Thermodynamics is a branch of science which deals with exchange of heat energy between bodies and conversion of the heat energy into mechanical energy and vice versa.

THERMODYNAMIC SYSTEM.

(i) It is a collection of an extremely large number of atoms or molecules.

(ii) It is confined within certain boundaries.

(iii) Anything outside the thermodynamic system to which energy or matter is exchange is called surrounding.

(iv) Types of thermodynamic system.

(a) Open system – It exchange both energy and matter with the surrounding.

(b) close system- It exchange only energy (not matter) with the surroundings.

(c) isolated system- It exchange neither energy nor matter with the surrounding.

THERMODYNAMIC VARIABLE AND EQUATION OF STATE.

A thermodynamic system can be described by specifying its pressure, volume, temperature, internal energy , number of moles and entropy. These parameters are called thermodynamic variables. The relation between the thermodynamic variables (P, V, T) of the system is called equation of state.

For n moles of an ideal gas, equation of state is PV = nRT and for 1 mole of an ideal gases it is PV = RT

THERMODYNAMIC EQUILIBRIUM.

In steady state thermodynamic variable are independent of time and the system is said to be in the state of thermodynamic equilibrium. For a system to be in thermodynamic equilibrium, the following condition must be fulfilled:

(i) Mechanical equilibrium: There is no unbalanced force between the system and surroundings.

(ii) Thermal equilibrium: There is a uniform temperature in all parts of the system and is same as that of surrounding.

(iii) Chemical equilibrium: There is a uniform chemical composition throughout the system and the surrounding.

THERMODYNAMIC PROCESS.

The process of change of state of a system involves change of thermodynamic variables such as pressure P, Volume V and temperature T of the system. The process is known as thermodynamic process. Some important process are isothermal (temp. constant), adiabatic (heat constant), isochoric (volume constant), cyclic (initial and final state are same while in non-cyclic these state are different), reversible and irreversible process.

INDICATOR DIAGRAM.

Whenever the state of gas (P, V, T) is changed, we say the gaseous system is undergone a thermodynamic process. The graphical representation of the change in state of a gas by a thermodynamic process is called indicator diagram. Indicator diagram is plotted generally in pressure and volume of gas. Each point in a P-V diagram represents a possible state of the system.

INTENSIVE PROPERTY.
If the value of a certain property of the whole system is same as its value for a part of that system, then that property is an intensive property. Examples: pressure, temperature, density, surface tension.

EXTENSIVE PROPERTY. If the value of a certain property of the whole system is different from its value for a part of that system, then that property is an extensive property.

Example: mass, amount of substance, volume, internal energy etc.

ENTHALPY. Enthalpy is a thermodynamic function of a system equal to the sum of its internal energy (U) and the product of its pressure (p) and volume (V).

i.e., $H = U + pV$

ZEROTH LAW OF THERMODYNAMICS

states that when two bodies A and B are in thermal equilibrium with a third body C separately, they (A and B) are in thermal equilibrium mutually also i.e. if $T_A = T_C$ and $T_B = T_C$ this implies $T_A = T_B$.

(i) The zeroth law leads to the concept of temperature. All bodies in thermal equilibrium must have a common property which has the same value for all of them. This property is called the temperature.

(ii) The zeroth law came to light long after the first and second laws of thermodynamics had been discovered and numbered. It is so named because it logically precedes the first and second laws of thermodynamics.

MECHANICAL EQUIVALENT OF HEAT.

According to Joule, work may be converted into heat and vice versa. The ratio of work done (W) to heat produced (Q) by that work without any wastage is always constant.

$\frac{W}{Q}$ = Constant, This constant is called

Mechanical Equivalent of heat (J).

Note that J is not a physical quantity, but a conversion factor whose value is

J = 4.186 joule/calorie.

i.e, 1 calorie = 4.2 joule.

WORK (ΔW): Suppose a gas is confined in a cylinder that has a movable piston at one end. If P be the pressure of the gas in the

cylinder, then force exerted by the gas on the piston of the cylinder F = PA (A= area of cross-section of piston)
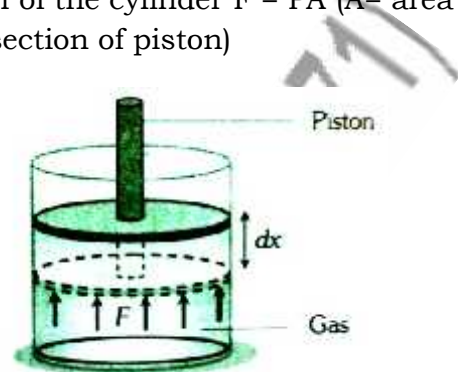
When the piston is pushed outward by an infinitesimal distance dx, the work done by the gas $dW = F.dx = P(Adx) = P.dV$

For a finite change in volume from V_i to V_f.
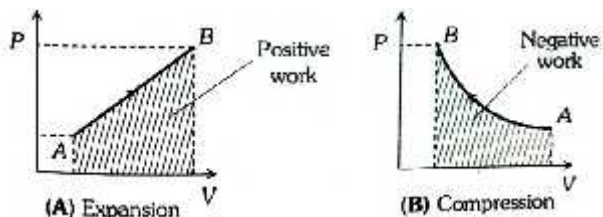
Total amount of work done

$W = \int_{V_i}^{V_f} PdV = P(V_f - V_i)$

**(i)** If we draw indicator diagram, the area bounded by PV graph and volume axis represents work done.
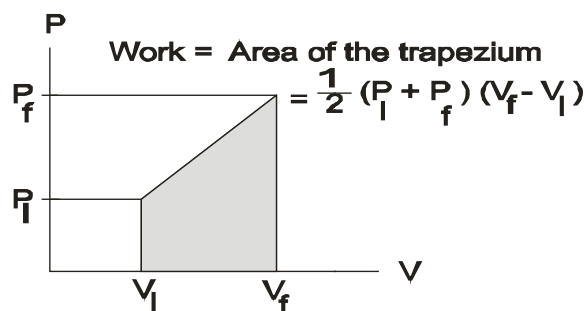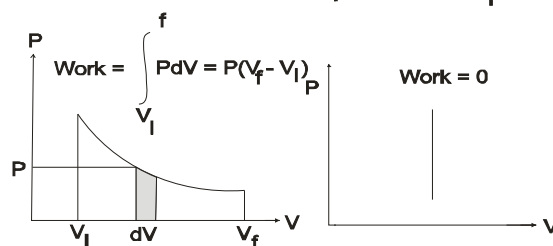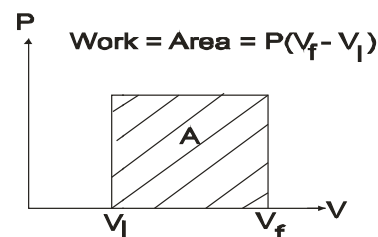
(ii) From $\Delta W = P\Delta V = P(V_f - V_i)$

If system expands against some external

force then $V_f > V_i \Rightarrow \Delta W$ = Positive. If system contract because of external force then $V_f < V_i \Rightarrow \Delta W$ = Negative.


(A) Expansion   **(B) Compression**

(iii) Like heat, work done also depends upon initial and final state of the system and path adopted for the process. In clock wise work will be +ve and in anticlock wise work will be –ve.

(A) Less area

(B) More area
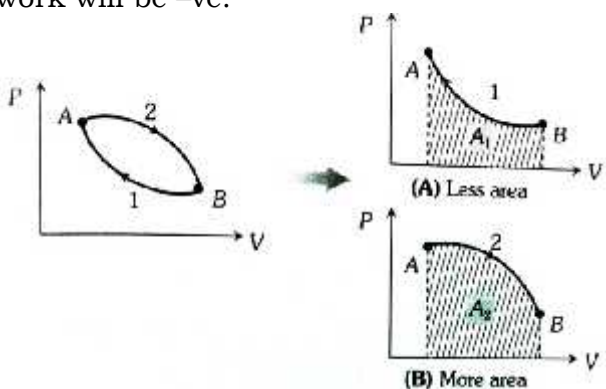
$A_1 < A_2 \Rightarrow W_1 < W_2$

(v) In cyclic process, work done is equal to the area of closed curve. It is positive if the cycle is clockwise and it is negative if the cycle is anticlock.

Work = Area of rectangle ABCD
= $AB \times AD$
= $(V_2 - V_i)(P_2 - P_1)$

Work = $\frac{\pi}{4}(P_2 - P_i)(V_2 - V_i)$
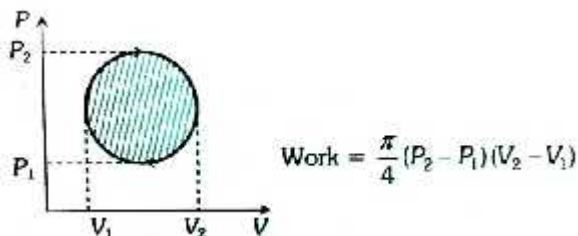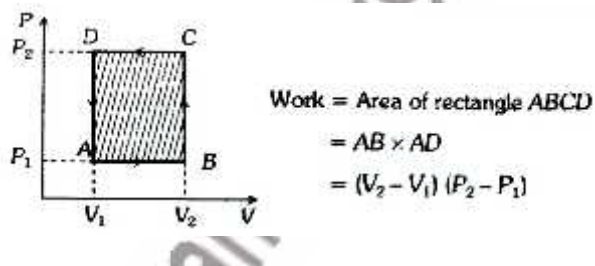
FIRST LAW OF THERMODYNAMICS.

It is based on conservation of energy and introduces the concept of internal energy. When heat energy dQ is supplied to a system, it is used up in two ways,

(i) in increasing internal energy of the system (dU)
(ii) in doing external work by the system on the surrounding (dW)
i.e,.   dQ = dU + dW
NOTE: dQ is taken as positive if the system expands or does work on the surrounding. When heat is drawn from the system, dQ is taken as negative and when gas is compressed (work is done on the gas), dW is taken as negative.

LIMITATION OF FLOT.

First law of thermodynamics does not indicate the direction of heat transfer. It does not tell anything about the conditions, under which heat can be transformed into work and also it does not indicate as to why the whole of heat energy cannot be converted into mechanical work continuously.

THERMODYNAMIC PROCESS.

(1) Quasistatic process
   If a process takes place in such a way that its state variables differ from those of the surroundings by an infinitesimally small amount all the time, it is called quasistatic .

(2) Isothermal process takes place at constant temperature. i.e., dT = 0

   (a) Essential conditions for isothermal process.
      (i) The walls of the container must be perfectly conducting to allow free exchange of heat between the gas and its surrounding.
   **(ii)** The process of compression or expansion should be so slow so as to provide time for the exchange of heat.
      Since these two conditions are not fully realized in practice, therefore, no process is perfectly isothermal.

   (b) Equation of state. In this process, P and V change but T = constant, Boyles law is obeyed,
      i.e., PV = Constant.$\Rightarrow P_1V_1 = P_2V_2$

   (c) Indicator diagram According to PV = constant, graph between P and V is a part of rectangular hyperbola. The graph at different temperatures parallel to each other are called isotherm.

$T_1 < T_2 < T_3$

Two isotherms never intersect
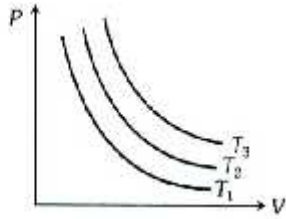
(i). Slope of isothermal curve : By differentiating PV = constant, we get

PdV + VdP = 0 ⇒ PdV = - VdP

⇒ Slope = $\tan\theta = \dfrac{d}{d} = -\dfrac{P}{V}$

.
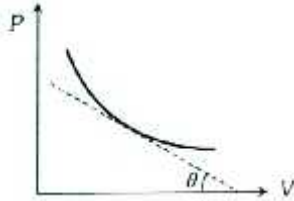
(ii). Area between the isotherm and volume axis represents the work done in isothermal process.

(c). Specific heat: Specific heat of gas during isothermal change is infinite. As

$C = \dfrac{Q}{m\Delta T} = \dfrac{Q}{m \times U} = \infty$ [As $T = 0$]

(d). Isothermal elasticity (E_θ):

$P = \dfrac{d}{-d/V} = \dfrac{S}{S} = E_\theta$

i.e., isothermal elasticity is equal to pressure.

At N.T.P.,

$E_\theta = A\mid \qquad p\mid \qquad = 1.0 \times 1 \ ^5 N/m^4$

(e). FLOT in isothermal process: From

dQ = dU + dW , dU = 0 (As T = 0)

dQ = dW

(f). Work done in isothermal process. work done by the gas
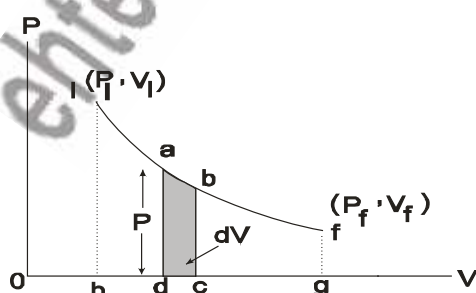
dW = F.dx = P(Adx) = P.dV

= area abcd

$W = \int_{V_i}^{V_f} P dV = \int_{V_i}^{V_f} \dfrac{\mu R}{V} dV$

(As PV = μRT)

$W = \mu RT \log_e \left(\dfrac{V_f}{V_i}\right) = 2.303 \mu RT \log_1 \left(\dfrac{V_f}{V_i}\right)$

= Area ifgh. OR

$W = \mu RT \log_e \left(\dfrac{P_i}{P_f}\right) = 2.303 \mu RT \log_1 \left(\dfrac{P_i}{P_f}\right)$

3. Adiabatic process: When a thermodynamic system undergoes a change in such a way that no exchange of heat takes place between system and surroundings, the process is known as adiabatic process.

In this process P, V and T changes but dQ = 0.

(a) Essential conditions for adiabatic process.

(i) There should not be any exchange of heat between the system and its surroundings. All walls of the container and the piston must be perfectly insulating.

(ii) The system should be compressed or allowed to expand suddenly so that there is no time for the exchange of heat between the system and its surroundings.

Since, these two conditions are not fully realized in practice, so no process is perfectly adiabatic.

(b) Examples of adiabatic process.

(i) Sudden compression or expansion of a gas in a container with perfectly non-conducting walls.

(ii) sudden bursting of the of the tube of bicycle tyre.

(iii) Propagation of sound waves in air and other gases.

(iv) Expansion of steam in the cylinder of steam engine.

(c) FLOT in adiabatic process:

dQ = 0, dW = - dU

If dW +ve then dU –ve (expansion)

If dW –ve then dU +ve (compression)

(d) Equation of state: It obey Poisson's law PV^γ = constant. Where $\gamma = \dfrac{C_p}{C_v}$

(i) For temperature and volume.

$TV^{\gamma-1}$ = constant $\qquad T_1 V_1^{1-\gamma} = T_2 V_2^{1-\gamma}$

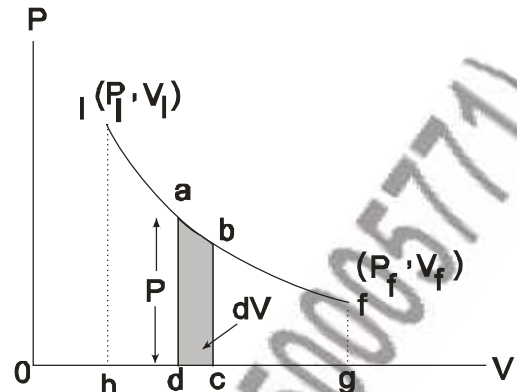or T $V^{\gamma-1}$

(ii) For temperature and pressure

$\dfrac{T^\gamma}{P^{\gamma-1}}$ = constant $\qquad T_1^\gamma P_1^{1-\gamma} = T_2^\gamma P_2^{1-\gamma}$ Or,
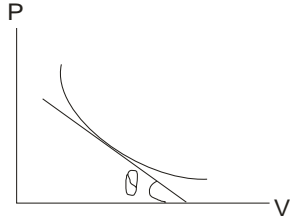
T $P^{\frac{\gamma-1}{\gamma}}$ Or, P $T^{\frac{\gamma}{\gamma-1}}$

TYPE OF GAS	$P \propto \dfrac{1}{V^\gamma}$	$P \propto T^{\frac{\gamma}{\gamma-1}}$	$T \propto \dfrac{1}{V^{\gamma-1}}$
Mono atomic $\gamma = 5/3$	$P \propto \dfrac{1}{V^{5/3}}$	$P \propto T^{5/2}$	$T \propto \dfrac{1}{V^{2/3}}$
Diatomic $\gamma = 7/5$	$P \propto \dfrac{1}{V^{7/5}}$	$P \propto T^{7/2}$	$T \propto \dfrac{1}{V^{2/5}}$
Poly atomic $\gamma = 4/3$	$P \propto \dfrac{1}{V^{4/3}}$	$P \propto T^{4}$	$T \propto \dfrac{1}{V^{1/3}}$

(d) **Indicator diagram.**
(i) From PV^γ = constant.
By differentiating, we get $\dfrac{d}{d} = -\gamma\left(\dfrac{P}{V}\right)$

Slope of adiabatic curve $\tan = -\gamma\left(\dfrac{P}{V}\right)$

(ii) But we also know that slope of isothermal curve $\tan = -\dfrac{P}{V}$
Hence $(Slope)_a = \times (slope)_i$
Or $\dfrac{(S)_A}{(S)_i} > 1$

(e) **Specific heat:** Specific heat of a gas during adiabatic change is zero.
As $C = \dfrac{d}{m} = \dfrac{u}{m} = 0$

(f) **Adiabatic elasticity (E):**
PV^γ = constant
Differentiating both side we get
$P = \dfrac{d}{-d/V} = \dfrac{S}{S} = (E)$
i.e., adiabatic elasticity is times that of pressure.
Also isothermal elasticity $E_\theta = P$
$\dfrac{E}{E_\theta} = = \dfrac{C_p}{C_v}$.

(g) **Work done in adiabatic process**
work done by the gas
$dW = F.dx = P(Adx) = P.dV = $ area abcd
$W = \int_{V_i}^{V_f} PdV = \int_{V_i}^{V_f} \dfrac{k}{V^\gamma} dV = \dfrac{(P_iV_i - P_fV_f)}{(\gamma-1)}$
$= \dfrac{\mu R(T_i - T_f)}{(\gamma-1)}$ = area ifgh.

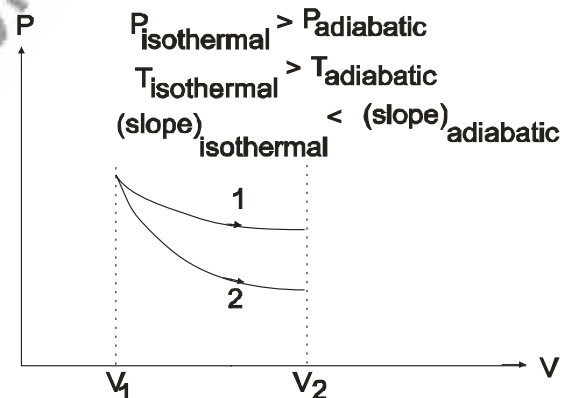i.e., $W \dfrac{1}{\gamma-1}$
hence, $\dfrac{m}{W_m} > \dfrac{d}{W_d} > \dfrac{t}{W_t}$

(h) Comparison between isothermal and adiabatic indicator diagrams:
(i) Equal expansion: Graph 1 represent isothermal process and 2 represents adiabatic process.
$W_{isothermal} > W_{adiabatic}$
$P_{isothermal} > P_{adiabatic}$
$T_{isothermal} > T_{adiabatic}$
$(slope)_{isothermal} < (slope)_{adiabatic}$

(ii) Equal compression: Graph 1 represents adiabatic process and 2 represents isothermal process.
$W_{isothermal} < W_{adiabatic}$
$P_{isothermal} < P_{adiabatic}$
$T_{isothermal} < T_{adiabatic}$
$(slope)_{isothermal} < (slope)_{adiabatic}$
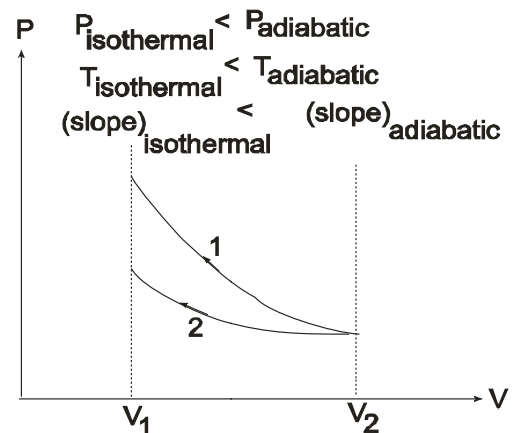
4. Isobaric process: When a thermodynamic system undergoes a physical change in such a way that its

pressure remains constant, then the change is known as isobaric process.

(i) Equation of state : In this process V and T changes but P remains constant. Hence Charle's law is obeyed in this process. V $\propto$ T $\quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$

(ii) Indicator diagram : Graph 1 represents isobaric expansion, graph 2 represents isobaric compression.

(A) Expansion   (B) Compression
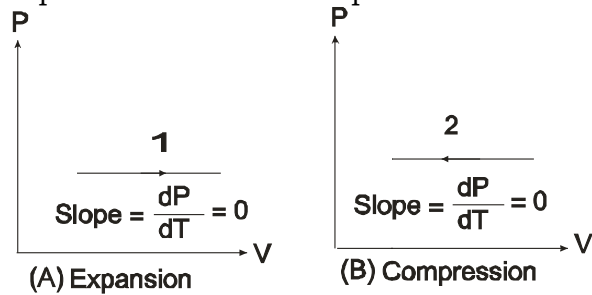
(iv) Specific heat: $C_P = \left(\frac{f}{2} + 1\right)R$

(v) Bulk modulus of elasticity:
$B = \frac{\Delta P}{-\Delta V/V} = 0$ (As $\Delta P = 0$)

(vi) Work done in adiabatic process :
$\Delta W = \int_{V_i}^{V_f} P dV = P \int_{V_i}^{V_f} dV = P(V_f - V_i)$

$\Rightarrow W = P(V_f - V_i) = \mu R(T_f - T_i) = \mu R \Delta T$

(vii) FLOT in isobaric process:
From dQ = dU + dW

$dU = \mu C_V dT = \mu \frac{R}{(\gamma-1)} dT$ and $dW = \mu R dT$

$\Rightarrow (dQ)_P = \mu \frac{R}{(\gamma-1)} dT + \mu R dT = \mu \left(\frac{\gamma}{\gamma-1}\right) R dT$

$\quad = \mu C_P dT$

(viii) Example of isobaric process :
All stae changes occure at constant temperature and pressure.

(a) Boiling of water.

Water $\longrightarrow$ Vapour
Temperature $\longrightarrow$ Constant
Volume $\longrightarrow$ Increases

A part of heat supplied is used to change volume (expansion) against external pressure and remaining part is used to increase its potential energy (kinetic energy remains constant).
From FLOT   dQ = dU + dW
   mL = dU + P(V_f – V_i)

(b) Freezing of water :
Heat is given by water itself. It is used to do work against external atmospheric pressure and to decreases the internal potential energy.

Water $\longrightarrow$ Ice
Temperature $\longrightarrow$ Constant
Volume $\longrightarrow$ Increases

From FLOT   dQ = dU + dW
   - mL = dU + P(V_f – V_i)

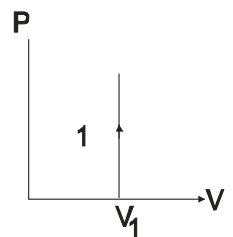**5. Isochoric Or Isometric process :**
In this process volume remain constant.

(i) Equation of state : In this process P and T changes but V = constant. Hence Gay-Lussac law is obeyed in this process i.e., P $\propto$ T $\quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$ = constant

(ii) Indicator diagram: Graph 1 and 2 represent isometric increase in pressure at volume V_1 and isometric decrease in pressure at volume V_2 respectively and slop of indicator diagram $\frac{dP}{dT}$ =
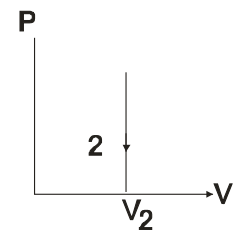
(a) isometric heating :

Pressure $\longrightarrow$ Increases
Temperature $\longrightarrow$ Increases
dQ $\longrightarrow$ Positive
dU $\longrightarrow$ Positive

(b) Isometric cooling :

Pressure $\longrightarrow$ Decrease
Temperature $\longrightarrow$ Decrease
dQ $\longrightarrow$ Negative
dU $\longrightarrow$ Negative

(c) Specific heat : $C_V = \frac{f}{2} R$

(d) Bulk modulus of elasticity:
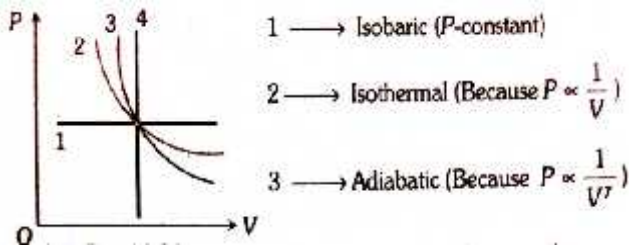$B = \frac{\Delta P}{-\frac{\Delta V}{V}} = \frac{\Delta P}{0} = \infty$

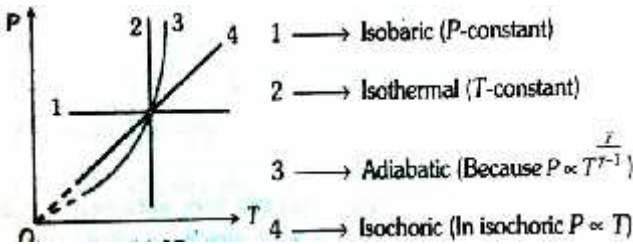**(e) Work done:** As V = constant, W = 0

(f) FLOT in isochoric process:
dQ = dU + 0

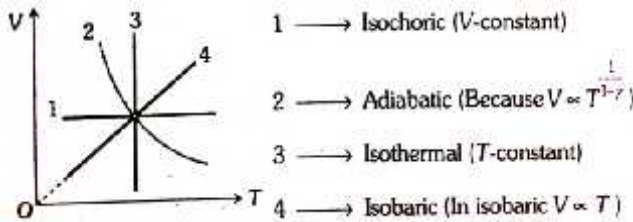$(dQ)_V = dU = \mu \frac{R}{\gamma-1} dT = \frac{P_f V_f - P_i P_i}{\gamma-1}$
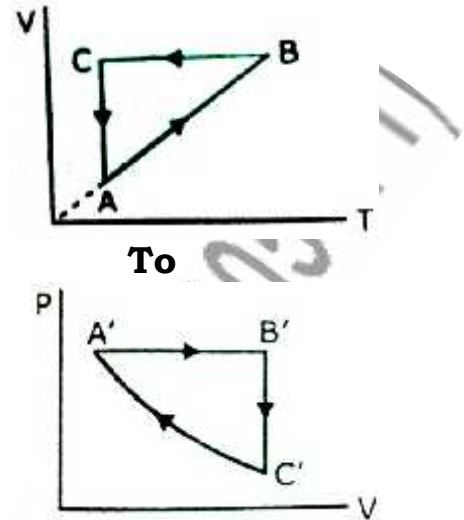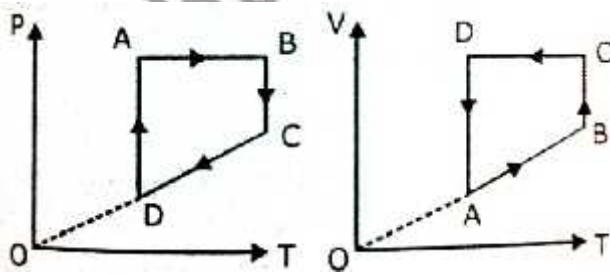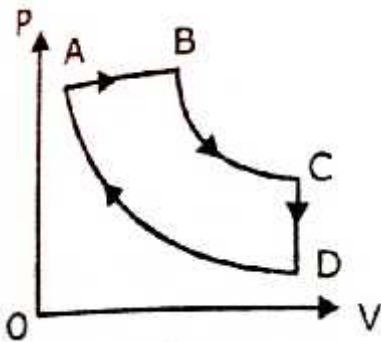
6. Mixed Graphical Representation:
P-V Graph

1 $\longrightarrow$ Isobaric (P-constant)

2 $\longrightarrow$ Isothermal (Because $P \propto \dfrac{1}{V}$)

3 $\longrightarrow$ Adiabatic (Because $P \propto \dfrac{1}{V^\gamma}$)

P-T Graph

1 $\longrightarrow$ Isobaric (P-constant)

2 $\longrightarrow$ Isothermal (T-constant)

3 $\longrightarrow$ Adiabatic (Because $P \propto T^{\frac{\gamma}{\gamma-1}}$)

4 $\longrightarrow$ Isochoric (In isochoric $P \propto T$)

V-T Graph

1 $\longrightarrow$ Isochoric (V-constant)

2 $\longrightarrow$ Adiabatic (Because $V \propto T^{\frac{1}{1-\gamma}}$)

3 $\longrightarrow$ Isothermal (T-constant)

4 $\longrightarrow$ Isobaric (In isobaric $V \propto T$)

7. Conversion of diagram.
(a) P-V diagram to P-T & V-T diagram

TO

(B) V-T to P-V diagram.

To

Reversible and Irreversible Process.

(a)   Reversible Process. A reversible process is one which can be reversed in such a way that all change occurring in direct process are exactly repeated in the opposite order and inverse sense and no change is left in any of the bodies taking part in the process or in the surroundings. For example if the heat is absorbed in the direct process, the same amount of heat should be given out in the reverse process. If the work is done on working substance in direct process then the same amount of work should be done by the working substance in the reverse process.

Condition of reversibility.

(i) There must be complete absence of dissipative force such as friction, viscosity, electric resistance etc.

(ii) The direct and reverse process must take place infinitely slowly.

(iii) The temperature of the system must not differ appreciably from its surroundings.

Example.

(a) All isothermal and adiabatic changes are reversible.

(b) An extremely slow extension or contraction of spring without setting up oscillations.

(c) When a perfectly elastic ball falls from some height on a perfectly elastic horizontal plane, the ball rises to the initial height.

(d) Very slow evaporation or condensation.

(e) Electrolysis is a reversible process; provide the electrolyte does not offer any

resistance to flow of current. If we reverse the direction of current, the direction of motion of ions is also reversed.

It should be remembered that the conditions mentioned for a reversible process can never be realised in practice. Hence, a reversible process is only an ideal concept. In actual process, there is always loss of heat due to friction, conduction, radiation etc.

(b) Irreversible process: Any process which is not reversible exactly is an irreversible process. All natural processes such as conduction, radiation, radioactivity decay, ware fall etc. are irreversible. All practical processes such as free expansion, Joule-Thomson expansion, electrical heating of wire are also irreversible.

W $C_P > C_V$. Let us consider one mole of an ideal gas. From first law of thermodynamics $dQ = dU + dW$ ......(1)

At constant volume $dW = 0$,

$dQ = 1 \times C_V \times dT$

Where C_V = Sp. heat of gas at constant volume.

Using equation (1) $C_V dT = dU + 0$

$$\boxed{C_V = \frac{d}{d}} \qquad ....(2)$$

At constant pressure $dW = PdV$,

$dQ = 1 \times C_P \times dT$

Where C_P = Sp. heat of gas at constant pressure

Using equation (1)

$C_P dT = dU + PdV$

$$\boxed{C_P = \frac{d + P}{d}} \qquad ....(3)$$

It is clear from equation (2) and (3)

$$C_P > C_V$$

Mayer's Formula $(C_P - C_V = R)$

Let us consider one mole of an ideal gas. From first law of thermodynamics $dQ = dU + dW$ ......(1)

At constant volume $dW = 0$,

$dQ = 1 \times C_V \times dT$

Where C_V = Sp. heat of gas at constant volume.

Using equation (1) $C_V dT = dU + 0$

$$\boxed{C_V = \frac{d}{d}} \qquad ....(2)$$

At constant pressure $dW = PdV$,

$dQ = 1 \times C_P \times dT$

Where C_P = Sp. heat of gas at constant pressure

Using equation (1)

$C_P dT = dU + PdV$

$$\boxed{C_P = \frac{d}{d} + \frac{P}{d}} \qquad ....(3)$$

using equation (2)

$C_P = C_V + \frac{P}{d}$

$$C_P - C_V = \frac{P}{d} \qquad ....(4)$$

We have $P V = R T$

Differentiating both side

$P\, dV + V\, dP = R\, dT + T\, dR$

But $dP = 0$ & $dR = 0$

$P\, dV = R\, dT$

using equation (4) we get

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

Second Law of Thermodynamics.

Second law of thermodynamics gives information about the direction of flow of heat.

(1) Clausius statement : It is impossible for a self acting machine, unaided by external agency to transfer heat from a cold body to a hot body. In other words, heat cannot itself pass from a colder to a hotter body.

(2) Kelvin-Planck statement. It is impossible for an engine working in a cyclic process to extract heat from a reservoir and convert it completely into work. In other words, 100% conversion of heat into work is impossible.

Carnot Engine . Carnot designed a theoretical engine which is free from all the defect of practical engine. This engine cannot be realised in actual practice, however, this can be taken as a standard against which the performance of an actual engine can be judged.

It consists of the following three parts as shown in figure.
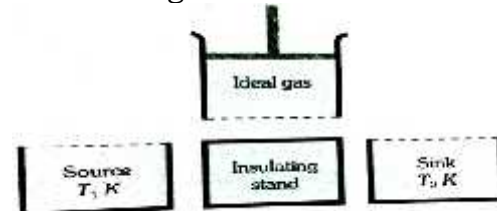
(i) Source. The source is at a fixed temperature T_1 from which the heat engine draws heat. It is supposed to possess infinite thermal capacity and as such any amount of heat can be drawn from it without changing its temperature.

(ii) Sink. The sink is at fixed lower temperature T_2 to which any amount of heat can be rejected by engine. It has also

infinite thermal capacity and as such its temperature remains constant at T_2 even if a lot of heat is given to it.

(iii) Working substance. A perfect gas acts as the working substance. It is contained in a cylinder with non-conducting sides and frictionless piston. *A part from these essential parts, there is provided a perfectly insulating stand with the engine so that the working substance can undergo adiabatic operation when desired.*

Carnot Engine/Cycle. A reversible heat engine operating between two temperature is called a Carnot Engine.
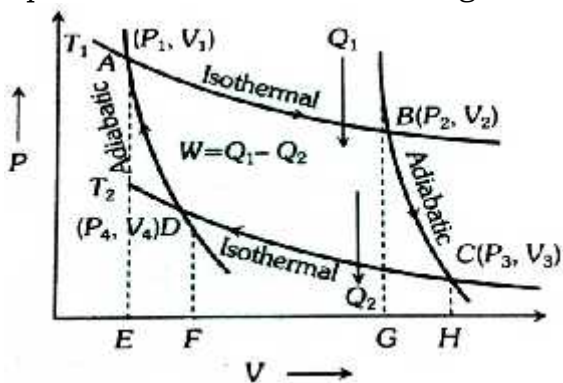
(a) Step A-B: Isothermal Expansion of the gas taking its state from (P_1, V_1, T_1) to (P_2, V_2, T_1). The heat absorbed by gas (Q_1) from the source at temperature T_1 is equal to work done (W_{A-B}) by the gas on the environment.

$$W_{A-B} = Q_1 = \mu RT_1 \log_e \left(\frac{V_2}{V_1}\right) = \text{Area ABGEA} \dots (1)$$

(b) Step B-C : Adiabatic expansion of the gas from (P_2, V_2, T_1) to (P_3, V_3, T_2),

$$W_{B-C} = \frac{\mu R(T_1 - T_2)}{\gamma - 1} = \text{Area BCHGB} \qquad \dots \dots (2)$$

(c) Step C-D : Isothermal compression of the gas from (P_3, V_3, T_2) to (P_4, V_4, T_2).

$$W_{B-C} = Q_2 = \mu RT_2 \log_e \left(\frac{V_3}{V_4}\right) = \text{Area CDFHC} \dots (3)$$

(d) Step D-A : Adiabatic Compression of the gas from (P_4, V_4, T_2) to (P_1, V_1, T_1).

$$W_{D-A} = \frac{\mu R(T_1 - T_2)}{\gamma - 1} = \text{Area DAEFD} \qquad \dots \dots (4)$$

Total Work done

$$W = W_{A-B} + W_{B-C} - W_{B-C} - W_{D-A}$$

$$W = \mu RT_1 \log_e \left(\frac{V_2}{V_1}\right) - \mu RT_2 \log_e \left(\frac{V_3}{V_4}\right) = Q_1 - Q_2$$

= Area ABCDA

The efficiency of the engine $= \frac{W}{Q_1}$

$$= 1 - \frac{Q_2}{Q_1} = 1 - \left(\frac{T_2}{T_1}\right)\frac{l_1 \ e\left(\frac{V_3}{V_1}\right)}{l_1 \ e\left(\frac{V_2}{V_1}\right)} \qquad \dots \dots (5)$$

Now, as step B-C is an adiabatic process

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1} \quad \frac{V_2}{V_3} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}} \dots \dots (6)$$

Similarly step D-A is an adiabatic process

$$T_2 V_4^{\gamma-1} = T_1 V_1^{\gamma-1} \quad \frac{V_1}{V_4} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}} \dots \dots (7)$$

Equating (6) & (7).

$$\frac{V_3}{V_4} = \frac{V_2}{V_1} \dots \dots \dots \dots \dots (8)$$

Using eq^n (8) in eq^n (5), $\boxed{= 1 - \frac{T_2}{T_1}}$

i.e., in Carnot cycle $\boxed{\frac{Q_1}{Q_2} = \frac{T_1}{T_2}}$

Carnot Theorem. No irreversible engine can have efficiency greater than Carnot reversible engine working between the same hot and cold reservoir and the efficiency of the Carnot engine is independent of the nature of the working substance.

Refrigerator. It is opposite of heat engine, it extract heat (Q_2) from a cold reservoir, does some work W on it and injects heat $(Q_1 = Q_2 + W)$ in the hot reservoir. The concept of efficiency does not apply in case of a refrigerator, because it is always more than 100% being equal to output upon input and output $(Q_2 + W)$ is always greater than the input Q_2.
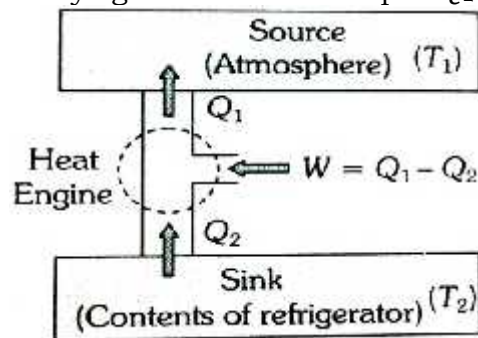
Coefficient of Performance : $\beta = \frac{Q_2}{W}$

$$= \frac{Q_2}{Q_1 - Q_2} = \frac{1}{\frac{Q_1}{Q_2} - 1} \qquad \text{But} \qquad \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

$$\boxed{= \frac{T_2}{T_1 - T_2}} \quad \text{Or} \quad \boxed{= \frac{1 - \eta}{\eta}}$$