Uma Charan Patnaik Engineering School
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LECTURE NOTES

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CHAPTER 1: INTRODUCTION AND BASIC CONCEPTS

Thermodynamics is the branch of science which deals with all forms of energy and the interconversion of different forms of energy.

(OR)

Thermodynamics is the branch of science which is concerned with the relations between heat and other forms of energy involved in physical and chemical processes.

In the study of thermodynamics, we are basically concerned with the four laws : the zeroth, first, second and third laws of thermodynamics. The laws of thermodynamics apply to matter in bulk (macroscopic systems) and not to individual atoms or molecules. The laws deal with the macroscopic changes of interest in the problem handled and because of this the study of thermodynamics is of direct benefit in the analysis of industrial problems. These laws are based on a large number of experimental observations and logical reasoning like all physical laws. The laws of thermodynamics have no mathematical proof (i.e., these laws cannot be proved as we prove mathematical theorems) and have not so far/yet been violated (no experimental evidence is available so far to doubt the validity of these laws). The laws of thermodynamics are merely a systematization of observations of common human experience. Several direct and indirect consequences of these laws may be deduced strictly on logical grounds with the application of a moderate knowledge of mathematics.

The zeroth law of thermodynamics deals with thermal equilibrium between a set of bodies and forms the basis for the measurement of temperature. The first law of thermodynamics indicates that there is an exact equivalence between the various forms of energy involved in any process. The second law of thermodynamics provides a means of predicting whether a given thermodynamic process is possible or not. It helps us to predict whether a given process is feasible or not. The first law of thermodynamics leads to the concept of internal energy, while the second law of thermodynamics leads to the concept of entropy. The third law of thermodynamics places a limitation upon the value of entropy. The law defines the absolute zero of entropy and helps us to calculate the absolute entropies of pure substances. The zeroth law of thermodynamics was formulated by Fowler in the year 1931. However, since the first and second laws of thermodynamics were already existed at that time, it was named as zeroth law of thermodynamics so that it proceeds the first and second laws to form a logical sequence. In case of internal energy and entropy functions, we are interested to know the changes in these functions. Actually, the first and second laws of thermodynamics do not give any idea/clue as to the method of finding the absolute values of the internal energy and entropy.

SCOPE AND LIMITATIONS OF THERMODYNAMICS

Thermodynamics tells us whether a given process, including a chemical reaction, is possible / feasible or not, under a given set of conditions (e.g., temperature, etc.). However, it does not tell anything about the rate at which a given process will take place/proceed. That is, thermodynamics cannot predict whether a specified change will occur in an acceptable period of time or not. Thermodynamics provides information regarding how far a given process may proceed (the maximum possible extent to which a given process can proceed) and the degree to which the energy present in a system can be utilized to cause a given process to occur / take place. It helps to make a preliminary choice of the process variables, their effect on the extent of a process and to find out thermal / heat effects associated / involved in a given process.

As far as chemical reactions are concerned, the aspects such as whether certain reactions can take place, to what extent chemical conversions can occur, the effect of parameters like temperature and pressure on the behaviour of a chemical reaction, the composition of product mixtures if equilibrium is reached and the amount of heat released / absorbed can be determined from thermodynamic calculations alone. However, thermodynamics cannot tell anything about the speed / rate of the reaction and the effect of the shape of the reactor used (kinetics provides this). A knowledge of both thermodynamics and kinetics is essential for a complete understanding of the unit processes. Thermodynamics of a chemical reaction must be known before its kinetics can be utilized. Before knowing how fast a chemical reaction will go / take place, one must know can it go at all / can it take place at all and, if so, how far (to what extent). Thermodynamics answers this. Thermodynamics enables us to calculate the maximum efficiency of a turbine or a refrigerator and the maximum achievable yield in a given chemical reaction.

System

The specified portion of the universe containing a definite quantity/amount of a specific substance or group of substances under study for the purpose of thermodynamic analysis of a problem is called a system (thermodynamic system).

Surrounding

The remaining part of the universe other than the system is called the surroundings - everything external to the system is called the surroundings.

TYPES OF SYSTEM:

Closed System:

- A system of fixed mass is called a closed system.
- A system which can exchange energy but not matter with its surroundings is called a closed system.

Open System:

- A system in which matter (and energy also) crosses the boundary of the system is called an open system.
- A system which can exchange matter as well as energy with its surroundings is called an open system.
- If both the mass and energy cross the boundaries of a system, it is called an open system.

Isolated System:

A system which can exchange neither matter nor energy through the boundaries with its surroundings is called an isolated system. It is of fixed mas and energy. This is a system which is not affected / influenced by the changes in its surroundings or environment. A perfectly isolated system is an ideal concept that cannot be observed or attained in practice. The combination of a system and its surroundings constitutes an isolated system. Therefore, the universe can be treated as an isolated system.

State of a System:

The thermodynamic state or, in brief, the state of a system is the condition of the system at any particular instant of time as described or measured by its macroscopic properties, such as temperature, pressure, volume and composition. Each unique condition of a system, as defined by its macroscopic properties, is called a state. State denotes the values of properties of a system at a particular instant of time. Therefore, when all the properties of a system have definite values, the system is said to exist in a definite state. A change in any one of these properties causes the system to change to a new state. Thus, the state of a system is fixed by its macroscopic properties. Stated differently, all properties are state or point functions

State Function:

The properties of a system are known as state functions as they have definite / fixed values for a particular state of the system and do not depend on the way / manner in which the state is reached / attained.

Pressure, volume, temperature, internal energy, enthalpy and entropy are state functions (point functions). The change in any state function accompanying a change in the state of a system depends on the initial and final states of the system and not on the path by which the state is brought about.

Path Function:

Thermodynamic functions / physical quantities which depend on the path followed by a system in reaching the final state from the given initial state are called path functions e.g., heat and work.

The values of heat and work accompanying a given change in state vary with the path from the initial state to the final state, i.e., the values of these quantities depend on the manner in which the change is brought about. Work and heat, as they depend on path, cannot be identified by points on a graph, but are represented by areas. As work and heat appear only when changes are caused in a system by a process, they are called properties of the process. They are not properties of a system.

Process:

- Whenever a system undergoes a change of state, it is said to undergo a process.
- A process is the means by which the given change in state is achieved (or the means by which a system changes from one state to another).
- A process is the means by which some sort of change or transformation, physical or chemical, takes place in the system under consideration.

During a process, the system changes from an initial state to a final state, through a series of intermediate states. This series of intermediate states through which a system passes during a process to reach the given final state from the given initial state is called the path of the process.

ENERGY:

Since thermodynamics deals with energy and its transformation, the concept of energy is essential in the understanding of thermodynamics. Energy is the capacity / ability of a body to do work. The forms of energy can be classified as :

- **Forms of energy related to the system**: These include energy possessed by material of the system - kinetic energy, potential energy, pressure / flow energy, internal energy, surface energy and magnetic energy.
- **Forms of energy associated with the process**: These include energy produced or transferred by the processing - heat and work

HEAT & WORK:

Heat is a form of energy which is transferred across a boundary due to the existence of a temperature difference.

Heat is the energy in transit (like work) between a hot source and a cold receiver. It appears at the boundary of a system, while a change is taking place within the system. The amount of heat transferred in a process depends on the way in which the process is carried out (it depends upon the intermediate states through which the system passes, i.e., path). Therefore, just as work, heat is a path function and not a state function.

The symbol Q is used for the amount of heat transferred. The unit of heat in the Si system is joule (J).

Heat flow into a system from the surroundings, by convention, is regarded as positive. Thus, Q is positive when the system gains energy as heat. Heat flow out of a system, that is, heat given up by the system to its surroundings, i.e., heat transferred from the system to its surroundings is taken as negative (since there is a corresponding decrease of energy of the system).

Heat added to a system = +Q ... taken as a positive quantity

Heat given up/rejected by a system = -Q ... taken as a negative quantity

A system exchanges energy with its surroundings in the form of heat and work, i.e., a system interacts with its surroundings by transfer of energy as heat and work. These energy interactions bring about changes in the properties of the system. Both heat and work are energy in transit and can be identified only when the process is in progress (only when a certain change is taking place).

Both are boundary phenomena and are associated with a process, not a state and have no meaning at a state. They are not properties of a system but are properties of a process.

According to the convention, Q and W are the heat absorbed and work done by the system.

Therefore, when

Q is + ve : heat has been added to the system

Q is – ve : heat has been removed from the system

(heat has been given up / rejected by the system)

W is + ve : Work has been done by the system

W is - ve : Work has been done on the system

Work done by the system = Work output of the system = Work produced

Work done on the system = Work required = Work input

If Q = 500 kJ …means heat added / absorbed by the system is 500 kJ

If Q = - 400 kJ …means heat removed from the system is 400 J

If W = 300 kJ …means work output of the system is 300 kJ

If W = -450 kJ …means work required is 450 kJ

Phase:

A pure substance is one which contains only one chemical species. Ice, water and steam have the same chemical species. So ice, water, steam, a system consisting of ice, water and steam, steam - water mixture are regarded as pure substances.

Three states of physical aggregation of matter are solid, liquid and gas. The different states in which a substance (matter) exists are called phases (liquid phase, gas phase, solid phase).

THERMODYNAMIC EQUILIBRIUM:

A system is said to be in a state of thermodynamic equilibrium if the properties on a macroscopic scale, i.e., the macroscopic properties (such as temperature, pressure, density, composition or concentration of species) are uniform throughout the system and do not undergo any change with time.

The state in which the macroscopic properties of a system are uniform throughout the system and do not undergo any noticeable change with time, under a given set of conditions, is said to be a state of equilibrium. This implies a balance of all potentials that tend to cause a change.

At equilibrium, all potentials tending to cause a change are balanced and hence there is no further tendency for a change to occur (all tendency towards change ceases). Thus, equilibrium refers to the absence of any tendency for a change to occur. Changes in a system are always caused by the action of some form of driving force, or potential difference. The driving force or potential difference in heat flow / transfer is temperature difference (temperature is one of the potentials). The driving force (or potential difference) in fluid flow is difference of pressure or head and in mass transfer it is concentration difference (true driving force - chemical potential). Thus, equilibrium implies the absence of driving force between the two interacting bodies (as at equilibrium any tendency towards change ceases).

A system is said to be in **thermal equilibrium** / in a state of thermal equilibrium if there is no flow of heat from one portion of the system to another. This is possible only if the temperature remains the same / uniform throughout the system. Thus, thermal equilibrium denotes uniformity of temperature or the absence of temperature gradient. In a state of thermal equilibrium, there is no temperature gradient within the system and there is no difference in temperature (driving force) between the system and its surroundings.

A system is said to be in a state of **mechanical equilibrium** if there is no imbalance of forces within the system. In a state of mechanical equilibrium, the system has a uniform pressure and there is no pressure difference between two interacting systems. Mechanical equilibrium denotes uniformity of pressure or the absence of unbalanced of forces.

A system is said to be in a state of **chemical equilibrium** if the composition of the components present in the system is uniform throughout the system and there is no tendency for the chemical reaction to occur within the system. Chemical equilibrium denotes equality of chemical potential.

The **criteria of equilibrium** are:

- Equality of temperature: Thermal equilibrium
- Equality of pressure : Mechanical equilibrium
- Equality of chemical potential : Chemical equilibrium

If the system is simultaneously in a state of thermal equilibrium, mechanical equilibrium and chemical equilibrium, then it is said to be in a state of **thermodynamic equilibrium**.

ZEROTH LAW OF THERMODYNAMICS:

Temperature is a thermal state of body, which distinguishes a hot body from a cold body.

Temperature is a measure of the degree of hotness or coldness of a body. A body which is hot is said to have a higher temperature than one which is cold. If a hot body is placed in contact with a cold body, then after a long time in contact, they attain a common temperature (both will be at the same temperature) and the two bodies are said to attained a state of thermal (or temperature) equilibrium or said to exist in thermal equilibrium. The temperature of the hot body has decreased, while that of the cold body has been raised (because of energy transfer as heat from the hotter body to the colder body) until at equilibrium the two bodies have equal/identical temperature.

If a body A is in thermal equilibrium with a body C and a body B is in thermal equilibrium with the body C, then the two bodies A and B are also in thermal equilibrium with each other.

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

REVERSIBLE AND IRREVERSIBLE PROCESSES:

The processes we normally come across can be divided into two classes:

- Reversible processes and
- Irreversible processes.

A **reversible process** is one

- in which the driving force causing the process is always infinitesimally greater than the opposing force (i.e., the force resisting the process).
- which is carried out extremely / infinitesimally slowly,
- which is free of dissipative effect (friction, viscosity, inelasticity and electrical resistance) of any form and
- which can be stopped and reversed at any stage so that both the system and its surroundings are restored to their respective initial / original states.

A process which is carried out with a finite driving force is called an irreversible process.

Since a reversible process is carried out infinitely slowly, with an infinitesimal driving force, the system is at all times infinitesimally near a state of thermodynamic equilibrium and thus every state passed through by the system is an equilibrium state.

A reversible process is thus a succession or series of equilibrium states. As these states can be described by thermodynamic properties (e.g., P, V, etc.), any reversible process can be represented on a thermodynamic diagram / can be plotted on thermodynamic coordinates.

If a process occurs in such a way that the system passes through non-equilibrium states (non-equilibrium intermediate states) though the initial and final states of the system are equilibrium states, it cannot be plotted on thermodynamic coordinates/cannot be represented on a thermodynamic diagram since because intermediate non-equilibrium states cannot be described by thermodynamic properties. Such a process is called an irreversible process.

When the system is in equilibrium at all the intermediate states between the initial and final states (which are also equilibrium states) only then the path followed by the system can be defined / can be traced. The path of a reversible process between the initial and final states is always represented by a continuous line as the path followed is certain, whereas the path of any irreversible process between the two states is always represented by a dotted line as the path is uncertain (the path of such a process cannot be traced).

A reversible process is an ideal or imaginary one since in this process all sources of energy dissipation are eliminated. Since reversible processes take place infinitesimally slowly, they would require infinite time for their completion. Therefore, reversible processes are not practicable. Inspite of impracticability of reversible processes, the study of these processes is of great value / importance since we get idea regarding the maximum efficiency obtainable in any given change. Thus, the ideal to be aimed at is known (the limit to the performance of an actual / real system).

Irreversible processes are those in which the condition of thermodynamic equilibrium is not satisfied and dissipative effects (e.g., fluid friction) are present. Since these processes take place fast with a measurable speed, finite time would be required for their completion. All actual processes that occur in nature are irreversible since they take place with finite driving forces (e.g., AT for heat transfer) between parts of the system or between the system and its surroundings. The irreversibility of a process may be caused due to lack of equilibrium during the process and / or presence of dissipative effects (friction, viscosity, electrical resistance).

Examples of reversible process: motion without friction, heat transfer with no temperature difference between the system and its surroundings.

Examples of irreversible process: motion with friction, unrestricted / free expansion of a gas), rusting of iron, mixing, heat transfer with a finite temperature difference.