Study Unit 1: Introduction to Thermodynamics, Basic Definition of term and Laws of Thermodynamics

Introduction

Most of this course will be concerned with understanding the patterns of energy change. More specifically, thermodynamics deals with (a) energy conversion and (b) the direction of change. Basis of thermodynamics is experimental observation. In that sense it is an empirical science. The principles of thermodynamics are summarized in the form of four laws known as zeroth, first, second, and the third laws of thermodynamics. The zeroth law of thermodynamics deals with thermal equilibrium and provides a means of measuring temperature. The first law of thermodynamics deals with the conservation of energy and introduces the concept of internal energy. The second law of thermodynamics dictates the limits on the conversion of heat into work and provides the yard stick to measure the performance of various processes. It also tells whether a particular process is feasible or not and specifies the direction in which a process will proceed. As a consequence, it also introduces the concept of entropy. The third law defines the absolute zero of entropy.

Learning Outcomes of Study Unit 1

At the end of this study unit you should be able to

1.1 Define thermodynamics and explain the basics terms associated with thermodynamics
1.2 Distinguish between the term state, process and system as they are applied to thermodynamics
1.3 Define the concepts of Heat, energy and work
1.4 Explain the concepts of heat, energy and work, stating their relationship with thermodynamics variables
1.5 Distinguish between microscopic and macroscopic Approaches
1.6 Discuss the concept of temperature and its measurement
1.7 Discuss in details the concept of reversibility and irreversibility
1.8 State and explain the first law of thermodynamics
1.9 Discuss the application of first law of thermodynamic
1.10   Solve problems associated with the first law of thermodynamics

1.1 Meaning and Definition of Thermodynamics

Thermodynamics is the science that deals with heat and work and those properties of substance that bear a relation to heat and work. Thermodynamics is the study of the patterns of energy change. Thermodynamics is the science that deals with the interaction between energy and materials system. It is the science of the regularities governing process of energy conversion. It can also be defined as an axiomatic science which deals with the relations among heat, work and properties of the system which they are in equilibrium. Thermodynamics describes state and changes in the physical systems.

1.2 Basic terms and concepts associated with thermodynamics

1.2.1 System, Surrounding, Boundaries, Universe, Types of Systems

A **system** is defined as a quantity of matter or a region in space chosen for study. The mass or region outside the system is called the **surroundings**. The real or imaginary surface that separates the system from its surroundings is called the **boundary**. The boundary of a system can be fixed or movable. Note that the boundary is the contact surface shared by both the system and the surroundings. Mathematically speaking, the boundary has zero thickness, and thus it can neither contain any mass nor occupy any volume in space. System and surroundings when put together result in **universe**. These terms are illustrated in figure 1.1.
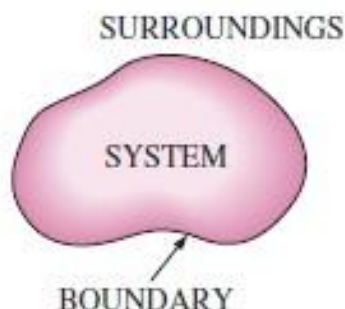

Figure 1.1: System, Surrounding and Boundary

Two types of exchange can occur between system and surroundings: (1) energy exchange (heat, work, friction, radiation, etc.) and (2) matter exchange (movement of molecules across the boundary of the system and surroundings).

Based on the types of exchange which take place or don't take place, there are three types of systems:

1.2.2 Closed system (also known as a control mass)

Consists of a fixed amount of mass, and no mass can cross its boundary. That is, no mass can enter or leave a closed system, as shown in figure 1.2. But energy, in the form of heat or work, can cross the boundary; and the volume of a closed system does not have to be fixed. Closed system is the system having only energy interactions at its boundary, for example, boiling water in a closed pan etc.
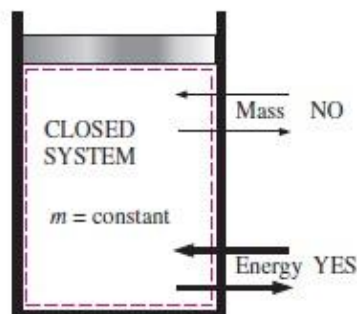

Figure 1.2: Closed System

1.2.3 Open system, or a control volume

As it is often called, is a properly selected region in space. It usually encloses a device that involves mass flow such as a compressor, turbine, or nozzle. Flow through these devices is best studied by selecting the region within the device as the control volume. Both mass and energy can cross the boundary of a control volume as shown in figure 1.3. The open system is one in which the energy and mass interactions take place at the system boundary, for example automobile engine etc.
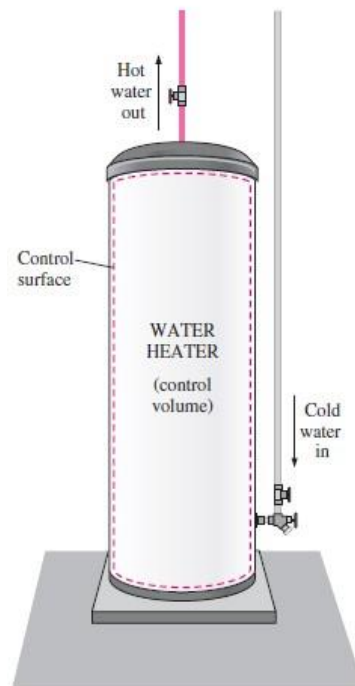
Figure 1.3: Closed System

Important note: some thermodynamics relations that are applicable to closed and open systems are different. Thus, it is extremely important to recognize the type of system we have before start analysing it.

1.2.4 Isolated system: A closed system that does not communicate with the surroundings by any means. Isolated system refers to the system which has neither mass interaction nor energy interaction across system boundary, for example Thermos Flask etc. Thus, the isolated system does not interact with the surroundings/systems in any way.

Rigid system: A closed system that communicates with the surroundings by heat only.

Control Volume: Control volume is defined as a volume which encloses the matter and the device inside a control surface. It can be further explained;

- Everything external to the control volume is the surroundings with the separation given by the control surface.
- The surface may be open or closed to mass flows and it may have flows from energy in terms of heat transfer and work across it.
- The boundaries may be moveable or stationary.
- In the case of a control surface that is closed to the mass flow, so that no mass can enter or escape the control volume, it is called a **control mass** containing same amount of matter at all times.

Concept of Continuum:

Matter is made up of atoms that are widely spaced in the gas phase. Yet it is very convenient to disregard the atomic nature of a substance and view it as a continuous, homogeneous matter with no holes, that is, a **continuum.**

Adiabatic system: A closed or open system that does not exchange energy with the surroundings by heat.

1.2.5 The State

The state of the system is described by its properties. Once a sufficient number of properties are specified, the rest of the properties assume some values automatically. The number of properties required to fix a state of a system is given by the state postulate:

The state of a simple compressible system is completely specified by two independent, intensive properties.

The system is called a simple compressible system in the absence of electrical, magnetic, gravitational, motion, and surface tension effects.

The state postulate requires that the two properties specified be independent to fix the state. Two properties are independent if one property can be varied while the other one is held constant. Temperature and specific volume, for example, are always independent properties, and together they can fix the state of a simple compressible system. Thus, temperature and pressure are not sufficient to fix the state of a two-phase system. Otherwise an additional property needs to be specified for each effect that is significant. An additional property needs to be specified for each other effect that is significant.

1.2.6 Equilibrium

- When the property of a system is defined, it is understood that the system is in equilibrium.
- If a system is in thermal equilibrium, the temperature will be same throughout the system.
- If a system is in mechanical equilibrium, there is no tendency for the pressure to change with respect to time. Mechanical Equilibrium occurs when there are no unbalanced forces within the system or between the surrounding.
- In a single phase system, if the concentration is uniform and there is no tendency for mass transfer or diffusion, the system is said to be in chemical equilibrium.
- A system which is simultaneously in thermal, mechanical, and chemical equilibrium is said to be in thermal equilibrium.

1.2.7 Property

- In thermodynamics a property is any characteristic of a system that is associated with the energy and can be quantitatively evaluated.

- The property of a system should have a definite value when the system is in a particular state.
- Thermodynamic property is a point function.
- Properties like volume of a system that depend on the mass of a system are called extensive properties.
- Properties like pressure or temperature which do not depend on the system mass are called intensive properties.
- The ratio of extensive property to the mass of the system are called specific properties and therefore become intensive properties.
- Substance can be found in three states of physical aggregation namely, solid, liquid and vapor which are called its phases.
- If the system consists of mixture of different phases, the phases are separated from each other by phase boundary.
- The thermodynamic properties change abruptly at the phase boundary, even though the intensive properties like temperature and pressure are identical.

Any characteristic of a system is called a **property.** Some familiar properties are pressure P, temperature T, volume V, and mass m. The list can be extended to include less familiar ones such as viscosity, thermal conductivity, modulus of elasticity, thermal expansion coefficient, electric resistivity, and even velocity and elevation.

Properties are considered to be either *intensive* or *extensive*.

Intensive properties are those that are independent of the mass of a system, such as temperature, pressure, and density.

Extensive properties are those whose values depend on the size or extent of the system. Total mass, total volume, and total momentum are some examples of extensive properties.

An easy way to determine whether a property is intensive or extensive is to divide the system into two equal parts with an imaginary partition. Each part will have the same value of intensive properties as the original system, but half the value of the extensive properties. Generally, uppercase letters are used to denote extensive properties (with mass m being a major exception), and lowercase letters are used for intensive properties (with pressure P and temperature T being the obvious exceptions). Extensive properties per unit mass are called **specific properties.** Some examples of specific properties are specific volume ($v = V/m$) and specific total energy ($e = E/m$).

1.2.9 Process
Any change that a system undergoes from one equilibrium state to another is called a **process,** and the series of states through which a system passes during a process is called the **path** of the process as shown in figure 1.4. To describe a process completely, one should specify the initial and final states of the process, as well as the path it follows, and the interactions with the surroundings.

A process is path followed by a system in reaching a given final state of equilibrium state starting from a specified initial state. An actual process occurs only when the equilibrium state does not exist. An ideal process can be defined in which the deviation from thermodynamic equilibrium is infinitesimal. All the states the system passes through during a quasi-equilibrium process may be

considered equilibrium states. For non-equilibrium processes, we are limited to a description of the system before the process occurs and after the equilibrium is restored. Several processes are described by the fact that one property remains constant. The prefix iso- is used to describe such processes. A process is said to be reversible if both the system and its surroundings can be restored to their respective initial states by reversing the direction of the process.

- Reversible: if the process happens slow enough to be reversed.
- Irreversible: if the process cannot be reversed (like most processes).
- Isobaric: process done at constant pressure

- Isochoric: process done at constant volume
- Isothermal: process done at constant temperature
- Adiabatic: process where q=0
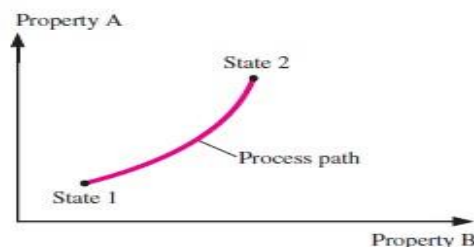- Cyclic: process where initial state is equal to final state

Figure 1.4: Process

A system is said to have undergone a **cycle** if it returns to its initial state at the end of the process. That is, for a cycle the initial and final states are identical.

1.2.10 Quasi-static Process

When a process proceeds in such a manner that the system remains infinitesimally close to an equilibrium state at all times, it is called a **quasi-static,** or **quasi-equilibrium, process.** A quasi-equilibrium process can be viewed as a sufficiently slow process that allows the system to adjust itself internally so that properties in one part of the system do not change any faster than those at other parts.

This is illustrated in figure: 1.5. When a gas in a piston-cylinder device is compressed suddenly, the molecules near the face of the piston will not have enough time to escape and they will have to pile up in a small region in front of the piston, thus creating a high-pressure region there. Because of this pressure difference, the system can no longer be said to be in equilibrium, and this makes the entire process non quasi-equilibrium. However, if the piston is moved slowly, the molecules will have sufficient time to redistribute and there will not be a molecule pileup in front of the piston. As a result, the pressure inside the cylinder will always be nearly uniform and will rise at the same rate at all locations. Since equilibrium is maintained at all times, this is a quasi-equilibrium process.
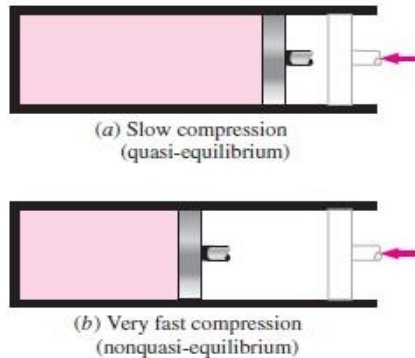
*(a) Slow compression
(quasi-equilibrium)*

*(b) Very fast compression
(nonquasi-equilibrium)*

Figure 1.5: Quasi Static Process

It should be pointed out that a quasi-equilibrium process is an idealized process and is not a true representation of an actual process. But many actual processes closely approximate it, and they can be modelled as quasi equilibrium with negligible error. Engineers are interested in quasi equilibrium processes for two reasons. First, they are easy to analyse; second, work-producing devices deliver the most work when they operate on quasi equilibrium processes. Therefore, quasi-equilibrium processes serve as standards to which actual processes can be compared. Note that the process path indicates a series of equilibrium states through which the system passes during a process and has significance for quasi equilibrium processes only. For nonquasiequilibrium processes, we are not able to characterize the entire system by a single state, and thus we cannot speak of a process path for a system as a whole. A nonquasiequilibrium process is denoted by a dashed line between the initial and final states instead of a solid line.

1.3 Concept of Energy, Work and Heat

1.3.1 Energy
In thermodynamics, we deal with change of the total energy only. Thus, the total energy of a system can be assigned a value of zero at some reference point. Total energy of a system has two groups: *macroscopic* and *microscopic*.

Macroscopic forms of energy: forms of energy that a system possesses as a whole with respect to some outside reference frame, such as kinetic and potential energy. The macroscopic energy of a system is related to motion and the influence of some external effects such as gravity, magnetism, electricity, and surface tension.

Kinetic energy: energy that a system possesses as a result of its relative motion relative to some reference frame, KE

$KE = \frac{mv^2}{2}$ (KJ) where V is the velocity of the system in (m/s).

Potential energy: is the energy that a system possesses as a result of its elevation in a gravitational field, PE

$PE = mgz$, where g is the gravitational acceleration and z is the elevation of the centre of gravity of the system relative to some arbitrary reference plane.

Microscopic forms of energy: are those related to molecular structure of a system. They are independent of outside reference frames. The sum of microscopic energy is called the *internal energy, U*. The total energy of a system consists of the kinetic, potential, and internal energies:

$$E = U + KE + PE = U + \frac{mv^2}{2} + mgz$$

where the contributions of magnetic, electric, nuclear energy are neglected. Internal energy is related to the molecular structure and the degree of molecular activity and it may be viewed as the sum of the kinetic and potential energies of molecules.

- The sum of translational, vibrational, and rotational energies of molecules is the kinetic energy of molecules, and it is also called the *sensible energy*. At higher temperatures, system will have higher sensible energy.
- Internal energy associated with the phase of a system is called *latent heat*. The intermolecular forces are strongest in solids and weakest in gases.
- The internal energy associated with the atomic bonds in a molecule is called *chemical* or *bond energy*. The tremendous amount of energy associated with the bonds within the nucleolus of atom itself is called *atomic energy*.
- Energy interactions with a closed system can occur via *heat transfer* and *work*.

In Macroscopic approach of thermodynamics, the substance is considered to be continuous whereas every matter actually comprises of myriads of molecules with intermolecular spacing amongst them. In engineering thermodynamics where focus lies upon the gross behaviour of the system and substance in it, the statistical approach is to be kept aside and classical thermodynamics approach be followed. In classical thermodynamics, for analysis the atomic structure of substance is considered to be continuous.

For facilitating the analysis this concept of continuum is used in which the substance is treated free from any kind of discontinuity. As this is an assumed state of continuum in substance so the order of analysis or scale of analysis becomes very important. Thus, in case the scale of analysis is large enough and the discontinuities are of the order of intermolecular spacing or mean free path then due to relative order of discontinuity being negligible it may be treated continuous. In the situations when scale of analysis is too small such that even the intermolecular spacing or mean free path are not negligible i.e. the mean free path is of comparable size with smallest significant dimension in analysis then it cannot be considered continuous and the microscopic approach for analysis should be followed.

For example, whenever one deals with highly rarefied gases such as in rocket flight at very high altitudes or electron tubes, the concept of continuum of classical thermodynamics should be dropped and statistical thermodynamics using microscopic approach should be followed. Thus, in

general it can be said that the assumption of continuum is well suited for macroscopic approach where discontinuity at molecular level can be easily ignored as the scale of analysis is quite large. The concept of continuum is thus a convenient fiction which remains valid for most of engineering problems where only macroscopic or phenomenological information are desired. For example, let us see density at a point as a property of continuum. Let us take some mass of fluid Δm in some volume ΔV enveloping a point P in the continuous fluid. Average mass density of fluid within volume ΔV shall be the ratio $(\Delta m/\Delta V)$. Now let us shrink the volume ΔV enveloping the point to volume ΔV. It could be seen that upon reducing the volume, ΔV may be so small as to contain relatively few molecules which may also keep on moving in and out of the considered very small volume, thus average density keeps on fluctuating with time. For such a situation the definite value of density cannot be given. Therefore, we may consider some limiting volume ΔV_{limit} such that the fluid around the point may be treated continuous and the average density at the point may be given by the ratio $(\Delta m/ \Delta V_{limit})$.

Thus, it shows how the concept of continuum although fictitious is used for defining density at a point as given below,
Average density at the point $= \lim \Delta V \to \Delta V limit (\Delta m/\Delta V)$

1.3.2 Work
Whenever a system interacts with its surroundings, it can exchange energy in two ways- work and heat. In mechanics, work is defined as the product of the force and the displacement in the direction of the force. Work done when a spring is compressed or extended: According to Hooke's law, Spring force $= - k (x – x_0)$

Where k is the spring constant, x_0 is the equilibrium position, and x is the final position. The negative sign shows that the direction of the spring force is opposite the direction of the displacement from x_0. The external force is equal in magnitude but opposite in sign to the spring force, so External force (force of your hands) $= k (x – x_0)$.

Now, we want to calculate the work done when we stretch the spring from position 1 to position 2.

$$W = F\, dx = k (x – x_0)\, d(x-x_0) = 1/2\, k [(x_2-x_0)^2 - (x_1-x_0)^2]$$
Work done when a volume is increased or decreased

Consider a gas in a container with a movable piston on top. If the gas expands, the piston moves out and work is done by the system on the surroundings. Alternatively, if the gas inside contracts, the piston moves in and work is done by the surroundings on the system. Why would the gas inside contract or expand? It would if the external pressure, P_{ex}, and the internal pressure, P_{in}, were different.

To calculate the work done in moving the piston, we know that the force = pressure times area and then work equals pressure times area times distance or work equals pressure times the change in volume. So,

W = the integral of (P$_{ex}$) dV

The differential work done (dW) associated with a differential displacement (dl) is given by
dW = F dl

For a piston cylinder assembly,
dW = F dl = PA (dl) = P dV

If the gas is allowed to expand reversibly from the initial pressure P to final pressure P, then the work done is given by
W = ∫ p dV

1.3.4 Heat

Heat like work, is a form of energy. The energy transferred between a system and its surroundings is called heat if it occurs by virtue of the temperature difference across the boundary. The two modes of energy transfer work and heat depend on the choice of the system. Heat energy moves from a hotter body to a colder body upon contact of the two bodies. If two bodies at different temperatures are allowed to remain in contact, the system of two bodies will eventually reach a thermal equilibrium (they will have the same temperature). A body never contains heat. Rather heat is a transient phenomenon and can be identified as it crosses the boundary.

Note that a quantity that is transferred to or from a system during an interaction is not a property since the amount of such a quantity depends on more than just the state of the system. Heat and work are energy transfer mechanisms between a system and its surroundings, and there are many similarities between them:

i.   Both are recognized at the boundaries of a system as they cross the boundaries. That is, both heat and work are boundary phenomena. 2. Systems possess energy, but not heat or work.
ii.   Both are associated with a process, not a state. Unlike properties, heat or work has no meaning at a state.
iii.   Both are path functions (i.e., their magnitudes depend on the path followed during a process as well as the end states).

Path functions have **inexact differentials** designated by the symbol d. Therefore, a differential amount of heat or work is represented by δQ or δW, respectively, instead of *dQ* or *dW*.

Properties, however, are **point functions** (i.e., they depend on the state only, and not on how a system reaches that state), and they have **exact differentials** designated by the symbol *d*. A small change in volume, for example, is represented by *dV*, and the total volume change during a process between states 1 and 2 is

$$\int_1^2 dV = V_2 - V_1 = \Delta V$$

That is, the volume changes during process 1–2 is always the volume at state 2 minus the volume at state 1, regardless of the path followed. The total work done during process 1–2, however, is

$$\int_1^2 \delta W = W_{12} \qquad (not\ \Delta W)$$

That is, the total work is obtained by following the process path and adding the differential amounts of work (δW) done along the way. The integral of δW *is not* $W2 \_ W1$ (i.e., the work at state 2 minus work at state 1), which is meaningless since work is not a property and systems do not possess work at a state.

1.4 Macroscopic and Microscopic Approaches

Microscopic approach uses the statistical considerations and probability theory, where we deal with "average" for all particles under consideration. This is the approach used in the disciplines known as kinetic theory and statistical mechanics.

In the **macroscopic** point of view, of classical thermodynamics, one is concerned with the time averaged influence of many molecules that can be perceived by the senses and measured by the instruments. The pressure exerted by a gas is an example of this. It results from the change in momentum of the molecules, as they collide with the wall. Here we are not concerned with the actions of individual molecules but with the time-averaged force on a given area that can be measured by a pressure gage.

From the macroscopic point of view, we are always concerned with volumes that are very large compared to molecular dimensions, and therefore a system (to be defined next) contains many molecules, and this is called continuum. The concept of continuum loses validity when the mean free path of molecules approaches the order of typical system dimensions.

1.5 Concept of Temperature

1.5.1 Temperature Measurement

Although we are familiar with temperature as a measure of "hotness" or "coldness," it is not easy to give an exact definition for it. Based on our physiological sensations, we express the level of temperature qualitatively with words like freezing cold, cold, warm, hot, and red-hot. However, we cannot assign numerical values to temperatures based on our sensations alone. Furthermore, our senses may be misleading. A metal chair, for example, will feel much colder than a wooden one even when both are at the same temperature.

Fortunately, several properties of materials change with temperature in a repeatable and predictable way, and this forms the basis for accurate temperature measurement. The commonly used mercury-in-glass thermometer, for example, is based on the expansion of mercury with temperature. Temperature is also measured by using several other temperature-dependent properties.

It is a common experience that a cup of hot coffee left on the table eventually cools off and a cold drink eventually warms up. That is, when a body is brought into contact with another body that is at a different temperature, heat is transferred from the body at higher temperature to the one at lower temperature until both bodies attain the same temperature as shown in figure 1.6. At that point, the heat transfer stops, and the two bodies are said to have reached **thermal equilibrium.** The equality of temperature is the only requirement for thermal equilibrium.
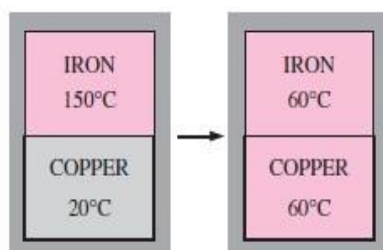
Figure 1.6: Thermal Equilibrium

1.5.2 Zeroth Law of Thermodynamics

We cannot assign numerical values to temperatures based on our sensations alone. Furthermore, our senses may be misleading. Several properties of material changes with temperature in a repeatable and predictable way, and this forms the basis of accurate temperature measurement. The commonly used mercury-in-glass thermometer for example, is based on the expansion of mercury with temperature. Temperature is also measured by using several other temperature dependant properties. Two bodies (eg. Two copper blocks) in contact attain thermal equilibrium when the heat transfer between them stops. The equality of temperature is the only requirement for thermal equilibrium.

The Zeroth Law of Thermodynamics: If two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other. This obvious fact cannot be concluded from the other laws of thermodynamics, and it serves as a basis of temperature measurement. By replacing the third body with a thermometer, the zeroth law can be restated two bodies are in thermal equilibrium if both have the same temperature reading even if they are not in contact.

1.5.3 Temperature Scales:

All temperature scales are based on some easily reproducible states such as the freezing and boiling point of water, which are also called the ice-point and the steam-point respectively. A mixture of ice and water that is in equilibrium with air saturated with water vapour at 1atm pressure is said to be at the ice-point, and a mixture of liquid water and water vapour (with no air) in equilibrium at 1atm is said to be at the steam-point.

Celsius and Fahrenheit scales are based on these two points (although the value assigned to these two values is different) and are referred as two-point scales.

In thermodynamics, it is very desirable to have a temperature scale that is independent of the properties of the substance or substances.

Such a temperature scale is called a thermodynamic temperature scale. (Kelvin in SI)

Ideal gas temperature scale

The temperatures on this scale are measured using a constant volume thermometer. Based on the principle that at low pressure, the temperature of the gas is proportional to its pressure at constant volume. The relationship between the temperature and pressure of the gas in the vessel can be expressed as

T = a + b.P

Where the values of the constants *a* and *b* for a gas thermometer are determined experimentally. Once *a* and *b* are known, the temperature of a medium can be calculated from the relation above by immersing the rigid vessel of the gas thermometer into the medium and measuring the gas pressure.

Ideal gas temperature scale can be developed by measuring the pressures of the gas in the vessel at two reproducible points (such as the ice and steam points) and assigning suitable values to temperatures those two points. Considering that only one straight line passes through two fixed points on a plane, these two measurements are sufficient to determine the constants a and b in the above equation. If the ice and the steam points are assigned the values 0 and 100 respectively, then the gas temperature scale will be identical to the Celsius scale. In this case, the value of the constant *a* (that corresponds to an absolute pressure of zero) is determined to be -273.15^0C when extrapolated.

The equation reduces to T = bP, and thus we need to specify the temperature at only one point to define an absolute gas temperature scale. Absolute gas temperature is identical to thermodynamic temperature in the temperature range in which the gas thermometer can be used. We can view that thermodynamic temperature scale at this point as an absolute gas temperature scale that utilizes an ideal gas that always acts as a low-pressure gas regardless of the temperature.

At the Tenth international conference on weights and measures in 1954, the Celsius scale has been redefined in terms of a single fixed point and the absolute temperature scale. The triple point occurs at a fixed temperature and pressure for a specified substance. The selected single point is the triple point of water (the state in which all three phases of water coexist in equilibrium), which is assigned the value 0.01 C. As before the boiling point of water at 1 atm. Pressure is 100.0 C. Thus the new Celsius scale is essentially the same as the old one. On the Kelvin scale, the size of Kelvin unit is defined as "the fraction of 1/273.16 of the thermodynamic temperature of the triple point of water, which is assigned a value of 273.16K". The ice point on Celsius and Kelvin are respectively 0 and 273.15 K.

Constant volume gas thermometer

The constant volume gas thermometer is the most accurate laboratory thermometer and is used for the calibration of other thermometers. When we heat a gas keeping the volume constant, its pressure increases and when we cool the gas its pressure decreases. The relationship between pressure and temperature at constant volume is given by the law of pressure. According to this law, the pressure of a gas changes by (1/273) of its original pressure at 0^0C for each degree centigrade (or Celsius) rise in temperature at constant volume.

If P_o is the pressure of a given volume of a gas at 0^oC and P_t is the pressure of the same volume of the gas (i.e., at constant volume) at t^oC, then

$$P_t = P_o + \frac{P_o}{273} \times t$$

$$P_t = P_o + (1 + \frac{t}{273})$$

$$P_t = P_o + (1 + \gamma_v \ t)$$

Where $\gamma_v = \frac{1}{273}$ is constant and is known as coefficient of increase of pressure.

It consists of a glass bulb B connected to a tube A, through a capillary glass tube „C". The tube A is connected to a mercury reservoir R which is clamped on the board and can be lowered or raised whenever required to keep the volume of the air constant. The capillary tube C is provided with a three-way stopper S and can be used to connect capillary and bulb as well as to disconnect tube from bulb B. A pointer is provided such that the end P is projecting inside from the upper part of A. A scale calibrated in 0oC is provided between A and R. It is as shown in figure 1.7.
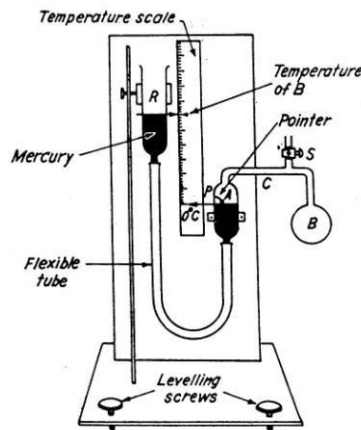

Figure 1.7: Constant Volume Gas Thermometer

The whole apparatus is levelled by adjusting the levelling screws. By adjusting the stopper, the bulb „B" is filled with air or some gas and the pointer is adjusted so that tip of the pointer just touches the level of mercury in the tube A. After filling the bulb, it is kept in an ice bath for some time till the air inside the bulb attains the temperature of ice at which the mercury level becomes stationary. Now the reservoir R is adjusted so that the level of mercury in the tube A just touches the tip of the pointer P. The difference between the mercury levels in the two tubes is noted and let it be ho. If Po is the pressure exerted by the air in the bulb, then

$$P_o = P + h_0$$

Now ice bath is removed and the bulb B is surrounded with steam. Again when the mercury level in both the tubes becomes stationary, tube R is adjusted so that the mercury column in this position in tube A touches the tip of the pointer. Let the difference between the mercury columns levels in A and R be h_{100}. The pressure of the enclosed gas in B will be given by,

-------- $$P_{100} = P_o + h_{100}$$ ----eq. (3)

$$P_{100} = P_o \quad (1 + \gamma_v 100)$$

$$P_{100} - P_o = P_0 \gamma_v \, 100$$

Finally, the bulb is brought in contact of the body whose temperature is to be found out. After the mercury level becomes stationary, the tube R is adjusted so that the mercury level touches the tip of the pointer again. Let h_t be the difference between the heights of mercury levels and if P_t is the pressure of the air inside the bulb B, then we have,

------------ $$P_t = P_o + h_t$$ --------eq. (5) --------------------eq. (6)

$$P_t = P_o \quad (1 + \gamma_v t)$$

Dividing equation (6) by equation (4), we get

$$P_t - P_o = P_0 \gamma_v t$$

$$\frac{P_t - P_o}{P_{100} - P_0} = \frac{P_0 \gamma_v t}{P_0 \gamma_v \, 100}$$

$$t = \frac{P_t - P_0}{P_{100} - P_0} \times 100$$

--------------------eq. (7)

Substituting P_t and P_{100} in equation (7), we get,

$$t = \frac{(P_0 + h_t) - (P_0 + h_0)}{(P_0 + h_{100}) - (P_0 + h_0)} \times 100$$

$$t = \frac{h_t - h_0}{h_{100} - h_0} \times 100$$

1.5.4 Joule's Experiments

Let us take a closed system which permits work interaction and heat interaction both, as in case of stirring in a container, as shown in figure 1.8. As a result of stirring it is seen that the temperature of water gets raised up. This rise in temperature can be accounted by quantifying the amount of heat supplied for raising this temperature. Thus, it is obvious that for any closed system undergoing a cycle

$$\oint W = J \cdot \oint Q, \text{ where } J \text{ is Joule's constant.}$$

i.e., the net heat interaction is proportional to the work interaction. Also the constant is known as "Joule's mechanical equivalent of heat". Joule's constant is described as;

$$\frac{W}{Q} = J = 4.18 \, \frac{\text{Joules}}{\text{Calories}}$$

Thus, J is a numerical conversion factor which could be unity if the heat is also given in joules. For any cyclic process in the closed system the relationship between heat and work shall be, (if the consistent units are used)
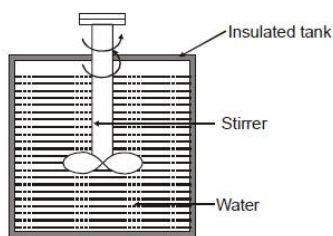
$$\oint \delta q = \oint \delta W.$$

Figure 1.8: Joule's Experiment

Other thermometers and their thermometric properties are as follows

Liquid in glass thermometer (Mercury or Alcohol)- Length of mercury or alcohol column

Bimetallic Thermometer-

Pressure Thermometer-

Thermocouple-

Resistance thermometer-

Optical Thermometer-

Activity – Complete the above by including their thermometric properties.

1.5.5 Conversion from one temperature scale to another

Fahrenheit to Celsius: $T_c = 5/9(T_f-32)$

Celsius to Fahrenheit - $T_f = 9/5T_c + 32$

Celsius to Absolute Temperature $T = Tc +273.15$

Also note, $T_c \frac{L_T - L_0}{L_{100} - L_0} \; x \; 100$-------------------------------------equation 1

The equation for computing the temperature Tc for liquid in glass thermometer. Where Tc is Temperature in Celsius, L_T is length at temperature T, L_{100} is length at steam point (upper fixed point) and L_0 is length at ice point (lower fixed point)

Activities: Consider equation 1 and compute for Platinum Thermometer, Constant Volume Gas thermometer and Thermocouple.

1.6 Reversibility and Irreversibility

1.6.1 Introduction

Thermodynamic processes may have the change of state occurring in two ways. One is the change of state occurring so that if the system is to restore its original state, it can be had by reversing the factors responsible for occurrence of the process. Other change of state may occur such that the above restoration of original state is not possible. Thermodynamic system that is capable of restoring its original state by reversing the factors responsible for occurrence of the process is called reversible system and the thermodynamic process involved is called reversible process. Thus, upon reversal of a process there shall be no trace of the process being occurred, i.e. state changes during the forward direction of occurrence of a process are exactly similar to the states passed through by the system during the reversed direction of the process. It is quite obvious that the reversibility can be realized only if the system maintains its thermodynamic equilibrium throughout the occurrence of process.

The irreversibility is the characteristics of the system which forbids system from retracing the same path upon reversal of the factors causing the state change. Thus, irreversible systems are those which do not maintain equilibrium during the occurrence of a process. Various factors responsible for the nonattainment of equilibrium are generally the reasons responsible for irreversibility. Presence of friction, dissipative effects etc. have been identified as a few of the prominent reasons for irreversibility. The reversible and irreversible processes are shown on *p-v* diagram in figure 1.9. by „1–2 and 2–1" and „3–4 and 4–3" respectively.
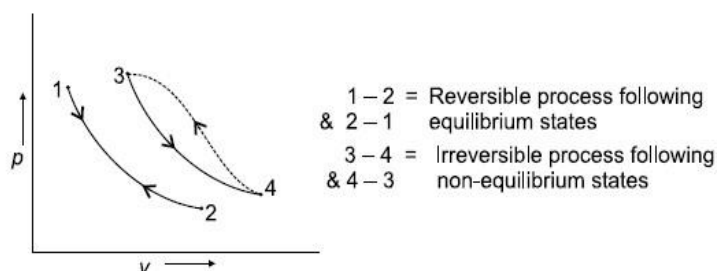

Figure 1.9: Reversible and Irreversible Processes

1.6.2 Causes for irreversibility
Generic types of irreversibility are due to;

(i) Friction,
(ii) Electrical resistance,
(iii) Inelastic solid deformations,
(iv) Free expansion
(v) Heat transfer through a finite temperature difference,
(vi) Non equilibrium during the process, etc.

Friction: Friction is invariably present in real systems. It causes irreversibility in the process as work done does not show equivalent rise in kinetic or potential energy of the system. Fraction of energy wasted due to frictional effects leads to deviation from reversible states.

*Electrical resistance***:** Electrical resistance in the system also leads to presence of dissipation effects and thus irreversibility. Due to electric resistance dissipation of electrical work into internal energy or heat takes place. The reverse transformation from heat or internal energy to electrical work is not possible, therefore leads to irreversibility.

Inelastic solid deformation: Deformation of solids, when of inelastic type is also irreversible and thus causes irreversibility in the process. If deformation occurs within elastic limits then it does not lead to irreversibility as it is of reversible type.

Free expansion: Free expansion as discussed earlier in chapter 3, refers to the expansion of un-resisted type such as expansion in vacuum. During this un-resisted expansion, the work interaction is zero and without expense of any work it is not possible to restore initial states. Thus, free expansion is irreversible.

Heat transfer through a finite temperature difference: Heat transfer occurs only when there exists temperature difference between bodies undergoing heat transfer. During heat transfer if heat addition is carried out in finite number of steps then after every step the new state shall be a non-equilibrium state. In order to have equilibrium states in between, the heat transfer process may be carried out in infinite number of steps. Thus, infinitesimal heat transfer every time causes infinitesimal temperature variation. These infinitesimal state changes shall require infinite time and process shall be of quasi-static type, therefore reversible. Heat transfer through a finite temperature difference which practically occurs is accompanied by irreversible state changes and thus makes processes irreversible.

Non equilibrium during the process: Irreversibility is introduced due to lack of thermodynamic equilibrium during the process. Non equilibrium may be due to mechanical in equilibrium, chemical in equilibrium, thermal in equilibrium, electrical in equilibrium etc. and irreversibility are called mechanical irreversibility, chemical irreversibility, thermal irreversibility, electrical irreversibility respectively. Factors discussed above are also causing non equilibrium during the process and therefore make process irreversible.

1.7 The First Law of Thermodynamics

The first law of thermodynamics, also known as the conservation of energy principle, provides a sound basis for studying the relationships among the various forms of energy and energy interactions. Based on experimental observations, the first law of thermodynamics states that energy can be neither created nor destroyed during a process; it can only change forms. Therefore, every bit of energy should be accounted for during a process.

Thus first law of thermodynamics states that "in a closed system undergoing a cyclic process, the net work done is proportional to the net heat taken from the surroundings" or "for any cycle of a closed system the net heat transfer equals the network".

For non-cyclic process: Let us now take up a system undergoing a non-cyclic process where transfer of heat and work take place and there is some change in the state of system i.e., initial and final states are different.

If we assume the system to have the heat interaction ΔQ and work interaction ΔW, then from the basic principles it can be said that: Energy lost = Energy gained; as the energy can neither be created nor destroyed.

Therefore, between states 1–2 one can write energy balance as,

$$Q1\text{–}2 - W1\text{–}2 = U1\text{–}2$$

Where $Q_{1\text{–}2}$, $W_{1\text{–}2}$ and $U_{1\text{–}2}$ are the heat, work and stored energy values. This stored energy is called as internal energy for a system having negligible electrical, magnetic, solid distortion and surface tension effects.

For elemental interactions, $dQ = dU + dW$

Thus, the first law of thermodynamics for non-cyclic processes can be given by

$$\int dQ = \int dU + \int dW$$

The first law of thermodynamics for cyclic process can be employed,

$$\oint (\delta Q - \delta W) = 0$$

1.7.2 Corollaries

First law of thermodynamics based on law of energy conservation has proved to be a powerful tool for thermodynamic analysis. But over the period of time when it was applied to some real systems, it was observed that theoretically first law stands valid for the processes which are not realizable practically. It was then thought that there exist certain flaws in first law of thermodynamics and it should be used with certain limitations. Say for example let us take a bicycle wheel and paddle it to rotate. Now apply brake to it. As a result of braking wheel comes to rest upon coming in contact with brake shoe. Stopping of wheel is accompanied by heating of brake shoe. Examining the situation from first law of thermodynamics point of view it is quite satisfying that rotational energy in wheel has been transformed into heat energy with shoe, thus causing rise in its temperature: Now, if we wish to introduce the same quantity of heat into brake shoe and wish to restore wheel motion then it is not possible simply, whereas theoretically first law permits the conversion from heat to work (rotation of wheel in this case) as well.

 Therefore, it is obvious that first law of thermodynamics has certain limitations as given below:
(*i*) First law of thermodynamics does not differentiate between heat and work and assures full convertibility of one into other whereas full conversion of work into heat is possible but the vice versa is not possible.

(*ii*) First law of thermodynamics does not explain the direction of a process. Such as theoretically it shall permit even heat transfer from low temperature body to high temperature body which is

not practically feasible. Spontaneity of the process is not taken care of by the first law of thermodynamics.

Perpetual motion machine of the first kind (PMM-I) is a hypothetical device conceived, based on violation of First law of thermodynamics. Let us think of a system which can create energy as shown below.
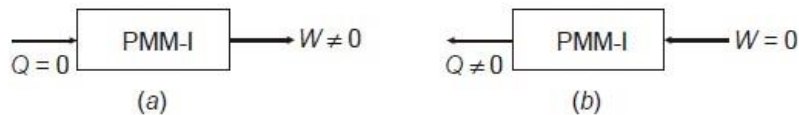
Here a device which is continuously producing work without any other form of energy supplied to it has been shown in figure 1.10 (*a*), which is not feasible. Similarly, a device which is continuously emitting heat without any other form of energy supplied to it has been shown in (*b*), which is again not feasible. Above two imaginary machines are called Perpetual Motion Machines of 1st kind.

1.7.3 First law applied to a Process and Flow System
Let us consider an open system as shown in figure 1.11having inlet at section 1–1 and outlet at section 2–2. The cross-section area, pressure, specific volume, mass flow rate, energy at section

1–1 and 2–2 are

Section 1–1 = $A1, p1, v1, m1, e1$

Section 2–2 = $A2, p2, v2, m2, e2$

Open system is also having heat and work interactions Q, W as shown in figure above.

Applying the energy balance at the two sections, it can be given as,

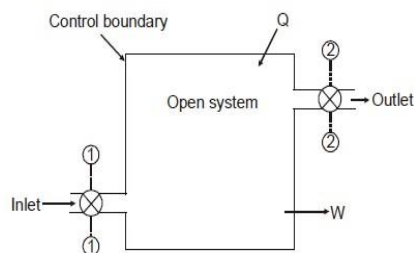Energy added to the system + Stored energy of the fluid at inlet = Stored energy of the fluid at outlet

Figure 1.10: First law as applied to open system

1.7.4 Steady Flow Energy Equation

Steady flow refers to the flow in which its properties at any point remain constant with respect to time. Steady system is the system whose properties are independent of time, i.e. any property at a point in system shall not change with time.

Let us take an open system having steady flow. Figure 1.12 shows steady flow system having inlet at section 1–1, outlet at section 2–2, heat addition Q and work done by the system W.
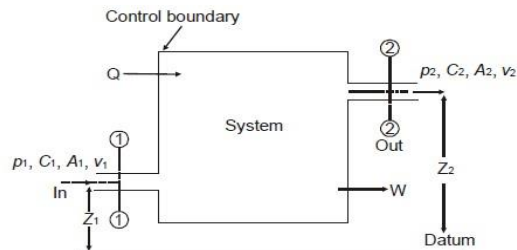

Figure 1.11: Steady Flow System

As described in earlier article the energy balance when applied to open system results in

$$Q + m_1(e_1 + p_1v_1) = W + m_2(e_2 + p_2v_2)$$

Substituting for e_1 and e_2

$$Q + m_1\left(u_1 + \frac{C_1^2}{2} + gz_1 + p_1v_1\right) = W + m_2\left(u_2 + \frac{C_2^2}{2} + gz_2 + p_2v_2\right)$$

and from definition of enthalpy,

$$h_1 = u_1 + p_1v_1$$
$$h_2 = u_2 + p_2v_2$$

therefore,

$$Q + m_1\left(h_1 + \frac{C_1^2}{2} + gz_1\right) = W + m_2\left(h_2 + \frac{C_2^2}{2} + gz_2\right)$$

Above equation is known as steady flow energy equation (S.F.E.E.). If the mass flow rates at inlet and exit are same, i.e. $m_1 = m_2 = m$

then,
$$Q + m\left(h_1 + \frac{C_1^2}{2} + gz_1\right) = W + m\left(h_2 + \frac{C_2^2}{2} + gz_2\right)$$

or, on unit mass basis the S.F.E.E. shall be:

$$q + h_1 + \frac{C_1^2}{2} + gz_1 = w + h_2 + \frac{C_2^2}{2} + gz_2$$

where
$$q = \frac{Q}{m},\ w = \frac{W}{m}$$

The steady flow energy equation can be used as a tool for carrying out thermodynamic analysis of engineering system with suitable modifications.

References

Physics for Scientists and Engineers 6th Edition by Serway Jewett
College Physics by Frederic J Bueche and Hugene Hecht