

# UNIT 5



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

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### 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

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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

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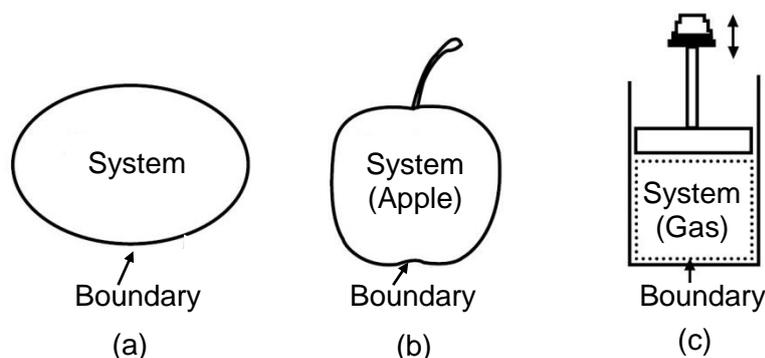
After studying this unit, you should be able to:

- ❖ 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

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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?

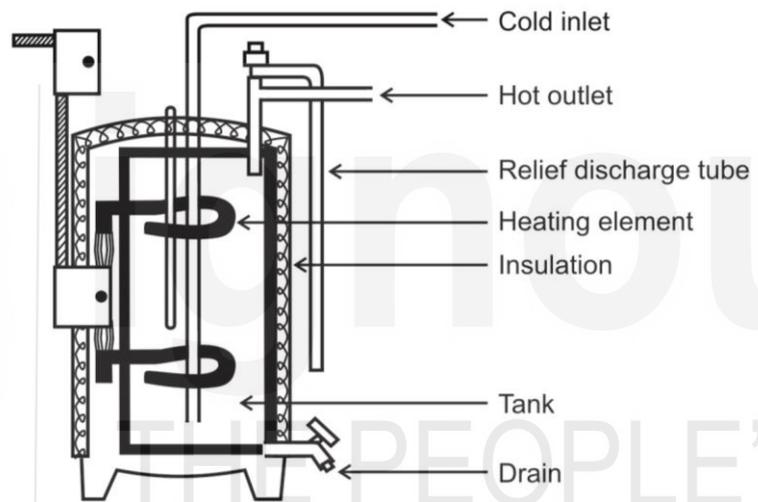


Fig. 5.2: Electrically operated water heater: An open system.

**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.

### 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.

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

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

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

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

- (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.

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### *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.
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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.

## Recap

## 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

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.

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.

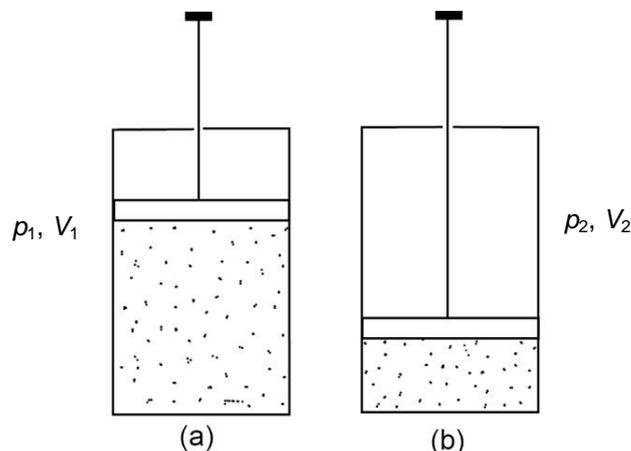


Fig. 5.3: Different states of a gaseous system are characterised by different values of pressure and volume.

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.

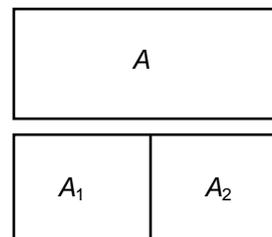


Fig.5.4: Intensive and extensive variables.

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 ( $\rho$ )	Mass ( $m$ ) Volume ( $V$ )
Paramagnetic solid	Flux density ( $B$ )	Intensity of magnetisation ( $M$ )
Stretched wire	Tension ( $F$ )	Length ( $L$ )
Surface film	Surface Tension ( $\sigma$ )	Area ( $A$ )
Electric Cell	emf ( $\varepsilon$ )	Charge ( $q$ )

We would now like you to answer an SAQ.

#### SAQ 2 – Thermodynamic variables

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

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

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  $60^\circ\text{C}$  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.

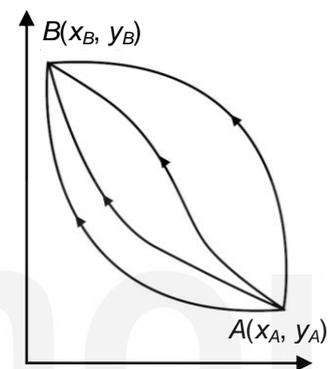
### 5.4.1 Reversible and Irreversible Processes

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

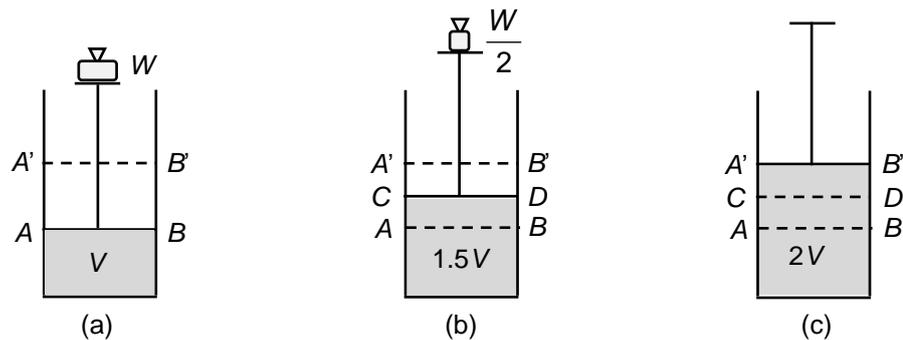


Fig. 5.6: Realising a reversible process.

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.

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### 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.

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#### 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.

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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.

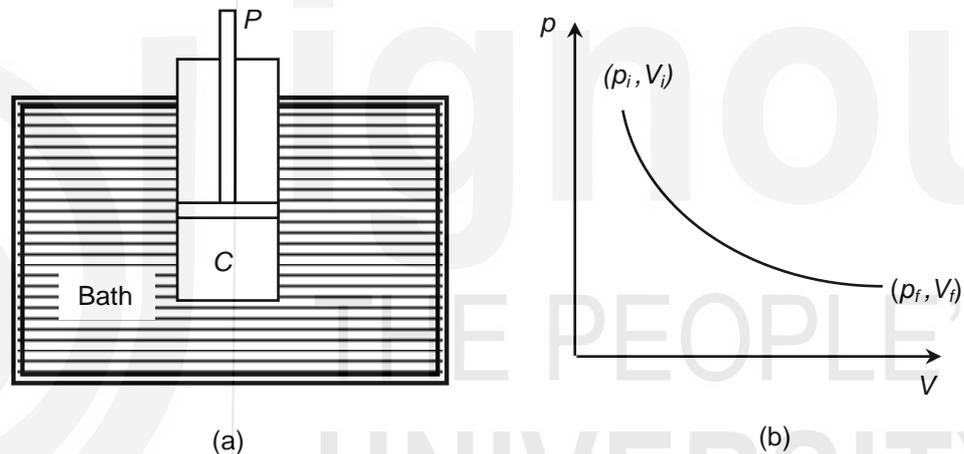
### 5.4.3 Representation of a Process on an Indicator Diagram

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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 diathermal 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).



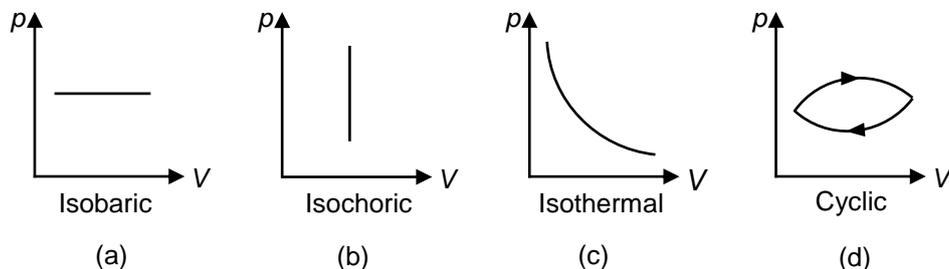
**Fig. 5.7:** a) Arrangement for isothermal expansion of a gas; b)  $p$  vs  $V$  diagram for a quasi-static isothermal expansion of a gas.

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  $2 \text{ m}^3$  of mercury at  $0^\circ\text{C}$  and 1 bar pressure at a place where  $g = 9.8 \text{ ms}^{-2}$  is  $2.67 \times 10^5 \text{ N}$ . 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.

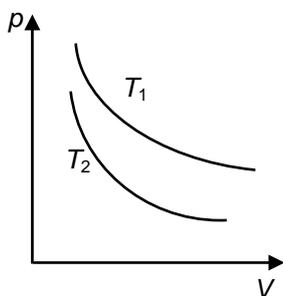


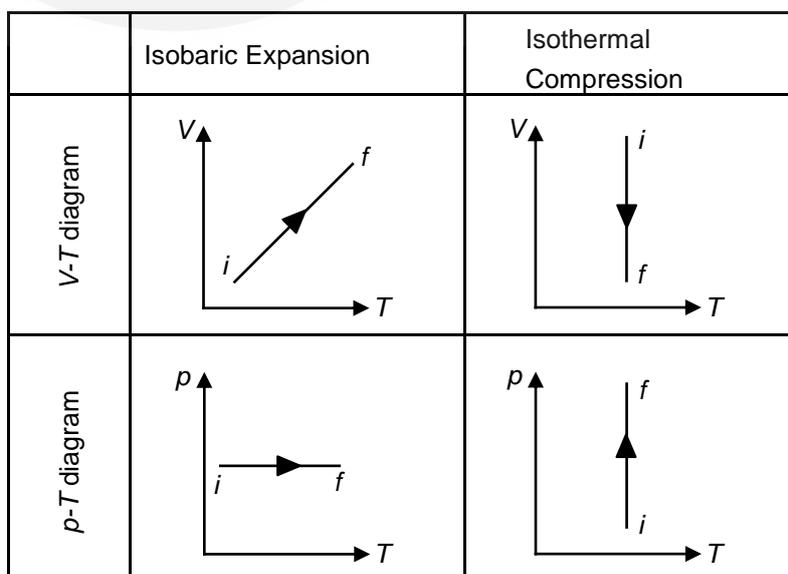
Fig. 5.9: Isotherms.

## 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.

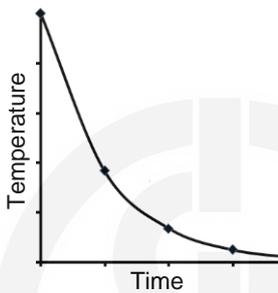


**Fig. 5.10: Representation of isobaric expansion and isothermal compression on V-T and p-T diagrams.**

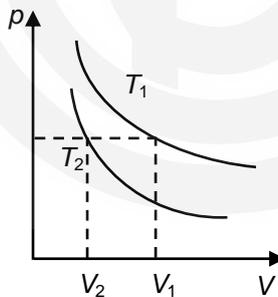
**Terminal Questions**

1. The rose plant in a garden is a system with soil, atmosphere and other plants as surroundings. It takes up sunlight and CO<sub>2</sub> from air in day time and gives out O<sub>2</sub>. 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 =  $2\text{ m}^3$ ,  
 Mass =  $2.67 \times 10^5\text{ N} / 9.8\text{ ms}^{-2} = 2.72 \times 10^4\text{ kg}$   
*Intensive variables :* Temperature =  $0^\circ\text{C}$ , Pressure = 1 bar,  
 density =  $2.72 \times 10^4\text{ kg} / 2\text{ m}^3 = 1.36 \times 10^4\text{ kg m}^{-3}$ ,  
 specific volume (volume per unit mass) =  $2\text{ m}^3 / 2.72 \times 10^4\text{ kg}$   
 $= 7.35 \times 10^{-5}\text{ m}^3\text{kg}^{-1}$ .



**Fig. 5.11: Newton's law of cooling.**



**Fig. 5.12: Isotherms.**

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.