

# THERMODYNAMICS

## Objectives

After studying this Unit, you will be able to

- explain the terms : system and surroundings;
- discriminate between close, open and isolated systems;
- explain internal energy, work and heat;
- state first law of thermodynamics and express it mathematically;
- calculate energy changes as work and heat contributions in chemical systems;
- explain state functions:  $U$ ,  $H$ .
- correlate  $\Delta U$  and  $\Delta H$ ;
- measure experimentally  $\Delta U$  and  $\Delta H$ ;
- define standard states for  $\Delta H$ ;
- calculate enthalpy changes for various types of reactions;
- state and apply Hess's law of constant heat summation;
- differentiate between extensive and intensive properties;
- define spontaneous and non-spontaneous processes;
- explain entropy as a thermodynamic state function and apply it for spontaneity;
- explain Gibbs energy change ( $\Delta G$ );
- establish relationship between  $\Delta G$  and spontaneity,  $\Delta G$  and equilibrium constant.

*It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown.*

**Albert Einstein**

Chemical energy stored by molecules can be released as heat during chemical reactions when a fuel like methane, cooking gas or coal burns in air. The chemical energy may also be used to do mechanical work when a fuel burns in an engine or to provide electrical energy through a galvanic cell like dry cell. Thus, various forms of energy are interrelated and under certain conditions, these may be transformed from one form into another. The study of these energy transformations forms the subject matter of thermodynamics. The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. Thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change. Laws of thermodynamics apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state. Macroscopic properties like pressure and temperature do not change with time for a system in equilibrium state. In this unit, we would like to answer some of the important questions through thermodynamics, like:

*How do we determine the energy changes involved in a chemical reaction/process? Will it occur or not?*

*What drives a chemical reaction/process?*

*To what extent do the chemical reactions proceed?*

## 6.1 THERMODYNAMIC TERMS

We are interested in chemical reactions and the energy changes accompanying them. For this we need to know certain thermodynamic terms. These are discussed below.

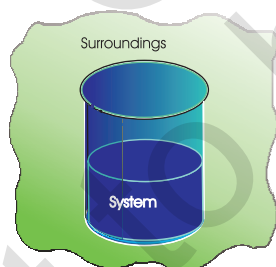
### 6.1.1 The System and the Surroundings

A **system** in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the **surroundings**. The surroundings include everything other than the system. System and the surroundings together constitute the universe .

The universe = The system + The surroundings

However, the entire universe other than the system is not affected by the changes taking place in the system. Therefore, for all practical purposes, the surroundings are that portion of the remaining universe which can interact with the system. Usually, the region of space in the neighbourhood of the system constitutes its surroundings.

For example, if we are studying the reaction between two substances A and B kept in a beaker, the beaker containing the reaction mixture is the system and the room where the beaker is kept is the surroundings (Fig. 6.1).



**Fig. 6.1** System and the surroundings

Note that the system may be defined by physical boundaries, like beaker or test tube, or the system may simply be defined by a set of Cartesian coordinates specifying a particular volume in space. It is necessary to think of the system as separated from the surroundings by some sort of wall which may

be real or imaginary. The wall that separates the system from the surroundings is called **boundary**. This is designed to allow us to control and keep track of all movements of matter and energy in or out of the system.

### 6.1.2 Types of the System

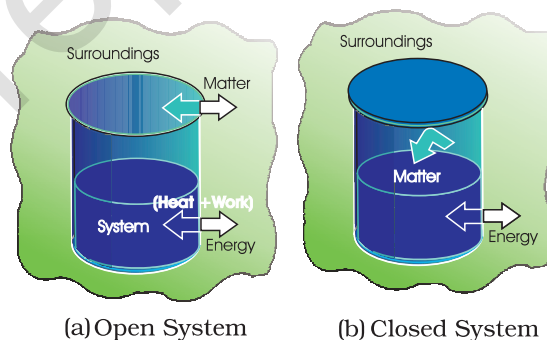
We, further classify the systems according to the movements of matter and energy in or out of the system.

#### 1. Open System

In an open system, there is exchange of energy and matter between system and surroundings [Fig. 6.2 (a)]. The presence of reactants in an open beaker is an example of an open system\*. Here the boundary is an imaginary surface enclosing the beaker and reactants.

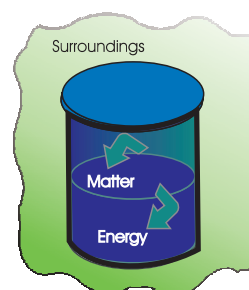
#### 2. Closed System

In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings [Fig. 6.2 (b)]. The presence of reactants in a closed vessel made of conducting material e.g., copper or steel is an example of a closed system.



(a) Open System

(b) Closed System



(c) Isolated System

**Fig. 6.2** Open, closed and isolated systems.

\* We could have chosen only the reactants as system then walls of the beakers will act as boundary.

### 3. Isolated System

In an isolated system, there is no exchange of energy or matter between the system and the surroundings [Fig. 6.2 (c)]. The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.

#### 6.1.3 The State of the System

The system must be described in order to make any useful calculations by specifying quantitatively each of the properties such as its pressure ( $p$ ), volume ( $V$ ), and temperature ( $T$ ) as well as the composition of the system. We need to describe the system by specifying it before and after the change. You would recall from your Physics course that the state of a system in mechanics is completely specified at a given instant of time, by the position and velocity of each mass point of the system. In thermodynamics, a different and much simpler concept of the state of a system is introduced. It does not need detailed knowledge of motion of each particle because, we deal with average measurable properties of the system. We specify the state of the system by **state functions** or **state variables**.

The **state** of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. We can describe the state of a gas by quoting its pressure ( $p$ ), volume ( $V$ ), temperature ( $T$ ), amount ( $n$ ) etc. Variables like  $p$ ,  $V$ ,  $T$  are called **state variables** or **state functions** because their values depend only on the state of the system and not on how it is reached. In order to completely define the state of a system it is not necessary to define all the properties of the system; as only a certain number of properties can be varied independently. This number depends on the nature of the system. Once these minimum number of macroscopic properties are fixed, others automatically have definite values.

The state of the surroundings can never be completely specified; fortunately it is not necessary to do so.

#### 6.1.4 The Internal Energy as a State Function

When we talk about our chemical system losing or gaining energy, we need to introduce

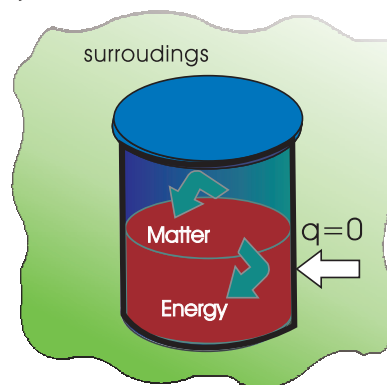
a quantity which represents the total energy of the system. It may be chemical, electrical, mechanical or any other type of energy you may think of, the sum of all these is the energy of the system. In thermodynamics, we call it the internal energy,  $U$  of the system, which may change, when

- heat passes into or out of the system,
- work is done on or by the system,
- matter enters or leaves the system.

These systems are classified accordingly as you have already studied in section 6.1.2.

#### (a) Work

Let us first examine a change in internal energy by doing work. We take a system containing some quantity of water in a thermos flask or in an insulated beaker. This would not allow exchange of heat between the system and surroundings through its boundary and we call this type of system as **adiabatic**. The manner in which the state of such a system may be changed will be called adiabatic process. Adiabatic process is a process in which there is no transfer of heat between the system and surroundings. Here, the wall separating the system and the surroundings is called the adiabatic wall (Fig 6.3).



**Fig. 6.3** An adiabatic system which does not permit the transfer of heat through its boundary.

Let us bring the change in the internal energy of the system by doing some work on it. Let us call the initial state of the system as state A and its temperature as  $T_A$ . Let the