2

Basic Concept of Thermodynamics

(System D...)

2.1 INTRODUCTION

The word 'Thermodynamics' is derived from (Thermo + dynamics) where thermo means heat and dynamics means movement. Hence, it is a science which deals with the energy possessed by gases and vapours or in other words the science which deals with heat and work (*i.e.*, mechanical energy) means transformation of energy which is governed by the various laws of thermodynamics based on experimentation which deals with the physical behaviour of the system by logical reasoning like a machine which is used for converting heat into mechanical work known as heat engine.

The thermodynamics is based on the four laws of thermodynamics known as zeroth, first, second, and third laws.

The application of thermodynamics is extremely wide and its principles are used in the designing of energy converting devices like steam engines. *i.e.*,engines, steam and gas turbines, as well in refrigerators and air conditioning etc.

2.2 THERMODYNAMIC SYSTEM

Thermodynamic system is defined as any portion of matter under consideration, which is separated from the surroundings by real or imaginary boundaries. The thermodynamic system may be homogeneous or heterogeneous, but has to be macroscopic.

2.2.1 Boundary

It is an envelope around the system known as boundary of the system.

The boundary may be real physical surface like *i.e.* engine cylinder or walls of a vessel. The boundary may be fixed or movable having some matter such as steam, gas and vapours on compression or expansion it can take any shape.

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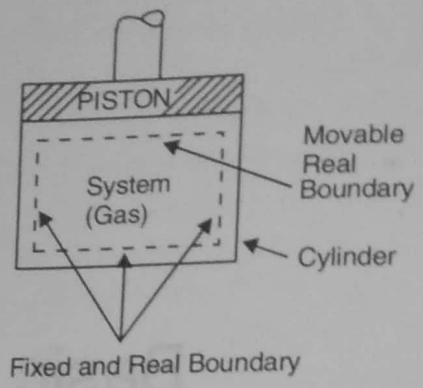

Fig.2.1 Representation of System Boundary and Surrounding

2.2.2 Surrounding

Everything outside the system boundary is called the surrounding.

2.2.3 Universe

When system and surrounding put together is called universe. Example piston cylinder arrangement.

2.3 TYPES OF SYSTEMS

There are three types of systems:

1. **Open System:** It is the system which is capable of exchanging both mass and energy (as heat) with the surrounding or across the boundary called open system.
2. **Closed System:** A system which is capable of exchanging only energy (as a heat or work) and mass remains constant with the surrounding called closed system. Example, a sealed gas container or piston cylinder.
3. **Isolated System:** It is the system which can exchange neither matter nor energy with the surroundings called isolated. Example, sealed thermoflask.

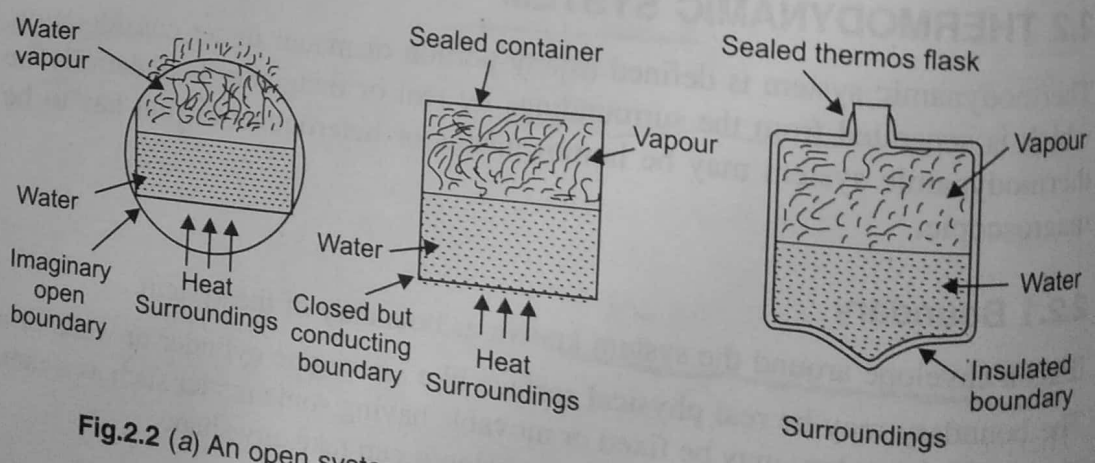

Fig.2.2 (*a*) An open system, (*b*) A closed system, (*c*) An isolated system

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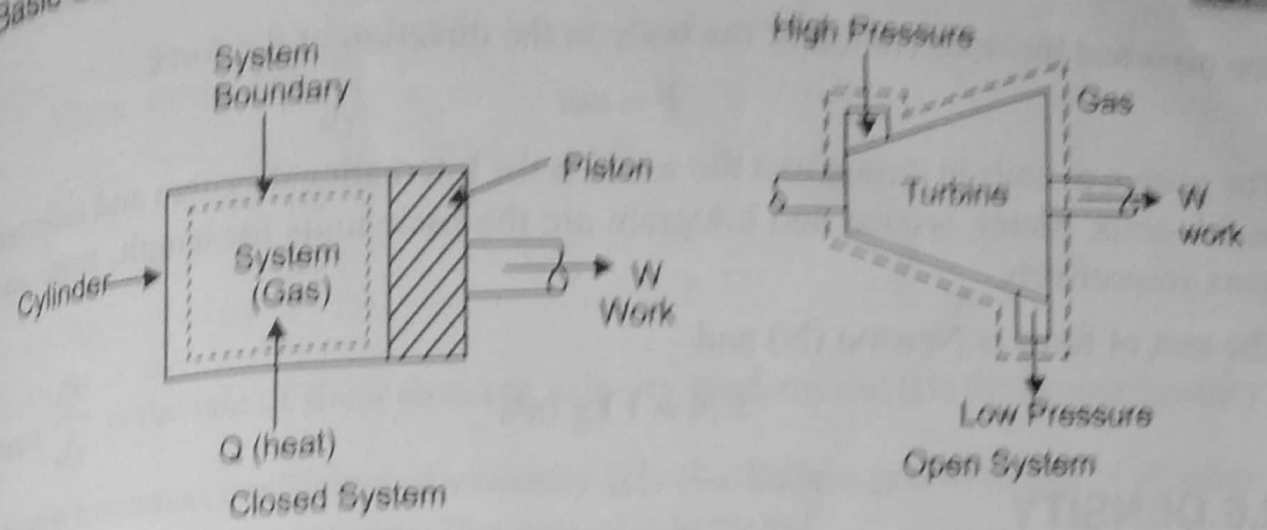

Fig. 2.3 Closed and open systems

2.4 PROPERTY

The quantitities which characterise the given state of the system are called properties or parameters. A property can be measured directly or indirectly while the system is in equilibrium. The value of the property depends only on the state and not on the process or path by which the state is achieved.

Properties are classified into two categories:

1. **Extensive Property:** It is the property which depends upon the amount of the substance present in the system. For example, total mass, volume, energy etc. of a system, since they cannot be determined without considering the system as a whole.
2. **Intensive Property:** It is the property which is independent of amount of substance present in the system. For example, viscosity, surface tension, refractive index, temperature, pressure, dielectric constant, density, specific gravity, specific heat, vapour pressure of a liquid, etc., are some of the important intensive properties.

Table 2.1. Some Intensive and Extensive Properties

Intensive properties		Extensive properties	
Temperature	Pressure	Mass	Enthalphy
Density	Refractive index	Number of moles	Entropy
Concentration	Surface tension	Energy	Internal energy
Specific heat	Boiling point	Volume	
Viscosity	Freezing point	Free energy	

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the mass and the acceleration of the body in the direction of the force,

$$F = ma$$

The system of units in throughout the world is the International system and related as S.I. units. Meter, second and kilogram are the basic units for length, time and mass respectively.

The unit of force is Newton (N) and

$$1 \text{ N} = 1 \text{ kg m/s}^2$$

2.6 DENSITY

Density is defined as the ratio of mass per unit volume. The density varies significantly for a gas with pressure and temperature but the variation is negligible for liquids.

$$\text{Density, } \rho = \frac{\text{mass}}{\text{volume}} \text{ in kg/m}^3$$

2.7 SPECIFIC WEIGHT

Specific weight (w) is defined as the ratio of weight per unit volume.

$$\text{Specific weight, } w = \frac{\text{weight}}{\text{volume}} \text{ in N/m}^3$$

2.8 SPECIFIC GRAVITY

Specific gravity of a liquid is defined as the ratio of specific weight of that liquid to the specific weight of water.

2.9 SPECIFIC VOLUME

Specific volume of a substance is defined as the volume per unit mass and the density is defined as the mass per unit volume, *i.e.*, the reciprocal of the specific volume. Specific volume and density are intensive properties. The SI unit for volume is Cubic metre. The other unit of volume is the litre and is equal to 0.001 cubic metres.

2.10 VISCOSITY

The property which controls the rate of flow of a liquid is known as viscosity. Viscosity is due to the cohesive force between the liquid particles and it is exhibited when the liquid is in motion.

Newton's law of viscosity states that the shear stress on a layer of a fluid is directly proportional to the rate of shear strain.

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Shear stress, $\tau \propto \frac{dv}{dy}$

$$\Rightarrow \quad \tau = \mu \frac{dv}{dy}$$

where $\frac{dv}{dy}$ is the rate of shear strain or velocity gradient and μ is the proportionality constant known as coefficient of viscosity. μ is also known as coefficient of absolute viscosity or dynamic viscosity. The unit of μ is Ns/m^2.

also

1 poise = 0.1 Ns/m^2 and

1 centipoise = (1/100) poise

$$\tau = \mu \frac{dv}{dy} = \frac{NS}{m^2}\frac{m/s}{m} = \frac{N}{m^2}$$

Kinematic viscosity of a liquid is the ratio of its absolute viscosity to its density.

Kinematic viscosity $\gamma = \mu/\rho$, m^2/s

1 stoke = 1/10000 $m^2/s = 10^{-4}$ m^2/s

1 centistoke = 1/100 stoke.

2.11 PRESSURE

Pressure is defined as the normal component of force per unit area. Pressure at a point in a fluid in equibrium is the same in all directions.

A fluid filled in a container exerts a force at all points on the sides and bottom of the container. This force per unit area is called pressure. The direction of this pressure is always normal to the surface with which the fluid comes in contact.

Atmospheric Pressure: The pressure exerted by the weight of air column on the surface of the earth is called as atmospheric pressure.

$$\text{Atmospheric Pressure} = \frac{\text{Weight of air column}}{\text{Area}}$$

$$= \frac{\text{Mass of air column} \times \text{Acceleration due to gravity}}{\text{Area}}$$

$$= \text{Volume of air column} \times \text{Density of air column} \times \text{Acceleration due to gravity}$$

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Since the acceleration due to gravity g is constant ($g = 9.81$ m/s ^{2}), the atmospheric pressure at any location depends on the height of air column and density of air at that place. The value of atmospheric pressure is considered as standard at the surface of the sea as it is horizontal everywhere. The maximum air column height exists at the sea level and value of standard atmospheric pressure is 1.03×10^5 N/rm^2 or 1.03 kg /cm^2. The value of atmospheric pressure will be less than this at any other place on earth due to its higher altitude from the sea level. The density of air is inversely proportional to temperature.

Gauge Pressure: Pressure measuring instruments are usually calibrated with respect to atmospheric pressure. They will read zero at atmospheric pressure. Pressure measured with these gauges is known as gauge pressure. Pressure gauges are used to measure pressure above atmospheric level and vacuum gauges are used to measure pressure below atmospheric level.

Absolute Pressure: Absolute pressure is the sum of gauge pressure and atmospheric pressure. Absolute pressure is zero at absolute vacuum.

Absolute Pressure = Gauge Pressure + Atmospheric Pressure

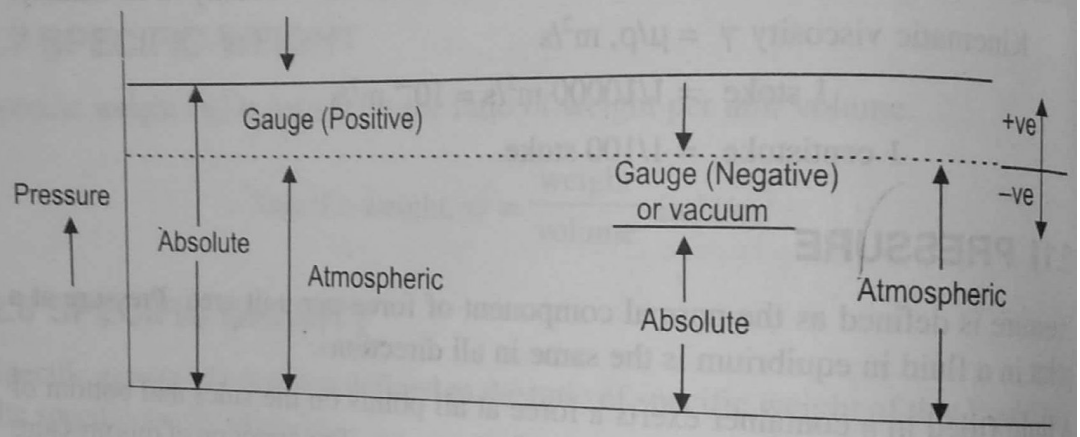

Fig. 2.4 Pressure Measurement

$$P_{abs} = P_{atm} + P_{vacuum} \qquad P_{abs} = P_{atm} - P_{vacuum}$$

The unit for pressure in the International System is (Force in Newton acting on a square metre area) called a Pascal (Pa).

$$1 \text{ Pa} = 1 \text{ N/m}^2$$

The other units are:

$$1 \text{ bar} = 10^5 \text{ Pa} = 0.1 \text{MPa}$$

$$1 \text{ atm} = 101325 \text{Pa} = 14.696 \text{ lbf/in}^2 \text{ or Psi}$$

$$1 \text{ kgf/cm}^2 = 0.980665 \text{ bar.}$$

$$1 \text{ torr} = 1 \text{ mm Hg.}$$

$$1 \text{ micron} = 1\ \mu = 10^{-6} \text{ m Hg} = 10^{-3} \text{ mm Hg}$$

$$1 \text{ mm of Hg} = 133.3 \text{ N/m}^2$$

$$1 \text{ N / mm}^2 = 10^6 \text{ N/m}^2$$

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2.12 THERMODYNAMIC EQUILIBRIUM AND NON-EQUILIBRIUM

A system is said to be in a state of thermodynamics equilibrium when the state variables remain constant throughout the system *i.e.*, state variables do not change with time and space. Thermodynamic equilibrium may be of following types:

1. **Thermal Equilibrium:** When the temperature in all parts of the system is uniform and is the same as that of the surroundings, the system said to be in thermal equilibrium.
2. **Mechanical Equilibrium:** A system is said to be in mechanical equilibrium when no mechanical work is done by one part of the system on any other part of the system *i.e.*, mechanical properties are uniform throughout the system.
3. **Chemical Equilibrium:** When the chemical composition of the system remains uniform and does not change with time, the system, is said to be in chemical equilibrium.

A system is said to be in a non-equilibrium state when the state variables have different values in different parts of system.

2.13 STATE

The state of the system is described by its properties such as pressure, temperature, density etc. This is shown on pressure-volume diagram as state 1 and 2.

Each property has a single value of each state *i.e.*, all properties are state or point functions.

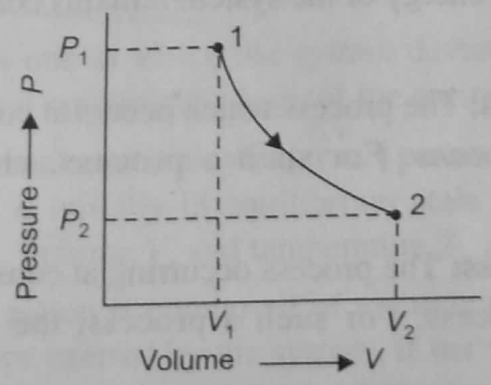

Fig. 2.5 State of a System

2.14 PATH

A thermodynamic system passing through a series of states is called a path.

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2.15 PROCESS

A process is defined when a system changes its state from one state to another state and the path is completely specified, such change of state is called a process.

In Fig. 2.6 state 1 is the initial state of the system. Then due to expansion of the system, the final state is 2. The line 1,2 is the process that has taken place.

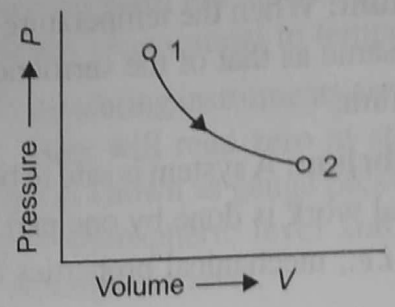

Fig.2.6 Representation of Process

2.16 TYPES OF THERMODYNAMIC PROCESS

An operation which brings about changes in the state of a system is called a thermodynamic process or simply a process.

A thermodynamic system may undergo following types of processes.

1. **Isothermal Process:** The process occurring at constant temperature is termed as an isothermal process. For such a process, δT (change in temperature) = 0.
2. **Adiabatic Process:** The process in which no heat is exchanged between the system and the surroundings is called adiabatic process. In such a process, the heat energy of the system remains constant and change in heat *i.e.*, $\delta q = 0$.
3. **Isobaric Process:** The process which occurs at constant pressure is termed as isobaric process. For such a process, change in pressure *i.e.*, $\delta P = 0$.
4. **Isochoric Process:** The process occurring at constant volume is known as a isochoric process. For such a process, the change in volume *i.e.*, $\delta V = 0$.
5. **Cyclic Process:** When initial and final states of a system in a process are the same, the process is called a cyclic process. In such a process, a system undergoes various processes and returns back to its initial state. Since internal energy, E and enthalhy, H are functions of state, we have $\delta E = 0$ and $\delta H = 0$ in a cyclic process.

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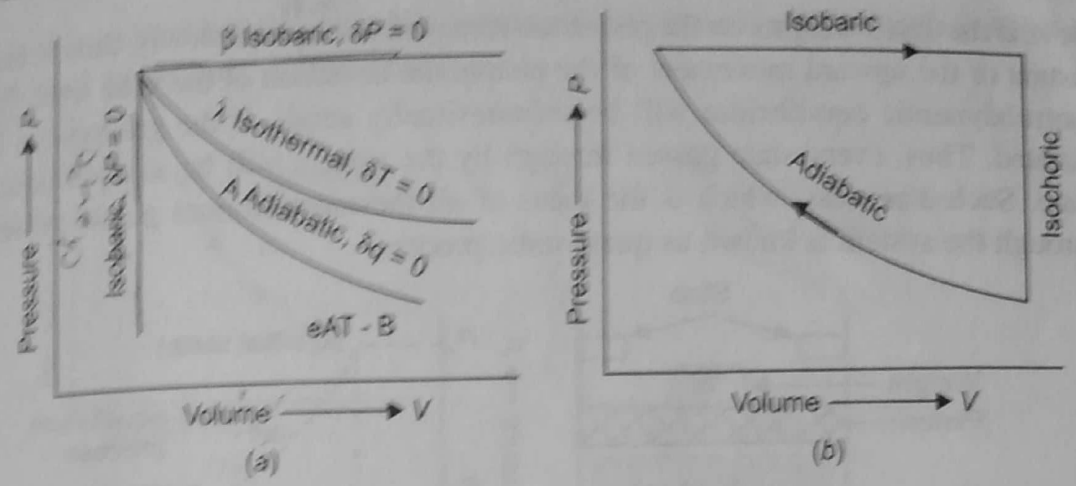

Fig. 2.7 (*a*) Isothermal, adiabatic and isobaric processes (*b*) a cyclic process

A graphical representation of these processes is shown in Fig. 2.7

2.17 CYCLIC PROCESS

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 then known as cyclic process.

A cyclic process may be represented on P-V diagram as shown in Fig. 2.8 if the various states and paths are known.

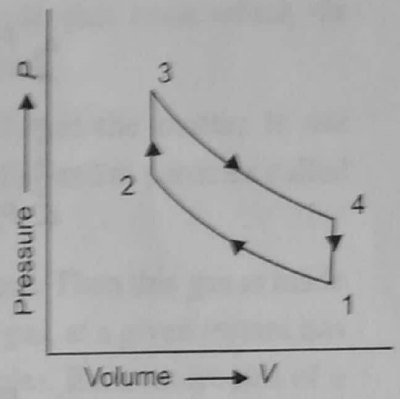

Fig.2.8 Cyclic process

2.18 QUASI-STATIC PROCESS (QUASI EQUILIBRIUM)

A quasi-static process is one in which the system deviates from one equilibrium state by only infinitesimal amounts throughout the entire process.

Consider a system (gas) enclosed in a cylinder and piston arrangement as shown in Fig.2.9. Let the system is initially in equilibrium state when the piston is at *A*, where the pressure is P_A, volume V_A and temperature T_A as shown in Fig.

The weight (W) on the piston is composed of a number of small weights which balances the upward force exerted by the system. If the whole weight is removed from the piston, then there will be unbalanced force between the system and the surroundings and the piston will be more upwards till it hits the stops at *B*. At this point *B*, the system again comes to an equilibrium state where the pressure is P_B, volume V_s and temperature T_s. But the intermediate state through which the system gets passed, are non-equilibrium states whose properties (pressure, volume and temperature) are not uniform throughout the system and thus the state of the system cannot be well-defined.

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Now, if the small weights on the piston are removed one by one slowly, then at any instant of the upward movement of the piston, the deviation of the state from the thermodynamic equilibrium will be infinitesimally small, if the gas system is isolated. Thus, every state passed through by the system will be in equilibrium state. Such a process, which is the locus of all these equilibrium points passed through the system is known as quasi-static process.

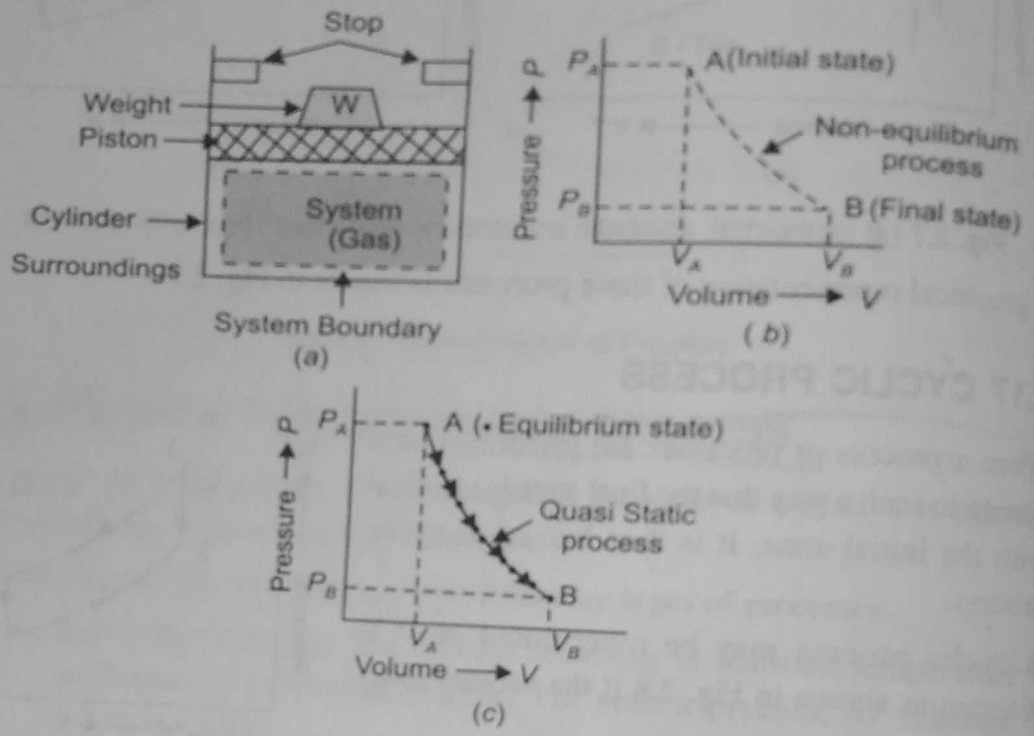

Fig.2.9 Quasi Static Process

2.19 REVERSIBLE AND IRREVERSIBLE PROCESSES

When a process is carried out infinitesimally slowly in such a way that each step remains in equilibrium with the previous step and the process could be reversed at any stage, it is called a reversible process.

A reversible process is supposed to take place in a series of infinitesimally small steps. If the process is carried out this way, the system remains in equibrium at each step and an infinitesimally change in the system can bring it back to the previous step.

Irreversible process is one in which the system or surroundings are not restored to their initial state at the conclusion of the reverse process. All naturally occurring processes are irreversible. They always tend to proceed in a definite direction and if left to themselves, they will never proceed in the opposite direction. For example, a clock always runs down and cannot rewind itself. Other common examples of irreversible process are : (1) flow of heat from a hotter to a colder body; (2) expansion of gases from high pressure regions to low pressure regions through orifices; (3) muting of two gases.

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Irreversible process are also called "spontaneous processes"; which means that the direction of the process is spontaneous.

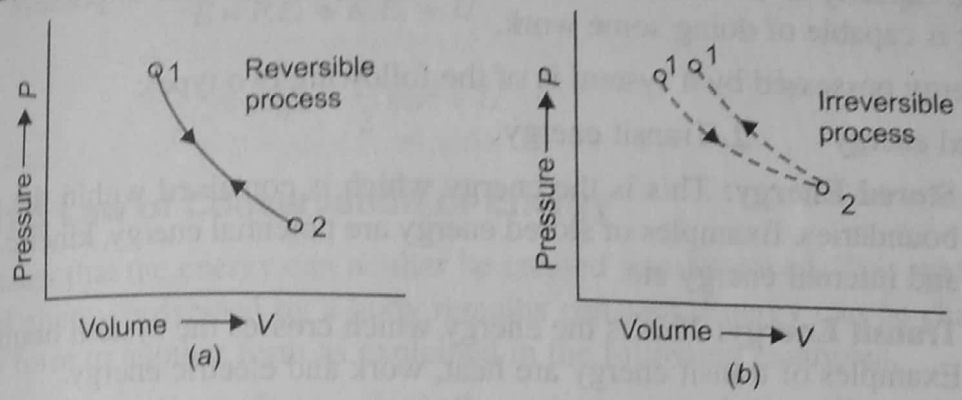

Fig. 2.10 Reversible and irreversible processes

2.20 MICROSCOPIC AND MACROSCOPIC POINT OF VIEW

There are two points of views, microscopic and macroscopic, from which the behaviour of matter or working of a system can be studied.

(*a*) **Microscopic Point of View:** It is considered that the matter is not continuous, but it is made up of a large number of identical particles called molecules.

For Example, consider a gas in a cylinder as system. Then this gas is made up of a number of molecules. Each molecule of a gas, at a given instant has certain position, energy, etc. and for each molecules. Each molecules of a gas, at a given instant has certain position, energy, etc. and for each molecule these changes rapidly because of the collisions (striking). The behaviour of the gas is described by summing up the behaviour of the molecules, statistical methods are employed and hence it is also called as statistical thermodynamics.

(*b*) **Macroscopic Point of View:** Certain quantity of matter is considered and the events that are taking place at the molecular level are not taken into account.

For example, let us consider a system of an I.C. engine, consisting of a charge in the engine cylinder. At any instant, the system has a certain volume depending upon position of the piston, this volume is easily measurable. Another quantity to describe the system is the pressure of the gas inside the cylinder. A pressure gauge can be used to measure the same. Similarly, temperature, chemical composition etc. may be described. Thus, in macroscopic point of view the system will be described large scale properties. It is also called "Classical Thermodynamics".

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2.21 ENERGY

It is the capacity to do work. In other words, a system is said to possess energy when it is capable of doing some work.

The energy possessed by a system is of the following two types:

1. Stored energy 2. Transit energy

1. **Stored Energy:** This is the energy which is contained within the system boundaries. Examples of stored energy are potential energy, kinetic energy and internal energy etc.
2. **Transit Energy:** This is the energy which crosses the system boundaries. Examples of transit energy are heat, work and electric energy.

2.21.1 Potential Energy

It is the energy, possessed by a body by virtue of its height above the earth surface (ground level) *e.g.*, a body raised to some height above the ground level possesses potential energy because it can do some work by falling on earth's surface.

Let W = Weight of the body

m = Mass of the body

z = Distance through which the body falls, and

g = Acceleration due to gravity = 9.81 m/s^2

$\therefore$ Potential energy, P.E. = Wz Nm

or P.E. = mgz Nm

$$\left[\begin{array}{l} \text{kg} \times \dfrac{\text{m}}{\text{s}^2} \times \text{m} = \text{N} - \text{m} \\ \because 1\text{N} = \dfrac{1\text{kg} - \text{m}}{\text{s}^2} \end{array}\right]$$

2.21.2 Kinetic Energy

It is the energy possessed by a body by virtue of its mass and velocity of motion.

Let m = Mass of the body, and

v = Velocity of the body

Kinetic Energy,

$$\text{K.E.} = \frac{1}{2} mv^2 Nm$$

$$\left[\begin{array}{l} \text{kg} \times \dfrac{\text{m}}{\text{s}^2} \times \text{Nm} \\ \because 1\text{N} = \dfrac{1\text{kg} - \text{m}}{\text{s}^2} \end{array}\right]$$

2.21.3 Internal Energy

It is the energy possessed by a body due to its molecular arrangement and motion of the molecules. It is usually represented by U.

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2.21.4 Total Energy

It is sum of potential, kinetic and internal energy.

$$E = P.E. + K.E. + U$$

$$= mgz + \frac{1}{2}mv^2 + U$$

2.21.5 Law of Conservation of Energy

It states that the energy can neither be created nor destroyed. This means that the total energy possessed by a body remains constant. Energy can be changed from one form to another form as explained in the following examples.

(*i*) Water flows from a tank through a vertical pipe -Potential energy is converted into Kinetic energy.

(*ii*) Brake is applied in an automobile-Kinetic energy of the wheel is converted into heat energy due to friction.

2.21.6 Law of Conservation of Mass

This law states that the mass can neither be created nor destroyed but can only be changed from one form to another form.

A substance can be changed from solid to liquid and liquid to gas or *vice-versa*.

2.22 HEAT

Heat is defined as this energy transformed without transfer of mass across the boundary of a system due to a temperature difference between the system and surrounding. It is expressed in Joule (J) or kilo joule (kJ) or in calorie for English system.

The amount of heat transferred during a process of work done by the system during the some process is dependent on the path followed during the process means the system from its initial state 1 to final state 2 by the two different paths 1-A-2 and 1-B-2. Thus, the heat and work are said to be path functions and not a point function.

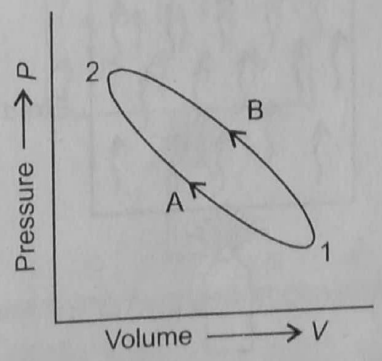

Fig. 2.11 Presure *v* volume

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The heat energy is generally transferred to three ways namely conduction, conservation and radiation.

1. **Conduction:** The transfer of energy from hot end to the cold end by molecules activity. Thus the mode of heat transfer without change of position of the molecules is known as conduction.
2. **Convection:** The transfer of heat only occurs in fluids. This mode of heat transfer takes place when hotter molecules colliding with the cooler molecules is known as convection.
3. **Radiation:** The transfer of heat by electromagnetic wave propagation from a hot body to a cold body is known as radiation.

2.23 SPECIFIC HEAT

The specific heat of a substance is defined as "the amount of heat required to raise the temperature of a unit mass of any substance through one degree."

It is generally denoted by c. In S.I., system of units, the unit of specific heat is taken as kJ /kg K. If m kg of a substance of specific heat, c is required to raise the temperature from an initial temperature T_1, to a final temperature of T_2, then

$$\text{Heat required} = mc\,(T_2 - T_1)\ \text{kJ}$$

where T_1 and T_2 may be either in °C or in K.

Since solid and liquid do not change the volume on heating, therefore they have only one specific heat. But the gases have the following two specific heats depending upon the process adopted for heating the gas.

1. Specific heat at constant pressure (c_p)
2. Specific heat at constant volume (c_v)

2.23.1 Specific Heat at Constant Volume

It is the amount of heat required to raise the temperature of a unit mass of gas through one degree when it is heated at a constant volume. It is generally denoted by c_v.

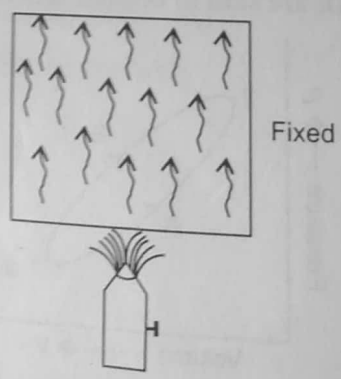

Fig.2.12 Heat being supplied at constant volume

Consider a gas contained in a container with a fixed lid as shown in Fig. 2.12. Now, if this gas is heated, it will increase the temperature and pressure of the gas in

the container. Since the lid of the container is fixed, therefore the volume of gas remains unchanged.

Let m = Mass of the gas

T_1 = Initial temperature of the gas and

T_2 = Final temperature of the gas

∴ Total heat supplied to the gas at constant volume

$$Q = \text{Mass} \times \text{Specific heat at constant volume} \times \text{Rise in temperature}$$
$$= mc_v(T_2 - T_1)$$

It maybe noted that whenever a gas is heated at constant volume, no work is done by the gas.

We know that,

work done, $W = PdV = P(V_2 - V_1)$

where P = Pressure of the gas

dV = Change in volume = $V_2 - V_1$

When there is no change in volume, then

$$dV = 0$$

Therefore, $W = 0$

2.23.2 Specific Heat at Constant Pressure

It is the amount of heat required to raise the temperature of a unit mass of a gas through one degree, when it is heated at constant pressure. It is generally denoted by c_p.

Consider a gas contained in a container with a movable lid as shown in Fig. 2.13. Now, if this gas is heated, it will increase the temperature and pressure of the gas in the container. Since the lid of the container is movable, therefore it will move upwards, in order to counterbalance the tendency for pressure to rise.

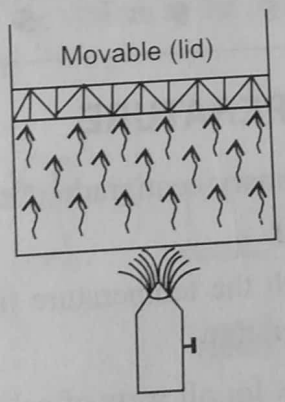

Fig. 2.13 Heat being supplied at constant pressure

Let m = Mass of the gas

T_1 = Initial temperature of the gas

T_2 = Final temperature of the gas

v_1 = Initial volume of the gas

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v_2 = Final volume of the gas

∴ Total heat supplied to the gas, at constant pressure

Q = Mass × Specific heat at constant pressure × Rise in temperature

$= m\, c_p (T_2 - T_1)$

2.24 TEMPERATURE

It is an intensive thermodynamic property, which determines the degree of hotness or coolness due to change in level of heat intensity. If the body is at high temperature. It shows high level heat intensity similarly if the body is at low temperature, it shows a low level of heat intensity.

An instrument used to measure the temperature is known as thermometer. Basically three scales are used to measure the temperature of a body.

1. Celsius or centigrade, 2. Fahrenheit scale, 3. Kelvin scale.

1. **Celsius Scale:** The freezing point of water is given zero value and boiling point is 100. It is represented by °C.
2. **Fahrenheit Scale**: The freezing point of water is 32 and boiling point is given 212. It is represented by °F.
3. **Kelvin Scale:** The freezing point of water is 273 and boiling point is given 273. It is represented by °K.

The relationship between Celsius, Fahrenheit and Kelvin scale is given as :

$$\frac{C-0}{100-0} = \frac{F-32}{212-32} = \frac{K-273}{373-273}$$

$$\boxed{\frac{C}{5} = \frac{F-32}{9} = \frac{K-273}{5}}$$

2.25 ABSOLUTE TEMPERATURE

The zero readings on the ordinary centigrade (Celsius) and Fahrenheit scale are chosen arbitarily for simplicity.

The temperature, below which the temperature of any substance cannot fall, is known as absolute zero temperature.

The absolute zero temperature, for all sorts of calculations, is taken as –273°C in case of Celsius scale and –460°C in case of Fahrenheit scale. The temperature measured from this zero are called absolute temperatue. The asbolute temperature in Celsius scale is called degree Kelvin (°K), such that K = °C + 273. Similarly, absolute temperature in Fahrenheit scale is called degree Rankine (°R) such that °R = °F + 460.

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2.26 WORK

Work is defined as a force acts upon a body causing a body to move along the direction of force or it is product of force (F) and distance moved (x) in the direction of force

$$W = F \times x$$

$$= \text{Force} \times \text{Distance Moved}$$

$$= \text{Pressure} \times \text{Area of Piston} \times \text{Distance}$$

The unit of work is Nm in S.I. system.

The work of (1Nm) is known as Joule because 1Nm = 1J

Thermodynamics Definition of the Work.

1. *"The energy transformed (without transfer of mass) across the boundary of a system due to the intensive propoerty difference other than temperature. That exits between the system and sourrounding"* Here the pressure difference means mechanical work and intensive property difference mean electrical work.

2. *"Work is energy in transition which flows from a system to the surroundings during a given process if the sole effect external to the system can be reduced to raising of a weight the work done, by the system is considered as positive work. While the work done on the system is considered as negative work."*

   Consider a sysem of battery and motor as shown Fig 2.14. The motor drives the fan in arrangement (a) The fan is replaced with the pulley and weight in arangement (b) When the motor runs, the weight is raised. The work is crossing the boundary of the system as the sole effect external to the system is for raising of a weight.

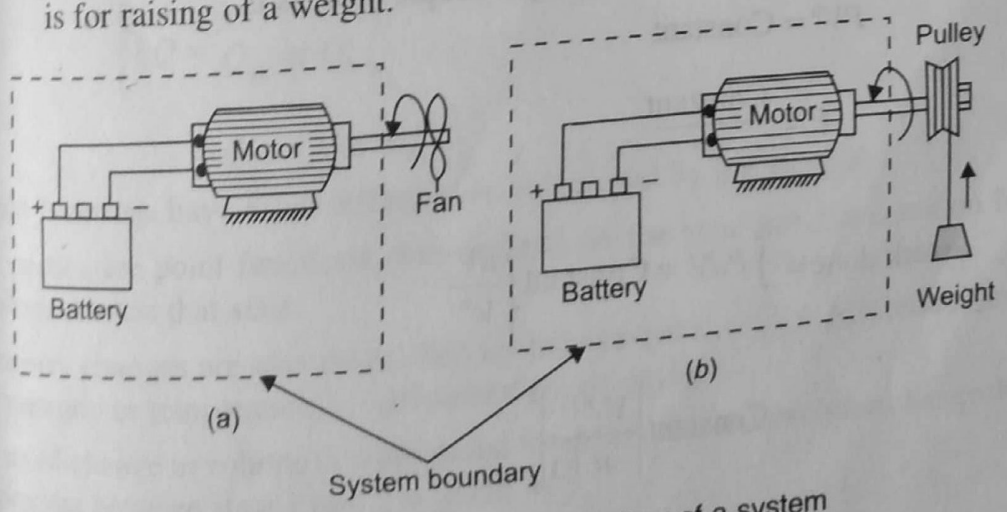

Fig.2.14 Work crossing the boundary of a system

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2.27 MOVING BOUNDARY WORK

Work can be done by the movement of the system boundary as the case of moving piston in a cylinder. Consider a system of the gas contained in a cylinder and piston as shown in Fig.2.15.

The total force on the piston is PA. Where P is the pressure of the fluid and A is area of the piston.

The work done is

$$\delta W = PA\,dl$$

The change in volume

$$dV = A.dl$$

$$\therefore \quad \delta W = P.dV$$

The work done at the moving boundary can be found by integrating the above equation if the relationship between P and V is known during this process.

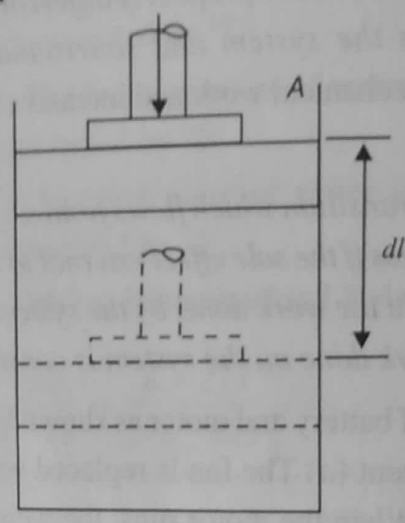

Fig. 2.15

The relationship between P and V in a polytropic process is

$$PV^n = \text{Constant}$$

$$P = \frac{\text{Constant}}{V^n}$$

$$\text{work done} = \int_1^2 PdV = \text{Constant}\int_1^2 \frac{dV}{V^n}$$

$$= \text{Constant}\left|\frac{V^{-n+1}}{-n+1}\right|_1^2$$

$$= \frac{\text{Constant}}{1-n}(V_2^{1-n} - V_1^{1-n})$$

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$$= \frac{P_2V_2^nV_2^{1-n} - P_1V_1^nV_1^{1-n}}{1-n}$$

$$= \frac{P_2V_2 - P_1V_1}{1-n}$$

The equation is valid for any exponent of n, except $n = 1$ when $n = 1$

$$PV = \text{Constant} = P_1V_1 = P_2V_2$$

and
$$\int_1^2 PdV = P_1V_1\int_1^2 \frac{dV}{V}$$

$$= P_1V_1 ln\frac{V_2}{V_1}$$

2.28 PATH AND POINT FUNCTIONS

Path functions have inexact differentials represented by the symbol δ, the magnitude of a path function depends on the path followed during a process as well as on the end states. Therefore, a differential amount of heat or work is represented by δQ or δW, instead of δQ or δW.

The total workdone during the process 1-2 is given by

$$\int_1^2 \delta W = W_{12} \text{ or } W_{1-2}$$

$$\neq W_2 - W_1 \text{ or } \delta W$$

Similarly,

$$\int_1^2 \delta Q = Q_{12} \text{ or } Q_{1-2}$$

$$\neq Q_2 - Q_1 \text{ or } \delta Q$$

Point functions have exact differentials designated by the symbol d.

Properties are point functions, they depend on the state only, and not on how a system reaches that state.

Property changes are also designated by the symbol d, *e.g.*, a differential amount of pressure or temperature is represented by dp or dT.

A small change in volume is represented by dV and the total volume change during a process between state 1 and 2 is given by

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

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2.31 ZEROTH LAW OF THERMODYNAMICS

Zeroth law states that when the two bodies are in thermal equilibrium with the third body individually, then these two will be in thermal equilibrium with each other.

Consider three bodies A, B, C as shown out when *A* and *B* are in thermal equilibrium with *C*. Then the two bodies *A* and *B* also be in thermal equilibrium with each other.

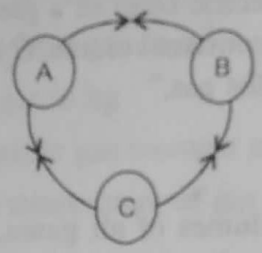

Fig.2.18 *A*, *B*, *C*, in thermal equilibrium

2.32 FIRST LAW OF THERMODYNAMICS

(*a*) **"Heat and mechanical work are mutually convertible:** It states that when closed system undergoes a cyclic process then net heat transfar is equal to net work transfer *i.e.*, the cyclic integral of heat transfer is equal to cyclic integral of work transfer."

Mathmatically.

$$\oint \delta Q = \oint \delta \omega$$

where $\oint$ = Cyclic integral

δQ = Amount of heat transfer

$\delta \omega$ = Amount of work transfer

(*b*) **Energy Conservation Law:** It state that "energy can neither be created nor destroyed but it can be converted from one form to another". When a system undergoes a change of state or energy exchange takes place (*i.e.*, heat and work transfer) during any process (not cyclic) then whole of the heat supplied is not converted in to work but some part of it is stored by the system itself called total energy of the system. It is denoted by *dE*.

Mathematically,

$$\delta Q - \delta W = dE$$

The symbol δ is used for a quantity which is inexact differential and *d* is used for a quantity which is an exact differential.

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The quantity E is an extensive property and represents the total energy of the system at a particular state.

On integrating the above expression for a change of state from 1 to 2.

We have

$$\int_1^2 \delta Q - \int_1^2 \delta W = \int_1^2 \delta E$$

$$Q_{1-2} - W_{1-2} = E_2 - E_1 \quad \text{... (i) } (Q, W \text{ and } E \text{ are in same units})$$

For a unit mass

$$Q_{1-2} - W_{1-2} = E_2 - E_1$$

where

Q_{1-2} = Heat transfer to the system during the process from state 1 to state 2.

W_{1-2} = Work done by the system on the surroundings during the process, and

E_1 = Total energy of the system at state 1

$$= PE_1 + KE_1 \times U_1$$

$$= mgz_1 + \frac{mV_1^2}{2} + U_1$$

where

PE is Potential Energy, KE is Kinetic energy and U is internal energy

E_2 = Total energy of the system at state 2

$$= PE_2 + KE_2 + U_2$$

$$= mgz_2 + \frac{mV_2^2}{2} + U_2$$

Thus, the above expression *i.e.*, Equation (*i*) may be written as

$$Q_{1-1} - W_{1-2} = (PE_2 + KE_2 + U_2) - (PE_1 + KE_1 + U_1)$$

$$= (PE_2 - PE_1) - (KE_2 - KE_1) + (U_2 - U_1)$$

$$= (mgz_2 - mgz_1) + \frac{mv_2^2}{2} - \frac{mv_1^2}{2} + (U_2 - U_1)$$

$$= mg(z_2 - z_1)\, m\left(\frac{v_2^2}{2} - \frac{v_1^2}{2}\right) + (U_2 - U_1)$$

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For unit mass, the expression is written as

$$q_{1-2} - w_{1-2} = (gz_2 - gz_1) + \left(\frac{v_2^2}{2} - \frac{v_1^2}{2}\right) + (U_2 - U_1)$$

When there is no change in potential energy of the system (*i.e.*, when the height of the system from the datum level is same), then $PE_1 = PE_2$. Thus, equation (*ii*) becomes

$$Q_{1-2} - W_{1-2} = (KE_2 - KE_1) = (U_2 - U_1) \quad (iii)$$

when there is no change of PE and also there is no flow of the mass into or out of the system, then $PE_1 = PE_2$ and $KE_1 = KE_2$. Thus, equation (*ii*) becomes

$$Q_{1-2} - W_{1-2} = U_2 - U_1 = dU \quad (iv)$$

For a closed or non-flow thermodynamic system,

$$PE = 0 \text{ and } KE = 0$$

Thus, equation (*iv*) is known as non-flow energy equation.

For an islolated system for which $Q_{1-2} = W_{1-2} = 0$ the equation (*i*) becomes $E_2 = E_1$. This shows that the first law of thermodynamic is the law of conservation of energy.

Limitations of the First Law of Thermodynamics:

(*i*) It is unable to tell direction of flow of heat.

(*ii*) It does not explain the physical and chemical processes occurring in a nutural direction.

(*iii*) It does not tell about the feasibility and direction of a process.

(*iv*) It is unable to tell about the extent of change of one form of energy into another.

2.33 APPLICATION OF FIRST LAW OF THERMODYNAMICS TO A CLOSED SYSTEM (NON-FLOW PROCESSES) INVOLVING PERFECT GASES

From first law of thermodynamics, equation for a closed system is given by

$$Q_{1-2} - W_{1-2} = E_2 - E_1 = dE$$

where

$$dE = dU + dKE + dPE$$

If dKE and dPE are negligible, then

$$Q_{1-2} - W_{1-2} = dU = U_2 - U_1$$

The analysis for first law of thermodynamics, for closed system (*i.e.*, non-flow system) which changes from one state to another and to develop some relations for thermodynamic are as given ahead:

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5. Change in Enthalpy

We know that change in enthalpy

$$dH = H_2 - H_1 = mc_p(T_2 - T_1)$$

Result:

Work done $(W_{1-2}) = \dfrac{P_2V_2 - P_1V_1}{n-1}$

Change in internal energy: $\delta U = mc_v(T_2 - T_1)$

Heat transfer $Q_{1-2} = \dfrac{\gamma - n}{1-\gamma} \times \left[\dfrac{(P_2V_2 - P_1V_1)}{n-1}\right]$

Change in enthalpy: $\delta H = mc_v(T_2 - T_1)$

Change in entropy: $\delta S = 2.3\, mc_v \times \left(\dfrac{\gamma - n}{n}\right)\log\left(\dfrac{P_1}{P_2}\right)$

2.33.6 Isentropic Process

The process, such as reversible adiabatic process, in which the entropy of the system remains constant is known as an isentropic process.

2.33.7 Hyperbolic Process

The process in which the product of the pressure of the gas and its volume remains constant V known as hyperbolic process. In the above case in isothermal process, PV = Constant.

So, the work done and heat transferred during hyperbolic process can be calculated by using the formula for the above isothermal process.

2.34 FLOW PROCESS

The process occurring in open system (or control volume) which permit the transfer of mass to and from the system, are known as flow process.

In a flow process, the mass *i.e.*, (working substance) enters the system and leaves after doing the work.

The flow process may be classified as:

1. Steady flow process
2. Unsteady flow process

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2.34.1 Steady Flow Process

Steady flow process is defined as a process in which the conditions within the control volume do not vary with time.

The following conditions must be satisfied in a steady flow process:

1. The mass rate within the system remains constant, *i.e.*, the mass rate at entrance and exit is same and do not vary with time.
2. The state of working substance at any point within the system is same at all times.
3. The rate at which heat and work transfer, across the system, does not vary with time, *i.e.* the rate of heat and work transfer is constant.
4. There is no change in the chemical composition of the system so no change in chemical energy is involved.
5. The state of energy of the working substance at the inlet or outlet of system does not vary with time.

2.34.2 Unsteady Flow Process

A process which does not satisfy the condition of steady flow *i.e.*, conditions vary with time is known as unsteady flow process.

2.35 FLOW ENERGY

The flow or displacement energy is the energy required to flow or move the working substance against its pressure. It is also known as flow work.

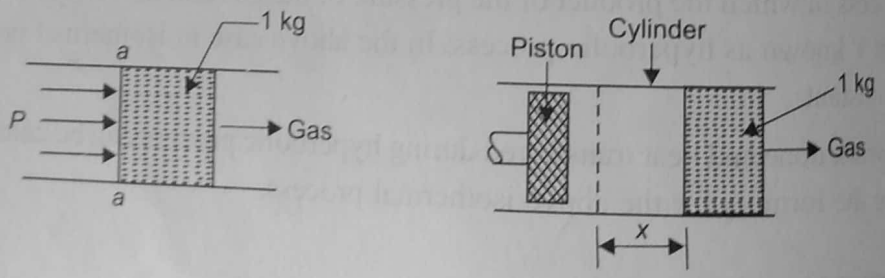

Fig. 2.28 Flow work

For Example, let the working substance with pressure in P (in N/ m^2) flow through area A (in m^2) and moves through a distance x (in metre).

∴ Energy or work required to flow the working substance,

$$\text{Flow energy} = \text{Force} \times \text{Distance}$$

$$= (P \times A) \times x \text{ kJ/kg}$$

$$= PV \text{ J/kg} \qquad (\because V = A \times x)$$

where V = Specific volume of the working substance in m^3/kg.

P = Pressure at section a, kN/m^2.

2.36 APPLICATION OF FIRST LAW OF THERMODYNAMICS TO OPEN SYSTEM (STEADY FLOW PROCESS)

Consider an open system through which the working substance flows at a steady rate, as shown in Fig. 2.29.

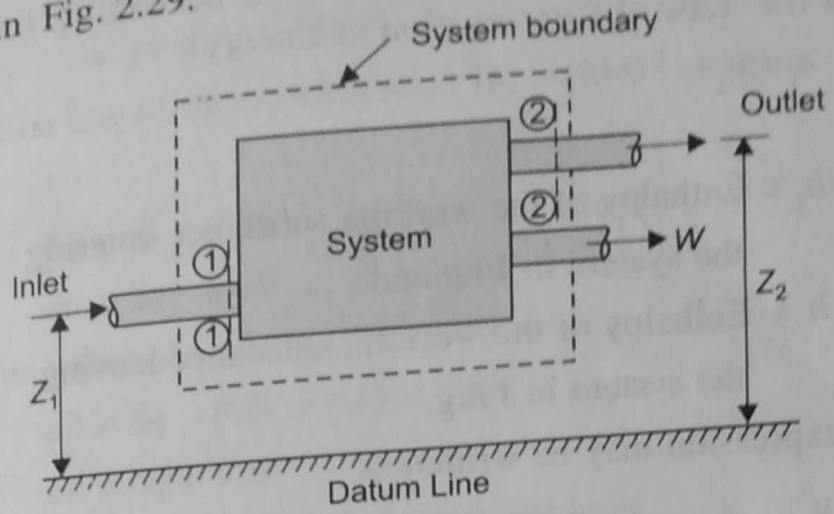

Fig. 2.29 Steady flow process

Let

P_1 = Pressure of the working substance entering the system in N/m^2.

V_1 = Specific volume of the working substance entering the system in m^3/kg.

v_1 = Velocity of the working substance entering the system in m/s.

u_1 = Specific internal energy of the working substance entering the system in J/kg.

Z_1 = Height above datum line for inlet in metres.

P_2, V_2, V_2, u_2, and Z_2 = Corresponding values for the working substance leaving the system.

q_{1-2} = Heat supplied to the system in J/kg

W_{1-2} = Work delivered by the system in J/kg.

Consider 1 kg of mass of the working substance,

We know that

Total energy entering the system per kg of the working substance

e_1 = Internal energy + Flow energy + Kinetic energy + Potential energy + Heat supplied.

$$= u_1 + P_1V_1 + \frac{v_1^2}{2} + gZ_1 + q_{1-2} \text{ J/kg}$$

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Similarly, Total energy leaving the system per kg of the working substance

$$e_2 = u_2 + P_2V_2 + \frac{v_2^2}{2} + gZ_2 + W_{1-2} \text{J/kg}$$

Assuming no loss of energy during flow, then according to first Law of Thermodynamics (*i.e.* Law of Conservation of Energy)

$$e_1 = e_2$$

We know that

$u_1 + P_1V_1 = h_1$ = Enthalpy of the working substance entering the system in J/kg and

$u_2 + P_2V_2 = h_2$ = Enthalpy of the working substance leaving the system in J /kg.

Thus, the above expression may be written as

$$h_1 + \frac{v_1^2}{2} + gZ_1 + q_{1-2} = h_2 + \frac{v_2^2}{2} + gZ_2 + W_{1-2} \quad \ldots(i)$$

or $$h_1 + ke_1 + Pe_1 + q_{1-2} = h_2 + ke_2 + Pe_2 + W_{1-2}$$

In equation (*i*) all terms represent the energy flow per unit mass of the working substance (*i.e.* in J /kg) and multiplied through *m* of the working substance to equation (*i*) which will represent the energy flow per unit time *i.e.* in J/sec.

Thus, the equation (*i*) may also be written as

$$m\left(h_2 + \frac{v_1^2}{2} + gZ_1 + q_{1-2}\right) = m\left(h_2 + \frac{v_2^2}{2} + gZ_2 + W_{1-2}\right) \quad \ldots(ii)$$

Both the equations (*i*) and (*ii*) are known as steady flow energy equations.

The steady flow energy equation (*i*) for unit mass flow may be written as:

$$q_{1-2} - W_{1-2} = (h_2 - h_1)\left(\frac{v_2^2}{2} - \frac{v_1^2}{2}\right) + (gZ_2 - gZ_1) \quad \ldots(iii)$$

$$= (h_2 - h_1) + (ke_2 - ke_1) + (Pe_2 - Pe_1)$$

In differential form, this expression is written as

$$\delta q - \delta W = dh + d\,(ke) + d\,(Pe) \quad \ldots(iv)$$

2.37 WORK DONE IN A STEADY FLOW PROCESS

We know that the steady flow equation for unit mass flow, in the differential form is

$$\delta q - \delta W = dh + d\,(ke) + d\,(Pe) \quad \ldots(i)$$

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