since water is flowing in and out across the boundary, the geyser is an open system. This is depicted in Fig. 5.2. Mathematically, we can write

$$\Delta E \neq 0, \ \Delta V = 0, \ \Delta m \neq 0$$

Can you name another physical open system?
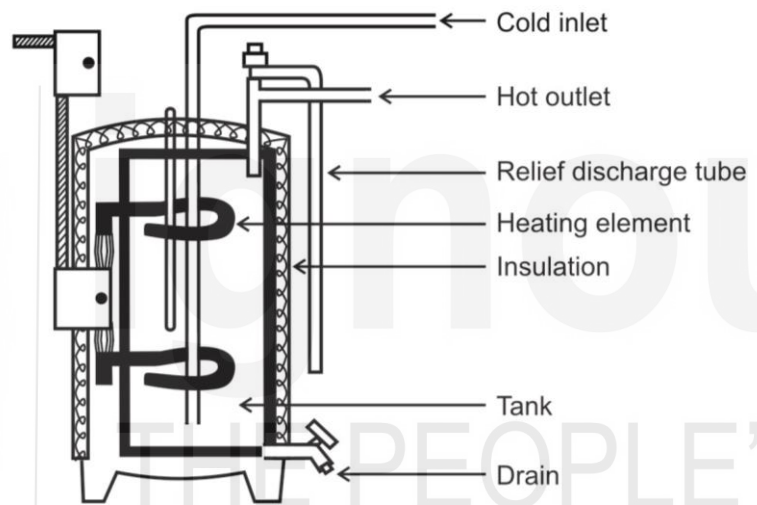
Fig. 5.2: Electrically operated water heater: An open system.

Isolated system: A system for which there is no exchange of energy or mass with the surroundings is said to be isolated. The content of an ideally sealed thermos-flask is an example of such a system. Mathematically, we can express it as

$$\Delta E = 0, \ \Delta V = 0, \ \Delta m = 0$$

It may be mentioned here that open systems find greater applications in practice.

While learning classification of systems, you must have realised that the characteristics of the boundary play an important role in determining the nature of the system. We now discuss different types of boundaries.

Mathematically we can represent closed, open and isolated systems, respectively, as

$$\Delta E \neq 0, \ \Delta V \neq 0, \ \Delta m = 0$$

$$\Delta E \neq 0, \ \Delta m \neq 0, \ \Delta V = 0$$

$$\Delta E = 0, \ \Delta m = 0, \ \Delta V = 0$$

5.2.2 Classification of Boundaries

(i)   **Diathermal Boundary:** If a boundary allows exchange of energy through it between the system and its surroundings, we say that the boundary is diathermal or thermally conducting. Note that such a boundary puts the system in thermal contact with the surroundings. A metallic (tea) pot provides a diathermal boundary to its contents.

(ii) **Adiabatic Boundary:** If a boundary does not allow any heat to flow across it, we call it an adiabatic boundary. An adiabatic boundary isolates the system thermally from its surroundings. The wall of an ideal thermos flask is adiabatic and a filled thermos flask with tight lid is a thermally isolated system.

(iii) **Rigid boundary:** If a boundary is such that it cannot be moved, even with large external mechanical force, it is said to be rigid. A system having a rigid boundary cannot be compressed or expanded. The surface of a spherical ball of steel, as used in 'shot put', is the closest approximation to a rigid boundary.

(iv) **Permeable Boundary:** If a boundary allows matter to flow through it, we call it permeable.

(v) **Semi-permeable Boundary:** If a boundary permits some constituents of the system to pass through selectively, it is called semi-permeable. Hot quartz is an excellent example of semi-permeable boundary; it allows only helium to pass through. In RO systems used for water purification, semi-permeable membranes are used to filter out impurities.

Now you may like to answer an SAQ to assess your understanding.

SAQ 1 – **System and boundaries**

a) Cite one example (different from what is given in the text) each of a system with (i) a real fixed boundary and (ii) a real moving boundary.

b) Hot water flows into the radiator of a car and flows out after cooling by radiation of heat. Should it be called an open or a closed system?

c) A bottle of water at room temperature is cooled by putting it in the refrigerator. Would you call the bottle and water an open or a closed system?

d) State the nature of a system (i.e. open, closed or isolated) enclosed by a (i) diathermal boundary and (ii) permeable boundary.

We hope that you now understand what we mean by a system and its surroundings. For a particular problem, these must be properly defined and the boundary must fulfil the conditions imposed. To illustrate this statement, suppose you want to assess the performance of a refrigerator kept in your dining room. Here the refrigerator along with its contents forms the system. Its walls define its boundary and the room in which it is placed constitutes its surroundings. But if we consider an air-conditioner installed in the same room, the room itself becomes the system, its walls, roof, floor, doors and windows constitute the boundary and its neighbouring rooms, corridor etc. become its surroundings.

Before proceeding further, we recapitulate the important terms and their definitions.

BASIC TERMINOLOGY

- **A thermodynamic system is a certain quantity of matter or a definite region of space, which is distinct from everything else that can influence it.**

- **The surface surrounding a thermodynamic system is called its boundary.**

- **Thermodynamic systems can be categorized as closed, open or isolated.**

- **The boundaries are classified as diathermal, adiabatic, rigid, permeable and semi-permeable.**

Once we select a thermodynamic system for study, we have to describe it precisely. This has analogy in mechanics, where we define the position and velocity of a particle in order to describe its motion, i.e. mechanical state of the particle. Likewise, we should know how to define thermodynamic states of different systems. This is the subject of discussion of the following section.

5.3 THERMODYNAMIC STATE OF A SYSTEM AND THERMODYNAMIC VARIABLES

We know that the pressure exerted by a gas is related to the average rate of change of momentum due to the collisions of gas molecules on a unit area of the walls of its container. Higher the rate of change of momentum, higher will be the pressure. Similarly, the temperature of a gas can be related to the average kinetic energy 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 are referred to as **microscopic properties** and are not directly perceptible.

In thermodynamics, a system is described by specifying its physical properties such as pressure, volume, temperature, mass, density etc. From Block 1, you may recall that a gas is characterised by its temperature, pressure and volume. These variables can be used to define its state. The state of a stretched wire is specified by its length and tension in it. These are called **thermodynamic variables.** The value of any property defining a system depends on its condition at the instant that property is measured. For example, the pressure and volume of a gas kept in a cylinder have fixed but different values in the two conditions shown in Fig. 5.3a and 5.3b. So we can say that the state of a system means specifying those properties of the system which uniquely define it at a particular instant.

p_1, V_1 $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ p_2, V_2

(a) $\quad\quad\quad\quad\quad\quad\quad$ (b)

Fig. 5.3: Different states of a gaseous system are characterised by different values of pressure and volume.

You must have realised that the pressure and temperature can be perceived. As such, these properties represent gross characteristics of the system and are called **macroscopic properties.**

5.3.1   Intensive and Extensive Variables

Refer to system A shown in Fig. 5.4. Suppose it is divided in two parts A_1 and A_2, each having same mass. If you measure the temperature of A and then of A_1 and A_2, you will find that its value is the same in all three cases. But the volumes of A_1 and A_2 are different from that of A. Variables whose value does not change when the system is subdivided or multiplied in size are called **intensive** and variables whose values change are said to be **extensive.** For a gaseous system, pressure, and temperature are intensive while mass and volume are extensive. The intensive variables are independent of **mass** whereas the extensive variables are dependent on mass. The intensive and extensive variables describing different systems are listed in Table 5.1.
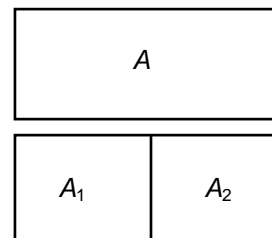
Fig.5.4: Intensive and extensive variables.

Table 5.1 : intensive and Extensive Variables for Typical Thermodynamic Systems

Thermodynamic System	Intensive Variables	Extensive Variables
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)	Length (L)
Surface film	Surface Tension (σ)	Area (A)
Electric Cell	emf (ε)	Charge (q)

We would now like you to answer an SAQ.

SAQ 2 – **Thermodynamic variables**

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

b)   List the thermodynamic variables required for specifying the following systems (i) Air inside a bicycle pump, and (ii) A dielectric substance placed in an electric field.

5.3.2   Thermodynamic Equilibrium

The state of a system may be completely specified even from a knowledge of some of its properties. It implies that we can use known properties to determine the unknown properties. For example, suppose we know the values of pressure (p), volume (V) and the number of moles (n) of an ideal gas.

Then we can obtain its temperature (T) by using the ideal gas equation:

$$pV = nRT \qquad\qquad (5.1)$$

An equation of this type is known as **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. We shall now discuss it in more detail.

Suppose you have some water at $60°C$ in a container. If this container is left to itself, it will gradually cool down to attain room temperature. This means that the container and water interact with the surroundings and temperature of water decreases with time. Once the system attains room (surroundings) temperature, no further change occurs. We then say that the container and water have attained **thermal equilibrium** with the surroundings.

If within the system, there are variations in pressure or elastic stress, its parts may move/expand/contract. Eventually when these movements cease, i.e. when no unbalanced force or torque acts on the system, it will be in **mechanical equilibrium**. For example, when a person steps on a weighing machine, the springs inside it are compressed and the pointer moves before it comes to rest showing the weight of the individual. It is then said to have attained a mechanical equilibrium.

Finally, suppose that a system contains substances that can react chemically. After a sufficient time, when all chemical reactions have stopped, the system is said to be in **chemical equilibrium**. In other words, a mixture of substances is in chemical equilibrium when they show no tendency for a chemical change to occur.

A system 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. In thermodynamics, the phrase 'state of a system' refers to an equilibrium state. Note that a system can be in different equilibrium states at different times.

Recap	**THERMODYNAMIC STATE OF SYSTEM**
	• **A thermodynamic system is described in terms of its physical properties such as pressure, volume, temperature, density etc. These properties are known as thermodynamic variables.**
	• **Thermodynamic variables are classified respectively as intensive and extensive variables, depending on whether or not they change when the system is sub-divided or multiplied.**
	• **A system simultaneously in thermal, mechanical and chemical equilibrium is said to be in thermodynamic equilibrium.**

You may ask: How does a system go from one equilibrium state to another? Let us discover the answer to this question.

5.4 THERMODYNAMIC PROCESSES

When the value of any thermodynamic variable associated with a system changes while going from one equilibrium state to another, the system is said to execute a **thermodynamic process**. Thus, a process signifies a 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 fitted with piston and maintained at constant pressure due to heating is a thermodynamic process. Again, suppose a wire is stretched tight between two rigid supports. It has certain tension and length. Now, if this wire is allowed to cool, it will try to shrink. Since it is not permitted to shrink, the tension in the wire will increase to keep it stretched at its initial length. The wire is then said to have executed a thermodynamic process.

In the subsequent units of this block, we will analyse thermodynamic processes. In order to do so, first we represent a thermodynamic process graphically. Suppose two variables x and y specify a system as shown in Fig. 5.5. 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). It is possible to reach from state A to state B in many different ways. Each of these curves is called a **path.**

Note that in whichever way you go, you would like that the intermediate states must also be defined by specific coordinates. What does that imply? It implies that all the intermediate states between A and B should be equilibrium states. But is this possible in practice? To answer this question, we first consider two types of thermodynamic processes.

Fig. 5.5: Graphical representation of several processes occurring between states A and B.

5.4.1   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 the final states are in equilibrium and if it is possible to execute the reverse process through the same equilibrium states, it is called **reversible.** If the above conditions are not satisfied, the process is called **irreversible.**

Let us now take an example to understand whether a reversible process can be executed in practice or not.

Consider a cylinder fitted with a piston and containing a gas, as shown in Fig. 5.6a. The gas occupies a volume V. We assume that weight W placed on the piston is such that on its removal, the piston will take the position $A´B´$, i.e., the volume of the gas will become $2V$ at constant temperature.

If we remove the weight W suddenly, the layer of the gas in immediate contact with the piston will expand first. This will result in instantaneous local drop in temperature and pressure. But other layers of the gas will remain relatively unaffected. This imbalance leads to an irreversible process.

Fig. 5.6: Realising a reversible process.

Now instead of having a single weight W, we put a weight equal to $W/2$. It is as if we have removed a weight $W/2$ from the configuration shown in Fig. 5.6a. The piston moves to position CD, midway between AB and $A'B'$ (Fig. 5.6b). Next, the weight $W/2$ is removed and the position goes to position $A'B'$ (Fig. 5.6c). This experiment shows that we get only one equilibrium state, CD, between the initial and the final states.

Similarly, by putting two weights, each equal to $W/3$, we can generate two intermediate states. By using n equal weights, each equal to W/n, we can have $(n-1)$ intermediate states. And for this expansion process to be reversible, all the intermediate states must be in equilibrium. For this, n must be infinitely large, i.e. the system should pass through an infinite number of equilibrium states. But this is impossible, which means that **a reversible process can only be idealized rather than achieved in practice**.

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

SAQ 3 – **Reversible and irreversible processes**

a) Classify the following processes as reversible or irreversible.

   (i)   A gas enclosed in a cylinder fitted with a frictionless piston is quickly compressed.

   (ii)   Mixing of glucose in water.

   (iii)   Oscillations of an ideal simple pendulum with a frictionless

            support in vacuum.

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

You have understood that a system can be restored to its initial state by a reversible process. When the process is completely reversible, the surroundings experience no resultant change. But, when the process is irreversible, some changes do occur in the surroundings. We may extrapolate this result to conclude that all natural processes are irreversible. This means that for such processes, the intermediate stages do not correspond to

equilibrium states and hence such processes cannot be represented by a path. But then its thermodynamic analysis is also not possible. This raises a vital question 'Can we not at all analyse natural processes thermodynamically?' The answer lies in the description of quasi-static processes. You will learn about these now.

5.4.2 Quasi-static Processes

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

Suppose we wish to heat a system from an initial temperature T_1 to a final temperature T_2. This could be done by enclosing the system in a diathermal boundary and maintaining the surroundings of the system at a temperature T_2. But this process would not be quasi-static because the temperature of the system near its boundary increases more rapidly than at points in the interior. To heat the system quasi-statically, the temperature of the surroundings should be kept initially at T_1 and then this temperature should be increased sufficiently slowly so that at all times it is infinitesimally higher than that of the system.

All real processes are non-quasi-static because during the process there is always a finite difference of pressure or temperature or both between several parts of the system. For dealing with such a process, we visualize it as being executed quasi-statically. You will be able to appreciate this statement when you solve the following SAQ.

SAQ 4 – Quasi-static processes

Classify with reason the following processes as quasi-static or non-quasi-static.

(i)   Air is being pumped in a tyre-tube slowly.

(ii)   The tyre-tube in which air is being pumped bursts suddenly.

(iii)   A small sapling grows into a big plant in two years, and we take observations of its height every day.

Now that you have learnt about quasi-static processes, you may ask: How do we represent an actual process on a diagram with different thermodynamic parameters as axes? You will learn this now.

5.4.3 Representation of a Process on an Indicator Diagram

You must have realized that the stages of a quasi-static process are a series of approximately equilibrium states. As you have seen in Fig.5.5, equilibrium

states are indicated by a series of points in the *xy*-plane, where *x* and *y* are any two thermodynamic variables. A curve through these points represents the path of the process. Such a representation is called an **indicator diagram**. Let us now learn to represent an actual process on an indicator diagram.

Refer to Fig. 5.7a. A gas is contained in a cylinder *C* fitted with a frictionless piston *P,* having dia-thermal walls. The cylinder is immersed in a constant temperature bath. 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 T_i in such a way that at any instant, the external pressure on the piston differs from the gas pressure by an infinitesimal amount. Let the final state of the gas be defined by (p_f, V_f, T_i). Note that while undergoing the change from the initial to the final state, the system passes through a series of values of *p* and *V*, which differ 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. 5.7b).

(a)   (b)
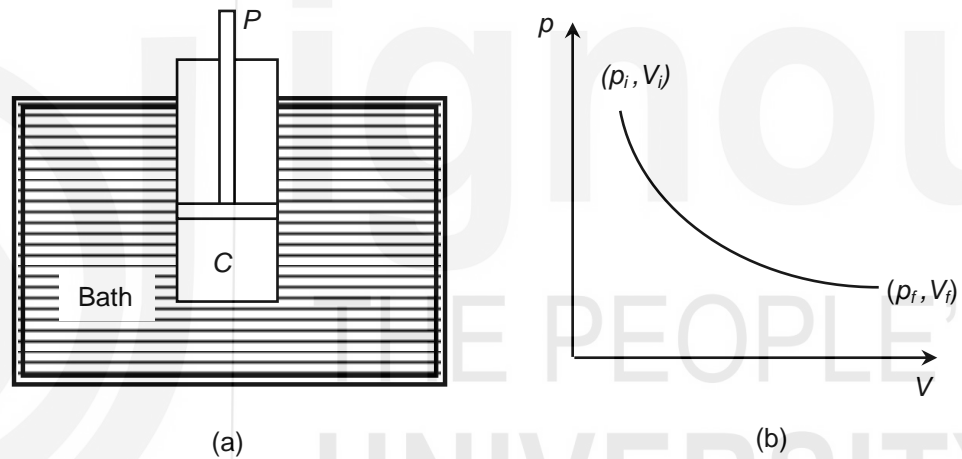
Fig. 5.7:   a) Arrangement for isothermal expansion of a gas; b) *p* vs *V* diagram for a quasi-static isothermal expansion of a gas.

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 property of the system that remains constant during the process. We code these processes by prefixing 'iso' before that property. For example, if the gas has been expanded at constant temperature, as in the example given above, the process is said to be **isothermal.** If the process takes place at constant pressure, it is called **isobaric.** A process taking place at constant volume is called **isochoric** or **isovolumic.** A change of state, e.g., melting of ice into water and water into steam, takes place at constant temperature and pressure. These are examples of isothermal-isobaric processes.

Furthermore, if the system has adiabatic boundaries, the process occurs without any exchange of heat between the system and its surroundings. We refer to such a process as an **adiabatic process**. For example, a single stroke of the piston of an internal combustion engine is very nearly adiabatic. This is because the duration of the process is extremely small and no heat can flow in or out of the system during this time.

If a process is such that the system returns to its original state along any path other than the initial one, we say that it has undergone a **cyclic process**. The working substances of all heat engines and refrigerators go through cyclic operation.

We have represented some of the above-mentioned processes on *p-V* diagrams in Fig. 5.8.
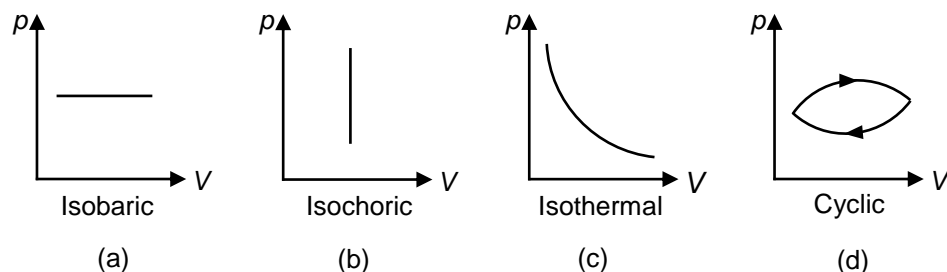
Fig. 5.8: Representation of an a) isobaric; b) isochoric; c) isothermal; d) a cyclic process on an indicator diagram.

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

SAQ 5 – **Thermodynamic processes**

Draw *V-T* and *p-T* diagrams for a perfect gas undergoing (i) isobaric expansion and (ii) isothermal compression.

Before completing this unit, we would like you to recapitulate what you have learnt in this section.

THERMODYNAMIC PROCESSES   Recap

- **When a thermodynamic system goes from one equilibrium state to another equilibrium state, it is said to execute a thermodynamic process.**

- **If all intermediate states between the initial and final states are equilibrium states and it is possible to execute the reverse process through exactly same states, the process is called reversible.**

- **If it is not possible to execute a reverse process through same intermediate states between initial and final states, the process is called irreversible.**

- **Depiction of a process on a *p-V* plot is called indicator diagram.**

5.5 SUMMARY

Concept	Description
Basic definitions	■ A region of space under study is called the **system** and everything else around it is the **surroundings**. An arbitrary surface enclosing the system is called the **boundary**.

Thermodynamic variables	■ The macroscopic quantities that determine the thermodynamic state of a system are called **thermodynamic variables**.
Extensive and intensive variables	■ Thermodynamic variables that depend on mass of the system are referred to as **extensive**. On the other hand, thermodynamic variables which do not depend on mass of the system are said to be **intensive**.
Equation of state	■ The variables of a system in thermodynamic equilibrium can be expressed in the form of a mathematical relationship called **the equation of state**.
Thermodynamic equilibrium	■ A system is said to be in **thermodynamic equilibrium** if it is in thermal, mechanical and chemical equilibria. It does not change with time in any way whatsoever.
Process	■ When any property of a system changes, the state of the system changes and the system is said to undergo a **process**.
Reversible and irreversible processes	■ A **reversible process** is one that is performed in such a way that at the conclusion of the process, both the system and the surroundings are in their respective initial **states without producing any change in the rest of the universe**. If the above condition is not satisfied, the process is called **irreversible.**
Quasi-static process	■ If a process is carried out in such a way that at any instant, the system departs only infinitesimally from an equilibrium state, the process is called **quasi-static**.

5.6 TERMINAL QUESTIONS

1. A rose plant in a garden is an example of an open system. Discuss.

2. Show that the specific value an extensive variable is an intensive property.

3. The weight of $2\,m^3$ of mercury at 0°C and 1 bar pressure at a place where $g = 9.8\,ms^{-2}$ is $2.67 \times 10^5\,N$. Write the two extensive and four intensive variables of this system.

4. Boiling water is kept in an open vessel to cool down to room temperature. Is this process quasi-static? Justify your answer.

5. Fig. 5.9 shows two isothermal processes at temperatures T_1 and T_2, respectively. By inspecting the curves, find out which of the two temperatures is higher.
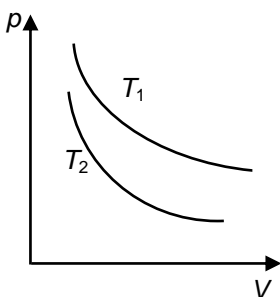
Fig. 5.9: Isotherms.

5.7 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. a) (i) A cricket ball (ii) an inflatable balloon.

   b) Open system, since the volume of water is constant.

c)   Closed system, since the mass is constant.

d)   (i) Closed (ii) open.

2. a)   Let *f* be the mass and *g* the volume of a homogeneous substance.
            Then *f* / *g* defines density, which is an intensive variable.

    b)   (i) Air inside a bicycle pump: Pressure, volume, temperature, mass
            and density;

        (ii) Dielectric in an electric field: Mass, volume, temperature, intensity
            of polarization, electric field Intensity.

3. a)   (i) Irreversible (ii) Irreversible (iii) Reversible.

    b)   Let us consider the case of compression of a gas contained in a
            cylinder by pushing the cylinder inwards. A part of the mechanical
            energy spent in pushing is used up to overcome friction between the
            piston and the cylinder. Part of the heat developed in the gas is
            conducted away through the wall of the cylinder. This process is
            irreversible and energy is dissipated in this process.

4. (i)   Quasi-static because due to slow pumping, the pressure in the tube
            increases in infinitesimally small amounts at a time and the pressure
            throughout the tube is almost uniform at any given time. This can be
            approximated to a system in equilibrium at any given point of time.

    (ii)   Non-quasi-static because after bursting of the tube, the air pressure
            in the tube as well as the volume occupied by the air changes
            suddenly and cannot be approximated to an equilibrium state.

    (iii) Quasi-static because when we take the readings of height every day,
            the increase is infinitesimally small and the state observed on each
            day can be treated as an equilibrium state.

5. The diagrams are shown in Fig. 5.10. Here *i* and *f* represent initial and
    final states respectively.

**Fig. 5.10: Representation of isobaric expansion and isotheral
        compression on *V-T* and *p-T* diagrams.**

Terminal Questions

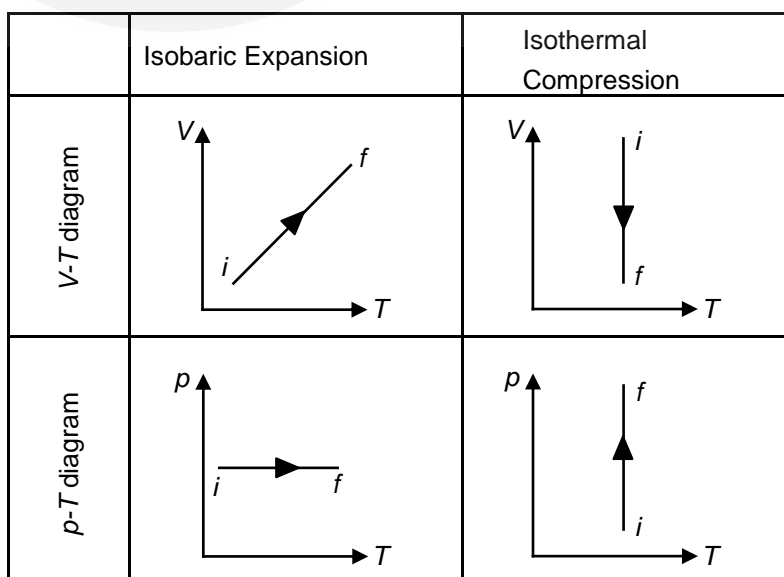1. The rose plant in a garden is a system with soil, atmosphere and other plants as surroundings. It takes up sunlight and CO_2 from air in day time and gives out O_2. It also takes nutrients and water from soil. Thus there is exchange of matter and energy with the surroundings. The rose plant is therefore an example of an open system.

2. An extensive variable, say *X*, is by definition, proportional to the mass so that it may be written as *km* where *k* is constant of proportionality. The corresponding specific value is X / m which is equal to *k*. It is independent of mass. From this we may conclude that specific value of an extensive variable is an intensive property.

3. *Extensive variables*: Volume = $2\,m^3$,
    Mass = $2.67 \times 10^5\,N / 9.8\,ms^{-2} = 2.72 \times 10^4\,kg$
    Intensive variables : Temperature = 0°C, Pressure = 1 bar,
    density = $2.72 \times 10^4\,kg / 2\,m^3 = 1.36 \times 10^4\,kg\,m^{-3}$,
    specific volume (volume per unit mass) = $2\,m^3 / 2.72 \times 10^4\,kg$
    $$= 7.35 \times 10^{-5}\ m^3 kg^{-1}.$$
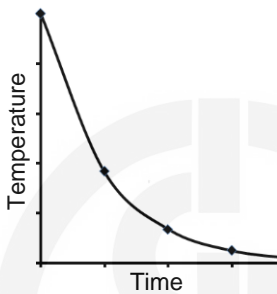
Fig. 5.11: Newton's law of cooling.
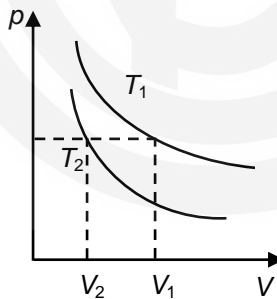
4. Non-quasi-static because the temperature of a cooling body follows the Newton's cooling law, which is exponential in nature. It falls sharply in the initial stages of cooling, and then slows down as shown in Fig. 5.11. Hence the rate of change of temperature is much higher in the initial stages of cooling and cannot be approximated to an equilibrium state.

5. In order to determine the higher of the two temperatures, draw a horizontal line parallel to volume axis, as shown in Fig. 5.12. This line represents a constant pressure. Find out the two volumes V_1 and V_2 corresponding to the intersections of the horizontal line with the two isotherms. From Boyle's law, at constant pressure, the larger volume of the gas corresponds to higher temperature. From the figure we have, $V_1 > V_2$. Hence, we can conclude that $T_1 > T_2$.

    You will notice that generally, the isotherm closer to the origin has lower temperature.

Fig. 5.12: Isotherms.
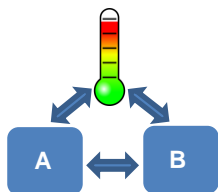
The Zeroth law of thermodynamics introduces us to the concepts of thermal equilibrium and temperature about which you will learn in this unit.

THE ZEROTH LAW

Structure

STUDY GUIDE

In the last unit, you have learnt the basic terminology used to describe a thermodynamic system. In this unit, you will learn about the Zeroth law of thermodynamics and how it helped to introduce the concept of temperature. You will also learn how to obtain parametric equation of state of a system. Parametric equation can be used to relate quantities such as the coefficient of volume expansion, compressibility and elasticity to thermodynamic variables. This would involve use of elementary calculus, including partial differentiation. You may have learnt these in your school mathematics classes. It will be useful if you refresh your knowledge about the differential equations before starting to study this unit.

We reiterate that you should answer SAQs and TQs yourself in order to check your understanding and enjoy the subject.

Heat energy of uniform temperature [is] the ultimate fate of all energy. The power of sunlight and coal, electric power, water power, winds and tides do the work of the world, and in the end, all unite to hasten the merry molecular dance.

Frederick Soddy

6.1 INTRODUCTION

The study of thermodynamics is based on four empirical laws, which are derived from experience and need no proof. That is why thermodynamics is a phenomenological science. Its laws find wide applications in the design of combustion engines, refrigeration and air conditioning systems, power generation and the like. With the help of these laws, we can determine the efficiency of all types of thermo-mechanical devices such as steam engines, thermal power plants and automobiles. These laws can also be applied to analyse energy transformations in chemical and geological systems.

In Block 1, we have used the term 'temperature' quite freely, since we are quite familiar with it. But have you ever thought as to how the concept of temperature was first introduced? Its basis lies in the *Zeroth* law of thermodynamics. We have discussed it in Sec. 6.2. The genesis of nomenclature of this law was in its formulation after the first and the second laws of thermodynamics had been established. And the concept of temperature was considered more basic than the internal energy and entropy. This law leads us to the equation of state. This equation can be represented in parametric form as discussed in Sec. 6.3. In Sec. 6.4, you will learn how to use the parametric equation of state to obtain mathematical relations between physical quantities such as coefficient of volume expansion, isothermal and adiabatic compressibilities/elasticities, etc.

| This nomenclature is due to RH Fowler. |

Expected Learning Outcomes

After studying this unit, you should be able to:

❖ state the Zeroth law of thermodynamics;

❖ explain how the Zeroth law introduces the concept of temperature;

❖ apply the parametric equation to describe different thermodynamic processes; and

❖ use the equation of state to solve problems in thermodynamics.

6.2 THE ZEROTH LAW OF THERMODYNAMICS

Refer to Fig. 6.1. Here, the adiabatic walls are denoted by solid lines and the diathermal walls are indicated by shaded lines.
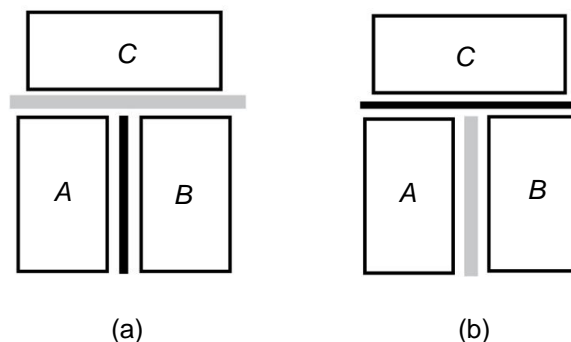

(a)   (b)

Fig. 6.1: The zeroth law of thermodynamics: a) *A* **and** *B* **are in thermal contact with** *C* ***separately*****; b)** *A* **and** *B* **are in thermal contact with one another.**

In Fig. 6.1a, *A* and *B* are separated by an adiabatic wall but are individually in thermal equilibrium with *C*. When these systems are insulated from *C* but put in thermal contact with one another as shown in Fig. 6.1b, they are seen to remain in thermal equilibrium.

We can summarise this observation as follows:

If two systems A and B are in thermal equilibrium independently with a third system C, then A and B will also be in thermal equilibrium with one another.

This is known as the **Zeroth law of thermodynamics**.

You may now like to know: What determines whether a number of bodies will be in thermal equilibrium or not when they are put in thermal contact? They must have a common property which has the same value for all systems. This property is called '**temperature'.** Thus, the temperature of a body is that property which determines whether or not it will be in thermal equilibrium with other bodies.

The phenomenon that two bodies in thermal contact tend towards a common temperature is so common that its importance was initially overlooked. When physicists finally appreciated its significance and fundamental nature, it was elevated to the status of a 'Law of Thermodynamics.' By that time the first and second laws of thermodynamics had already been enunciated. So, in order to place it ahead of the first and second laws, it was named the 'zeroth law.' The significance of this law lies in the fact that **it introduces the concept of temperature.**

You are familiar with the equation of state. The relation $pV = nRT$ (Eq.(5.1)) is one such equation of state for *n* moles of an ideal gas. Can such relations exist for other thermodynamic systems as well? From the zeroth law it can be established mathematically that relations do exist between the temperature and the other thermodynamic variables associated with a system. All such relations are the **equations of state**. Let us now study these equations in detail.

6.3 THE EQUATION OF STATE

You know that temperature of a system can be expressed in terms of two other thermodynamic variables. If *x* and *y* (pressure *p*, volume *V*, say) are the two parameters, then mathematically we can write

$$T = f_1(x, y) \tag{6.1a}$$

Eq. (6.1a) can be solved for *x* in terms of *T* and *y* or for *y* in terms of *T* and *x*. Then we get the relations of the form

$$x = f_2(T, y) \tag{6.1b}$$

and $$y = f_3(T, x) \tag{6.1c}$$

Eqs. (6.1 a, b and c) can be expressed as a composite relation as

$$f(x, y, T) = 0 \tag{6.2}$$

Eq. (6.2) is parametric as the form of the function *f* is not given. But the equation of state for an ideal gas (Eq. 5.1) is exact. Likewise, we have

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equations of state of other systems like a real gas, a stretched wire, etc. In Table 6.1, we quote equations of state for a few typical physical systems.

Table 6.1: Equations of state for various systems

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)	$f(M, B, T) = 0$	$M = CB / T$, 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)	$f(L, F, T) = 0$	$L = L_0 [1 + q_1 F + q_2 (T - T_0)]$ 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, q_1 and q_2 are constants.

The parametric forms of the equations 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 so now. This exercise will enable you to handle thermodynamic relations involving partial derivatives. You will encounter several such relations, particularly in Block 3 of this course.

6.4 DEDUCTIONS FROM THE EQUATION OF STATE

Before we proceed to study the characteristics using the equation of state, we need to learn about partial differentiation, which is an extension of the idea of ordinary differentiation. You have learnt about it in the second semester course entitled Electricity and Magnetism (BPHCT 133). We come across such differentiation when a quantity is 'a function of more than one variable and we need to know 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 change of temperature with respect to pressure for an isochoric (volume = constant) process. In this case, we are seeking the partial derivative of T with respect to p at constant V, denoted by $(\partial T / \partial p)_V$. On the other hand, if we seek the rate of variation of T with respect to V for an isobaric (pressure = constant) process, the appropriate partial derivative will be $(\partial T / \partial V)_p$.

We shall now work out the mathematical relationship between partial derivatives involving any three variables. These will be very useful to you in doing the relevant deductions involving any three variables.

Note that instead of using the symbol 'd', as in case of ordinary differentials, we use '∂' (pronounced as 'del') in case of partial differentials.

Let us assume that a gas is defined by pressure p, volume V and temperature T. So, V may be taken as a function of p and T, i.e., we can write $V = V(p, T)$. The change in volume can be expressed as

$$dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT \tag{6.3a}$$

where the first term indicates the change of volume due to change of pressure alone and the second term indicates the change of volume due to change of temperature alone. Similarly, we can write $p = p(V, T)$ and the total differential dp for change of pressure due to changes in volume and temperature as

$$dp = \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT \tag{6.3b}$$

On substituting the expression for dp from Eq. (6.3b) in Eq. (6.3a), we get

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

On collecting the coefficients of dV and dT, we can write

$$\left[1 - \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T\right] dV - \left[\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_p\right] dT = 0 \tag{6.4}$$

Note that of the three variables p, V and T, only two are independent. Let us choose V and T as the independent variables. Then, Eq. (6.4) must be true for all sets of values of dV and dT. So, for any two states which are at the same temperature ($dT = 0$), but have different volumes ($dV \neq 0$), Eq. (6.4) implies that

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

or $$\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{\left(\frac{\partial p}{\partial V}\right)_T} \tag{6.5}$$

This means that the partial derivative of any variable can be replaced by the reciprocal of the inverted partial derivative with the same variable (here T) held constant. There is another important relation which you will derive in the following SAQ.

$\mathcal{SAQ}\,1$ – **Equation of state**

Imposing the conditions $dV = 0$ and $dT \neq 0$ in Eq. (6.4), prove that thermodynamic variables are connected through the relation

$$\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p = -1 \tag{6.6}$$

We shall now discuss how to use Eqs. (6.5) and (6.6) to obtain some results of physical interest. To do so, we first define thermal expansivity or the isobaric coefficient of volume expansion, α, the bulk modulus or isothermal elasticity, E_T and the isothermal compressibility $(\beta_T = 1/E_T)$:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{6.7}$$

and

$$E_T = \frac{1}{\beta_T} = -V\left(\frac{\partial p}{\partial V}\right)_T \tag{6.8}$$

Note the negative sign in Eq. (6.8). It has been put to give E_T [or (β_T)] a positive value since pressure decreases as volume increases, i.e., $(\partial p / \partial V)_T$ is negative for all systems.

You may like to attempt an SAQ to find out the values of β_T and α for an ideal gas.

SAQ 2 – **Isothermal compressibility and volume expansion coefficient**

Show that for an ideal gas

$$\beta_T = \frac{1}{p} \quad \text{and} \quad \alpha = \frac{1}{T}$$

On combining Eqs. (6.7) and (6.8), we can write

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

or

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

Using this result in Eq. (6.6), we get

$$\left(\frac{\partial p}{\partial T}\right)_V = \alpha E_T \tag{6.9}$$

Similarly, an infinitesimal change in pressure may be expressed in terms of changes in temperature and volume as

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

Using Eqs. (6.8) and (6.9), we can write

$$dp = \alpha E_T \, dT - E_T \frac{dV}{V}$$

At constant volume, if change in temperature is small but finite, β and E_T may be assumed to be constant. Hence, the change in pressure Δp, corresponding to a finite change in temperature, ΔT, at constant volume is given by

$$\Delta p = \alpha E_T \Delta T \tag{6.10}$$

We now take up a numerical example to illustrate Eq. (6.10).

$\mathcal{E}$XAMPLE 6.1: ISOCHORIC PROCESS

The temperature of a block of copper is increased from 400K to 410K. What change in pressure is necessary to keep the volume constant? Given, for copper, $\alpha = 5 \times 10^{-5} \text{K}^{-1}$ and $E_T = 1.3 \times 10^{11} \text{Nm}^{-2}$.

SOLUTION ■ In Eq. (6.10), we have $\Delta T = 10\text{K}$.

So $\Delta p = (5 \times 10^{-5} \text{K}^{-1})(1.3 \times 10^{11} \text{Nm}^{-1}) \times 10\text{K}$

       $= 6.5 \times 10^7 \text{Nm}^{-2}$

Let us now sum up what you have learnt in this unit.

6.5 SUMMARY

Concept	Description
Zeroth law of thermodynamics and temperature	■ The **zeroth law of thermodynamics** states that *if systems A and B are separately in thermal equilibrium with a system C, then A and B will be in thermal equilibrium with one another.* This nomenclature has genesis in the fact that it introduces the concept of **temperature**, which has fundamental significance.
Thermal equilibrium	■ All systems in **thermal equilibrium** are characterized by the same temperature.
The general equation of a gaseous system	■ The general equation of any gaseous system is given by $$f(p, V, T) = 0,$$ where *f* is a single valued function of pressure *p*, volume *V* and absolute temperature *T*.
Coefficients of isobaric volume expansion, isothermal elasticity and isothermal compressibility	■ In terms of partial derivatives, the coefficients of isobaric volume expansion (α), isothermal elasticity (E_T) and isothermal compressibility (β_T) are defined as $$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \quad E_T = -V\left(\frac{\partial p}{\partial V}\right)_T, \quad \beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$ These are related to pressure through the relations $$\Delta p = \alpha E_T \, dT - E_T \frac{dV}{V}, \quad dp = \alpha E_T \, dT - \frac{1}{\beta_T}\frac{dV}{V}$$

6.6 TERMINAL QUESTIONS

1. Write down the relation between thermodynamic variables expressed by Eq. (6.6) for (i) a paramagnetic solid and (ii) a stretched wire.

2. A stretch of railway track is laid without expansion joints in Thar desert where day and night temperatures differ by 25K. The cross-sectional area of the rails is $3.6 \times 10^{-3} \text{m}^2$. The Young's Modulus, Y, of its material is $2 \times 10^{11} \text{Nm}^{-2}$ and the coefficient of linear expansion, α, is $8 \times 10^{-6} \text{K}^{-1}$.

    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, calculate the change in its length between day and night.

    (Hint: Use $Y = \frac{L}{A}\left(\frac{\partial F}{\partial L}\right)_T$ and $\alpha = -\frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_F$ where *L, F* and *T* denote

    length, tension and temperature, respectively.)

3. The density of a substance is ρ. Show that

    (i) $\beta_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T$ and   (ii) $\alpha = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p$

4. Prove that for a *pVT*-system

    $$\frac{dV}{V} = \alpha dT - \beta_T dp$$

5. Calculate the coefficient of volume expansion and isothermal compressibility for a van der Waals' gas.

6. The isothermal compressibility and expansivity of a substance are, respectively, given by

    $$\beta_T = \frac{aT^3}{p^2} \qquad \text{and} \qquad \alpha = \frac{bT^2}{p}$$

    Obtain the equation of state of the system under consideration.

6.7 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. Imposing the condition dV = 0, d$T \neq 0$ in Eq. (6.4), we get

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

    Since $\left(\frac{\partial V}{\partial T}\right)_p = +\frac{1}{\left(\frac{\partial T}{\partial V}\right)_p}$, we can write

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

2. We know that isothermal compressibility is defined as

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \qquad\qquad\qquad\qquad\qquad\text{(i)}$$

For a perfect gas, $V = \dfrac{RT}{p}$

so that $\left(\dfrac{\partial V}{\partial p}\right)_T = -\dfrac{RT}{p^2}$

On using this result in Eq. (i), we get

$$\beta_T = \frac{RT}{p^2 V} = \frac{1}{p}\cdot\frac{RT}{pV} = \frac{1}{p}$$

Similarly, volume expansion coefficient is defined as

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

For one mole of a perfect gas, $pV = RT$

so that

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p}$$

$$\therefore \quad \alpha = \frac{R}{pV} = \frac{1}{T}$$

Terminal Questions

1. (i) Paramagnetic solid: $\left(\dfrac{\partial M}{\partial B}\right)_T \left(\dfrac{\partial B}{\partial T}\right)_M \left(\dfrac{\partial T}{\partial M}\right)_B = -1$

   (ii) Stretched wire: $\left(\dfrac{\partial L}{\partial F}\right)_T \left(\dfrac{\partial F}{\partial T}\right)_L \left(\dfrac{\partial T}{\partial L}\right)_F = -1$

2. a)   Let L = length, F = tension and T = temperature of the track.
        Since $f(L,F,T) = 0$, following the relation for stretched wire
        obtained in TQ-1 (ii), we can write

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

Using the relations for Y and α given in the question, we can write,

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

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

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

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

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

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

$$= (2\times10^{11}\,\text{Nm}^{-2})\times(3.6\times10^{-3}\,\text{m}^2)\times(8\times10^{-6}\,\text{K})\times25\text{K}$$

$$= 1.44\times10^{5}\,\text{N}$$

As the temperature falls during night, the track tries to contract. However, since it is not permitted to contract, the tension increases to keep it stretched to its original length. Therefore, ΔF is positive.

b) Since $L = L(F,T)$, $\quad dL = \left(\dfrac{\partial L}{\partial F}\right)_T dF + \left(\dfrac{\partial L}{\partial T}\right)_F dT$

If the track is free to expand, $dF = 0$. $\Delta T = -25K$.

The change in length in terms of the coefficient of linear expansion is defined as

$$\Delta L = \alpha L\Delta T = (8\times10^{-6}\,\text{K}^{-1})\times(15\times10^{3}\,\text{m})\times(-25\text{K}) = -3\,\text{m}$$

Thus the track will contract by 3m.

3. (i) We know that isothermal compressibility is defined as

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V}\left(\frac{\partial V}{\partial \rho}\right)_T\left(\frac{\partial \rho}{\partial p}\right)_T \qquad (i)$$

Since $V = \dfrac{m}{\rho}$, we can write

$$\left(\frac{\partial V}{\partial \rho}\right)_T = -\frac{m}{\rho^2} \qquad (ii)$$

Using this result in (i), we get

$$\beta_T = -\frac{1}{V}\left(-\frac{m}{\rho^2}\right)\left(\frac{\partial \rho}{\partial p}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T \qquad (iii)$$

(ii) We know that volume expansivity at constant pressure is given by

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

On substituting for $(\partial V/\partial \rho)_p$ from (ii), we get

$$\alpha = -\frac{m}{V\rho^2}\left(\frac{\partial \rho}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \qquad (v)$$

4. For a pVT-system, we choose volume as independent variable and write

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

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

$$= V\alpha dT - V\beta_T dp$$

or $\qquad \dfrac{dV}{V} = \alpha dT - \beta_T dp$

5. We know that for one mole of a gas, van der Waals equation of state is

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \qquad\qquad\qquad\text{(i)}$$

Further the coefficient of volume expansion and isothermal compressibility are defined as

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

and $\qquad \beta = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_T \qquad\qquad\qquad\text{(iii)}$

Hence, from Eq. (i) we can write

$$\left[\left(p + \frac{a}{V^2}\right) - \frac{2a}{V^3}(V - b)\right]\left(\frac{\partial V}{\partial T}\right)_p = R$$

or $\qquad \left(\dfrac{\partial V}{\partial T}\right)_p = \dfrac{R}{\left(p + \dfrac{a}{V^2}\right) - \dfrac{2a}{V^3}(V - b)}$

To simplify, we multiply the numerator as well as the denominator on the right-hand side by $(V - b)$ and use Eq. (i), this gives

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R(V - b)}{RT - \dfrac{2a}{V^3}(V - b)^2} = \frac{V - b}{T\left(1 - \dfrac{2a(V - b)^2}{RTV^3}\right)}$$

$$= \frac{RV^3(V - b)}{RTV^3 - 2a(V - b)^2}$$

$$\therefore \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{RV^2(V - b)}{RTV^3 - 2a(V - b)^2} \qquad\qquad\text{(iv)}$$

To obtain the expression for β_T, we rewrite Eq. (i) as

$$p = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$\therefore \qquad \left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V - b)^2} + \frac{2a}{V^3}$$

and $\qquad -V\left(\dfrac{\partial p}{\partial V}\right)_T = E_T = +\dfrac{RTV}{(V - b)^2} - \dfrac{2a}{V^2} = \dfrac{RTV^3 - 2a(V - b)^2}{(V - b)^2 V^2}$

Hence $\beta_T = \dfrac{1}{E_T} = \dfrac{V^2(V-b)^2}{RTV^3 - 2a(V-b)^2}$ (v)

6. The equation state is a relation between any two variables out of p, V and T. Therefore, we first establish the relation between p and V. To do so, we write

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

An infinitesimal change in V corresponding to infinitesimal change in p and T can be expressed as

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

In terms of α and β_T, we can rewrite this equation as

$$dV = -V\beta_T\, dp + V\alpha\, dT$$

or $\dfrac{dV}{V} = -\beta_T\, dp + \alpha\, dT$ (iii)

For an isothermal process, $dT = 0$ and Eq. (iii) reduces to

$$\frac{dV}{V} = -\beta_T\, dp$$

On substituting the given value of β_T, we get

$$\frac{dV}{V} = -\frac{aT^3}{p^2}\, dp$$

On integration, we get the following expression:

$$\ln V = \frac{aT^3}{p} + \ln V_0$$

On taking antilogarithm, we get the equation of state for an isothermal process as

$$V = V_0\, \exp\left(\frac{aT^3}{p}\right)$$ (iv)

For an isobaric process, $dp = 0$ and Eq. (iii) reduces to

$$\frac{dV}{V} = \alpha dT = \frac{b}{p}T^2 dT$$

On integration we get

$$\ln V = \frac{b}{3p}T^3 + \ln V_0$$

On taking antilogarithm, we get the equation of state for an isobaric process as

$\therefore$ $V = V_0\, exp\left(\dfrac{b}{3p}T^3\right).$ (v)
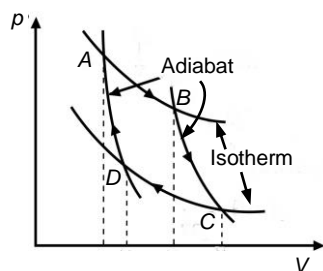
Ideally a sequence of isothermal and adiabatic processes can result in a reversible cyclic process, about which you will learn in this unit.

THE FIRST LAW AND ITS APPLICATIONS

Structure

STUDY GUIDE

In Unit 6, the concept of temperature was introduced through the Zeroth law of thermodynamics. In this unit, you will learn about the nature of heat. You are aware of the thermodynamic concept of work from your school physics curriculum. We will build upon that knowledge to introduce the concept of internal energy and formulate the first law of thermodynamics. You will appreciate that this law is universal and explains various phenomena observed in nature as well as in a laboratory – from fall in temperature with height in outer atmosphere to pressure oscillations in sound waves. This will require a basic knowledge of ordinary as well as partial differentiation and it will be a good idea to revise your prior knowledge up-front.

To enable you to grasp various important concepts and develop problem solving skills, we have interspersed solved examples in the text. Try to solve these SAQs and TQs on your own.

"Suppose we take a quantity of heat and change it into work. In doing so, we haven't destroyed the heat, we have only transferred it to another place or perhaps changed it into another energy form."

Isaac Asimov

7.1 INTRODUCTION

From your +2 physics curriculum you know that a question that puzzled the best brains of the 19th century for a long time and confronted them with many conceptual problems was 'what is the nature of heat?' The answer to this and other related questions was ultimately provided by Joule through a series of classical experiments when he concluded that '*heat is some form of motion'.* It tells us that heat is equivalent to other forms of energy. Much of our world works because of this equivalence. The electrical energy that lights our houses, operates machines and runs trains originates in heat released in burning of coal, oil, gas, etc.

We begin this unit by discussing the nature of heat in Sec. 7.2. This is followed by a discussion of work done on or by a system in Sec. 7.3. In Sec. 7.4, you will obtain the expression for the work done by a gaseous system. The efforts made to develop analytical theory of heat based on dynamical view-point led to introduction of the concept of *internal energy*, which is defined as the sum of the energies of the individual constituents of the system. (You have learnt about molecular nature of matter in Block 1 of this course.) This is discussed in Sec. 7.5.

The recognition of heat as a form of energy led to the formulation of the first law of thermodynamics, which is essentially a statement about the conservation of energy for thermodynamic systems. This constitutes the subject matter of discussion in Sec. 7.6. The first law of thermodynamics is universal and has been successfully used to understand diverse physical phenomena observed in the nature as well as in a laboratory. Using this law, we can explain interesting phenomena like the pressure oscillations in a sound wave and fall in the temperature as we move upward in the outer atmosphere.

In Sec.7.7, we begin by considering applications of the first law of thermodynamics and obtain the expression for the difference in molar heat capacities of a gas at constant pressure and constant volume. For a typical substance, the difference between heat capacities can be related to measurable quantities like volume expansion coefficient and bulk modulus of elasticity.

In Sec. 7.8, we have used this law to derive the equation of state for adiabatic processes. You know that the sound waves are propagated in a medium due to pressure oscillations. This is an adiabatic process. You will learn here to correlate the thermodynamic parameters with the speed of sound.

Expected Learning Outcomes

After studying this unit, you should be able to:

❖ explain the nature of heat;

❖ discuss the thermodynamic concept of work and obtain expressions for work done by different thermodynamic systems;

❖ define internal energy and use it to formulate the first law of thermodynamics;

❖ apply the first law of thermodynamics to obtain an expression for the difference between heat capacities of a gas at constant pressure and at constant volume;

❖ derive the equation of state for an adiabatic process; and

❖ obtain the expressions for speed of sound in air.

7.2 NATURE OF 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 temperature of a closed system − water or tea in this case − is different from that of the surroundings, energy is exchanged till such time that thermal equilibrium is established. That is, energy transfer continues till the body and the surroundings are at the same temperature. We also know that in the case of cold water, energy flows spontaneously from the surroundings to the glass, whereas in the case of hot tea, energy flows from the cup to the environment. In other words, the natural direction of energy transfer is always from the body at higher temperature to 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 the *source* and the one at lower temperature is called the *sink.*)

In 1840, Joule performed a classical experiment on the equivalence of heat and mechanical work. In the apparatus used by him, heat was produced by churning water contained in a cylinder by means of brass paddles. It means that the mechanical energy of the paddles was converted into heat. Joule argued that the heat must have been produced through chaotic motion of water molecules. Thus, he established that *molecular motion was associated with heat.*

We often say that a cup of hot coffee has heat or there is tremendous heat in the Sun. But henceforth, we shall use the word 'heat' only when it enters or leaves a system. **Heat is a form of energy in transit**. It is wrong to say heat 'in' a body. You will learn soon that when we speak of heat in a body, we essentially mean its internal energy. You will learn about the difference between 'heat' and 'internal energy' a little later in this unit.

Since heat is a directional quantity, we adopt a sign convention to represent it. Heat transferred to a system is taken as positive whereas heat taken out of a system is taken as negative. If there is no heat transfer in a process, it is said to be **adiabatic**.

Now go through the following example to grasp the ideas discussed so far.

Source of heat at temperature T is a body or a system which supplies heat to its surroundings or a body in its contact and continues to remain at constant temperature T, without exchange of any work. A *sink* of heat at temperature T is a body which receives heat from its surroundings or a body in contact with it without any change of temperature or exchange of work.

$\mathcal{E}$ *XAMPLE 7.1* : **HEAT TRANSFER IN A THERMODYNAMIC SYSTEM**

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

SOLUTION ■ The skin of the potato can 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 of the potato in the form of heat.

Recap

HEAT

- Heat is a form of energy in transit;

- The natural direction of energy transfer is always from the body at higher temperature to that at lower temperature;

- Energy is transferred in the form of heat by virtue of temperature difference; and

- Heat is closely connected to the molecular motion.

7.3 WORK

We now know that if the cause of transfer of energy is temperature difference between the system and the surroundings, then that form of energy is heat. But it is possible that energy interaction is not caused by temperature difference between the system and the surroundings. When energy crosses the boundary of a system and it is not in the form of heat, it is work.

If a system as a whole exerts force on its surroundings so that a displacement takes place, the work that is done 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.* In thermodynamics, internal work is of no consequence. Let us take an example of a storage battery. When it is not in operation, the changes that take place in its cells, such as internal-diffusion of chemicals, are not accompanied by the performance of any work, and so are not significant for us.

We adopt the convention that 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, whereas the work consumed by compressors or mixers is negative.

You may now like to answer an SAQ.

SAQ 1 - **Work done by a system**

a) Explain whether any work is done or not in the following processes.

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

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

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

7.4 EXPRESSION FOR WORK

In thermodynamics, we express the work in terms of the state variables of the
system. This permits simple mathematical analysis. To do so, we have to
ensure that the system is always near an equilibrium state, i.e. the process is
quasi-static. With this understanding, we now proceed to obtain the
corresponding expressions for work done on/by gaseous system .for different
processes.

7.4.1 A Gaseous System

Refer to Fig. 7.1, which shows a cylinder fitted with a frictionless piston and
filled with a gas of mass M. Let the area of cross-section of the piston be A
and the pressure exerted on it by the system at any instant be p. Obviously,
the force acting on the piston will be equal to pA. This force pushes the piston

$F = pA$

f

i
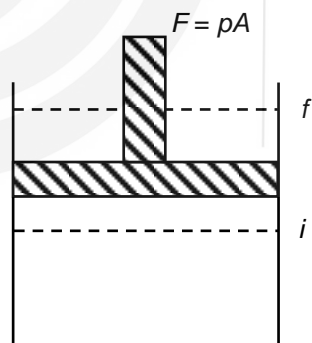
**Fig. 7.1: Work done during expansion of a gaseous system. Here *i* and *f* stand
for the initial and final states, respectively.**

outwards. If the piston moves in the direction of the force through dx, we can
write down the work done by the system as

$$\delta W = p \, A \, dx$$

Note that $A \, dx$ signifies the increase in volume of the system due to outward
movement of the piston and we can write dV for $A \, dx$. Thus, the work done by
the system when the piston moves outward through dx is given by

$$\delta W = p \, dV \tag{7.1}$$

> You will learn that the
> internal energy (U) is a
> function of the state
> whereas work (W) and
> heat (Q) are not. An
> infinitesimal change in a
> quantity which is not a
> function of state is
> indicated by putting the
> symbol δ (pronounced
> as delta) on the left of
> the quantity of interest.
> The infinitesimal
> change in a quantity
> which is a state function
> is indicated by putting
> 'd' on the left of the
> quantity. Hence, an
> infinitesimal amount of
> work is denoted by δW,
> an infinitesimal amount
> of heat by δQ. And an
> infinitesimal amount of
> internal energy is
> denoted by dU.

If the system expands quasi-statically from initial volume V_i to final volume V_f, the total work done by the gaseous system on its surroundings is given by

$$W = \int_{V_i}^{V_f} p\,dV \tag{7.2}$$

Fig. 7.2: *p-V* **diagram for a gaseous system undergoing expansion.**

For evaluating the integral in Eq. (7.2), we need to know how p varies with V, which depends on the nature of the process. The pressure p and the volume V at any instant can be shown on an indicator diagram (Fig. 7.2) as a point. The curve joining a series of such points gives the path of the process of expansion or compression. The nature of the curve depends on how p varies with V. Note that pdV is represented by 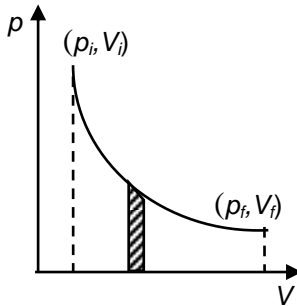the area of the shaded strip in the figure. The total work done W between the initial and final states is the sum of the areas of strips obtained for all the infinitesimal changes from the initial to the final state. This is equal to the total area under the *p-V* curve of the system.

Work done in an isothermal process

Let us now calculate the work done in an isothermal expansion (or compression) of an ideal gas. You will recall that n mole of ideal gas obeys the perfect equation of state:

$$pV = nRT \tag{7.3}$$

On substituting for p from Eq. (7.3) in Eq. (7.2), we obtain the expression for total work done:

$$W_{isotherm} = \int_{V_i}^{V_f} (nRT\,/\,V)\,dV$$

$$= nRT\,\ln(V_f\,/\,V_i) = 2.303\,nRT\,\log_{10}(V_f\,/\,V_i) \tag{7.4}$$

From this equation we note that when an ideal gas expands isothermally, the work done by it depends on the temperature T and the expansion ratio of final to initial volumes rather than the difference $(V_f - V_i)$. We know that during expansion, $V_f > V_i$ and $\ln(V_f\,/\,V_i) > 0$. It means that the work done by the system when it expands isothermally is positive.

However, in the case of compression, $V_f < V_i$ so that $\ln(V_f\,/\,V_i) < 0$ and $W_{isotherm}$ is negative. This means that when a system is compressed isothermally, work is done on the system.

You may now like to answer an SAQ to check your progress.

SAQ 2 – **Work done by a gaseous system**

a) Express Eq. (7.4) in terms of pressure.

b) Obtain the expression for work done in expanding the gas from volume V_i to V_f in an isobaric process.

Work done in an isochoric process

Next let us consider a gas that undergoes an isochoric process. In this case, $dV = 0$, and hence, $\delta W = pdV = 0$. So, no work is done either on or by the system in an isochoric process.

We now give a solved example to help you grasp the concept.

$\mathcal{E}$*XAMPLE 7.2*: **WORK DONE BY AN IDEAL GAS**

Two mole perfect gas at STP is expanded isothermally to twice its original volume. The gas is then made to undergo an isochoric change to attain its initial pressure. Calculate the total work done. Given: $R = 8.3\,\text{JK}^{-1}\text{mol}^{-1}$.

SOLUTION ■ Here $V_f / V_i = 2$. Hence work done by the gas in the isothermal expansion is

$$nRT \ln(V_f/V_i) = (2\ \text{mol}) \times \left(8.3\ \text{JK}^{-1}\text{mol}^{-1}\right) \times (273\ \text{K}) \times (\ln 2) = 3.1 \times 10^3\ \text{J}$$

Since no work is done during an isochoric process, the total work done by the gas $= 3.1 \times 10^3$ J.

7.4.2 Path Dependence of Work and Heat

You know 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. Refer to Fig. 7.3, which depicts three processes *ACB, ADB* and *AEB* between initial and final states defined by *A* and *B* on an indicator diagram. The path *ACB* indicates a general process. The path *ADB* is the combination of an isochoric and an isobaric process, whereas the path *AEB* is the combination of an isobaric and isochoric process. The work done for the process *ACB* is equal to the area *ACBFG*. Similarly, the work done during the processes *ADB* and *AEB* are given by areas *DBFG* and *AEFG,* respectively. Since these areas are not equal, we can say that that the work done between the same initial and final states during these processes is not the same. It means that *the work done by a system between any initial and final state depends on the path taken*. In other words, **work is not a function of the state**.

Fig.7.3: The points *A* and *B*, are connected by different paths.

Is the same true about heat content? To understand this let us take an example. Suppose you have a glass of milk at 30ºC and you wish to have its temperature raised by 5ºC. This can be done by adding heat to it or churning it vigorously or by a combination of heating and churning. However, in all the cases we ultimately arrive at a state which can be defined as 'milk at 35ºC'. In all the cases, the initial state was 'milk at 30ºC'. The processes connecting these states were different and the quantities of heat given to the system in the three processes were not the same. So we can say that *heat given to the system depends on the process*, i.e*., the path followed between the initial and the final state*. Hence, **heat is not a function of the state**.

Before proceeding further, you should recapitulate what you have learnt so far in this unit.
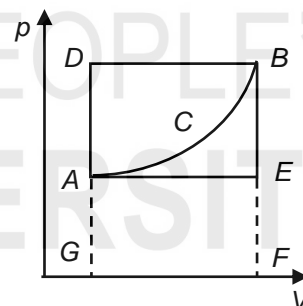
Recap

WORK DONE BY AN IDEAL GAS

- The work done by a gaseous system on its surroundings is given by

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

- For an isothermal process $W_{iso} = 2.303\, nRT\, log_{10}\left[V_2 / V\right]_1$

- Heat and work are function of the path followed, i.e., these depend on the process rather than the state.

So, we now know that work and heat are not functions of the state. You may now ask: Is there any function which is independent of the path followed between the initial and final states? Yes, such a function does exist. It is known as *internal energy*. You will now learn about it in some detail.

7.5 INTERNAL ENERGY

We know that on heating, ice melts to form water at 0ºC. On the basis of the kinetic theory of gases we can say that if temperature remains constant, the kinetic energy remains constant. Since energy has to be conserved, what can you say about the added thermal energy? When ice is converted into water, its specific volume changes from 0.92 cc g^{-1} to 1 cc g^{-1}. To bring about this change, work is done at the expense of added energy.

However, the major share of the additional energy is used up in breaking the bonds of intermolecular attraction in ice and this energy is stored in water. (It is released when water freezes into ice.) The energy apparently shown by a system during a phase transition is termed as **internal energy**.

In thermodynamics, it is not necessary to know the source of internal energy. But it can be easily understood that the sum of kinetic energies of all the molecules in a system defines *internal kinetic energy*. Also, due to the inter-atomic/ intermolecular attractions, each atom / molecule making up the system possesses potential energy.

The total energy stored in the system due to the interactions defines *total internal potential energy*. *The sum of internal kinetic and potential energies of all the molecules constitutes the internal energy of the system*. We denote it by the symbol *U*.

The internal energy depends only on the state variables like pressure, temperature and volume. It is therefore a 'state function'. In SAQ 3, you will learn that for a cyclic process, there is no change in the internal energy. In fact, this result holds for all functions of state.

You can now answer an SAQ on the concept of internal energy.

$\mathcal{SAQ}$ 3 – **Internal energy of a cyclic process**

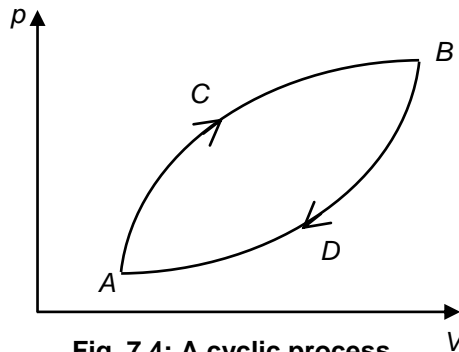Show that the change in the internal energy during a cyclic process depicted in (Fig, 7.4) is zero.

Fig. 7.4: A cyclic process.

We now know 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 Figs. 7.5a and b, we have shown schematically two methods, viz. adding heat energy and doing work on it, respectively, by which the internal energy of a system can change. We shall now invoke the well-known 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.

(a)   (b)
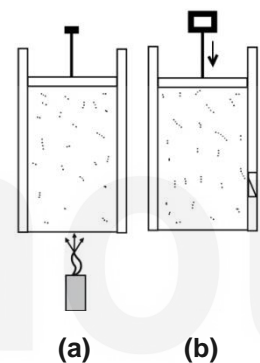
Fig. 7.5: Internal energy of a system can be changed by a) Adding thermal energy; b) by doing work on it.

7.6   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 the universe) remaining constant. According to this principle, we cannot get energy out of nowhere. *If energy of a system increases, there must have been an equivalent loss of energy of the surroundings.*

Let us again consider the example of raising the temperature of a cup of milk. We can say that the internal energy of the milk can be increased in three ways: (i) by way of heat input only, (ii) by way of work input only and (iii) by way 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 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 $-\Delta W$. However, the change in internal energy is the same in each case. Let us denote it by ΔU. Here all the quantities are expressed in heat units. From the principle of conservation of energy, we have

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

Mathematically, we can write

$$\Delta U = \Delta Q + (-\Delta W) = \Delta Q - \Delta W \qquad (7.5)$$

When heat is converted into other forms of energy (as in a steam engine) or vice versa (as in an electric heater), in each form it is equivalent. If a quantity of heat, Q, is converted entirely into work, W, then W is equivalent to Q and W/Q = constant known as the mechanical equivalent of heat. It is denoted by J and its value is approximately equal to 4.2 J cal^{-1}. Thus, one calorie of heat is equivalent to 4.2J of work. Likewise, work can be expressed in heat units. We shall express both work and heat by the same units.

This is the mathematical form of the first law of thermodynamics. The formal statement of the first law is: '*Internal energy of a system is a function of the state of the system and any change in it during a thermodynamic process is equal to the sum of the heat given to the system and the work done on the system.*' According to this law, we can say that for a thermodynamic process taking place between two particular states, the difference between the heat absorbed and the work done by the system is always constant; equal to the change in internal energy of the system.

You may recall that the heat required to convert 1 g of water at 100°C to 1 g of steam at 100°C is 540 cal at normal atmospheric pressure. This is termed as latent heat as it does not induce temperature rise. You may naturally wonder, as to what happens with this heat? A part of it is utilised in performing external work by the system. The rest is utilised in breaking up intermolecular bonds so that water is converted from liquid to vapour state, i.e. to raise the internal energy of the system. Let us now look at this from a quantitative point of view. Go through the following numerical example carefully.

$\mathcal{E}$*XAMPLE* *7.3* : **PHASE CHANGE AND INTERNAL ENERGY**

1g of water and steam at normal atmospheric pressure (1.013×10^5 Nm^{-2}) occupy 1 cm^3 and 1671 cm^3 volumes, respectively. Calculate the change in internal energy for vaporisation of 1g of water at 100°C. (Latent heat of steam is 540 cal and mechanical equivalent of heat $= 4.2\,$Jcal^{-1}).

SOLUTION ■ For 1g of water vaporising to steam, $\Delta U = \Delta Q - \Delta W$, where $\Delta Q = 540$ cal, $\Delta W = p\,(V_2 - V_1)$, and V_1 and V_2 are volumes of water and steam, respectively.

Here, $p = 1.013 \times 10^5$ Nm^{-2}, $V_1 = 1$ cm^3, $V_2 = 1671$ cm^3.

$\therefore \Delta W = (1.013 \times 10^5$ Nm$^{-2}) \times (1671 - 1) \times 10^{-6}$ m$^3 = 169.2$ J $= 40.3$ cal.

and, $\Delta U = (540 - 40.3)$ cal $= 499.7$ cal.

Thus we see that out of 540 cal, only 40.3 cal is spent in doing external work, while the rest goes to raise the internal energy of the system. ΔU ($= 499.7$ cal) for this process is often referred to as the internal latent heat.

Now before proceeding further, attempt the following SAQ.

Fig. 7.6: Change of state of a system along different paths.

$\mathcal{SAQ}$ *4* – **First law of thermodynamics**

Refer to Fig. 7.6. When a system is taken from state i to state f following the path iaf, it is found that $\Delta Q = 45$J and $\Delta W = 20$J. But along the path ibf, $\Delta Q = 30$J.

a) What is ΔW along the path ibf ?

b) If $\Delta W = -13$J for the curved return path fci, what is ΔQ for this path?

c) Taking $U_i = 10$ J, what is U_f?

d) If $U_b = 21$ J, what are ΔQ's for the processes ib and bf ?

To study further applications of the first law of thermodynamics, we need to know the differential form of the law. You will now learn about it.

7.6.1   Differential Form of the First Law

You now know that functions like work and heat are path dependent and so will be the changes in these. But the change in internal energy is independent of path.

We may now extend Eq. (7.5) to write the differential form of the first law of thermodynamics as

$$dU = \delta Q - \delta W$$

or,

$$\delta Q = dU + \delta W \tag{7.6}$$

Eq. (7.6) is the *differential form of the first law of thermodynamics.*

You may now like to work out an SAQ on the first law of thermodynamics.

> If a physical quality is a function of state rather than the path, it is said to be exact differential. On the other hand, if a physical quality depends on the path, it is said to be an inexact differential. In order to indicate this difference mathematically, we put 'd' before the exact differential U, while we put 'δ' before the inexact differentials (Q and W).

SAQ 5 – **Mathematical form of the first law**

a) Write down the mathematical form of 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 used in the text write down the differential form of the first law for a gas in a cylinder fitted with a piston.

c) 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.

Significance of the First Law

So far, we have learnt that the first law of thermodynamics is very significant since it defines 'internal energy' as a function of the state of the system and heat as energy in transit. Being an extension of the principle of conservation of energy, it rules out the possibility of constructing a machine which can work on its own, without any input. There are several physical situations, where this law can be successfully applied. In the next sections we will discuss some important applications of the first law.

7.7   HEAT CAPACITIES OF A GAS

You may recall that according to kinetic theory, molar heat capacity of an ideal gas is independent of its nature, i.e., for all gases of given atomicity, molar heat capacity at constant volume or at constant pressure is same. But, physical conditions under which heat is given introduce change in the value of heat capacity of a gas. Let us, therefore, obtain an expression for the difference in the heat capacities of an ideal gas at constant pressure and constant volume. Assume that one kilomole of a gas is contained in a cylinder fitted with a frictionless piston. In Unit 5, you have learnt that the state of a gas

You may recall that heat capacity of a substance varies with temperature as well as amount of the substance. The amount of substance is expressed in **kg** or by **number of moles. The corresponding measures of heat capacity are specific heat capacity and molar heat capacity.** At constant volume, the specific heat capacity is denoted by small letter c_v and molar heat capacity is denoted by C_V. These are connected through the relation

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

where m is the mass of one kilomole of the substance. The specific heat capacity is measured in $J\,kg^{-1}\,K^{-1}$ and molar heat capacity is measured in the units of $J\,kmol^{-1}\,K^{-1}$.

can be described in terms of any two thermodynamic variables 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 sum of its partial differential with respect to T at constant V multiplied by dT and that with respect to V at constant T multiplied by dV:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad (7.7)$$

The symbol ∂ (pronounced as del) denotes a partial derivative. On combining Eqs. (7.6) and (7.7), and expressing the work done by the gas as $\delta W = pdV$, that you have worked out in SAQ 5b, we can write

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV \qquad (7.8)$$

Now suppose that the piston was 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, its temperature. **The heat required to raise the temperature of one kilo 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 generally expressed in $J\,kmol^{-1}\,K^{-1}$. For such a system, Eq. (7.8) reduces to

$$C_V = \left(\frac{\delta Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad (7.9)$$

Note that different symbols have been used to depict changes in heat, internal energy and temperature because heat is not a function of state. Now suppose that the piston was 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 given to the surroundings. So, to achieve the same rise in temperature, more heat has to be supplied to the gas in a constant pressure (isobaric) 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 kilo mole of a gas by one degree.** It is denoted by the symbol C_p. Mathematically, we can write

$$C_p = \left(\frac{\delta Q}{\partial T}\right)_p \qquad (7.10)$$

On combining Eqs. (7.8 and 7.10), we can write

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

The first term on the right-hand side of this result is molar heat capacity at constant volume [Eq. (7.9)]. Then on rearranging terms, we can write

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p \qquad (7.11)$$

Let us pause for a while and interpret this result. The first term in the square brackets on the right-hand side tells us that the internal energy of a gas may vary with volume even when temperature is kept fixed. This implies that for change in volume, work has to be done against intermolecular forces in the gas. It means that knowledge of the difference of heat capacities at constant pressure and at constant volume gives us information about variation of internal energy of a substance with volume.

We recall that according to kinetic theory, there are no intermolecular forces in an ideal gas. This implies that internal energy of a perfect gas is wholly kinetic and $(\partial U / \partial V)_T = 0$. Using this result in Eq. (7.11), we get

$$C_p - C_V = p\left(\frac{\partial V}{\partial T}\right)_p \tag{7.12}$$

This shows that the difference in the molar heat capacities of a gas depends on how the volume of a system changes with temperature at constant pressure. We expect this difference to be substantial since a small change in temperature brings about significant change in the volume of a gas. Using the gas law $(pV = RT)$, we can write

$$p\left(\frac{\partial V}{\partial T}\right)_p = R$$

Using this result in Eq. (7.12), we get

$$C_p - C_V = R \tag{7.13}$$

This result is known as **Mayer's formula**. It shows that the difference between constant pressure and constant volume molar heat capacities is equal to the molar gas constant; independent of temperature; and same for all gases.

You may now ask: How do these predictions compare with the observed results? To know the answer to this question, refer to Table 7.1, where we have given molar heat capacities of some gases (in units of R) at constant pressure as well as at constant volume.

Table 7.1: Molar heat capacities of a few gases at constant pressure and constant volume

Type of Gas	Gas	C_p / R	C_V / R	$\left(C_p - C_v\right)/R$
Monoatomic	He	2.5	1.5	1.0
	Ar	2.5	1.5	1.0
Diatomic	H_2	3.45	2.45	1.0
	O_2	3.53	2.53	1.0
	Cl_2	4.17	3.09	1.08
Polyatomic	CO_2	4.43	3.42	1.01
	NH_3	4.42	3.34	1.08
	C_2H_6	6.21	5.18	1.03

You must have noted that but for Cl_2 and polyatomic gases, Mayer's formula holds rather well. Before proceeding further, you should answer an SAQ.

$\mathcal{SAQ}$ 6 – Heat capacities of gases and the first law

a) For hydrogen, the molar heat capacities at constant pressure and constant volume are 28.8 J mol^{-1} K^{-1} and 20.5 J mol^{-1} K^{-1}, respectively. Calculate the gas constant.

b) The constant pressure molar heat capacity of a gas is 160 J mol^{-1}K^{-1}. Calculate the ratio of specific heat capacities at constant pressure to that at constant volume.

c) Show that for an ideal gas, the first law of thermodynamics can also be written as

$$\delta Q = C_V\, dT + p dV \quad \text{and} \quad \delta Q = C_p\, dT - V dp$$

Proceeding further, we recall that a real gas is made up of molecules having small but finite size and non-zero inter-molecular forces. This suggests that we should use the van der Waals' equation of state. The mathematical steps are somewhat cumbersome and we will just quote the result (TQ 4):

$$C_p - C_V = R\left(1 + \frac{2a}{VRT}\right) \tag{7.14}$$

On comparing Eqs. (7.13) and (7.14) we note that the difference between heat capacities at constant pressure and at constant volume is more for a real gas than for a perfect gas. Did you not expect this result? We know that for a real gas, the internal energy changes with volume because work has to be done against the intermolecular forces. Also, at high pressures, molecules experience a repulsive force. Thus, we may expect some change, howsoever small, in temperature when a real gas is made to undergo expansion/compression.

You may now ask: Do we distinguish heat capacities at constant volume and constant pressure for solids and liquids as well? For these substances, such a distinction is of little significance because they are incompressible. In fact, for solids and liquids, measured values are quoted at constant pressure. Before proceeding further, let us summarise what you have learnt about the heat capacities of different substances.

Recap

HEAT CAPACITIES OF A GAS

- The molar heat capacity of a gas at constant pressure (volume) is defined as the amount of heat required to raise the temperature of one kilo mole of a gas by one degree.

- For one mole of an ideal gas, the difference in molar heat capacities at constant pressure and constant volume is given by Mayer's formula:

$$C_p - C_V = R$$

- For a van der Waals' gas, we have: $C_p - C_V = R\left(1 + \dfrac{2a}{VRT}\right)$

- For solids and liquids, the difference in molar heat capacities at constant pressure and constant volume is almost negligible.

So far, we have obtained the expression for the difference between molar heat capacities at constant pressure and constant volume for an ideal and a van der Waal's gas. Let us now consider a process in which no heat is exchanged between the system and surroundings. You may have experienced that if you let air out of a tyre, you feel that the air is cool. You can do a simple activity yourself. 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.

You may be aware of some adiabatic processes occurring around you. Sound propagation in air, drop in temperature with altitude, existence of Deep Ocean currents are a few important examples of adiabatic processes. Here, we will consider propagation of sound in air. To be able to do so, we must know the equation of state for an adiabatic process. We now derive it using the first law of thermodynamics.

7.8   EQUATION OF STATE FOR AN ADIABATIC PROCESS

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

$$dU + \delta W = 0 \tag{7.15}$$

From this expression we note that internal energy will decrease in an adiabatic expansion. Since internal energy is a function of temperature, a fall in internal energy implies drop in temperature, i.e., the system cools. You may now ask: 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. We will not discuss this here but those of you who are interested in details should read the books given in the references at the end of this volume.

Proceeding further, let us suppose that one mole of an ideal gas is made to undergo quasi-static adiabatic expansion. Then, using the result obtained in SAQ 6c, we can write

$$C_V dT + p dV = 0 \tag{7.16}$$

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 $p = RT/V$ in Eq. (7.16), dividing throughout by $C_V T$ and rearranging the resulting expression, we get

$$\frac{dT}{T} = -\frac{R}{C_V}\frac{dV}{V} \tag{7.17}$$

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). Therefore, it is pertinent to assume that C_V remains independent of temperature.

For a quasi-static 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. (7.17) to obtain

$$\ln T = -\frac{R}{C_V} \ln V + \ln K \tag{7.18}$$

where $\ln K$ is constant of integration.

Taking antilog and rearranging terms, we get

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

Using Eq. (7.13) we can rewrite it as

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

From Block 1, you may recall that the ratio of heat capacity at constant pressure to that at constant volume is denoted by the Greek symbol gamma; $\gamma = C_p / C_V$. It is referred to as *adiabatic index*. So, we can rewrite the equation for an adiabatic transformation as

$$TV^{\gamma - 1} = K \tag{7.19}$$

This relation tells us that when a perfect gas undergoes a quasi-static adiabatic change and temperature increases, volume will decrease and vice versa. Note that the change is not linear. This is an important result.

You may now ask: Can we similarly relate pressure and temperature or pressure and volume for an adiabatic process? To get the answer to this question, we would like you to solve an SAQ.

$\mathcal{SAQ}$ 7 – **Other equations of state for an adiabatic process**

Starting from Eq. (7.19), show that

$$\frac{T^{\gamma}}{p^{\gamma - 1}} = K_1 \tag{7.20}$$

and $\qquad\qquad pV^{\gamma} = K_2 \tag{7.21}$

where K_1 and K_2 are constants.

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

Eq. (7.20) predicts that during an adiabatic process, change in pressure is accompanied by a corresponding change in temperature. What can you say about Eq. (7.21)?

Note that Eqs. (7.19), (7.20) and (7.21) are equivalent forms of the so-called *adiabatic equation*. These equations will hold provided

i)   the initial and final states are equilibrium states,

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

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

Before proceeding further, you should assess your understanding by answering the following SAQ.

SAQ 8 – **Application of adiabatic process**

Differentiate Eq. (7.21) w.r.t. V and calculate $(dp/dV)_{ad}$. Also calculate the corresponding expression for an isothermal change. Compare the results. What do you conclude?

While answering SAQ 8 you must have noted that an adiabat is steeper than an isotherm by a factor of γ. You will obtain the same result if you plot Eq. (7.21) on a p-V diagram (Refer to Fig. 7.7).
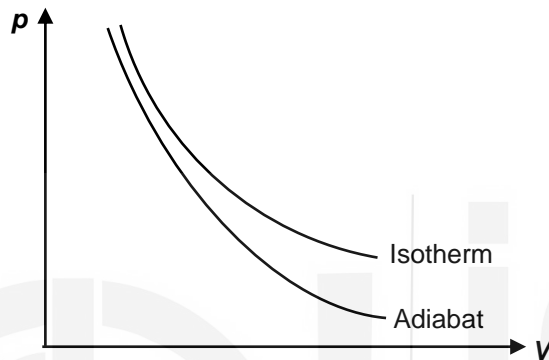

Fig. 7.7: Plot of Eq. (7.21)

From the solution of SAQ 8 you will recall that $(\partial p / \partial V)_S$, which defines the slope of an adiabat, is equal to $-\gamma(p/V)$. It is γ times the slope $(\partial p / \partial V)_T$ of an isotherm. It implies that relative change in volume in an adiabatic process is less than that in an isothermal process.

Before proceeding further, you should carefully go through the example given below based on adiabatic change.

Since the physical properties of a gas depend on the physical conditions under which a process is carried out, we put a suffix to denote the type of change. It is for this reason that p and V were used to denote heat capacities at constant pressure and constant volume. Similarly, for adiabatic and isothermal processes we put the suffixes S and T, respectively with the physical quantity of interest.

EXAMPLE 7.5 : **ADIABATIC CHANGE**

The nozzle of a bicycle pump 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 of magnitude F reducing the volume to one-third. No air escapes from the pump. Assume the change to be adiabatic. Taking γ for air to be 1.4, calculate the final temperature of air in the pump.

SOLUTION ◼ For an adiabatic change, we use Eq. (7.21) and write

$$p_i V^\gamma = p_f \left(\frac{V}{3}\right)^\gamma$$

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

$$p_f = p_i 3^\gamma = 4.66 p_i.$$

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Using the perfect gas equation of state, you can write: $\dfrac{p_i V}{T_i} = \dfrac{p_f (V/3)}{T_f}$

or $\qquad T_f = \dfrac{p_f}{3 p_i} T_i = \dfrac{4.66}{3} T_i = 1.55 \times (300\,\text{K}) = 465\,\text{K}$

Note that 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. This is a vivid demostration of theoretical prediction that adiabatic compression produces heating.

You may now like to answer an SAQ.

$\mathcal{SAQ}$ 9 – Adiabatic expansion

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

Earlier in this unit, you have learnt how to obtain an expression for work done in an isothermal and isochoric processes. Let us now obtain the expression for work done in an adiabatic change.

7.8.1 Work done in an Adiabatic Change

Suppose that one mole of a perfect gas undergoes adiabatic change and its volume changes from V_1 to V_2 and pressure changes from p_1 to p_2. We know that during an adiabatic process, a system is thermally insulated from its surroundings.

So, when a gas expands from volume V_1 to V_2, the work done by it is given by

$$W_{ad} = \int_{V_1}^{V_2} p\, dV$$

On substituting the value for pressure from Eq. (7.21) in this expression, we obtain

$$W_{ad} = \int_{V_1}^{V_2} \frac{K}{V^\gamma}\, dV = \frac{K}{1-\gamma}\left(\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}} \right) = \frac{1}{1-\gamma}\left[p_2 V_2 - p_1 V_1 \right]$$

$$= \frac{R(T_1 - T_2)}{\gamma - 1} \tag{7.22}$$

An important manifestation of adiabatic process is found in the troposphere in that as we move up, the temperature gradually drops. This is referred to as *adiabatic lapse rate*. You can read about it in Appendix 7A.

Another important manifestation of adiabatic processes is the transmission of sound in air. You will now find out the relationship between the speed of sound and thermodynamic parameters.

7.8.2   The Speed of Sound

In your school physics classes, you have studied propagation of sound in air. This essentially consists of pressure oscillations in the medium and are accompanied by local changes in temperature. However, the total energy of the system is conserved. That is, we can say that adiabatic changes occur in air when sound propagates. You may now like to know as to how the speed of sound is related to the properties of the medium. It is given by

$$v_S = \sqrt{\frac{E_s}{\rho}}$$
(7.23)

where E_s and ρ, respectively, denote the adiabatic bulk modulus of elasticity and density of the medium. By definition, the bulk modulus of elasticity is given by

$$E = \frac{\text{Stress}}{\text{Volume strain}} = \frac{\Delta p}{(\Delta V / V)} = V\left(\frac{\Delta p}{\Delta V}\right)$$

In the language of calculus, we can write: $E = -V\dfrac{dp}{dV}$

The negative sign appears because for all known systems, *V decreases* as *p* increases. Therefore, we can write the expression for the adiabatic bulk modulus of elasticity as:

$$E_S = -V\left(\frac{\partial p}{\partial V}\right)_S$$
(7.24)

From Eq. (7.21), we know that $pV^\gamma = K$. On differentiation, we get

$$\gamma p V^{\gamma-1}dV + V^\gamma dp = 0$$

which gives $\left(\dfrac{\partial p}{\partial V}\right)_S = -\dfrac{\gamma p}{V}$

Using this result in Eq. (7.24), we get

$$E_S = \gamma p$$
(7.25)

This shows that adiabatic elasticity is γ times pressure. Upon using this result in Eq. (7.23), you will get the expression for speed of sound in terms of pressure:

$$v_S = \sqrt{\frac{\gamma p}{\rho}}$$
(7.26)

This expression for speed of sound is known as *Laplace formula*. For air, $\gamma = 1.4$, $\rho = 1.29$ kg m^{-3} and $p = 1.01 \times 10^5$ N m^{-2} so that Eq. (7.26) gives speed of sound in air to be $v_S = 331$ ms^{-1}. This value is in excellent agreement with the measured value of 332 ms^{-1}. From this we can conclude that thermodynamic arguments work really well in this case.

You may now like to answer an SAQ.

SAQ 10 – **Speed of sound**

Newton proposed that when sound wave propagates in air, isothermal changes take place. Then speed of sound can be defined as

$$v = \sqrt{\frac{E_T}{\rho}}$$

Using this definition, derive the relation equivalent to Eq. (7.26) and estimate the percentage difference from the value obtained using Laplace formula.

Using the equation of state in Eq. (7.26) for one mole of air, the expression for speed of sound can also be written as

$$v = \sqrt{\frac{\gamma RT}{V\rho}} = \sqrt{\frac{\gamma RT}{M}} \tag{7.27}$$

This result shows that speed of sound in air is directly proportional to square root of temperature and inversely proportional to square root of the molecular weight of air. Do these predictions agree with the observations? Indeed, there is remarkable agreement.

We now recapitulate important results obtained in this section.

Recap

ADIABATIC PROCESS

- The equation of state for an adiabatic process is given by $pV^\gamma = $ constant. Other equivalent forms are $TV^{\gamma-1} = $ constant and $T^\gamma p^{1-\gamma} = $ constant.

- The work done in an adiabatic process is given by

$$W_{ad} = \frac{1}{\gamma - 1}(p_2 V_2 - p_1 V_1) = \frac{1}{\gamma - 1}R(T_2 - T_1)$$

Let us now sum up what you have learnt in this unit.

7.9 SUMMARY

Concept	Description
Heat	■ Heat is a 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 from the system is considered as negative.

Work	■ If an energy interaction takes place between a system and its surroundings, not by way of difference of temperature, then it is called work.
	■ Work done *by* a thermodynamic system is taken as positive and that done *on* the system is taken as negative.
	■ The expressions of work done in different systems undergoing finite changes are:

- Expansion of a gaseous system from volume V_i to V_f:

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

- Isothermal expansion of a perfect gas from volume V_i to V_f:

$$W = nRT \ln(V_f / V_i)$$

■ Work done by or on the system during a process as well as heat absorbed or evolved by a system during a process are path dependent. Therefore, work and heat are not functions of the state of the system.

Internal energy

■ The internal energy of a system is the sum of the energies of individual constituents of the system. It is a function of the state of the system.

The first law of thermodynamics

■ The 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 processes connecting the same initial and final states. The differential form of the first law is:

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

Heat capacities

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

$$C_p - C_V = R$$

Equation of state of an adiabatic process

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

$$TV^{\gamma-1} = \text{constant}$$

In terms of temperature and pressure, it is:

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

In terms of pressure and volume, it is:

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

where γ is ratio of heat capacities at constant pressure and constant volume and is known as adiabatic index.

Propagation of sound in air

■ The propagation of sound in air is an adiabatic process. The expression for the speed of sound is

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

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

7.10 TERMINAL QUESTIONS

1. Two moles of a perfect gas occupy a volume of 0.050 m³ and exert a pressure of 2.6×10^5 Nm⁻². It is compressed isobarically to a volume of 0.035 m³. Determine the work done on/by the gas and the change in its temperature. (Given R = 8.3 JK⁻¹ mol⁻¹).

2. A perfect gas at 300K occupies a volume of 0.2 m³ at a pressure of 5×10^6 Nm⁻². It is allowed to expand isothermally until its volume is 0.5 m³. Next the gas is compressed isobarically up to its original volume. And finally, the pressure is increased isochorically until the gas returns to its initial state. Calculate the work done during the cycle.

3. A person consumes a diet of 10^4J per day and spends total energy of 1.2×10^4J per day. Determine the daily change in the internal energy. If the net energy spent comes from sucrose at the rate of 1.6×10^4J kg⁻¹, in how many days will the person reduce his mass by 1 kg?

4. Obtain the expression for the difference in the heat capacities for a real gas given by Eq. (7. 14).

5. Starting from the first law of thermodynamics, show that

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

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

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

where E_T is isothermal elasticity and α is volume expansion coefficient.

6. Isothermal compressibility (β_T) is inverse of isothermal elasticity. Calculate β_T for (i) an ideal gas, and (ii) a van der Waals' gas.

7. A reversible cyclic process consists of four steps: isothermal expansion (*AB*) at temperature T_1, adiabatic expansion (*BC*), isothermal compression (*CD*) at temperature T_2 and adiabatic compression (*DA*) as shown in Fig. 7.8. Using the first law of thermodynamics, obtain an expression for the total work done.

Fig. 7.8: A reversible cyclic process.

8. Two identical gaseous systems, each containing 0.06 mol of ideal gas, are at 300K and 2.0 atm. The ratio of heat capacities of the gas is 1.4. One of the gases is made to expand adiabatically and the other isothermally till they reach atmospheric pressure. Calculate the final volume in each case.
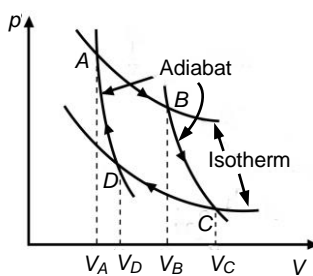
7.11   SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. a) (i) When the magnetic domains are realigned against frictional forces inside a magnet, some work is done. This work results in the rise in the temperature of the magnet.

    (ii) In this case, current flows in the coil and it gains kinetic energy. So work is done.

  b) (i) +ve (ii) –ve.

2. a) For an ideal gas undergoing isothermal process from state (p_i, V_i) to state (p_f, V_f), we have $p_iV_i = p_fV_f$. Therefore $V_f / V_i = p_i / p_f$. Substituting this in Eq. (7.4), we get

$$W_{iso} = nRT \ln (p_i / p_f)$$

  b) Since the system expands from volume V_i to V_f at constant pressure, we can write

$$W_p = \int_{V_i}^{V_f} \delta W = \int_{V_i}^{V_f} pdV = p(V_f - V_i) = p\Delta V$$

3. Refer to Fig. 7.4. 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 of *U* during the cyclic process is $(U_B - U_A) + (U_A - U_B) = 0$.

4 a) We know that $U_f - U_i$ = constant independent of path joining *i* and *f*. For *iaf*, $\Delta Q = 45$ J and $\Delta W = 20$J. So from Eq. (7.5), we get

    $\Delta U = (45 - 20)$ J = 25J and hence, $U_f - U_i = 25$ J.

    Therefore, for *ibf*, we have 25 J = 30 J $- \Delta W$ or $\Delta W = 5$ J

  b) $U_f - U_i = 25$ J. So, for the return path *fci*, we have

      $- 25$ J $= \Delta Q - \Delta W = \Delta Q + 13$ J

    or $\Delta Q = (- 25 - 13)$ J $= - 38$J

  c) $U_f - U_i = 25$ J. Hence, $U_f = U_i + 25$ J = 10 J + 25 J = 35 J

  d) We have already obtained in (a) that ΔW for *ibf* = 5 J. But *bf* being an isochoric process, no work is done in it. Hence, for *ib*, $\Delta W = 5$ J.

    Now, $\Delta Q - 5$ J $= U_b - U_i = 21$ J $- 10$ J = 11 J

    $\therefore$ For *ib,* $\Delta Q = 16$ J. Again for *bf*, $\Delta W = 0$J,

    $\therefore \Delta Q = \Delta W + U_f - U_b = 0 + 35$ J $- 21$ J = 14 J

5. a) For a thermally insulated system, $\delta Q = 0$. Then Eq. (7.6) implies that $dU = - \delta W$. Therefore, increase in internal energy is equal to the work done on the system. Alternatively, the work done by the system equals the decrease in internal energy i.e. the system does work at the cost of its internal energy.

  b) $\delta Q = dU + pdV$

   c) $\delta W \approx 0$, since change in volume is negligible; δQ is negative since the system loses heat and dU is negative since temperature decreases.

6. a) We know that $C_p - C_V = R$. On substituting the given values, we get $R = 8.3\,\mathrm{Jmol^{-1}K^{-1}}$.

   b) It is given that molar heat capacity at constant pressure is $160\,\mathrm{Jmol^{-1}K^{-1}}$. Using Eq. (7.13) we can calculate C_V:

   $$C_V = C_p - R$$

   Since $R = 8.3\ \mathrm{J\,mol^{-1}\,K^{-1}}$, we find that

   $$C_V = (160\ \mathrm{J\,mol^{-1}\,K^{-1}}) - (8.3\ \mathrm{J\,mol^{-1}\,K^{-1}}) = 151.7\ \mathrm{J\,mol^{-1}\,K^{-1}}$$

   Hence, $\gamma = \dfrac{C_p}{C_V} = \dfrac{160\,\mathrm{J\,mol^{-1}K^{-1}}}{151.7\,\mathrm{J\,mol^{-1}K^{-1}}} = 1.05$

   c) The first law of thermodynamics is

   $$\delta Q = dU + pdV \qquad\qquad\text{(i)}$$

   Using Eq. (7.9) you can write: $dU = C_V dT$

   Hence, $\delta Q = C_V dT + pdV \qquad\qquad\text{(ii)}$

   From the equation of state for an ideal gas, $pV = RT$ we get

   $$pdV + Vdp = RdT \quad\Rightarrow\quad pdV = RdT - Vdp$$

   Using this result in (ii) we get

   $$\delta Q = (C_V + R)\,dT - Vdp = C_p\,dT - Vdp \qquad\qquad\text{(iii)}$$

7. From Eq. (7.19), we recall that

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

   For a perfect gas, the equation of state is $pV = RT$. On substituting for V we get

   $$T\left(\frac{RT}{p}\right)^{\gamma-1} = K \quad\text{or}\quad \frac{T^{\gamma}}{p^{\gamma-1}} = \frac{K}{R^{\gamma-1}} = K_1 \qquad\qquad\text{(ii)}$$

   Similarly, on substituting for T in (i) you will get

   $$pV^{\gamma} = KR = K_2 \qquad\qquad\text{(iii)}$$

8. From Eq. (7.21), for an adiabatic process, we have $pV^{\gamma} = K$. On differentiation

   $$\gamma pV^{\gamma-1}dV + V^{\gamma}\,dp = 0$$

   $$\therefore \qquad\qquad \left(\frac{dp}{dV}\right)_S = -\gamma\left(\frac{p}{V}\right) \qquad\qquad\text{(i)}$$

   For an isothermal process, $pV = $ constant

   $$\therefore \quad pdV + Vdp = 0 \quad\text{or}\quad \left(\frac{dp}{dV}\right)_T = -\left(\frac{p}{V}\right) \qquad\qquad\text{(ii)}$$

   These results show that the curve depicting an adiabatic process is steeper than the one corresponding to an isothermal process since $\gamma > 1$. In fact, the slope of an adiabat is γ times the slope of an isotherm.

9. Since the change is adiabatic and we have to compute the variation in temperature, we use Eq. (7.20): $\dfrac{T^\gamma}{p^{\gamma-1}} = K_1$

So, for initial and final states defined by (T_i, p_i) and (T_f, p_f) we can write

$$\frac{T_i^\gamma}{p_i^{\gamma-1}} = \frac{T_f^\gamma}{p_f^{\gamma-1}} \quad \text{or } T_f = \left(\frac{p_f}{p_i}\right)^{(\gamma-1)/\gamma} T_i$$

It is given that the initial pressure in the tube is 2 atm. When it bursts, it attains atmospheric pressure. On substituting the given data, we get

$$T_f = \left[\frac{1}{2}\right]^{(1.4-1)/1.4} \times (300\,\text{K}) = 0.82 \times 300\,\text{K} = 246.1\,\text{K}$$

This result shows that temperature drops in an adiabatic expansion.

10. We are told that according to Newton, the expression for speed of sound should be $v = \sqrt{\dfrac{E_T}{\rho}}$

For a perfect gas, $pV = RT$ and so, $\left(\dfrac{\partial p}{\partial V}\right)_T = -\dfrac{RT}{V^2}$

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

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

Substituting for air, $\rho = 1.29\ \text{kg m}^{-3}$ and $p = 1.01 \times 10^5\,\text{N m}^{-2}$ we find that

$$v = \sqrt{\frac{1.01 \times 10^5\,\text{Nm}^{-2}}{1.29\,\text{kg m}^{-3}}} = 280\ \text{ms}^{-1}$$

The difference between the values obtained by Laplace and Newton formulations is

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

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

Terminal Questions

1. Work done by the gas under isobaric condition is given by $\Delta W_p = p\,(V_f - V_i)$. Inserting the given values, we get

$$\Delta W_p = 2.6 \times 10^5\,(0.035 - 0.050)\ \text{J} = -3.9 \times 10^3\ \text{J}.$$

The negative sign implies that work is done on the gas. Now for a perfect gas $pV = nRT$, so that

$$\Delta W_p = nR\,\Delta T$$

The change in the temperature is given by

$$T = \Delta W_p / nR = -3.9 \times 10^3\,\text{J} / (2\ \text{mol} \times 8.3\ \text{J mol}^{-1}\text{K}^{-1}) = -235\ \text{K}$$

2. The equation of state of a perfect gas is $pV = nRT$.

    $\therefore$ $n = pV / RT = (5 \times 10^6 \times 0.2) / (8.3 \times 300) = 400$ moles.

    (i) For the isothermal path, $V_i = 0.2$ m^3, $V_f = 0.5$ m^3, p $= 5 \times 10^6$ Nm^{-2}.

        $\therefore$ $p_f = p_i V_i / V_f = 5 \times 10^6$ Nm$^{-2} \times 0.2$ m$^3 / 0.5$ m^3 $= 2 \times 10^6$ Nm^{-2}

        $\therefore$ Work done by the gas, $\Delta W_T = nRT \ln (V_f / V_i)$

            $\Delta W_T = 400$ mol $\times 8.3$ J mol^{-1} K$^{-1} \times 300$K $\times \ln (0.5 / 0.2)$

                $= 9.1 \times 10^5$ J

    (ii) Work done on the gas in compressing it from 0.5m^3 to 0.2m^3 at constant pressure of 2×10^6 Nm^{-2} is

        $\Delta W_p = -p \Delta V = -2 \times 10^6$ Nm$^{-2} \times (0.5 - 0.2)$ m$^3 = -6 \times 10^5$ J

    (iii) No work is done along the isochoric path.

        Hence, total work done by the gas

            $= (9.1 - 6.0) \times 10^5$ J $= 3.1 \times 10^5$J.

3. The calorie content of the diet consumed is the heat supplied and energy spent is the work done by the system. Thus,

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

    $\therefore$ $dU = \delta Q - \delta W$

            $= 1.0 \times 10^4 - 1.2 \times 10^4 = -2000$ J.

    The decrease corresponds to loss of sucrose. The amount of sucrose lost per day is 2000J / (1.6 $\times 10^4$ J kg^{-1}) = 0.125 kg.

    Required number of days = 1 kg / 0.125 kg = 8.

4. For one mole of a van der Waals' gas, the equation of state is

    $$\left(p + \frac{a}{V^2} \right)(V - b) = RT \qquad \qquad \text{(i)}$$

    where a and b are van der Waals' constants for a gas.

    If we assume that internal energy of a real gas is given by

    $U = -\dfrac{a}{V} +$ constant, we can write

    $$\left(\frac{\partial U}{\partial V} \right)_T = +\frac{a}{V^2}$$

    Using this result in Eq. (7.11), we get

    $$C_p - C_V = \left(p + \frac{a}{V^2} \right)\left(\frac{\partial V}{\partial T} \right)_p \qquad \qquad \text{(ii)}$$

    To proceed further, we differentiate Eq. (i) with respect to T and obtain

    $$\left[\left(p + \frac{a}{V^2} \right) - \frac{2a}{V^3}(V - b) \right]\left(\frac{\partial V}{\partial T} \right)_p = R$$

We can rewrite it as

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{\left(p + \frac{a}{V^2}\right) - \frac{2a}{V^3}(V - b)}$$

On multiplying both sides of this expression by $\left(p + \frac{a}{V^2}\right)$, we can write

$$\left(p + \frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_p = \frac{R\left(p + \frac{a}{V^2}\right)}{\left(p + \frac{a}{V^2}\right) - \frac{2a}{V^3}(V - b)} = \frac{R}{1 - \frac{2a(V - b)}{V^3\left(p + \frac{a}{V^2}\right)}}$$

On using this result in Eq. (ii), and replacing $\left(p + \frac{a}{V^2}\right)$ in the

denominator of above equation by $\frac{RT}{(V - b)}$, we get

$$C_p - C_V = \frac{R}{1 - \frac{2a}{V^3 RT}(V - b)^2} \approx \frac{R}{1 - \frac{2a}{VRT}}$$

since *a* and *b* are very small.

Using binomial expansion with *n*=1, we obtain the required result:

$$C_p - C_V = R\left(1 + \frac{2a}{VRT}\right) \qquad\qquad \text{(iii)}$$

Binomial expansion is

$$\frac{1}{(1 - x)^n} = 1 + nx$$

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

5.   From Eq. (7.11) 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 Eq. (6.7) as

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

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

On rearranging terms, we get the required result:

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

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

To know pressure variation of internal energy you have to rewrite (i) as

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

By definition, isothermal elasticity is given by Eq. (6.8) as

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

Using this result in (iii), we get pressure variation of internal energy:

$$\left(\frac{\partial U}{\partial p}\right)_T = \frac{pV}{E_T} - \frac{C_p - C_V}{\alpha E_T} \tag{iv}$$

6. For an ideal gas, the equation of state is

$$pV = RT \tag{i}$$

Hence, $\quad (\beta_T)_{ideal} = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{p}{RT} \times \left(-\frac{RT}{p^2}\right) = \frac{1}{p}$ (ii)

That is, $(\beta_T)_{ideal}$ is the inverse of pressure for an ideal gas. You may have expected this result from Eq. (7.25). Similarly, for a van der Waals' gas

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \tag{iii}$$

or $\quad p = \frac{RT}{V - b} - \frac{a}{V^2}$

So, $\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$ and $-V\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{\beta_T} = -\frac{2a}{V^2} + \frac{RT}{(V-b)^2}V$

On using (iii), we find that $\quad \frac{1}{\beta_T} = -\frac{2a}{V^2} + \frac{\left(p + \dfrac{a}{V^2}\right)V}{V - b}$

If we ignore b in comparison with V, we get

$$\frac{1}{\beta_T} = -\frac{2a}{V^2} + \left(p + \frac{a}{V^2}\right) = \left(p - \frac{a}{V^2}\right) \quad \text{or} \quad (\beta_T)_{Van} = \frac{1}{p - \dfrac{a}{V^2}}$$

This shows that $(\beta_T)_{Van} > (\beta_T)_{Ideal}$. This is physically expected because of the presence of inter-atomic forces in a real gas.

7. For an isothermal process, $dU = 0$ so that all heat absorbed during this process is converted into work: $\delta Q = pdV$

Hence, $W_{A \to B} = \int\limits_{V_A}^{V_B} pdV = RT_1 \int\limits_{V_A}^{V_B} \frac{dV}{V} = RT_1 \, ln\left(\frac{V_B}{V_A}\right)$ (i)

where T_1 is the temperature at which heat is absorbed by the system.

For an adiabatic expansion, $\delta Q = 0$ and increase in volume tends to decrease internal energy and hence temperature so that $T_2 < T_1$. Hence

$$W_{B \to C} = \int_{V_B}^{V_C} p\,dV = \int_{V_B}^{V_C} \frac{K\,dV}{V^\gamma} = -\frac{K}{\gamma - 1}\left[\frac{1}{V_C^{\gamma - 1}} - \frac{1}{V_B^{\gamma - 1}}\right]$$

Using the equation of state for an adiabatic process, we can rewrite it as

$$W_{B \to C} = \frac{R(T_1 - T_2)}{\gamma - 1} \qquad (ii)$$

Similarly, for isothermal compression you can readily show that

$$W_{C \to D} = RT_2 \ln\left(\frac{V_D}{V_C}\right) = -RT_2 \ln\left(\frac{V_C}{V_D}\right) \qquad (iii)$$

whereas for adiabatic compression

$$W_{D \to A} = -\left(\frac{R(T_1 - T_2)}{\gamma - 1}\right) \qquad (iv)$$

On combining results contained in (i) to (iv), you will get

$$W = W_{A \to B} + W_{B \to C} + W_{C \to D} + W_{D \to A} = RT_1 \ln\left(\frac{V_B}{V_A}\right) - RT_2 \ln\left(\frac{V_C}{V_D}\right)$$

8. The initial volume of both gases may be obtained using the ideal gas law, $pV = nRT$. On solving for V, we get

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

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

For the isothermal process, temperature remains constant at 300K. So when pressure drops to half the initial value, the equation $pV = \text{const}$ implies that the volume will double. So the final volume will be $1.5 \times 10^{-3}\ \text{m}^3$. That is,

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

For the adiabatic process, we have $p_i V_i^\gamma = p_f V_f^\gamma$

On solving for V_f, we get

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

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

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.

APPENDIX-7A: ADIABATIC LAPSE RATE

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. (7.20). For one mole of the gas, Eq. (7.20) in logarithmic form becomes:

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

On differentiation, we can write the resultant expression as:

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

which can be rearranged as:

$$\frac{dp}{p} = \frac{\gamma}{\gamma - 1} \frac{dT}{T} \tag{7A.1}$$

Let us now pause for a moment 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, for one mole of air, we can use the equation of state $p = RT / V$ in the above expression. This gives:

$$\frac{dp}{p} = -\frac{Mg}{RT} dh \tag{7A.2}$$

where $M = \rho V$ is the mass of one mole of air . ($M = m N_A$, where m is the average mass of one air molecule.) On combining Eqs. (7.A.1) and (7.A.2), we get:

$$\frac{dT}{dh} = -\left(\frac{\gamma - 1}{\gamma}\right) \frac{Mg}{R} \tag{7A.3}$$

This is the expression for adiabatic lapse rate. The negative sign on the RHS indicates that temperature decreases as we move upwards.

Typically, $\dfrac{dT}{dh} = 9.8 \times 10^{-3}$ K m^{-1}. This means that over one kilometre, the temperature falls by about 10K.

FURTHER READINGS

1. **Thermal Physics: Kinetic Theory, Thermodynamics and Statistical Mechanics** by Garg, S.C., Bansal, R.M. and Ghosh, C.K., McGraw Hill Education (India) Pvt. Ltd., 2nd Edition, Seventh Reprint (2018).

2. **A Treatise on Heat** by Saha, M.N. and Srivastava, B.N., The Indian Press, 5th Edition (1969).

TABLE OF PHYSICAL CONSTANTS

Symbol	Quantity	Value
c	Speed of light in vacuum	3.00×10^{8} ms^{-1}
μ_0	Permeability of free space	1.26×10^{-6} NA^{-2}
ε_0	Permittivity of free space	8.85×10^{-12} C^{2}N^{-1}m^{-2}
$1/4\pi\varepsilon_0$		8.99×10^{9} Nm^{2}C^{-2}
e	Charge of the proton	1.60×10^{-19} C
$-e$	Charge of the electron	-1.60×10^{-19} C
h	Planck's constant	6.63×10^{-34} Js
$\hbar$	$h/2\pi$	1.05×10^{-34} Js
m_e	Electron rest mass	9.11×10^{-31} kg
$-e/m_e$	Electron charge to mass ratio	-1.76×10^{11} Ckg^{-1}
m_p	Proton rest mass	1.67×10^{-27} kg (1 amu)
m_n	Neutron rest mass	1.68×10^{-27} kg
a_0	Bohr radius	5.29×10^{-11} m
N_A	Avogadro constant	6.02×10^{23} mol^{-1}
R	Universal gas constant	8.31 Jmol^{-1}K^{-1}
k_B	Boltzmann constant	1.38×10^{-23} J K^{-1}
G	Universal gravitational constant	6.67×10^{-11} Nm^{2}kg^{-2}

LIST OF BLOCKS AND UNITS: BPHCT-135

BLOCK 1:   KINETIC THEORY OF GASES

Unit 1   **Ideal and Real Gases**

Unit 2   **Molecular Velocity Distribution Function**

Unit 3   **Mean Free Path and Transport Phenomena**

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BLOCK 2:   THE ZEROTH AND THE FIRST LAWS OF THERMODYNAMICS

Unit 5   **Thermodynamic Description of a System**

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BLOCK 4:   STATISTICAL MECHANICS

Unit 12   **Basic Concepts of Statistical Mechanics**

Unit 13   **Classical Statistics**

Unit 14   **Quantum Statistics**

SYLLABUS: THERMAL PHYSICS AND STATISTICAL MECHANICS (BPHCT-135)

4 Credits

Kinetic Theory of Gases: Expression for pressure (no derivation), kinetic interpretation of temperature and derivation of gas laws, real gases (van der Waals equation, qualitative discussion). Derivation of Maxwell's law of distribution of velocities and its experimental verification, expression for average speed $(\bar{v})$, most probable speed (v_p), and root mean square (v_{rms}), law of equipartition of energy (no derivation) and its applications to specific heat of gases, monoatomic and diatomic gases. Mean free path (zeroth order). Transport phenomena, viscosity, conduction and diffusion (discussion of physical implications only, no derivation). Brownian motion (no derivation) and its significance, sedimentation, Perrin's experiment.

The Zeroth Law and The First Law of Thermodynamics: Boundaries, variables, processes (reversible and irreversible), graphical description. Statement of zeroth law, introduction of concept of temperature, applications of the zeroth law. Compressibility and expansion coefficient. First law of thermodynamics, statement, parametric form, mathematical form (integral and differential), relation between c_p and c_v, work done during isothermal and adiabatic processes, velocity of sound.

The Second and Third Law of Thermodynamics: Heat engines, conversion of heat into work, Carnot cycle, efficiency of a Carnot engine, Carnot theorem, Kelvin-Planck and Clausius statements of second law of thermodynamics, equivalence of Kelvin-Planck and Clausius statements. Entropy, second law and entropy, entropy changes in reversible and irreversible processes, entropy-temperature diagram, statement and consequences of the third law of thermodynamics (unattainability of absolute zero temperature, etc.). Thermodynamic potentials, enthalpy, Gibbs, Helmholtz and internal energy functions, Maxwell's relations and their applications, Clausius-Clapeyron equation, Joule Thomson effect, *TdS* equations. Black body radiation, spectral distribution, concept of energy density, derivation of Planck's law, deduction of laws of radiation (Wien's distribution law, Rayleigh-Jeans law, Stefan Boltzmann law and Wien's displacement law).

Statistical Mechanics: Phase space, macrostate and microstate, entropy and thermodynamics probability, distribution function. Maxwell-Boltzmann law, partition function of a monoatomic gas and deduction of thermodynamic functions. Need for quantum statistics, Bose-Einstein distribution function, Bose-Einstein photon gas, Fermi-Dirac distribution function, strongly degenerate Fermi system, Fermi energy, electronic heat capacity, comparison of the three statistics.