THERMODYNAMICS

Since Ancient times man has been inquisitive about the nature and natural phenomena occurring around himself and has tried to understand them. In the attempt of unveiling the mysteries of nature two major questions were raised.

1. How does a portion of matter behave under changing ambient conditions?

2. Why does it behave in that particular manner?

For an answer to the first question some portion of matter has to be selected for investigation. This portion is called **a system.** After specifying the system its interaction with surrounding systems should be observed. All the surrounding systems with which our chosen system interacts are collectively called its **environment. For an answer to the second question, one has to go down to the molecular level and structure of matter.**

Macroscopic point of view:

The study of the whole system and its interaction with the environment is called the macroscopic point of view. A system can be described by specifying certain quantities like temperature, pressure, mass, composition, volume etc. which refers to the gross characteristics or large scale properties of the system and provide a macroscopic description. These quantities are therefore called **macroscopic coordinates.** The macroscopic coordinates of a system should possess the following characteristics in common:

1. They should involve no special assumption regarding the structure of matter.

2. Only a few coordinates are needed to provide a complete macroscopic description. For example only four coordinates : Pressure, Volume, Temperature and Mass completely describes some amount of gas.

3. They are suggested more or less directly by our sense of perception.

4. They can in general be directly measured by suitable measuring instruments.

In general, macroscopic description of a system involves the specification of a few fundamental properties of the system.

Microscopic point of view:

Microscopic point of view is based on molecular or atomic point of view. The microscopic coordinates of a system should possess the following characteristics in common:

1. Assumptions are made concerning the structure of matter, for example existence of molecules is assumed.

2. Many coordinates are needed to be specified provide a complete macroscopic description. For example to find the average molecular speed it is required to know the speeds of each individual molecule.

3. The quantities specified are not suggested directly by our sense of perception.

4. These quantities can not be directly measured

The study of velocity of gas molecules, their moment of inertia, structure of a crystalline solids etc. based on atomic and molecular phenomena involve microscopic point of view.

Scope of Thermodynamics:

Thermodynamics is that branch of Physics which deals with thermal and mechanical properties of matter on macroscopic basis. In thermodynamics a macroscopic point of view is adopted but only those macroscopic quantities are considered which have a bearing on the internal state of the system. **Macroscopic quantities bearing a relation with the internal state of the system are called Thermodynamic coordinates.** Such coordinates determine the internal energy of the system. It is the purpose of thermodynamics to generate some relations between thermodynamic coordinates, the relations being consistent with the fundamental laws of nature. For example pressure, volume, temperature, entropy etc. These coordinates are also time independent, provided the ambient conditions remain unaltered.

Inexact differential: Let ‘X’ be a physical quantity associated with a system. If the difference of ‘X’ between two terminal states of the system depends on the process or path connecting the two states then ‘X’ is called a **Path dependent quantity.** The change of ‘X’ between two terminal states is called an **inexact differential** and denoted by ‘**δX**’

Exact differential: Let ‘X’ be a physical quantity associated with a system. If the difference of ‘X’ between two terminal states of the system is independent of the process or path connecting the two states then ‘X’ is called a **Path independent quantity.** The change of ‘X’ between two terminal states is called an **exact differential** and denoted by ‘**dX**’

Extensive variables: A quantity in a macroscopic system that is proportional to the size of the system. Examples of extensive variables include the volume, mass, and total energy.

Intensive variables: An intensive variable is one which is independent of system size (like temperature, pressure, or density). Usually, the ratio of two extensive variables, give an intensive variable. For example the ratio of mass to volume of a system is its density, which is an intensive variable. Intensive variables tell us much more about the system than extensive variables.

State functions: These coordinates are time independent, provided the ambient conditions remain unaltered and are also path independent functions are called **state functions.**

Thermodynamic system: A system that may be described in terms of thermodynamic coordinates is called a **thermodynamic system**

Change of state: A system suffers interactions with the environment and its internal state as determined by its thermodynamic coordinates undergoes changes. This change is called **change of state.**

Process: The method via which the system undergoes changes in its thermodynamic coordinates is called a **process.**

THERMODYNAMIC EQUILIBRIUM

In Thermodynamics, the only permissible interactions between a system and environment are

1. Mechanical interaction
2. Thermal interaction
3. Chemical or diffusive interaction

Any interaction involves an energy transfer between different parts of the system or between the system and environment.

Mechanical interaction and mechanical equilibrium: When there is an unbalanced force or pressure between the system and environment or between different parts of the system, energy transfer occurs in form of **work.** Work energy flows from region of high pressure to low pressure. This process is called **Mechanical interaction.** The process continues till the pressure difference between different parts of the system or between the system and environment vanishes and no further transfer of work energy occurs. Under this condition the system is said to be in **mechanical equilibrium.**

Thermal interaction and thermal equilibrium: When there is an unbalanced temperature between the system and environment or between different parts of the system, energy transfer occurs in form of **heat**. Heat energy flows from region of high temperature to low temperature. This process is called **Thermal interaction**. The process continues till the temperature difference between different parts of the system or between the system and environment vanishes and no further transfer of heat energy occurs. Under this condition the system is said to be in **thermal equilibrium.**

Chemical interaction and Chemical equilibrium: When there is an unbalanced concentration between the system and environment or between different parts of the system, energy transfer occurs in form of mass. Mass flows from region of high concentration to low concentration. This process is called **Thermal interaction**. The process continues till the temperature difference between different parts of the system or between the system and environment vanishes and no further transfer of heat energy occurs. Under this condition the system is said to be in **Chemial equilibrium.**

A system which is simultaneously in all three states of equilibrium(mechanical, thermal and chemical) is said to be in **thermodynamic equilibrium.** In other words, a system is said to attain thermodynamic equilibrium, if there are no unbalanced potentials(mechanical, thermal and chemical) between different parts of the system or between the system and environment. The thermodynamic coordinates do not change with time for a system in thermodynamic equilibrium. So the state of a system can be described in terms of specific values of thermodynamic coordinates for a system in thermodynamic equilibrium. It is not possible to describe a system in non equilibrium in the same way as the thermodynamic coordinates will continuously change with time.

Hence the science of thermodynamics is restricted only to systems in equilibrium and to such processes which occur keeping the state of the system very little different from equilibrium state.

Equation of state: For a system in equilibrium, there exists a well defined mathematical relation connecting its thermodynamic coordinates. This relation is called **equation of state.** An equation of state expresses the individual peculiarities of one system in contradistinction to another and should be determined either experimentally or from molecular theory. For example the equation of state of ideal gas is : $PV = nRT$, where the symbols have their usual meaning. Every thermodynamic system in equilibrium has its own individual equation of state, though it has not been possible till now to find the exact equation for all of them. A general theory like thermodynamics based on general laws of nature is incapable of explaining the behavior of one material as opposed to another. An equation of state is therefore not a theoretical deduction from thermodynamics but an experimental addition to it. No equation of state exists for a system which is not in thermodynamic equilibrium, since such a state can't be described in terms of thermodynamic coordinates. The equation of state for a fixed mass gaseous system can be written in the form : $f(P,V,T) = 0$, where 'P' is the pressure exerted by the system, 'V', the volume occupied by it and 'T', the temperature of the system. The equation shows that if any two variables are fixed at some arbitrary value, the third variable must also assume a definite value. So two variables are independent while the third one, is dependent on the other two. Hence any two variables are sufficient to specify the system completely.

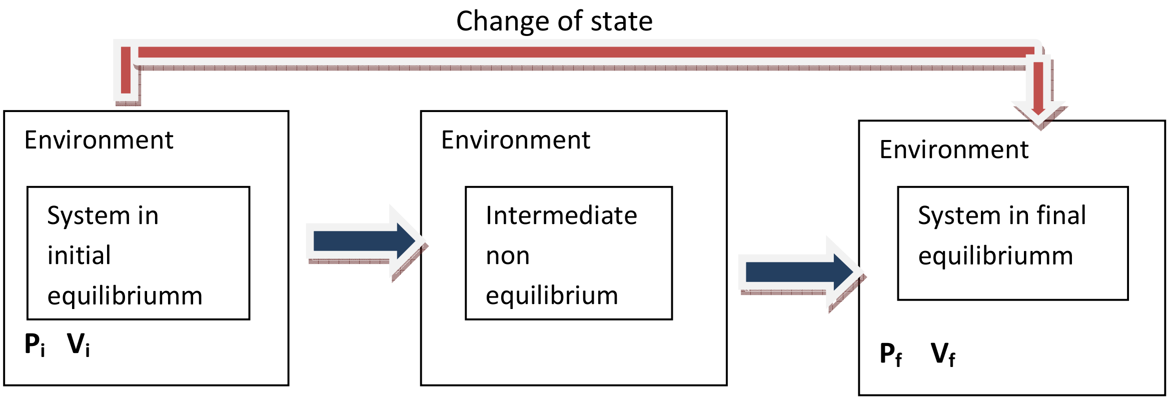

Fig. 1.1: The initial and final equilibrium states are specified by two coordinates (P_i, V_i) and (P_f, V_f) respectively, while no such specification is obtained for intermediate non equilibrium state.

Indicator Diagram: Let 'X' and 'Y' be any two physical properties describing the state of the system. A graphical representation is considered using two mutually perpendicular axes to represent 'X' and 'Y'. In this graph a single point represents the state of the system at a particular instance of equilibrium. Such a representation is called an indicator diagram.

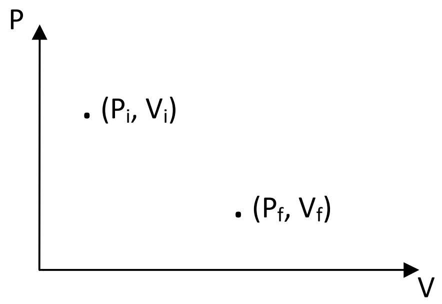

Fig. 1.2: P-V indicator diagram of the change of state shown in Fig. 1.1

Non equilibrium states can't be plotted on an indicator diagram.

DIFFERENT TYPES OF PROCESSES

1. **Quasi static process:** **A quasi static process is an idealized process which involves infinitesimal(extremely small) changes in the thermodynamic coordinates of a system as compared to the absolute values of the coordinates, brought about by an infinitesimal unbalanced potential(Mechanical, chemical or thermal) between different parts of the system or between the system and environment. At each step of a quasi static process the system is always very near to its preceding equilibrium state.** Hence at every step the system is practically in an equilibrium state. Hence the state of a system undergoing a quasi static process can be described at any instant by means of thermodynamic coordinates referring to the system as a whole.. An equation of state is therefore applicable to all states, in a quasistatic process. **For a process to be quasi static it should be a very slow one.**

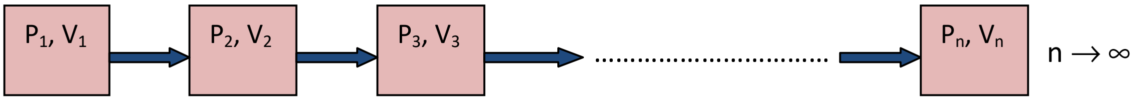

Fig. 1.3. Demonstrating Quasistatic process from (P_1, V_1) to (P_n, V_n)

Here(P_1, V_1) ≈ (P_2, V_2) ≈ (P_3, V_3) ≈ ……………………………………….(P_n, V_n) but the difference between (P_1, V_1) and (P_n, V_n), i.e a finite difference gets divided into an infinite number of divisions each differing from the preceding one by a negligible amount as compared to the absolute values of (P,V).

{**example to understand**: Suppose volume changes from 10cc to 25cc. The amount of change is 15cc, which is a finite amount. Consider the changes to take place in steps of 0.001cc, i.e 10cc, 10.001cc, 10,002cc, 10.003cc ………………………………25cc, then each value is very near to its preceding value, the difference(0.001) being negligible compared to the magnitudes of volume(10, 25). Such a change can be considered as a quasi static volume change. But if the volume of the system instantly jumps to 25cc from 10cc without passing through the intermediate small steps, then the process is no longer quasi static}

Cyclic process: A **cyclic process** is a process in which, a system starting from an initial thermodynamic state ,returns to the same state at the end of the process.

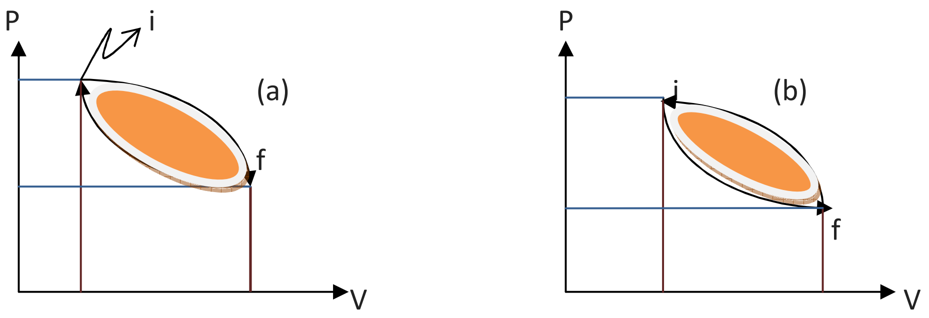

Fig. 1.4 : P-V diagram of a cyclic process.

The net work involved is the enclosed area on the P-V diagram. If the cycle goes counterclockwise, work is done by the system every cycle(fig. 1.2a). If the cycle goes counterclockwise, work is done on the system every cycle(fig. 1.2b). An example of such a system is a refrigerator or air conditioner.

Reversible Process: A reversible process is a process, which if desired can be retraced back along the same path to the initial point so as to restore the system as well as its surroundings to the initial state, without causing any change anywhere in the universe. For a process to be reversible, it must be quasi-static so that the system passes through states in equilibrium, which may be traversed just as well in one direction, as in opposite direction. If, in addition there are no dissipative effects, then all the work done by a system during process in one direction will be quenched(restored to the system) during the process in reverse direction. So the two conditions for a process to be reversible are:

1. The process should be quasi static.

2. The process should not be accompanied by any dissipative effects.

{Note well: Do not confuse between a reversible process and cyclic process. In a cyclic process the system actually returns to the initial state though the surrounding undergoes some change. But in a reversible process the initial and final state might be different. Only if desired, it is possible to take the system back to the initial state along with its surroundings.}

Since all intermediate stages of a reversible process are in equilibrium, hence the whole of the process can be plotted on a P-V indicator diagram by a continuous line.

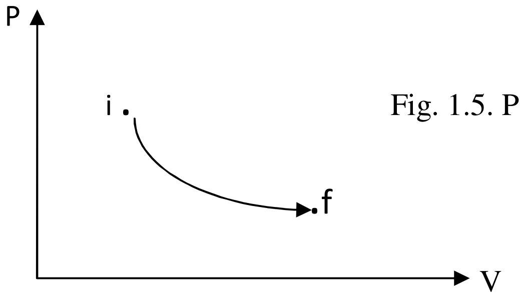

Fig. 1.5. P-V diagram of a reversible process.

The process from i to f is a reversible process. This means that if the process is retraced backwards from ‘f’ to ‘I’ along the same path then not only the system but also the surrounding with which the system is interacting, will return to the initial state.

Irreversible process: A process which is either non quasi static or is accompanied by some dissipative effects or both is called an irreversible process. For an irreversible process it is not possible for the system to return back to initial state by retracing the same path. All natural processes are irreversible.

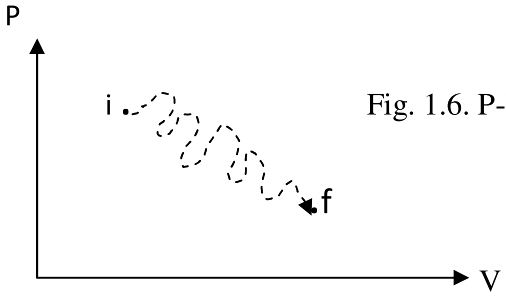

Fig. 1.6. P-V diagram of a irreversible process.

Note: If a cyclic process is such that all steps of the cycle is reversible and it can be then the cycle is called reversible cycle. If a reversible cycle, proceeds in clockwise sense, producing some change of energy, then during the corresponding anticlockwise cycle along the same path will counterbalance that change. It even a small part of the cyclic process is irreversible then the cycle is called irreversible cycle.

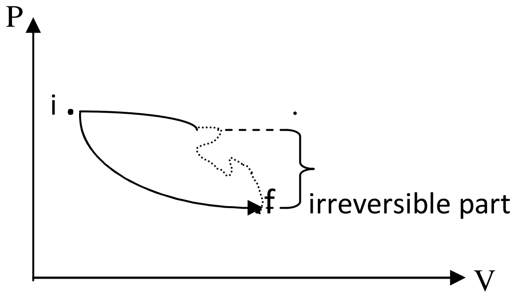

Fig. 1.7(a) Irreversible cycle

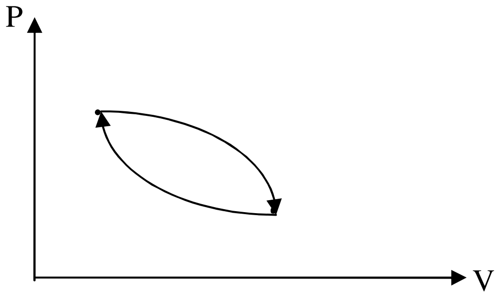

Fig. 1.7(b) Rreversible cycle

{Note: An irreversible process does not necessarily mean that it is impossible to restore the sy6stem back to the initial equilibrium state. By any process the system can be reverted back to the initial state if desired but in that case the environment will never return to the initial state. Some changes will be produced in the universe.}