Chapter 1

1.1 Definition

The word thermodynamics stems from the Greek words *therme* (heat) and *dynamis* (force/power), which is most descriptive of the early efforts to convert heat into power: the capacity of hot bodies to produce work.

Today, Thermodynamics is defined as the study of energy, its forms and transformations and the interactions of energy with matter. Hence, thermodynamics is concered with

- the concept of energy
- the law that governs the conversion of one form of energy into another
- the properties of the working substances or the media used to obtain the energy conversion.

1.2 Value of Energy to Society

The availability of energy and people's ability to harness that energy in useful ways have transformed our society. A few hundred years ago, the greatest fraction of the population struggled to subsist by producing food for local consumption. Now, in many countries a small fraction of the total work force produces abundant food for the entire population, and much of the population is freed for other jobs. We are able to travel great distances in short times by using a choice of transport means; we can communicate instantaneously with persons anywhere on earth; and we control large amounts of energy at our personal whim in the form of automobiles, electric tools and appliances, and comfort conditioning in our dwellings.

It is very hard to imagine the present life without electricity and other forms of energy. The energy available and consumed data exhibit the perspective picture of the economic condition and scope and the level of advancement of living people's civilization.

1.3 Macroscopic versus Microscopic Viewpoint

It is well-known that a substance consists of a large number of particles called molecules. The properties of the substance naturally depend on the behavior of these particles.

There are two points of view from which the behavior of matter can be studied: the macroscopic and the microscopic approach.

a) Macroscopic Approach

This is the approach to the thermodynamics is concerned with gross or overall behavior. The properties of the substance/matter is considered without taking into account the events occurring at the molecular level.

For example, the pressure of a gas in a container is the result of momentum transfer between the molecules and the walls of the container. However, one does not need to know the behavior of the gas particles to determine the pressure in the container. It would be sufficient to attach a pressure gauge to the container. Hence, instruments are used to find the value of the thermodynamic properties.

This macroscopic approach to the study of thermodynamic that does not require knowledge of the behavior of individual particles is called **classical thermodynamics**. It provides a direct and easy way to the solution of engineering problems. The values of the properties of the systems are their average values like pressure, temperature etc.

b) Microscopic approach

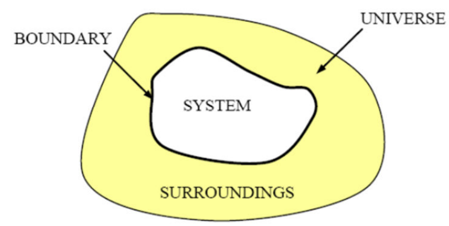
A more elaborate approach, based on the average behavior of large groups of individual particles is called microscopic approach or **statistical thermodynamics**. The properties like velocity, momentum, impulse etc. are studied by this approach. It required advanced statistical and mathematical method since they are not easily measured by instruments.

1.4 Concept and Definitions

1.4.1 System and Surrounding

Universe: is defined as the totality of matter that exists.

A system and its surroundings together comprise a universe.



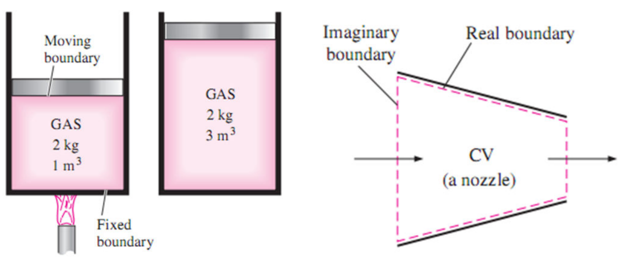
System: is a quantity of matter or a region in space selected for examination and analysis (study). The system is a specified region wherein changes due to transfers of mass and energy or both are to be studied.

It is not necessary that the volume or shape of the system should remain fixed.

Surrounding: It is the part of universe external to the system which strongly interacts with the system under study.

Boundary: The real or imaginary surface that separates system from its surroundings is called boundary. The boundary of a system can be fixed or movable. It is a contact surface shared by both the system and surrounding.

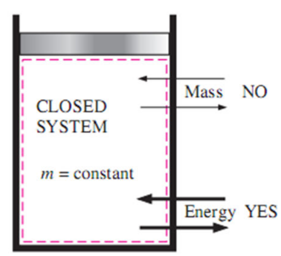
Note: all transfers of mass and energy between the system and surroundings are evaluated at the boundary.



The thermodynamic system may be classified into the following three groups: (a) Closed system; (b) Open system; and (c) Isolated system.

a) Closed system

A system with fixed amount of matter (mass) i.e. no matter (mass) can cross its boundary but the energy, in the form of heat or work can cross the boundary. It is also referred to as **control mass (CM)**.

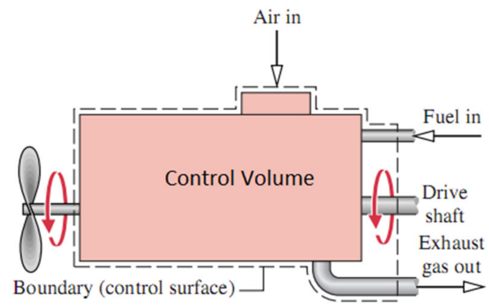


b) Isolated System

If neither mass nor energy is allowed to cross the boundary of a system is called an isolated system. It is a special type of closed system that does not interact in any way with its surrounding. E.g. any closed rigid insulated box.

c) Open system

If both mass and energy cross the boundary of a system, it is called open system. An open system permits both mass and energy cross the boundaries and the mass within the system may not remain constant. It is also called **control volume (CV)**.



Note: When the terms control mass and control volume are used the system boundary is often referred to as a ***control surface****.*

1.4.2 Thermodynamic Property

The parameter to define the characteristic of system is called thermodynamic property. A thermodynamic property is a macroscopic characteristic of a system such as mass, volume, energy, pressure, and temperature to which a numerical value can be assigned at a given time without knowledge of the previous behavior (history) of the system.

The thermodynamic properties of a system may be divided into the following two general classes.

a) Extensive properties

A property is called extensive if its value for an overall system is the sum of its values for the parts into which the system is divided i.e. it is additives. The value of a property is proportional to the mass of the system. Mass, volume, energy, and several other properties introduced later are extensive. Extensive properties depend on the size or extent of a system. The extensive properties of a system can change with time.

b) Intensive properties

If the value of a property is independent of the size or extent of a system i.e. independent of the mass of the system, it is referred as intensive properties. Intensive properties are not additive in the sense previously considered. It may vary from place to place within the system at any moment. Thus, intensive properties may be functions of both position and time.

The ratio of an extensive property 'X' to the mass 'm' is called the specific value 'X/m' of that property. Thus, $v=V/m$ is the specific volume, specific total energy ($e = E/m$).

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).

1.4.3 Thermodynamic state and Thermodynamic Equilibrium

The word state refers to the condition of a system as described by its properties such as pressure, volume, temperature, mass etc. At a given state, all the properties of a system have fixed values. If the value of even one property changes, the state will change to a different one. Hence, each unique condition of system is called a state. State is the condition of the system as all the properties can be measured or calculated throughout the entire system, which gives us a set of properties that completely describes the condition.

On the basis of the above discussion we can determine if a given variable is a property or not by applying the following tests:

(a) A variable is a property if, and only if, it has a single value at each equilibrium state.

(b) A variable is a property if, and only if, the change in its value between any two prescribed equilibrium states is single valued.

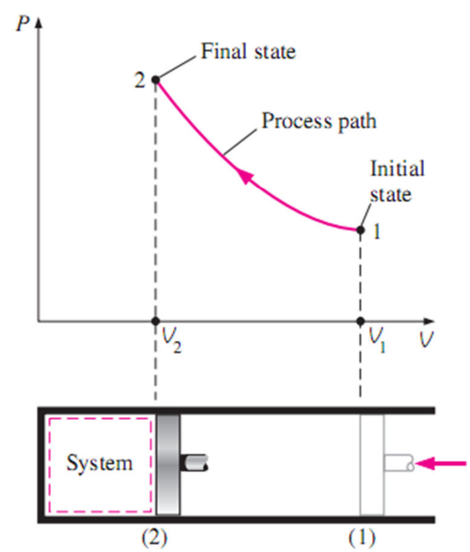
Thermodynamics deals with equilibrium states. The word equilibrium implies a state of balance. In an equilibrium state there are no unbalanced potentials (or driving forces) within a system. For a system, the properties describing the state will be constant if the system is not allowed to interact with the surroundings or it the system is allowed to interact completely with unchanging surroundings. Such a state is termed an equilibrium state and the properties are equilibrium properties.

A system will be in a state of thermodynamic equilibrium, if the condition for the following three types of equilibrium are satisfied

a) Mechanical equilibrium: a system is in mechanical equilibrium if there is no change in pressure at any point of the system with time.
b) Thermal equilibrium: a system is in thermal equilibrium if the temperature is the same throughout the entire system
c) Chemical equilibrium: a system is in chemical equilibrium if its chemical composition does not change with time, that is, no chemical reactions occur

1.4.4 Thermodynamic Process and cycles:

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.

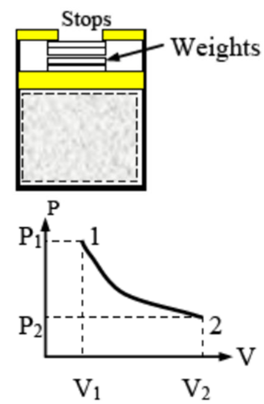


When a process proceeds in such a manner that the system remains infinitesimally (very very) close to an equilibrium state at all times, it is called a quasi-static, or quasi- equilibrium, process. A quasi-equilibrium process can be

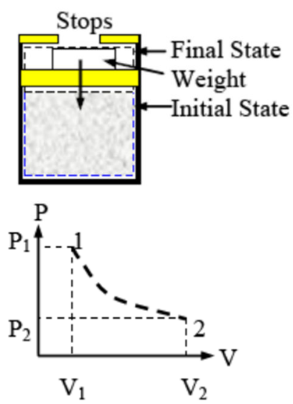
viewed as a sufficiently slow process and also called reversible process. It should be pointed out that a quasi-equilibrium process is an idealized process and is not a true representation of an actual process. But many actual processes closely approximate it. It is important because:

a) they are easy to analyze
b) serves as standards to which actual process can be compared.

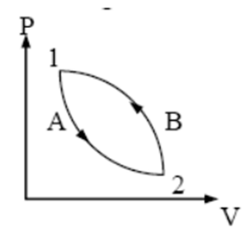
Let us consider a system of gas contained in a cylinder. The system initially is in equilibrium state, represented by the properties P_1, V_1, T_1. The weight on the piston just balances the upward force exerted by the gas. If the weights are removed one by one very slowly from the top of the piston, at any instant of the upward travel of the piston, considering gas system is isolated, every state passed through by the system will be an equilibrium state. Such a process, which is locus of all the equilibrium points passed through by the system, is known as quasi-static or quasi-equilibrium process. A quasi-static process is thus a succession of equilibrium states and represented by a continuous line.



If the weight is single and is removed, there will be an unbalanced force between the system and the surroundings, and under gas pressure, the piston will move up till it hits the stops. The system again comes to an equilibrium state, being described by the properties P_2, V_2, T_2. Thus, the intermediate states passed through by the system are non-equilibrium states which cannot be described by thermodynamic properties. such process is called non quasi-equilibrium process or irreversible process denoted by a dashed line between initial and final states.



When a process or processes are performed on a system in such a way that the final state is identical with the initial state, it is the known as a thermodynamic cycle or cyclic process. In Figure, 1 –A –2 and 2 – B – 1 are processes whereas 1 –A –2 – B – 1 is a thermodynamic cycle.



1.4.5 Some Common Properties:

a) Pressure:

It is defined as the normal force exerted per unit area.

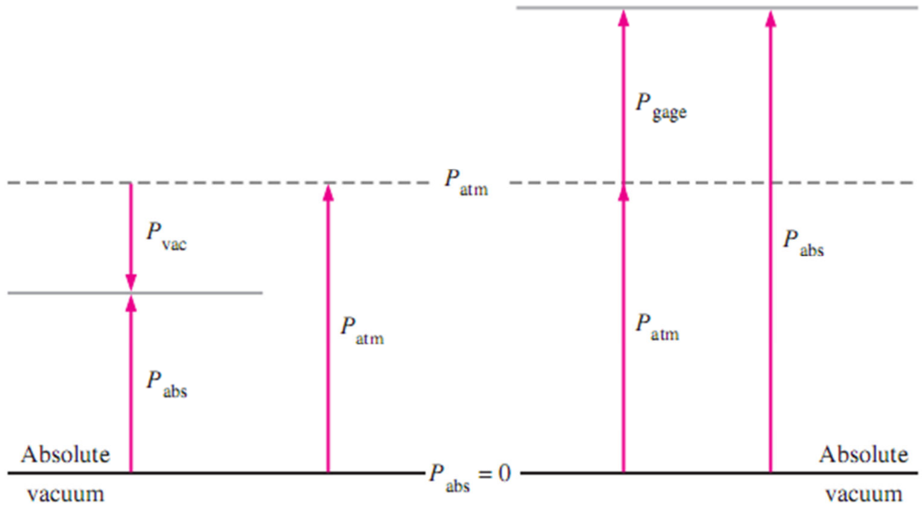
With the restriction that area over which the force is applied must not smaller than some minimum value a , the mathematical definition of the local pressure is

$$P = \lim_{\Delta A \to a} \frac{\Delta F_N}{\Delta A} \; \left(\frac{N}{m^2}, Pa\right)$$

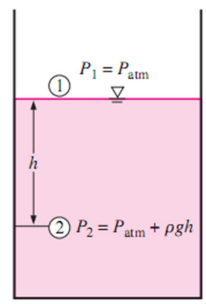
The actual pressure at a given position is called **absolute pressure** and it is measured relative to absolute vacuum i.e. absolute zero pressure. The difference between absolute pressure and local atmospheric pressure is called **gauge pressure**. Gauge pressure may be positive or negative. Pressure below atmospheric pressure is called **vacuum pressure**.

Pabs = Patm+ Pgauge

Pvac = Patm - Pabs



Pressure Variation with depth



For fluids whose density changes significantly with elevation, a relation for the variation of pressure with elevation can be obtained by

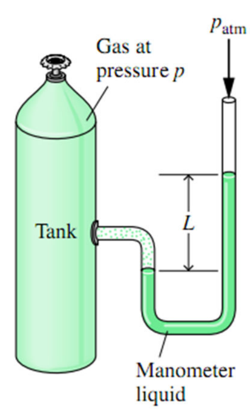
$$\frac{dP}{dz} = -\rho g$$

The negative sign is due to our taking the positive z direction to be upward so that dP is negative when dz is positive since pressure decreases in an upward direction. When the variation of density with elevation is known, the pressure difference between points 1 and 2 can be determined by integrating

$$\Delta P = P_2 - P_1 = -\int_1^2 \rho g dz = -\rho g(z_1 - z_2) = \rho gh$$

$$P_2 - P_{atm} = \rho gh = P_{gauge}$$

Manometer



A manometer is a device to measure the pressure difference based on the principle of variation of pressure with depth.

$$P_{gas} - P_{atm} = \rho gL$$

where, ρ is the density of the manometer liquid and L is the pressure head.

b) Specific Volume:

The specific volume (v) of a substance is defined as the volume per unit mass and is measured in m^3/kg. Thus, mathematical definition of specific volume is

$v = V/m$

Hence, specific volume is the reciprocal of the density, i.e.,

$v = 1/\rho$

c) Temperature

It is an intensive thermodynamic property, which determines the degree of hotness or the level of heat intensity of a body. A body is said to be at a high temperature or hot, if it shows high level of heat intensity in it. Similarly, a body is said to be at a low temperature or cold, if it shows a low level of heat intensity.

The instrument used to measure the temperature is called thermometer. For most

Temperature Scales:

Temperature Scales enable us to use a common basic for temperature measurements. All temperature scales are based on some easily reproducible states such as the freezing and boiling point of water.

The two scales (Kelvin and Rankin scale) most useful in thermodynamics are so called absolutes scales. The absolute scale for SI is the Kelvin scale. This scale is a one point scale based on the second law of thermodynamics. The single point is the triple point of water, where ice, liquid water, and water vapor coexist in a closed system in the absence of air. Rankin scale is related to Kelvin scale by

$1.8^{o}R=1K$

Two other commonly used scales are the Fahrenheit scale and the Celsius scale.

1.4.6 Equality of Temperature and Zeroth Law of thermodynamics

The zeroth law of thermodynamics states that if two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other. It serves as a basis for the validity of temperature measurement.