SRI RANGANATHAR INSTITUTE OF POLYTECHNIC COLLEGE,
ATHIPALAYAM- 641 110

DEPARTMENT OF AUTOMOBILE ENGINEERING

2nd YEAR / 4th SEMESTER
N – SCHEME

NOTES OF LESSON

4021440 – AUTOMOTIVE ENGINES

CHAPTER 1
FUNDAMENTAL CONCEPTS

INTRODUCTION TO THERMODYNAMICS

Thermodynamics is branch of physics which deals with temperature, heat and their relation to energy, radiation, work, and properties of matter. The thermodynamic term is derived from two Greek words 'thermes' meaning heat, and 'dynamis' meaning motion. Thermodynamics means heat in motion. The key concept is that heat is a form of energy corresponding to a definite amount of mechanical work. The study of thermodynamics is comprised of important laws of thermodynamics namely first law of thermodynamics, second law of thermodynamics, third law of thermodynamics and Zeroth law of thermodynamics.

The application of thermodynamic laws are found in all field of energy transfer, mainly in steam and nuclear power plants, internal combustion engine, gas turbine, air conditioning and refrigeration, air compressor and chemical process plants etc.

THERMODYNAMIC STATE

The condition of a system at any instant of time described by its physical properties is known as state of system. An operation in which properties of system change is called a change of state.

THERMODYNAMIC SYSTEM

A quantity of the matter or part of the space which is under thermodynamic study is called as system. It is shows in fig.1.1
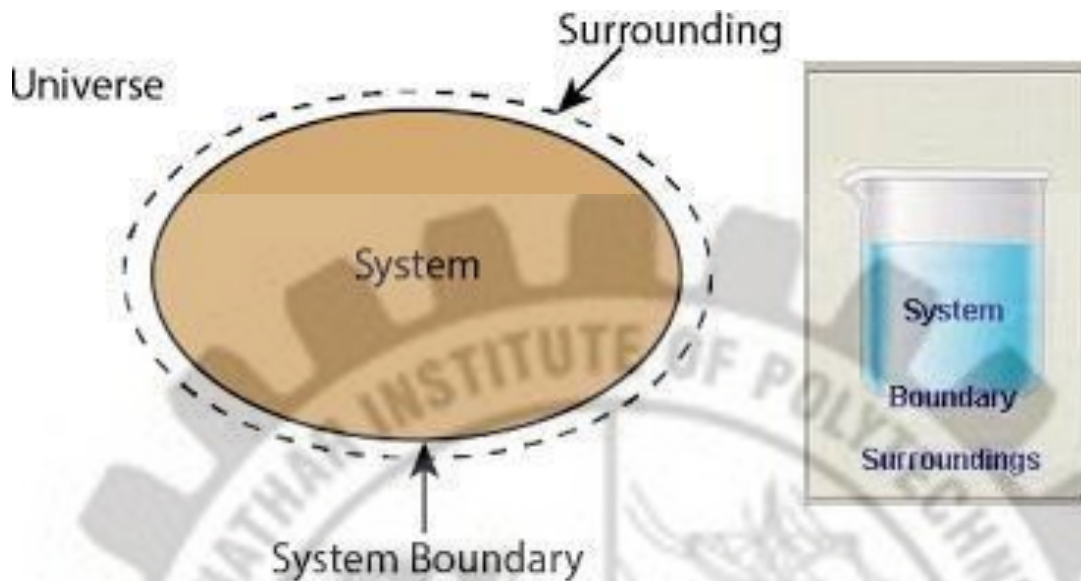
Fig. 1.1: Thermodynamic system

BOUNDARY

System and surroundings are separated by a definite border called boundary. It can be fixed or movable. System, surroundings and boundary constitute the universe.

SURROUNDING

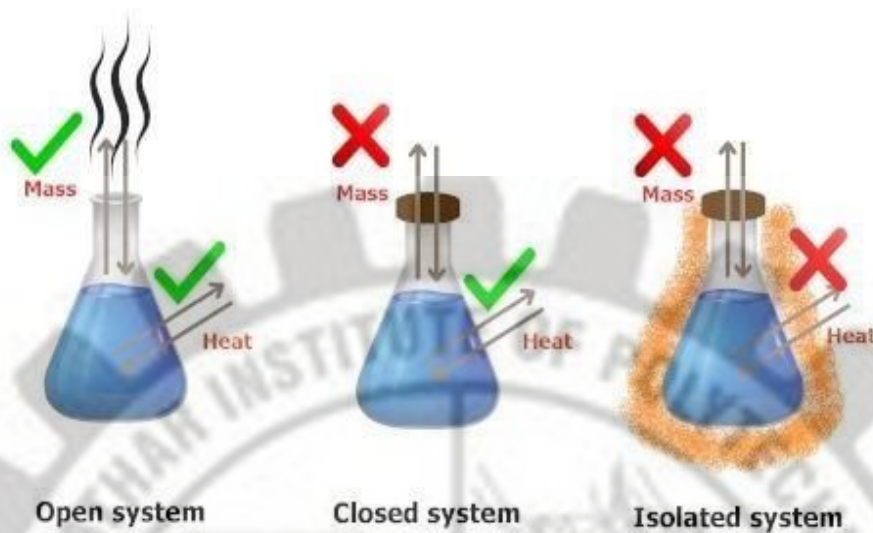Everything external to a thermodynamic system is called surroundings.

UNIVERSE

The system and the surroundings together make up the universe.

TYPES OF THERMODYNAMIC SYSTEMS

Thermodynamic systems can be broadly classified into three types. They are:

1. Open System
2. Closed system
3. Isolated system

In fig. 1.2 shows the types of thermodynamic system.

Fig. 1.2: Types of thermodynamic system

1. Open system

An open system is a thermodynamic system which allows both mass and energy to flow in and out of it, across its boundary.

2. Closed system

A closed system allows only energy (heat and work) to pass in and out of it. It does not allow mass transfer across its boundary.

3. Isolated system

It does not allow both mass and energy transfer across its boundary. It is more restrictive. In reality, complete isolated systems do not exist. However, some systems behave like an isolated system for a finite period of time.

However, there are some other terms by which the system or characteristics of a sytem are described. Thear are as below:

4. Adiabatic

The process during which work is done and no heat is transferred across the system boundary is known as adiabatic process.

5. Homogeneous

The system that has single or uniform phase such as like solid or liquid or gaseous is called as homogeneous system.

6. Heterogeneous

The system that has more than one phase i.e. the combination of solid, liquid and gaseous state is called as heterogeneous system.

7. Macroscopic

In this approach a certain quantity of matter is considered without taking into account the events occurring at molecular level. In other words this approach to thermodynamics is concerned with gross or all behavior. This is known as classical thermodynamics.

The values of the properties of system are their average values. For example consider a sample of a gas in a closed container. The pressure of the gas is the average value of the pressure exerted by millions of individual molecules.

8. Microscopic

In microscopic study, the behavior of individual atoms and molecules of a substance considered. This approach considers that the systems are made up of a very large numbers of discrete particles known as molecules. These molecules have different velocities and energies. The values of these energies are constantly changing with time.

PROPERTIES OF THE SYSTEM

The characteristics by which the physical condition of the system is described are called as properties of system. Some examples of these characteristics are: temperature, pressure, volume etc. are called as properties of system.

The system properties are of two types: extensive and intensive properties.

1. Extensive properties of system

The properties of the system that depend on the mass or quantity of the system are called extensive properties. Some examples of extensive properties are: mass, volume, enthalpy, internal energy, entropy etc.

2. Intensive properties of the system

These properties do not depend on the quantity of matter of the system. Some of the examples of intensive properties are: freezing point temperature, boiling point, temperature of the system, density, specific volume etc.

THERMODYNAMIC EQUILIBRIUM

A state of thermodynamic equilibrium is said to be exist in a system if no change in any macroscopic properties is registered and the system is assumed to be isolated from its surroundings. A system will be in state of thermodynamic equilibrium, if following three equilibrium conditions are satisfied:

1. Mechanical equilibrium
2. Chemical equilibrium
3. Thermal equilibrium

1. Mechanical equilibrium

A state of mechanical equilibrium is that state in which it experiences no pressure or elastic stress within it and there is no unbalanced force between the system and surrounding.

2. Thermal equilibrium

In the state of thermal equilibrium of the system, there is no exchange of heat energy between the system and surrounding. Such a state is characterized by same value of the temperature of the system and surrounding.

3. Chemical equilibrium

In the state of chemical equilibrium system does not undergo a spontaneous change in its internal composition i.e. no chemical reaction takes place in it and no transfer of matter takes place from one part of it to another part.

QUASI-STATIC PROCESS

The state of a system can change as a result of its interaction with the environment. The change in a system can be fast or slow and large or small. The manner in which a state of a system can change from an initial state to a final state is called a thermodynamic process. For analytical purposes in thermodynamics, it is helpful to divide up processes as either quasi-static or non-quasi-static. A quasi-static process refers to an idealized or imagined process where the change in state is made infinitesimally slowly so that at each instant, the system can be assumed to be at a thermodynamic equilibrium with itself and with the environment. For instance, imagine heating 1 kg of water from a temperature 20ºC to 21ºC at a constant pressure of 1 atmosphere. To heat the water very slowly, we may imagine placing the container with water in a large bath that can be slowly heated such that the temperature of the bath can rise infinitesimally slowly from 20ºC to 21ºC. If we put 1 kg of water at 20ºC directly into a bath at 21ºC the temperature of the water will rise rapidly to 21ºC in a non-quasi-static way.
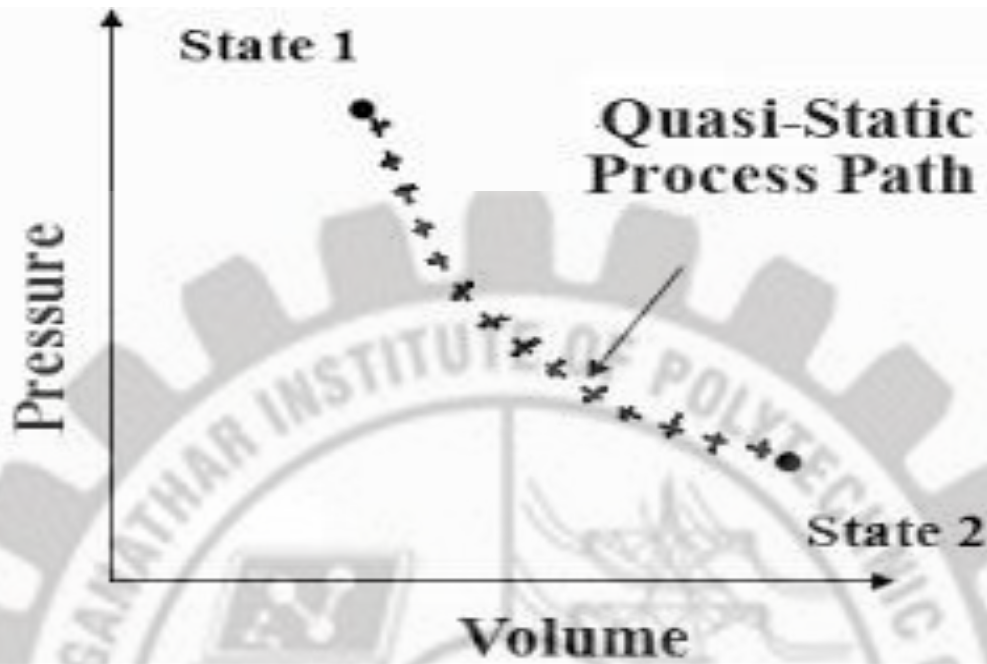
Fig. 1.3: Quasi-static process

Quasi-static processes are done slowly enough that the system remains at thermodynamic equilibrium at each instant, despite the fact that the system changes over time. The thermodynamic equilibrium of the system is necessary for the system to have well-defined values of macroscopic properties such as the temperature and the pressure of the system at each instant of the process. Therefore, quasi-static processes can be shown as well-defined paths in state space of the system. Since quasi-static processes cannot be completely realized for any finite change of the system, all processes in nature are non-quasi-static.

REVERSIBLE AND IRREVERSIBLE PROCESSES

A process which can be reversed in direction and the system retraces the same path and the same equilibrium state is known as reversible process. Fig. 1.4 shows a reversible process.
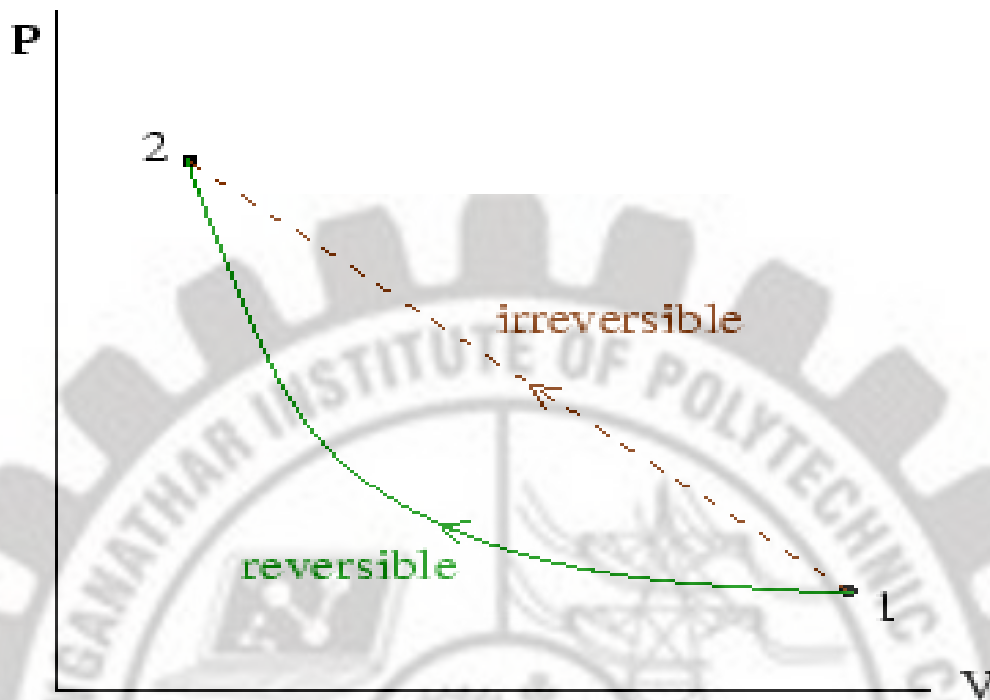
Fig. 1.4: Reversible and irreversible processes

A process said to be irreversible if a system passes through a sequence of non-equilibrium states. An irreversible process cannot come back to the original state, if made to proceed in reverse direction. Fig. 4 shows an irreversible process with dotted lines.

ZEROTH LAW OF THERMODYNAMICS

The Zeroth law of thermodynamics states that if two bodies are each in thermal equilibrium with some third body, then they are also in equilibrium with each other. Thermal equilibrium means that when two bodies are brought into contact with each other and separated by a barrier that is permeable to heat, there will be no transfer of heat from one to the other.
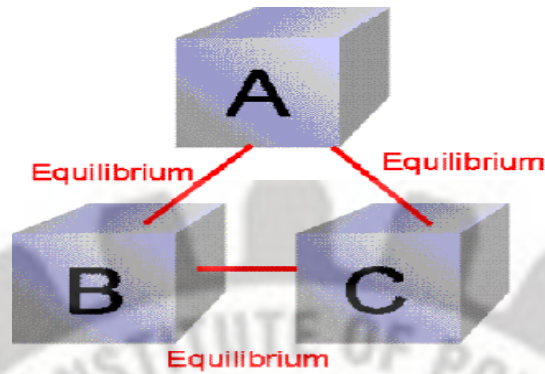
Fig. 1.5: Zeroth law of thermodynamics

PRESSURE

Pressure is a measure of the force exerted per unit area on the boundaries of a substance. The standard unit for pressure in the SI system is the Newton per square meter or pascal (Pa). Mathematically:

$$P = F/A$$

Where F is the normal force and A is the area on which force is exerted.

Atmospheric Pressure

The pressure exerted by atmospheric air on the earth surface is called atmospheric pressure. The atmospheric pressure varies with temperature and altitude above sea level.

Absolute pressure

When pressure is measured with reference to absolute vacuum pressure then it is called absolute pressure. At this pressure, the molecular momentum is zero.
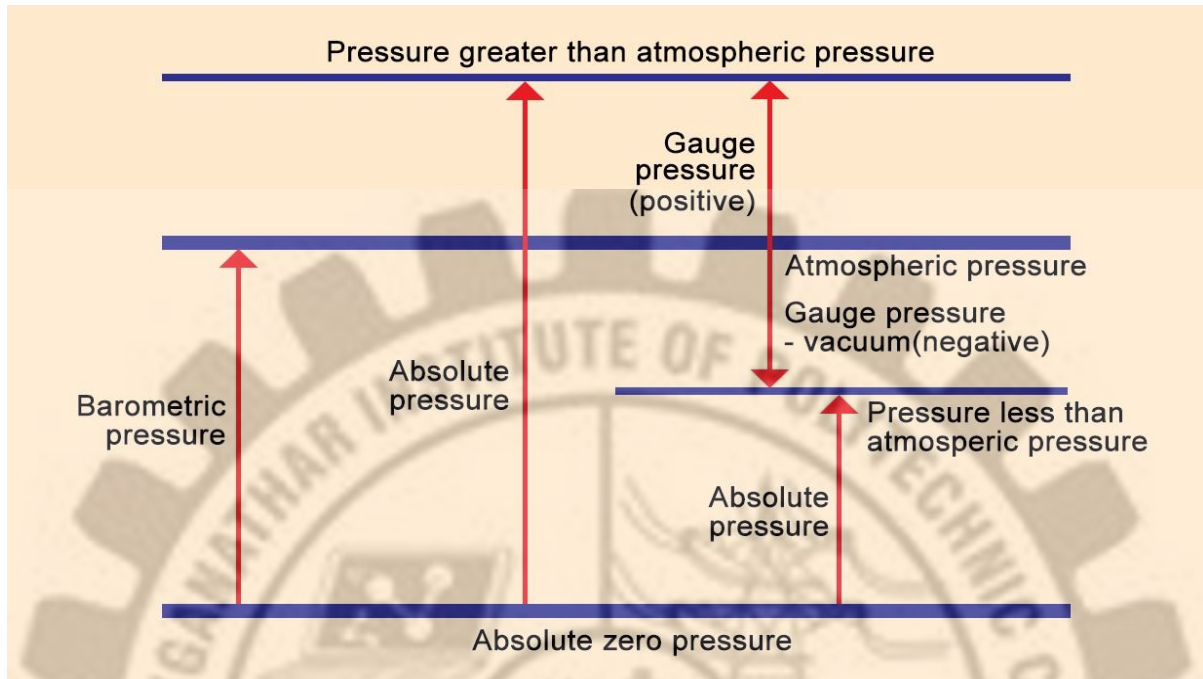
Fig. 1.6: Absolute pressure, gauge and vacuum pressure

Gauge pressure

This is the pressure measured by of pressure measuring instruments, in which atmospheric pressure is taken as datum. The atmospheric pressure is taken as zero this system. The instrument used to measure this pressure is known as pressure gauge. The pressure always used to indicate the pressure above atmospheric pressure.

Vacuum pressure

Measurement of pressure below the atmospheric pressure, in which atmospheric pressure taken as reference. This is also known as negative pressure or suction pressure. The instrument used to measure vacuum pressure is known as vacuum gauge.

VOLUME

The amount of space occupied by any substance is called volume. Its unit is m³.

TEMPERATURE

It is an intensive property which determines the degree of hotness or the level of heat intensity of a body. The temperature of a body is measured with the help of an instrument known as thermometer.

For the measurement of temperature of body, following types of scales are used:

1. Centigrade temperature scale (ºC)

Centigrade temperature scale also called Celsius temperature scale, is the scale based on 0 for the freezing point of water and 100 for the boiling point of water. Invented in 1742 by the Swedish astronomer Anders Celsius, it is sometimes called the centigrade scale because of the 100-degree interval between the defined points. The Celsius scale is in general use wherever metric units have become accepted, and it is used in scientific work everywhere.

2. Fahrenheit scale (ºF)

Fahrenheit temperature scale is a scale based on 32 for the freezing point of water and 212 for the boiling point of water, the interval between the two being divided into 180 parts. The relationship between centigrade and fahrenheit scale is given by

3. Absolute temperature

It is temperature below which the temperature of any substance cannot fall. For calculations, the absolute zero temperature is taken as -273ºC in case of Celsius scale and -460ºF in case of fahrenheit scale. The absolute temperature in Celsius scale is called degree Kelvin (K) and in fahrenheit scale is called degree of Rankine (ºR).

$$T (K) = T (ºK) + 273$$

$$T (ºR) = T (ºF) + 460$$

ENTHALPY

It is the sum of the internal energy added to the product of the pressure and volume of the system. It reflects the capacity to do non-mechanical work and the capacity to release heat. Enthalpy is denoted as H; specific enthalpy denoted as h.

$$H = U + PV$$

INTERNAL ENERGY

It is the energy stored in a body or a system due to its molecular arrangement and motion of molecules. It is generally denoted by U. it is function of temperature. Internal energy is given by

$$\Delta U = mC_v (T_2 - T_1)$$

CHAPTER 2
LAWS OF PERFECT GASES

DEFINITION OF GASES

A gas may be defined as a state of a substance, whose evaporation from its liquid state is complete. A perfect gas or an ideal gas may be defined as a gas which obeys all the gas laws under all conditions of temperature and pressure. In actual practice, no gas is perfect gas, but some real gases like oxygen, nitrogen and air etc. may be regarded as perfect gases within certain temperature and pressure limits.

EXPLANATION OF PERFECT GAS LAWS

There are mainly three variables which control the physical properties of gas:

(i)Temperature of the gas (T), (ii) Pressure exerted by gas (P), (iii) Volume occupied by gas (V).

Any change in above mentioned variables is given by various laws which are based upon the experimental results.

(i) Boyle's law,   (ii) Charle's law,   (iii) Gay-Lussac law

I.   Boyle's law

This law states, at constant temperature, the volume of an ideal gas is inversely proportional to its absolute pressure. Mathematically,
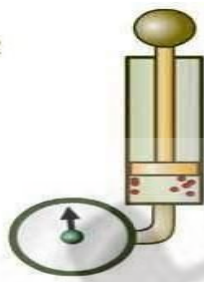
$$P \propto \frac{1}{V}$$

Or   PV = Constant

The more useful form of the above equation is

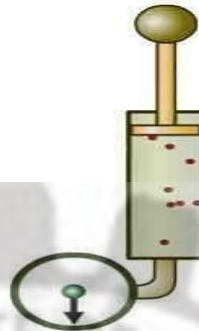$P_1V_1 = P_2V_2 = P_3V_3 = ...= $ constant.

The product of pressure and volume is constant for a fixed mass of ideal gas at fixed temperature.

Before After

$$P_1V_1 = k \qquad P_2V_2 = k$$

$$P_1V_1 = P_2V_2$$

II. Charle's law

At constant pressure, the volume of an ideal gas is directly proportional to its absolute temperature. The simplest statement of the law is:

$$V \propto T$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

V = volume
T = absolute temperature
(assumes pressure constant and closed system)

T = Temperature of the gas
V = Volume of the gas

Pressure must be constant

All perfect gases change in volume by $1/273^{th}$ of its original volume at 0 °C for every 1 °C change in temperature, when the pressure remains constant.

Let $\qquad$ V_o = Volume of a given mass of gas at 0 °C

$\qquad$ V_t = Volume of a given mass of gas at t °C

Then according to above statement,

$$V_t = V_o + \frac{1}{273} V_o \times t$$

$$= V_o \times \left(\frac{273+t}{273}\right) = V_o \times \frac{T}{T}$$

$$\frac{V_t}{T} = \frac{V}{T}$$

The above statement shows that the volume of a gas goes on decreasing by $1/273^{th}$ of its original volume for every 1 °C decrease in temperature. Now at a

temperature of -273°C, the volume of the gas would become zero and this temperature is called absolute zero temperature.

III. Gay-Lussac law

At constant volume, the pressure of an ideal gas is directly proportional to its absolute temperature. Mathematically,

$$P \propto T \quad \text{or} \quad \frac{P}{T} = Constant$$

$$\text{Or} \quad \frac{P1}{T1} = \frac{P2}{T2} = \frac{P3}{T3} = \dots\dots\dots\dots\dots\dots = Constant.$$

AVOGADRO'S LAW

It implies that under similar conditions of pressure, volume and temperatures all gases will have an equal number of molecules, independent of the weight and density of the gas.
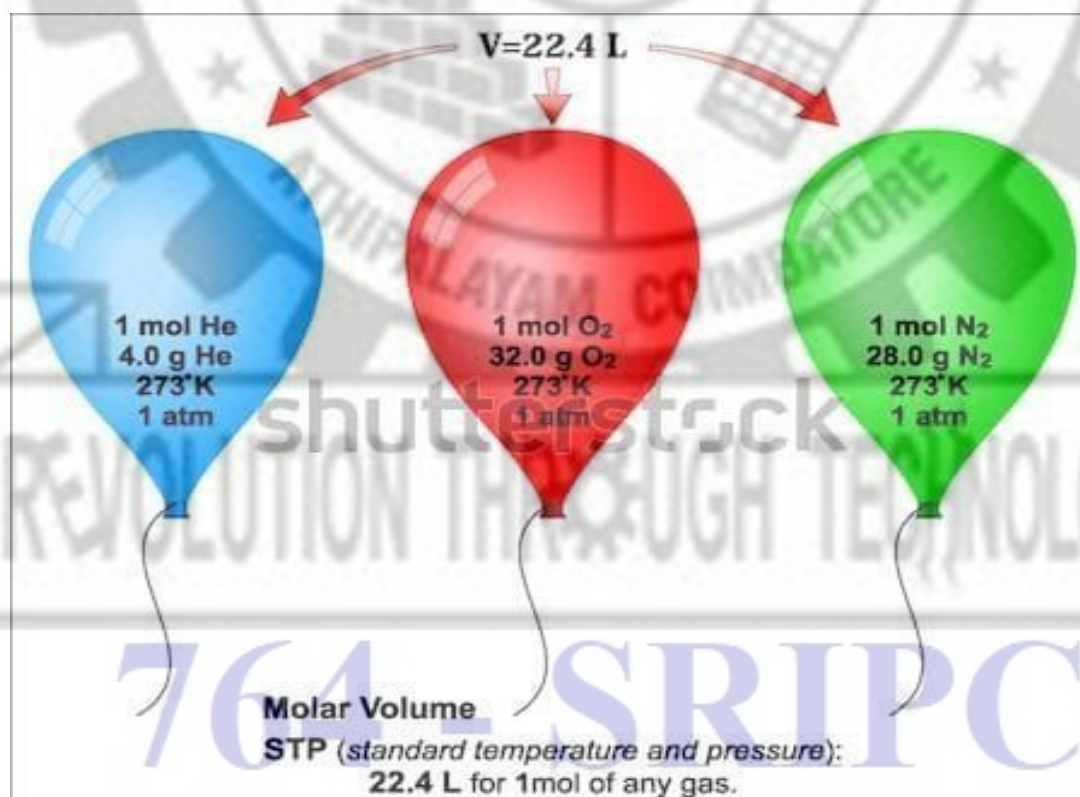
Equal volumes of all gases at conditions of same temperature and pressure have the same number of molecules', written as:

$$V \propto n \text{ or } V/n = K$$

Where   V=volume of gas;

                                n= Number of moles

REGNAULT'S LAW

It is states that the specific heat capacity of a gas at constant pressure (C_p) and the specific heat capacity of a gas at constant volume (C_v) do not change with change in pressure and temperature. According to this law, C_p and C_v values of a gas remain constant.

UNIVERSAL GAS CONSTANT (R)

When the molecular mass of any gas is multiplied by its specific gas constant/ characteristic gas constant (R). R is explained in the next topic. It is observed that the product R is always the same for all gases. This product is called universal gas constant and it is denoted as R. In SI system the value of the universal gas constant is 8.314 kJ/mole.K.

$$R_u = MR$$

Where   M = molecular mass of gas in kg mole,

            R = Gas constant.

            R_u = 8314.3J/kg mole/K

GENERAL GAS EQUATION & CHARACTERISTIC GAS CONSTANT

The Combined gas law or General Gas Equation is obtained by combining Boyle's law, Charles's law, and Gay-Lussac's law. If temperature and pressure

are kept constant, then the volume of the gas is directly proportional to the number of molecules of gas.

Let us consider the pressure exerted by the gas to be 'P'

The volume of the gas be – V

Temperature be – T

Universal gas constant – R

According to Boyle's Law,

$$P \propto \frac{1}{V} \quad \text{or} \quad V \propto \frac{1}{P}$$

According to Charles' Law,

$$V \propto T$$

From above two laws, we have

$$V \propto \frac{1}{P} \text{ and T both}$$

$$V \propto \frac{T}{P}$$

$$PV \propto T$$

$$PV = CT$$

Where C is a constant and value of C depends upon the mass and other properties of the gas. The general gas equation may be written as:

$Pv = RT$

If m is the mass of gas in kg, then the equation can be written as:

$PV = mRT$

Where,

R is the gas constant, called characteristic gas constant which has a value of 287 J/kgK.

SPECIFIC HEATS

The amount of heat required to raise the temperature of its unit mass through one degree. Solid and liquid have only one specific heat. Gas has mainly two types of specific heat:

a) Specific heat at constant pressure (C_p)

The amount of heat required to raise the temperature of its unit mass through one degree, when its pressure is kept constant.

$Q = mC_p dT$

b) Specific heat at constant volume (C_v)

The amount of heat required to raise the temperature of its unit mass through one degree, when its volume is kept constant.

$Q = mC_v dT$

c) Specific Index

It is the ratio of specific heat at constant pressure to specific heat at constant volume is known as specific heat index. It is denoted by γ.

$$\gamma = C_p/C_v$$

DERIVATION OF SPECIFIC HEATS WITH CHARISTICS GAS CONSTANT/

RELATIONSHIP BETWEEN C_P, C_V AND R

Let us consider m kg of a gas enclosed in a container and is being heated at constant pressure.

Let T_1 = Initial temperature of the gas,

                     T_2 = Final temperature of the gas,

                     V_1 = Initial volume of gas,

                     V_2 = Final volume of gas,

C_p = Specific heat at constant pressure,

C_v = Specific heat at constant volume,

P = Absolute constant pressure.

We know that heat supplied to the gas at constant pressure,

$$Q = mC_p (T_2-T_1) .... (i)$$

We also know that a part of this heat is utilisec in doing external work, while the remaining part of heat is used in increasing the internal energy of gas.

i.e. $$Q = W + dU .... (ii)$$

now heat utilised for external work,

$$W = P(V_2 - V_1) .... (iii)$$

And increase in internal energy

$$dU = mC_v (T_2 - T_1) .... (iv)$$

Putting the values of W and dU in equation (ii)

$$Q = P(V_2 - V_1) + mC_v(T_2 - T_1) .... (v)$$

Using characteristic gas equation, we have

$PV_1 = mRT_1$ (For initial condition)

$PV_2 = mRT_2$ (For final condition)

$$P (V_2 - V_1) = mR (T_2 - T_1)$$

Putting the value of P (V2 – V1) from equation (vi) in equation (v), we get

$$Q = mR(T_2 - T_1) + mC_v(T_2 - T_1)$$

Now putting the value of Q from equation (i) in above equation, we get

$$mC_p (T_2 - T_1) = mR(T_2 - T_1) + mC_v(T_2 - T_1)$$

or $C_p = R + C_v$

or $C_p - C_v = R$

The equation may be written as

$$C_v [\frac{Cp}{Cv} - 1] = R$$

$$C_v(\gamma - 1) = R$$

$$C_v = \frac{R}{\gamma-1}$$

The value of r in S.I. unit is taken as 287 J/kg K

The equation may also be written as

$C_p = C_v + R$

Dividing both sides by C_v , we get

$$\frac{Cp}{Cv} = 1 + \frac{R}{Cv}$$

$$\gamma = 1 + \frac{R}{Cv}$$

CHAPTER 3
THERMODYNAMIC PROCESSES

INTRODUCTION

When the system changes from one thermodynamic state to the final thermodynamic state due to change in pressure, temperature, volume etc, the system is said to have undergone thermodynamic process. The various types of thermodynamic processes are: isothermal process, adiabatic process, isochoric process, isobaric process and reversible process.
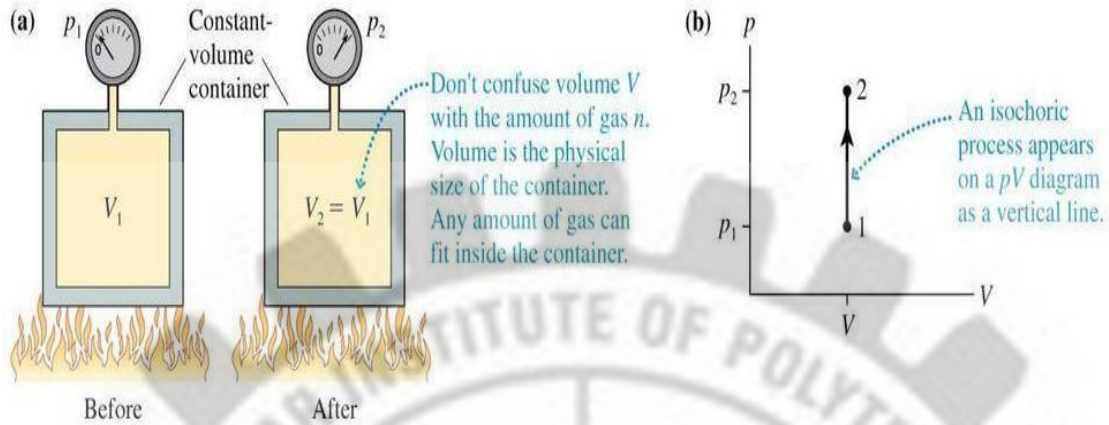
TYPES OF THERMODYNAMIC PROCESSES

The important thermodynamic processes are:

A. Reversible non-flow processes

1. Isochoric process (Constant volume process)
2. Isobaric process (Constant pressure process)
3. Isothermal process (Constant temperature process)
4. Adiabatic process
5. Hyperbolic process
6. Polytropic process
7. Throttling process

Isochoric process (Constant volume process)

In this process the volume of system remains constant. The main characteristic of this process is that the displacement work is eliminated. An example of this process is the heating or cooling of a gas stored in a rigid cylinder. Since the volume of the gas does not change, no external work is done, and work transferred W is zero.

Therefore from 1st law of thermodynamics for a constant volume process:

$$Q_{1\text{-}2} - W_{1\text{-}2} = U_2 - U_1$$

But, $\qquad W_{1\text{-}2} = \int_{1}^{2} PdV = U_2 - U_1$ .... $(dV = 0)$

$$Q_{1\text{-}2} = U_2 - U_1$$

$$Q_{1\text{-}2} = mC_v(T_2 - T_1)$$

Thus, during a constant volume process, the heat transfer equals the change in internal energy of the system.

Isobaric process (Constant pressure process)

The process, during which the pressure of the system remains constant, is called as isobaric process. If the temperature of a gas is increased by the addition of heat while the gas is allowed to expand so that its pressure is kept constant, the volume of the gas will be increase in accordance with Charles law. Since the volume of the gas increases during the process, work is done by the gas at the same time that its internal energy also changes. Therefore for constant pressure process, assuming constant specific heats and ideal gas behaviour,

The mass maintains a constant pressure in the cylinder.

V_i Initial

V_f Final

M

M

Pressure

i ————→ f

W > 0

Volume
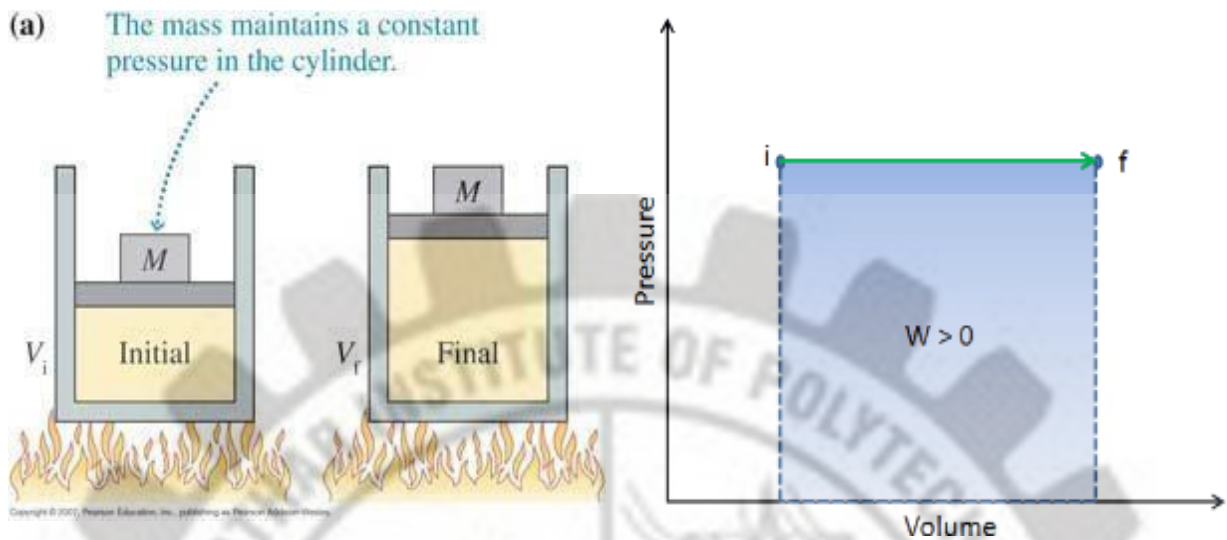
If the work is carried out quasi-statically,

$$\int_1^2 \delta W = \int_1^2 P dV$$

Then, from first law of thermodynamics,

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

Or

$$\int_1^2 \delta Q = \int_1^2 \delta W + \int_1^2 dU$$

$$= \int_1^2 P dV + \int_1^2 dU$$

$$= \int_1^2 d(U + PV)$$

$$\int_1^2 \delta Q = \int_1^2 dH$$

Also

$$\int_1^2 \delta Q = \int_1^2 mC_p dT$$

Or

$$Q_{1-2} = mC_P (T_2 - T_1)$$

Thus, the heat supplied at constant pressure is equal to change in enthalpy of the system.

Isothermal process (Constant temperature process)

According to Boyle's law, when a gas is compressed or expanded at constant temperature, the pressure will vary inversely with the volume. Since the gas does work as it expands, if the temperature is to remain constant, energy to do the work must be supplied from an external source. When a gas is compressed, work is done on the gas and if the gas is not cooled during the process the internal energy of the gas will increase by an amount equal to the work of compression. Therefore if the temperature of the gas is to remain constant during the process gas must reject heat to the surroundings. Since there is no temperature increase in the system change in internal energy becomes zero. And the amount of work done will be the amount of heat supplied.

From first law of thermodynamics,

$$\delta Q - \delta W = dU$$

But

$$dU = mC_v dT$$

Now as

$$dT = 0$$

$$dU = 0$$

$$\delta Q - \delta W = 0$$

Or

$$\delta Q = \delta W$$

For quasi-static process,

$$\int_1^2 \delta W = \int_1^2 P dV$$

Or

$$W_{1-2} = \int_1^2 P dV = \int_1^2 \frac{PV dV}{V}$$

Or

$$Q_{1-2} = PV \log_e \left(\frac{V_2}{V_1}\right)$$

Or

$$Q_{1-2} = P_1 V_1 \log_e \left(\frac{V_2}{V_1}\right)$$

Or

$$Q_{1-2} = mRT_1 \log_e \left(\frac{V_2}{V_1}\right)$$

Hence, the heat supplied during isothermal process is equivalent to non-flow work during the process.

Adiabatic process

The process during which work is done and no heat is transferred across the system boundary is known as adiabatic process.

Heat transferred, $Q_{1-2} = 0$

From first law of thermodynamics,

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

Or $\quad Q_{1-2} - W_{1-2} = \Delta U$ .... $Q_{1-2} = 0$
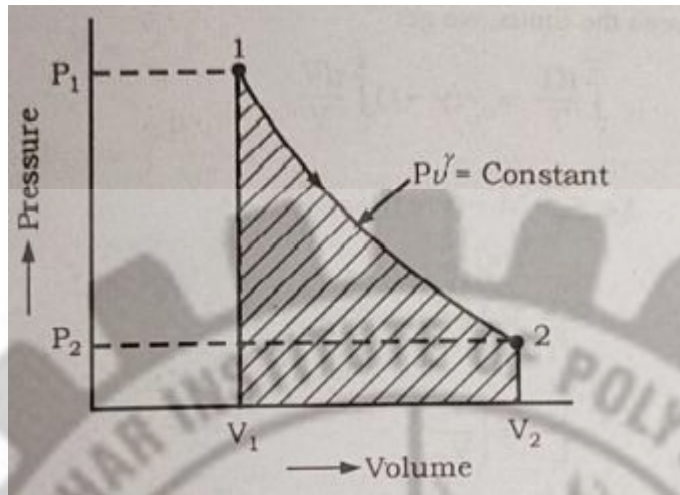
Or $\quad - W_{1-2} = \Delta U$ .... (i)

Work done = Change in internal energy

For perfect gases, we know that

$\Delta U = m \times C_v \times (T_2 - T_1)$ .... (ii)

Also $\quad W_{1-2} = \int_1^2 P dV$ .... (iii)

Putting the values of ΔU and W1-2 from equations (ii) and (iii) in equation (i), we get

$$-\int_{1}^{2} PdV = m.C_V (T_2 - T_1)$$

Or

$$PdV = -m. C_V \, dT \qquad \dots\dots\dots \text{(iv)}$$

But

$$PV = mRT$$

Or

$$P = \frac{mRT}{V} \qquad \dots\dots\dots\text{(v)}$$

Putting the value of P from equation (v) in equation (iv), we get

$$\frac{mRT}{V} dV = -m.C_V.dT$$

Or

$$\frac{dT}{T} = \frac{-R}{C_V} \times \frac{dV}{V} \qquad \dots\dots \text{(vi)}$$

Now

$$R = C_P - C_V$$

$$\frac{R}{C_V} = \frac{C_P - C_V}{C_V}$$

$$= \frac{C_P}{C_V} - 1$$

$$= \gamma - 1 \qquad \text{………. (vii)}$$

Putting the value of R/C_v from (vii) in equation (vi), we get

$$\frac{dT}{T} = -(\gamma - 1)\frac{dV}{V}$$

Integrating between the limits, we get

$$\int_1^2 \frac{dT}{T} = -(\gamma - 1)\int_1^2 \frac{dV}{V}$$

$$\log_e \frac{T_2}{T_1} = -(\gamma - 1)\log_e \frac{V_2}{V_1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{-(\gamma-1)}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{(\gamma-1)}$$

$$TV^{\gamma-1} = \text{Constant}$$

$$\frac{V_1}{V_2} = \frac{P_2 T_1}{P_1 T_2}$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \times \frac{T_1}{T_2}\right)^{(\gamma-1)}$$

$$\frac{T_2}{T_1} \times \left(\frac{T_2}{T_1}\right)^{\gamma-1} = \left(\frac{P_2}{P_1}\right)^{\gamma-1}$$

$$\left(\frac{T_2}{T_1}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

$$\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

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

$$W_{1-2} = \int_{1}^{2} P\,dV$$

$$PV^{\gamma} = P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

$$P = \frac{P_1 V_1^{\gamma}}{V^{\gamma}}$$

$$W_{1-2} = \int_{1}^{2} \frac{P_1 V_1^{\gamma}}{V^{\gamma}}\,dV$$

$$= P_1 V_1^{\gamma} \int_{1}^{2} V^{-\gamma}\,dV = P_1 V_1^{\gamma}\left[\frac{V^{-\gamma+1}}{-\gamma+1}\right]_{1}^{2}$$

$$= \frac{P_1 V_1^{\gamma}}{1-\gamma}\left[V_2^{1-\gamma} - V_1^{1-\gamma}\right]$$

$$= \frac{P_1 V_1^{\gamma}\cdot V_2^{1-\gamma} - P_1 V_1^{\gamma}\cdot V_1^{1-\gamma}}{1-\gamma}$$

$$= \frac{P_2 V_2 - P_1 V_1}{1-\gamma} \qquad \left(\because P_1 V_1^{\gamma} = P_2 V_2^{\gamma}\right)$$

$$= \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$$

$$W_{1-2} = \frac{mR(T_1 - T_2)}{\gamma - 1}$$

It should be noted that during reversible adiabatic process, entropy remains constant, so the process is also known as isentropic process.

Condition for isentropic process:

1. The process should be frictionless.
2. No heat should be transferred.
3. Work should be done by the gas or on the gas.
4. In real practice, isentropic process is not possible.

Isentropic Process

If an adiabatic process is reversible then it is called Isentropic process i.e., reversible adiabatic process is known as isentropic process. For an adiabatic process to qualify as isentropic process, then it should be frictionless. All the other properties of this process are same as that of adiabatic process.

Polytropic process

It is found that in actual practice many processes approximate to a reversible process of the PV^n = Constant, where n is called polytropic index. Both vapours and perfect gases follow this type of process closely. Work done during the process from state 1 to state 2 by system,

$$\int\limits_{1}^{2} \delta W = \int\limits_{1}^{2} PdV = \int\limits_{1}^{2} \frac{P_1 V_1^n}{V^n} dV$$

$$W_{1-2} = P_1 V_1^n \left[\frac{V_2^{-n+1} - V_1^{-n+1}}{-n+1} \right]$$

$$W_{1-2} = \frac{P_1 V_1^n V_2^{-n+1} - P_1 V_1^n V_1^{-n+1}}{-n+1}$$

$$W_{1-2} = \frac{P_2 V_2^n V_2^{-n+1} - P_1 V_1^n \cdot V_1^{-n+1}}{-n+1} \qquad \left(\because P_1 V_1^n = P_2 V_2^n \right)$$

$$W_{1-2} = \frac{P_2 V_2 - P_1 V_1}{-n+1}$$

$$W_{1-2} = \frac{P_1 V_1 - P_2 V_2}{n-1}$$

Throttling process

The throttling process is an irreversible steady flow expansion process in which a perfect gas is expanded through an orifice of minute dimensions such as a narrow throat or as lightly opened valve.

Due to fall in pressure during expansion, the gas should come out with a large velocity, but due to high frictional resistance between the gas and the walls of the aperture, there is no considerable change in velocity. The kinetic energy of the gas is converted into heat which is utilized in warming the gas to its initial temperature. Since no heat is supplied or rejected during the throttling process and also no work is done. There is no change in enthalpy from one state to another, $h_1 = h_2$; no work is done, $W = 0$; and the process is adiabatic, $Q = 0$.

Free expansion process

The expansion of gas in perfect vacuum is called free expansion. Consider a properly insulated cylinder with a partition and stopper. Now place some gas on one side and evacuate other side. When stopper is removed the gas expands freely to the other side of cylinder. This process is called free expansion or irreversible isothermal process.
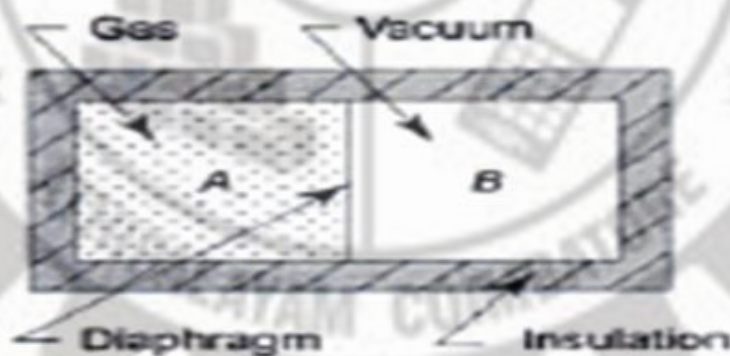
Since it is properly insulated no heats enters or leave the cylinder (adiabatic) and temperature of gas remains constant i.e., isothermal. The matter inside cylinder does not cross the system boundaries (walls of cylinder) hence work done is 0. Since temperature is constant, there is no change in internal energy of system.

$$\delta Q + \delta W = dU$$

Since, $dU = 0$, Thus, internal energy of system remains constant.

$$H = U + PV$$

CHAPTER 4
LAWS OF THERMODYNAMICS

LAW OF CONSERVATION OF ENERGY

The law of conservation of energy states that energy can neither be created nor destroyed - only converted from one form of energy to another. This means that a system always has the same amount of energy, unless it's added from the outside. Some examples of conservation of energy are as follow:
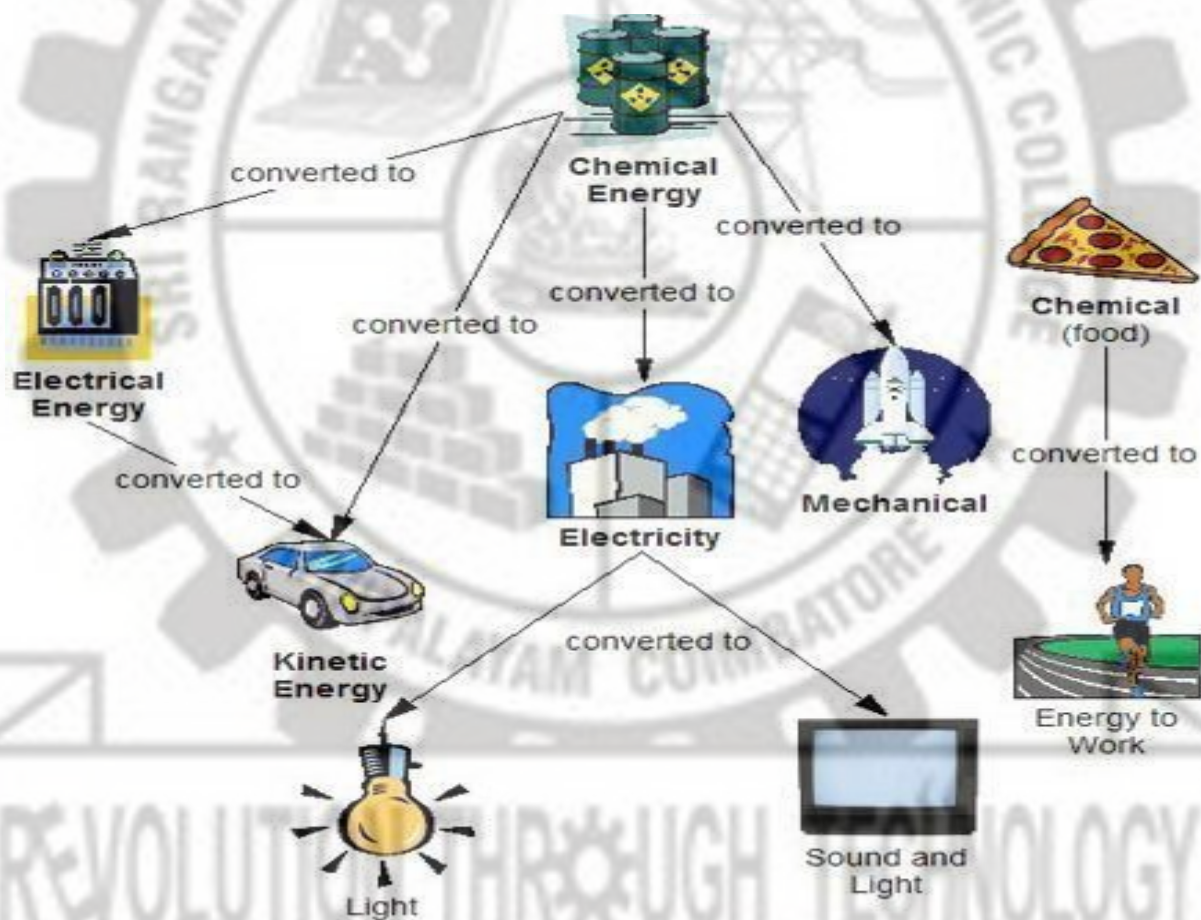
1. Conversion of electrical energy into heat energy by flowing of current through a resistance.
2. Conservation of water energy into heat energy during power generation in a hydroelectric power plant.

FIRST LAW OF THERMODYNAMICS (JOULE's EXPERIMENT)

It is special case of law of conservation of energy and may be explained as follow for the following systems:

First law for a closed system undergoing a cycle

Let us consider a closed system which consist of a known mass of water, (m) contained in an adiabatic vessel having a thermometer and a paddle wheel as shown in fig.
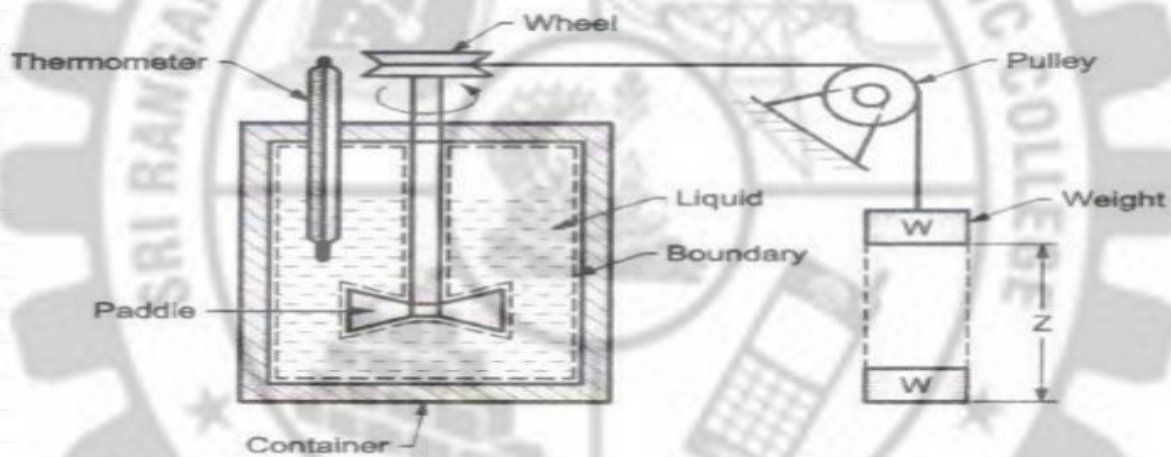

Fig. 4.1 Joule experiment apparatus

Let a certain amount of work (W_{1-2}) be done upon the system by the paddle wheel. The quantity of work can be measured by the fall of weight which derives the paddle wheel through a pulley. The system initially was at temperature (T_1), the same as that of the atmosphere and after the work transfer let the temperature rise to (T_2). The process 1-2 undergone by the system is shown in the figure 8, in generalized thermodynamic coordinates X, Y.
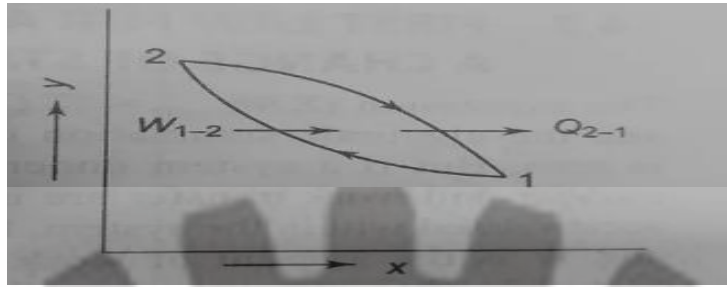
Fig. 4.2 Cyclic process

The system and the surrounding interact by heat transfer till the system returns to the original temperature (T_1), attaining the condition of thermal equilibrium with the atmosphere. The amount of heat transfer (Q_{2-1}) from the system during the process (2-1) shown in the figure above, can be estimated from,

$$Q_{2-1} = mC_p (T_2 - T_1)$$

The systems thus execute a cycle, which consist of a definite amount of work input (W_{1-2}) to the system followed by the transfer of an amount of heat (Q_{2-1}) from the system.

$$\left(\sum W\right)_{cycle} = J \left(\sum Q\right)_{cycle}$$

The work (W_{1-2}) is always proportional to the heat (Q_{2-1}) and constant of proportionality is called the Joule's equivalent or mechanical equivalent of heat. If the cycle involves many more heat and work quantities, the same result will be found,

$$\oint dW = J \oint dQ$$

Where,

J = Joule's equivalent.

$\oint$ = Denotes the cyclic integral for the closed path.

This is the first law for a closed system undergoing a cycle. It is accepted as a general law of nature, since no violation of it has ever been demonstrated. In this, the algebraic summation of all energy transfer i.e. heat energy transfer and work energy transfer across the system boundaries will be zero.

First law for a closed system undergoing a change of state

Let we have one closed system which is undergoing a change of state and energies i.e. work energy and heat energy both are crossing the system boundaries. Net energy will be stored within the system in the form of internal energy. The Q heat energy enters the system from surrounding and work energy W leave the system or we can also say that system is doing work W on the surrounding by taking Q amount of heat energy from the surrounding.
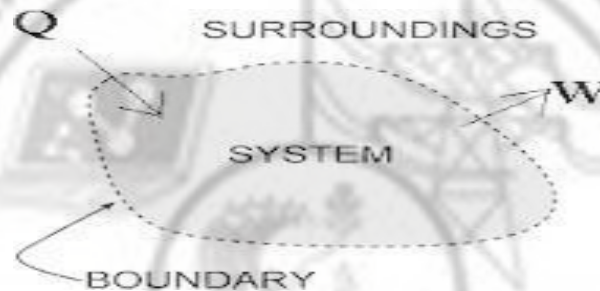

(Q-W) will be the net energy and it will be accumulated within the system and hence there will be increment in internal energy of the system as (Q-W) amount of energy will be stored within the system during this process. Therefore according to the first law of thermodynamics, we have following equation for above thermodynamic process where system is under a change of state.

$$Q - W = \Delta U$$

Where, ΔU is increase in internal energy of the system during the process.

Let we have one system where multiple energies are crossing the system boundary in a process as shown in figure, "Sign convention used for heat and work energy transfer across the system boundary "and we will write here the equation of energy transfer across the system boundary according to the first law of thermodynamics for this process.
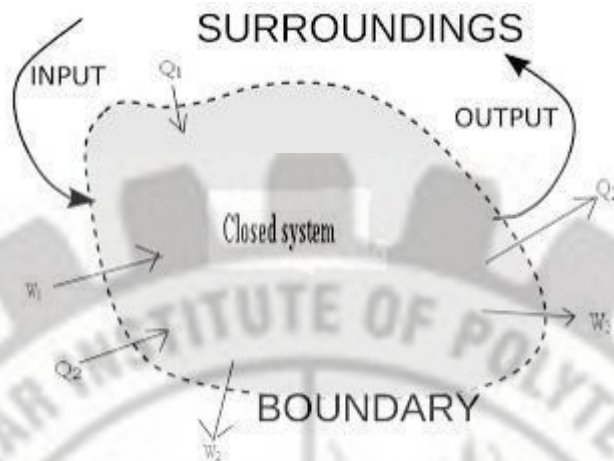
$$Q_1 + Q_2 - Q_3 - W_1 + W_2 + W_3 = \Delta U$$

This equation shows the change in internal energy or change of system energy.

Limitations of First law first law of thermodynamics (Joule's experiment)

1. No restriction on the direction of the flow of heat: the first law establishes definite relationship between the heat absorbed and the work performed by a system. The first law does not indicate whether heat can flow from a cold end to a hot end or not. For example: we cannot extract heat from the ice by cooling it to a low temperature. Some external work has to be done.

2. Does not specify the feasibility of the reaction: first law does not specify that process is feasible or not for example: when a rod is heated at one end then equilibrium has to be obtained which is possible only by some expenditure of energy.

3. Practically it is not possible to convert the heat energy into an equivalent amount of work.

To overcome this limitations, another law is needed which is known as second law of thermodynamics. The second law of thermodynamics helps us to predict whether the reaction is feasible or not and also tell the direction of the flow of heat.

STEADY FLOW ENERGY EQUATION

Before going for the energy equation, let us first discuss the conditions which must be satisfied for the steady flow process.

1. The mass flow through the system remains constant.
2. Fluid is uniform in composition.
3. The only interaction between the system and surroundings are work and heat.
4. The state of fluid at any point remains constant with time.
5. In the analysis only potential, kinetic and flow energies are considered.

Fig. 4.3 Steady flow process

Let   P1, P2 = Pressure of working substance at inlet and outlet of system,

Z1, Z2 = Datum height at inlet and outlet,

C1, C2 = Velocity of working substance at inlet and outlet,

Q = Heat supplied to the system,

W = Work delivered by the system,

V1, V2 = Volume of working substance entering and leaving the system,

U1, U2 = Internal energy of working substance at inlet and outlet,

m = Mass of working substance

We know that energy entering the system is

$$E_{entering} = U_1 + \frac{mC_1^2}{2} + mZ_1 g + P_1 V_1 + Q$$

Similarly, energy leaving the system is

$$E_{outlet} = U_2 + \frac{mC_2^2}{2} + mZ_2 g + P_2 V_2 + W$$

From assumption

$$E_{entering} = E_{outlet}$$

$$U_1 + \frac{mV_1^2}{2} + mZ_1 g + P_1 V_1 + Q = U_2 + \frac{mC_2^2}{2} + mZ_2 g + P_2 V_2 + W$$

Also, we know that,

$$H_1 = U_1 + P_1 V_1$$
$$H_2 = U_2 + P_2 V_2$$

And

$$H_1 + \frac{mC_1^2}{2} + mZ_1 g + Q = H_2 + \frac{mC_2^2}{2} + mZ_2 g + W$$

The above equation is known as steady flow energy equation. Mass flow rate (m) of the working substance in a steady flow is given by

$$\dot{m} = \frac{A_1 V_1}{v_1} = \frac{A_2 V_2}{v_2}$$

APPLICATIONS OF GENERAL STEADY FLOW EQUATION

Some of the important applications of general steady flow equations are as follows:

1. Turbine

A turbine is a rotary steady state steady flow machine whose purpose is the production of shaft power at the expense of the pressure of the working fluid. Two general classes of turbines are steam and gas turbines depending on the working substance used. Usually, changes in potential energy are negligible, as

is the inlet kinetic energy. Often the exit kinetic energy is neglected (if in a problem, the flow velocities are specified, the kinetic energy term should be included). Normally, the process in the turbine is adiabatic and the work output reduces to decrease in enthalpy from the inlet to exit states.

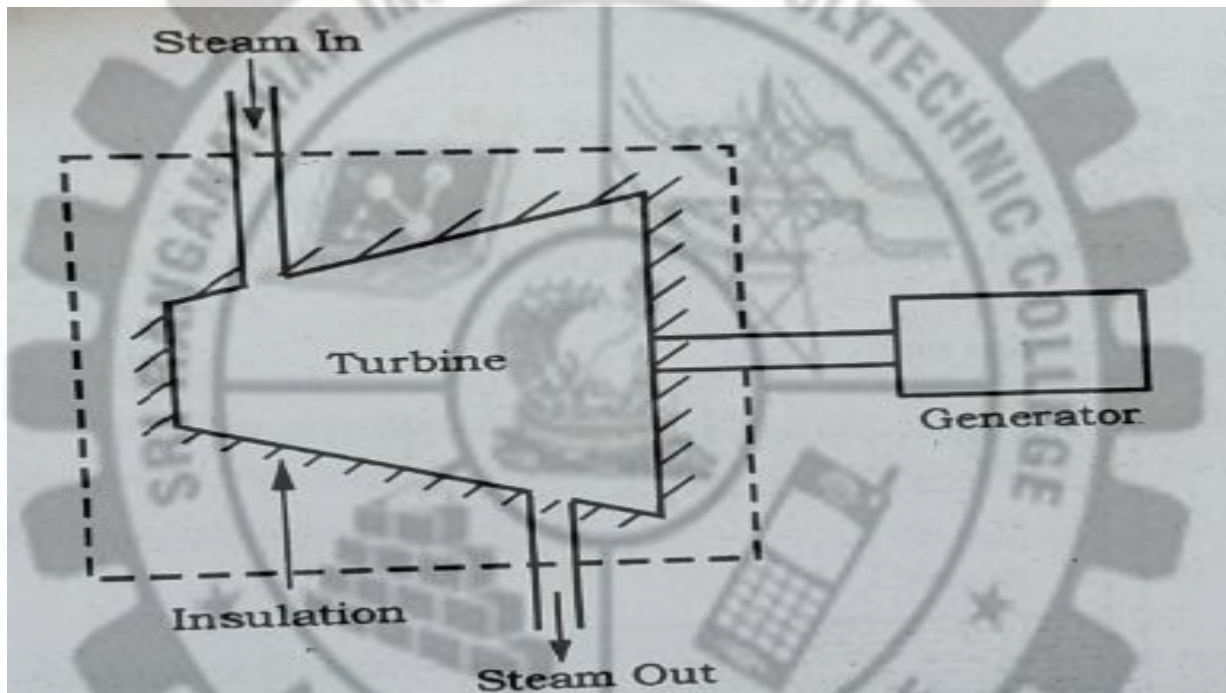$$H_1 + \frac{mC_1^2}{2} + mZ_1g = H_2 + \frac{mC_2^2}{2} + mZ_2g + W$$

Fig. 4.4 Turbine

$$H_1 = H_2 + W$$

$$W = H_1 - H_2$$

This shows that the work done by the system is due to the decrease in enthalpy of working substance.

2. Pump

A pump is a device which lifts the water from lower level and delivers it to higher level as shown in fig. the pump is run by an external device, therefore work is –ve in this case. Also the change in internal energy of water is zero i.e. $Q = 0$ and $U_1 - U_2 = 0$.
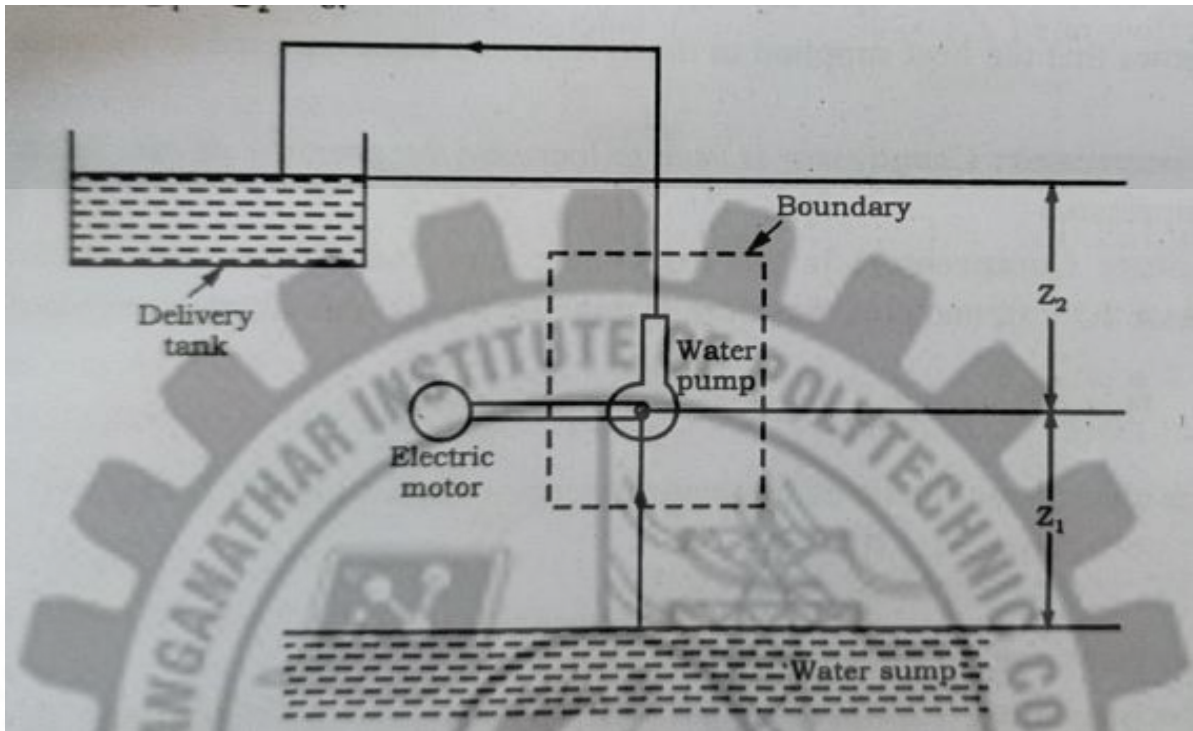
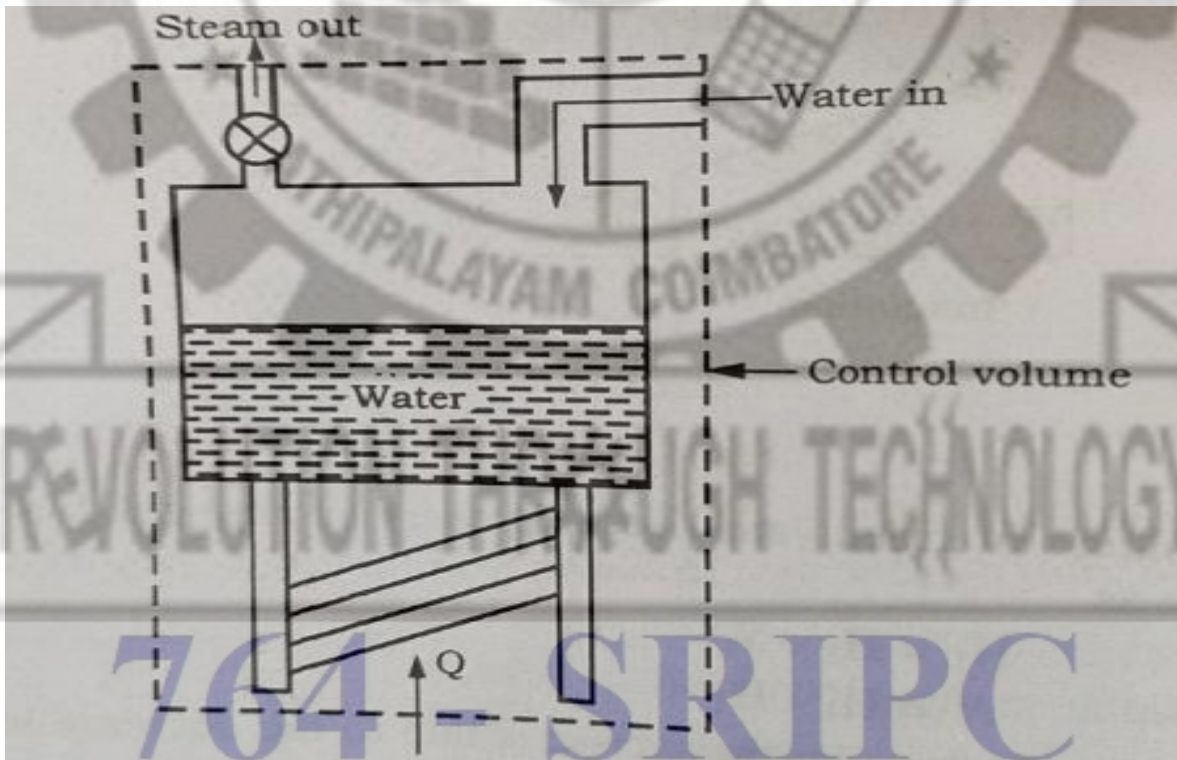**Fig. 4.5 Pump**

3. Boiler

Fig. 4.6 Boiler

A boiler is a device shown in fig which is used to generate the steam after heating the water. In this system, there is no change in kinetic energy and potential energy. Also there is no work done by system.

Therefore, from general energy equation,

$$H_1 + Q = H_2$$

$$Q = H_2 - H_1$$

This show that the heat supplied to the system in a boiler is used to increase the enthalpy of the system.

4. Compressor

Compressor is used to increase the pressure of air. There are mainly two types of compressors:

a) Rotary compressor

In this case, the compressor is insulated, so that no transfer of heat takes place ($Q = 0$) and also, the work is done on the system. From energy equation

$$H_1 + \frac{mC_1^2}{2} + mZ_1g = H_2 + \frac{mC_2^2}{2} + mZ_2g - W$$

Also the change in K.E. and P.E. are negligible.

$$H_1 = H_2 - W$$

$$W = H_2 - H_1$$

It shows that work is done to increase enthalpy.

b) Reciprocating compressor

The rate of flow is low as compared to rotary compressor, so there is large area in contact with surroundings. Amount of heat transfer in appreciable and cannot be ignored.

Therefore,

$$H_1 - Q = H_2 - W$$

The –ve sign of Q and W indicate that in reciprocating compressor, heat is rejected and work is done on the system.

5. Nozzle

It is a device which is used to increase the velocity of working substance at the cost of pressure drop. The nozzle is considered to be insulated so that there is no transfer of heat from or to the system (Q = 0). Also there is no change in potential energy and no external work is done by the system. From general energy equation,
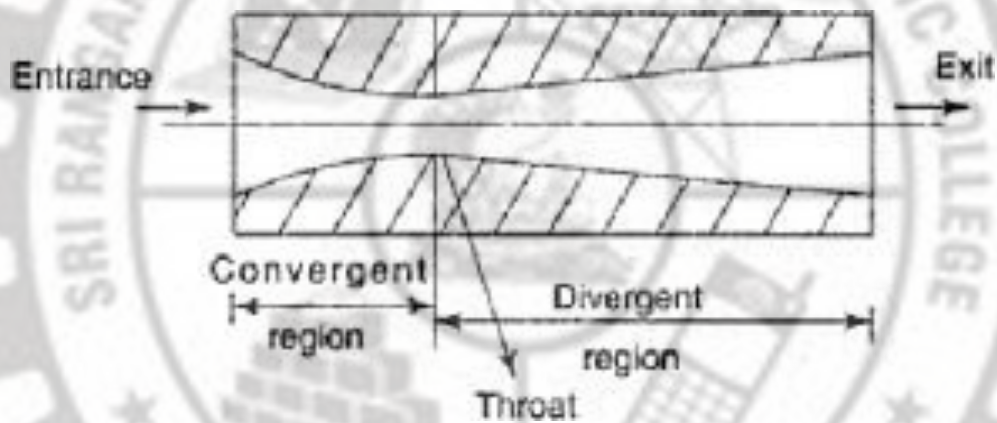

Fig. 4.7 Nozzle

$$H_1 + \frac{mC_1^2}{2} = H_2 + \frac{mC_2^2}{2}$$

$$H_1 - H_2 = \frac{mC_2^2}{2} - \frac{mC_1^2}{2}$$

Now, C_1 is very small as compared to C_2, so C_1 may be ignored. From general energy equation,

$$C_2 = \sqrt{\frac{2(H_1 - H_2)}{m}}$$

Above relation shows that the increase in K.E. will results in decrease in enthalpy.

6. Evaporator

It is device which is used in refrigeration system. In evaporator, liquid refrigerant receives heat and leaves as vapors refrigerant. In thus system, kinetic energy and potential energy can be neglected. Also there is no work done by the system.
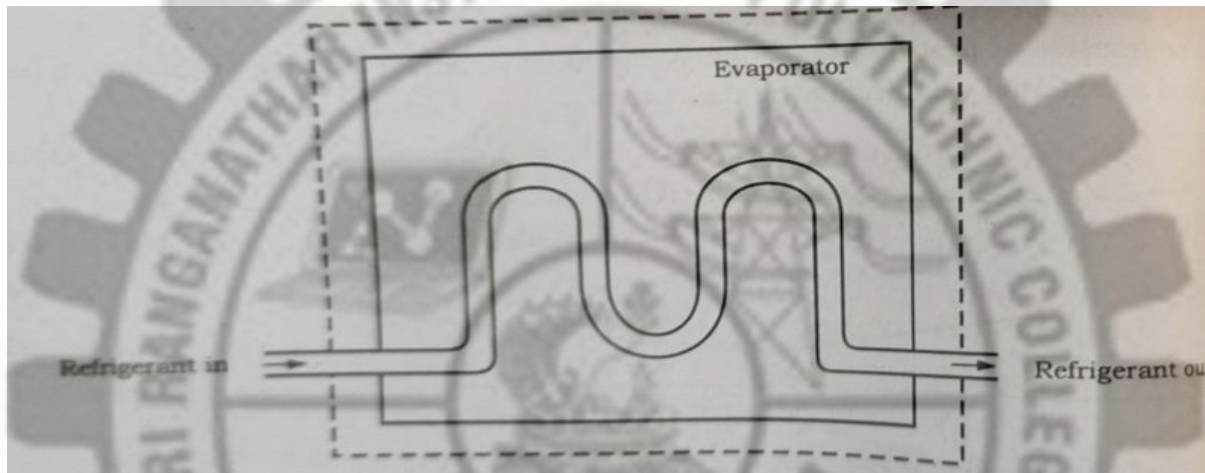

Fig. 4.8 Evaporator

$$H_1 + Q = H_2$$
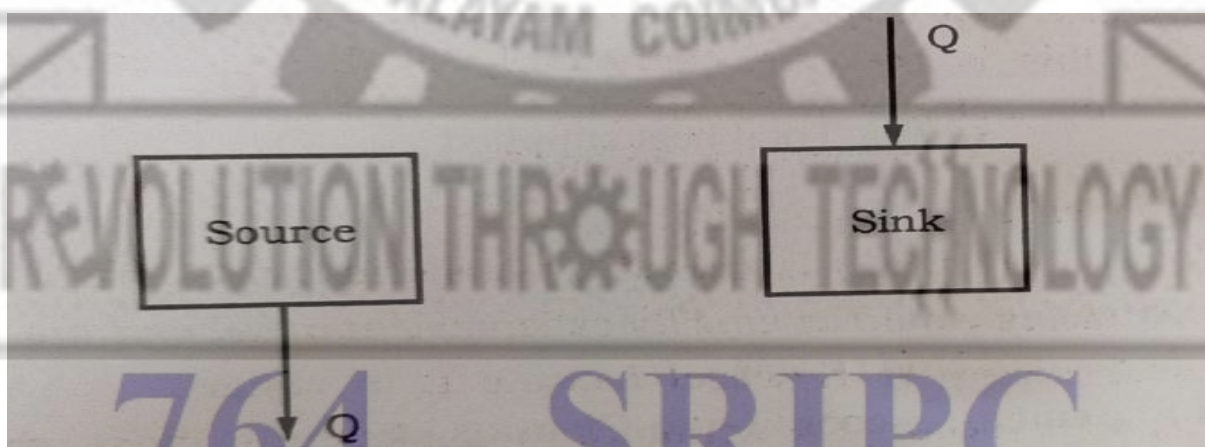
$$Q = H_2 - H_1$$

HEAT SOURCE AND HEAT SINK

Fig. 4.9 Heat Source and heat Sink

Ideally sink and source are thermal reservoirs of infinite thermal capacities. This means you can extract (source) or reject (sink) heat from them without changing their temperature. Practically such device does not exist; these are just concepts to make study of thermodynamic systems like heat engine and refrigerator easy.

STATEMENT OF SECOND LAW OFTHERMODYNAMICS

The Second Law of Thermodynamics states that the state of entropy of the entire universe, as an isolated system, will always increase over time. The second law also states that the changes in the entropy in the universe can never be negative. However, in some cases where the system is in thermodynamic equilibrium or going through a reversible process, the total entropy of a system and its surroundings remains constant. The second law is also known as the law of degradation of energy.

There are two statements on the second law of thermodynamics which are;

1. Kelvin- Plank statement
2. Clausius statement
3.

(A) Kelvin – Planck statement

It is impossible for any device that operates on a cycle, to receive heat from a single reservoir and produce a net amount of work. In other words, no heat engine converts or can convert whole of the heat energy into mechanical work and there will always be a heat rejection.

Let us assume that heat energy (Q_1) at temperature T_1 is supplied to heat engine from source and heat energy (Q_2) at temperature T_2 is rejected to the sink. Then remaining or net energy ($Q_1 – Q_2$) will be converted into mechanical work (W_{net}). The ratio of maximum mechanical work obtained to the total heat supplied to the engine is known as thermal efficiency of heat engine.
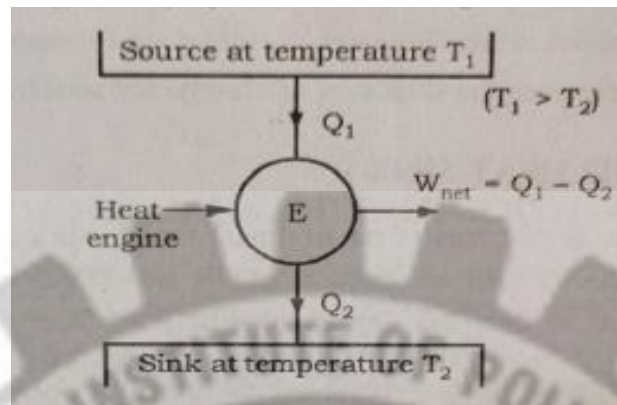
Fig. 4.10 Heat engine

$$\eta_{th} = \frac{W_{net}}{\text{Total heat supplied}} = \frac{Q_1 - Q_2}{Q_1}$$

$$\eta_{th} = 1 - \frac{Q_2}{Q_1}$$

If $Q_2 = 0$ (i.e., $W_{net} = Q_1$, or efficiency $= 1$), the heat engine produces work in a complete cycle by exchanging heat with only one reservoir, thus violating the Kelvin-Planck statement of second law is known as perpetual motion machine of second kind (PMM-II).

(B) Clausius statement

It is impossible to construct a device operating in a cycle that can transfer heat from a colder body to warmer without consuming any work. Therefore, heat cannot flow is itself from a body at a higher temperature. The applications of this law are found in a heat pump and refrigerator.

(C) Equivalency of Kelvin Planck's and Classius statements
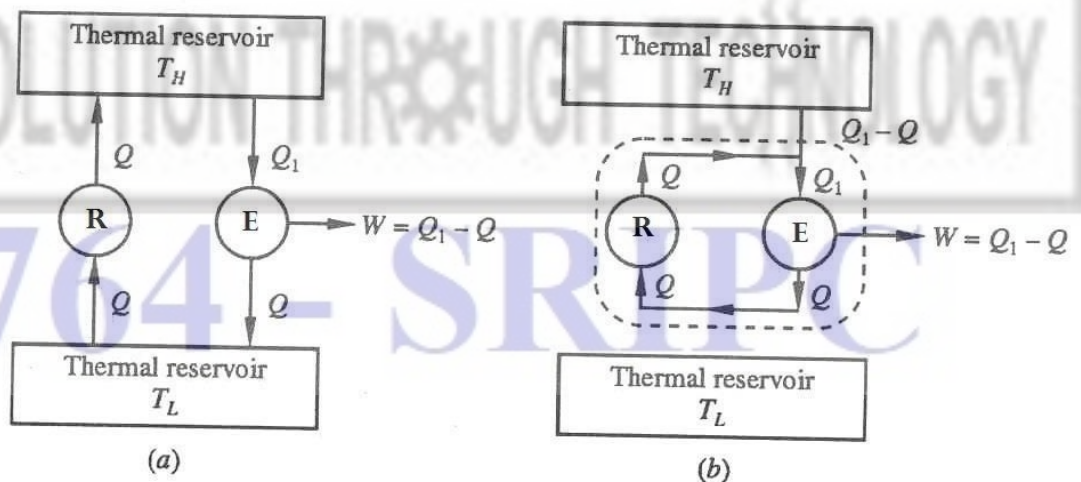
To prove that violation of the Kelvin-Planck Statement leads to a violation of the Clausius Statement, let us assume that Kelvin-Planck statement is incorrect.

Consider a cyclically working heat engine (E), which absorbs energy Q_1 as heat from a thermal reservoir at T_H. Equivalent amount of work W (W = Q_1) is performed.

Consider refrigerator (R) operating as a cycle, which absorbs energy Q_L as heat from a low temperature thermal reservoir at T_L and rejects energy Q_H ($Q_H = Q_L + W$). Such a device does not violate Clausius statement.

(a)   (b)
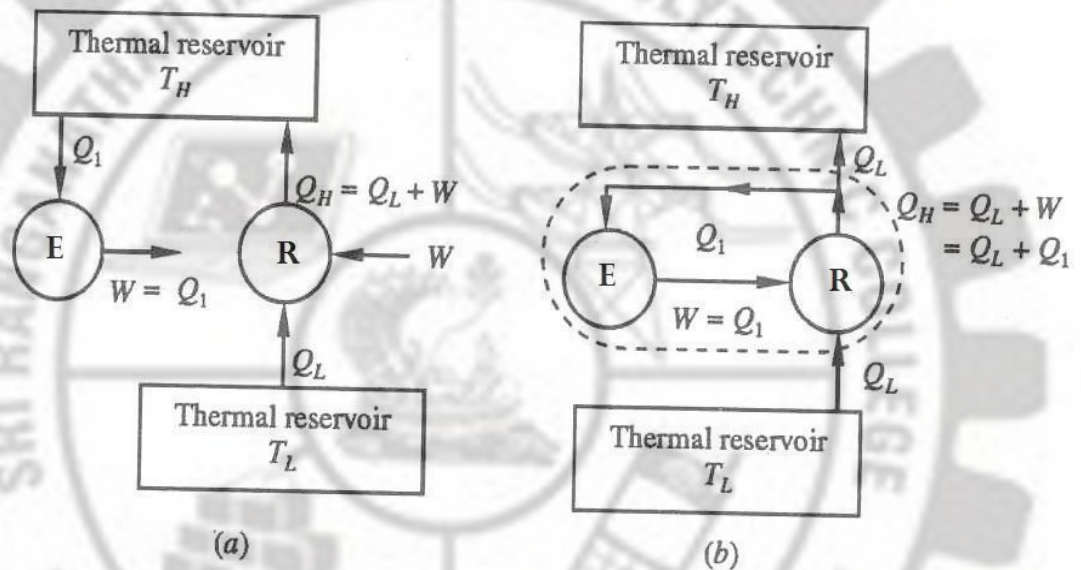
If the two devices are now combined, the combined device (enclosed by the dotted boundary) transfers heat Q_L from the low temperature reservoir at T_L to a high temperature reservoir at T_H without receiving any work from an external device, which is the violation of the Clausius statement.

(a)   (b)

Likewise let us assume that the Clausius statement is incorrect. So we have a refrigerator (R), cyclically working transferring heat Q from a low temperature reservoir at T_L to a high temperature thermal reservoir at T_H. Consider heat engine (E), which absorbs heat Q_1 from a high temperature reservoir at T_H does work W and rejects energy Q as heat tot the low temperature reservoir at T_L as shown in figure.

If the two devices are combined (shown in figure by a dotted enclosure), then the combined device receives energy (Q_1-Q) as heat from a thermal reservoir and delivers equivalent work ($W=Q_1$-Q) in violation of the Kelvin-Planck statement. Therefore violation of Clausius statement leads to the violation of the Kelvin-Planck statement. Hence, these two statements are equivalent.

(D)Heat pump: It is a device operating in cyclic process which maintains the temperature of a hot body at a temperature higher than the temperature of surroundings. Heat pump operates between atmospheric temperature and hot body temperature. Performance of a heat pump is measured by a term known as coefficient of performance which is defined as the ratio of maximum heat transfer to the amount of work done.
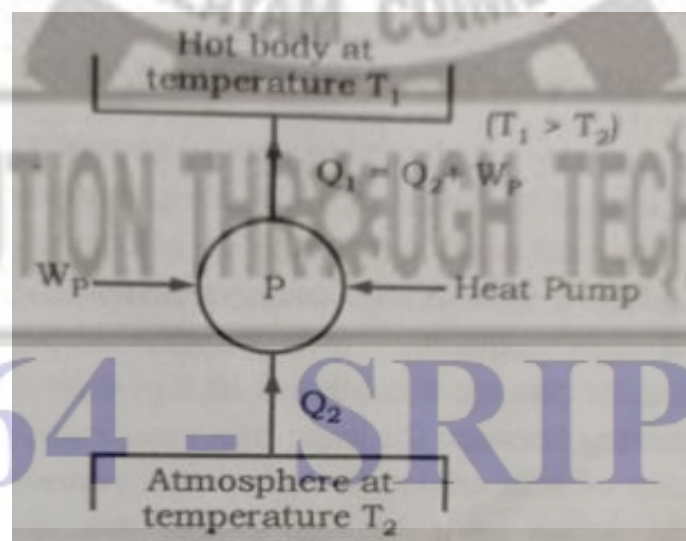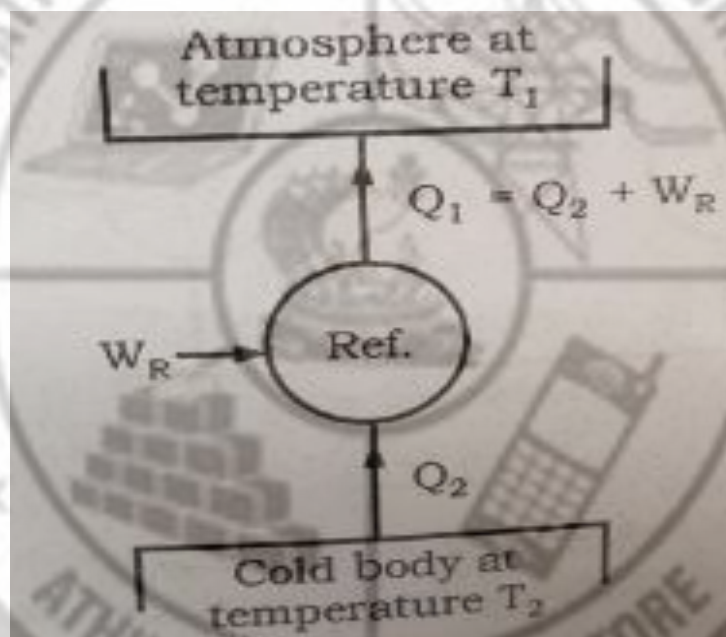

Fig.4.11 Heat pump

$$(C.O.P)_{H.P.} = \frac{Q_1}{W_P} = \frac{Q_1}{Q_1 - Q_2}$$

(D) **Refrigerator:** A refrigerator is a device operating in a cycle which maintains a body at a temperature lowers than the temperature of the surroundings. A refrigerator works between the cold body temperature and the atmospheric temperature.
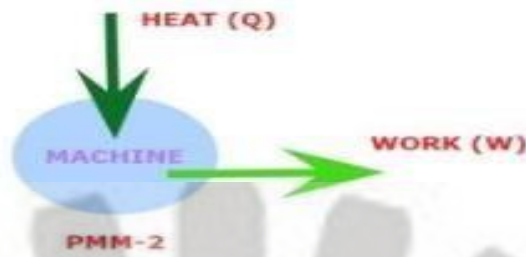

Fig. 4.12 Refrigerator

PERPETUAL MOTION MACHINE (PMM)

A device that violates the first law of thermodynamics (by creating energy) is called a Perpetual motion machine of the first kind.


A device that violates the second law of thermodynamics is called a Perpetual motion machine of the second kind.

CARNOT ENGINE

Carnot engine is a theoretical thermodynamic cycle proposed by Leonard Carnot. It gives the estimate of the maximum possible efficiency that a heat engine during the conversion process of heat into work and conversely, working between two reservoirs, can possess. It is an idealized engine whose working is perfectly reversible. This engine uses an ideal gas as the working substance and performs a 4-stroke process to complete one cycle. The reversible cycles cannot be achieved in practice because of irreversibility's associated with real processes. But, the reversible cycles provide upper limits on the performance of real cycles.
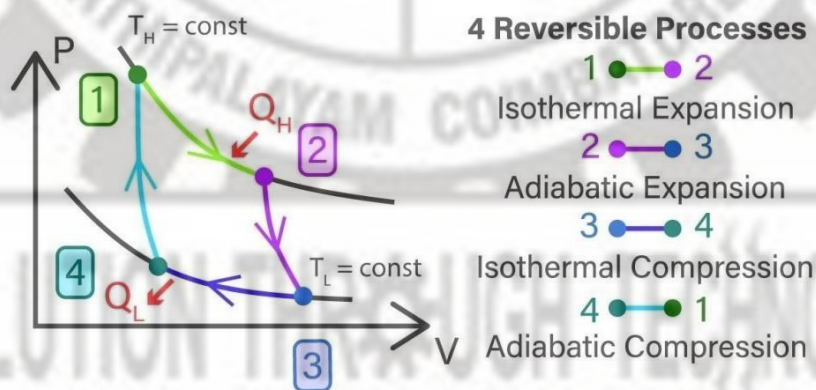
Consider a gas in a cylinder-piston (closed system). The Carnot cycle has four processes:

1. Reversible isothermal expansion (1-2): The cylinder containing ideal gas is working substance allowed to expands slowly at this constant temperature (T_H).

2. Reversible adiabatic expansion (2-3): The cylinder-piston is now insulated (adiabatic) and gas continues to expand reversibly (slowly). So, the gas is doing work on the surroundings, and as a result of expansion the gas temperature reduces from T_H to T_L.

3. Reversible isothermal compression (3-4): The gas is allowed to exchange heat with a sink at temperature TL as the gas is being slowly compressed. So, the surroundings are doing work (reversibly) on the system and heat is transferred from the system to the surroundings (reversibly) such that the gas temperature remains constant at T_L.

4. Reversible adiabatic compression (4-1): The gas temperature is increasing from T_L to T_H as a result of compression.

$$\eta_{max} = \eta_{Carnot} = 1 - \frac{T_C}{T_H}$$

THIRD LAW OF THERMODYNAMICS

This law states, 'At absolute zero temperature, the entropy of system is zero'. Zero entropy means the absence of all molecular, atomic, nuclear and electronic disorders. It has two important consequences, it defines the sign of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature.

CONCEPT OF IRREVERSIBILITY

A process is said to be reversible if both the system and the surroundings can be restored to their respective initial states, by reversing the direction of the process. A reversible process is a process that can be reversed without leaving a trace on the surroundings. Processes that are not reversible are called Irreversible processes.

Irreversibilities

The factors that cause a process to be irreversible are called irreversibilities.

1. Friction
2. Unrestrained expansion
3. Mixing of two gases
4. Heat transfer across a finite temperature difference
5. Spontaneous chemical reactions
6. Expansion or Compression with finite pressure difference
7. Mixing of matter at different states

CONCEPT OF ENTROPY

The term entropy means transformation. It is a function of quantity of heat which shows the possibility of conversion of that heat into work. As a matter of fact, it is difficult to define entropy. But change of entropy of a substance can be easily defined. In a reversible process, over a range of temperature, the increase or decrease of entropy when multiplied by the absolute temperature gives the heat absorbed or rejected by the working substance. Mathematically,

$$\delta O = TdS$$
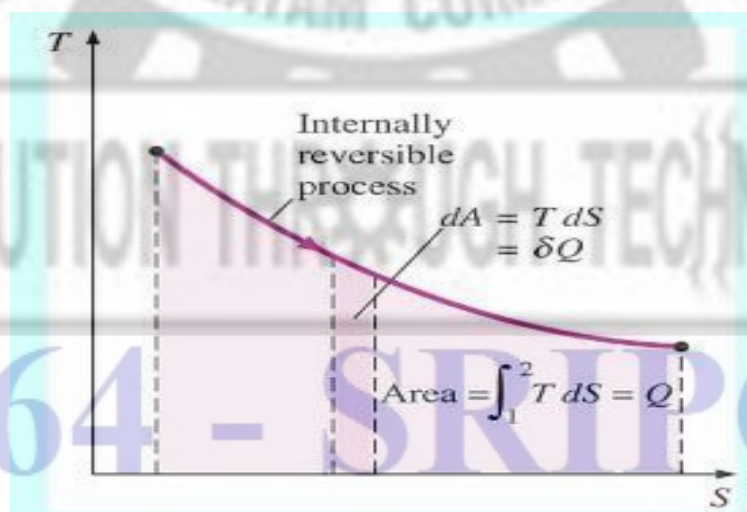
Where, T = Absolute temperature, dS = Change in entropy

Fig. 4.13 T-S diagram

The relation between heat and entropy is given by Clausius. To prove this, let us consider the heating of a working substance by reversible process. Entropy is represented on the abscissa and absolute temperature on the ordinate. This diagram is known as temperature – entropy diagram.

$$dS = \frac{\delta O}{T}$$

Importance of entropy: The change in entropy represents the maximum amount of work done per degree drop in temperature. In other words, change in entropy may be regarded as the rate of availability or unavailability of heat for transformation into work.