

# UNIT-1 Fundamental Ideas of Thermodynamics

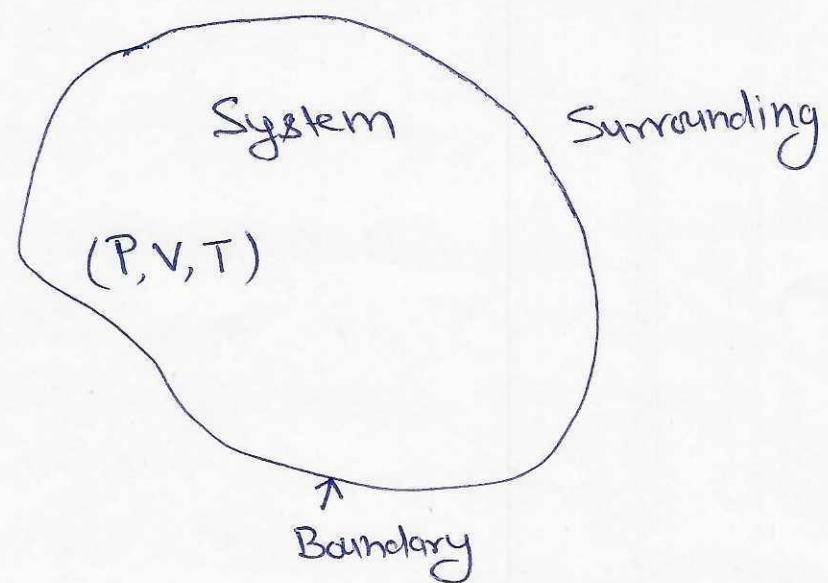
Thermodynamics is a branch of Science which deals with Study of heat, temperature and their relation to other form of Energy.

Heat — Heat is the form of Energy that is transferred between Systems or objects with different temperatures. Flowing from the high temperature System to the low temperature System.

Temperature — The degree of hotness or coldness of the substance.

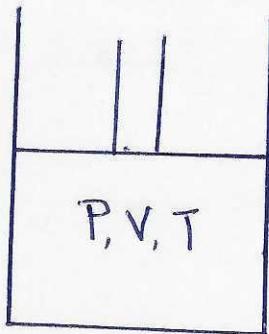
# The Concept of a "System", "State", "Equilibrium" and "Process" —

System — A Thermodynamic System is a body of matter and/or radiation confined in Space by walls which separate it from its Surroundings having a Certain Value of pressure, Volume and Temperature Called Thermodynamic System.

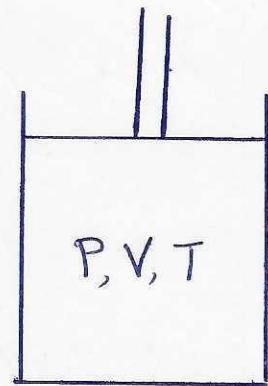


State — State is the condition of the System identified by thermodynamic properties.

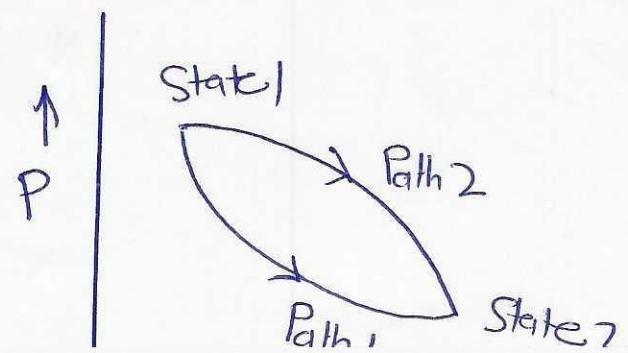
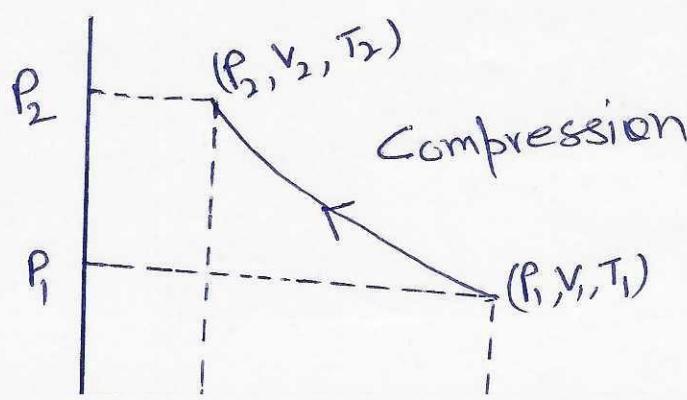
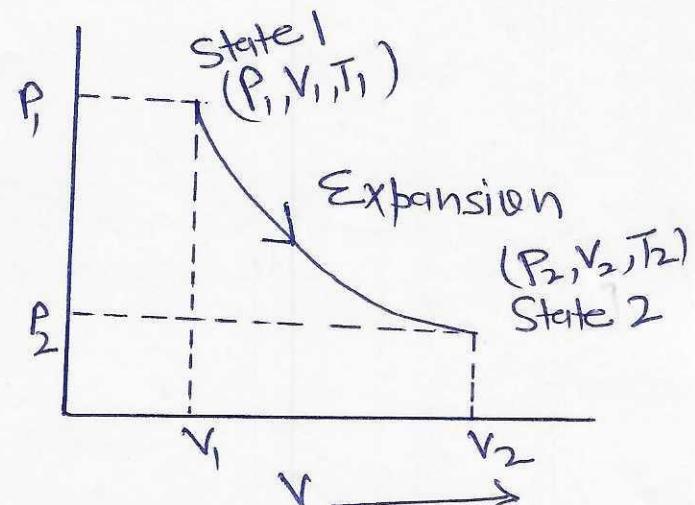
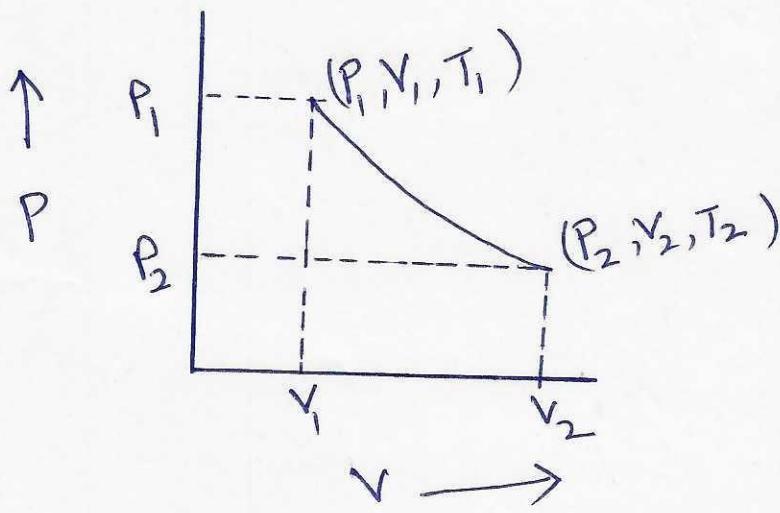
An operation in which properties of the System changes is called Change of State.



State 1

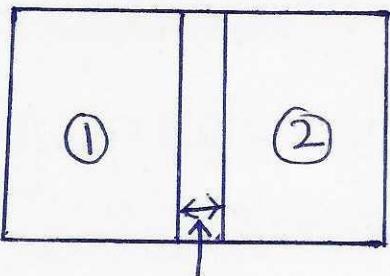


State 2

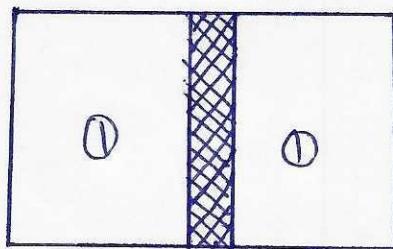


## Thermal Equilibrium —

Two Systems are in Thermal Equilibrium if there is no net flow of Thermal Energy between them when they are connected by a path permeable to heat. Thermal Equilibrium obeys the Zeroth Law of Thermodynamics.



Gas Vessel ① and ② Separated by an adiabatic wall



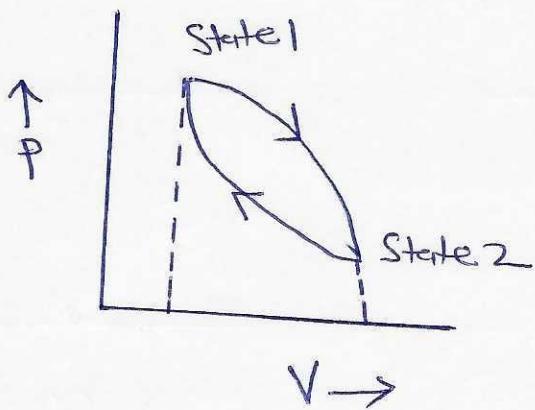
Gas Vessel ① and ② Separated by a diathermic Wall

Let the pressure and volume of the gases be  $(P_1, V_1)$  and  $(P_2, V_2)$  respectively. If the two vessels are separated by an adiabatic wall (does not allow the flow of heat) then any possible pair of values  $(P_1, V_1)$  will be in equilibrium with any possible pair of values  $(P_2, V_2)$ . If ① and ② are now separated by a diathermic wall (allows heat to flow through it) then the pressure and volume of ~~the same~~ two gases change to  $(P'_1, V'_1)$  and  $(P'_2, V'_2)$  such that the new states of ① and ② are in equilibrium with each other. There is no more flow of heat. The two

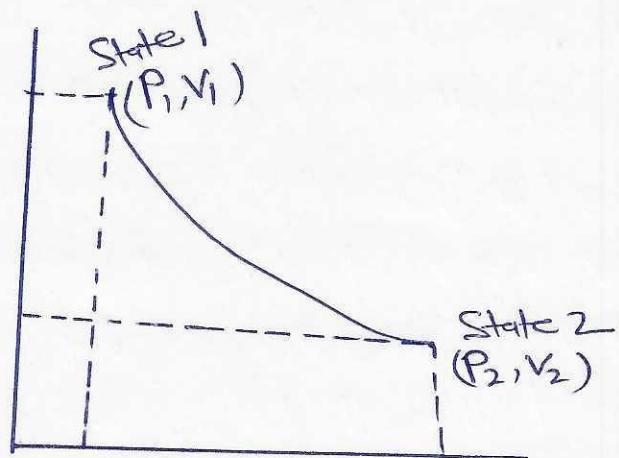
## Thermodynamic Process

Thermodynamic process represents a transition in which a system changes from one state to another

Cyclic process — Any process in which the system returns to its initial state after undergoing a series of changes is known as a cyclic process.



Non-Cyclic process — A non-cyclic process is one in which the system does not return to its initial state



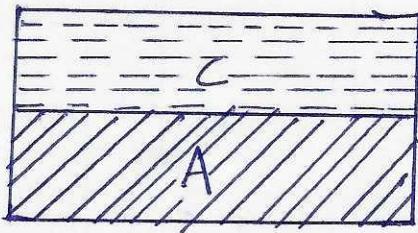
## Equation of State —

The mathematical relation between the pressure, Volume and temperature of the thermodynamic System is called its equation of state.

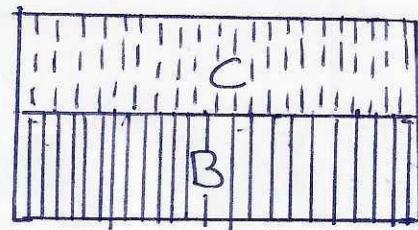
for example, the equation of state for n moles of an ideal gas can be written as

$$PV = nRT.$$

## Zeroth Law of Thermodynamics —



fig①



fig②

Mathematically,

A is thermal equilibrium with C  
B also with C

So, A is also thermal equilibrium with B.

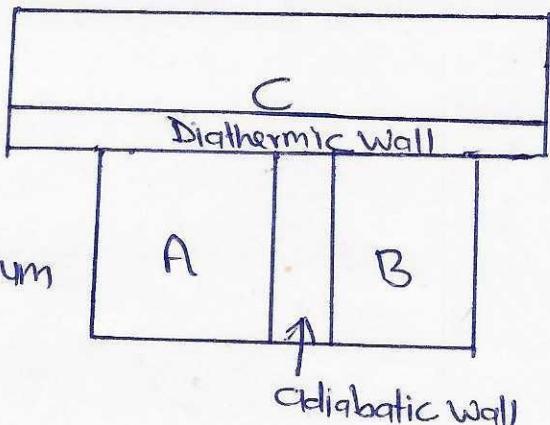


fig ③

It states that if two systems A and B are separately in thermal equilibrium with the third system C then A and B are also in thermal equilibrium with each other.

Figure ③ Shows two Systems A and B Separately by an adiabatic wall. They are separated from System C by a diathermic wall. The Systems A and C and B and C will reach thermal equilibrium separately. If adiabatic wall between A and B is removed, there will be no exchange of heat showing that A and B are already in thermal equilibrium.

From Fig ① and ②

A is thermal equilibrium with C

$$\text{So } T_A = T_C$$

B is also thermal equilibrium with C

$$\text{So, } T_B = T_C$$

So we can say

$$T_A = T_C = T_B$$

This Shows that

$$T_A = T_B$$

Temperature of System A = Temperature of System B

## First Law of Thermodynamics

According to the First Law of Thermodynamics, if some heat is supplied to a system which is capable of doing work, then the quantity of heat absorbed by the system will be equal to the sum of the increase in its internal energy and the external work done by the system on the surroundings.

Let  $dQ$  is the heat supplied to the system by the surroundings,  $dw$  is the work done by the system on the surroundings and  $dU$  is the change in the internal energy of the system

Then

$$dQ = dU + dw$$

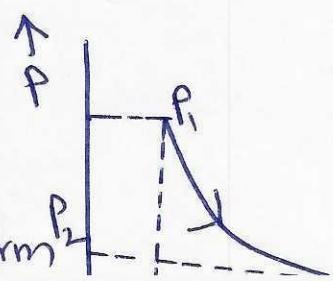
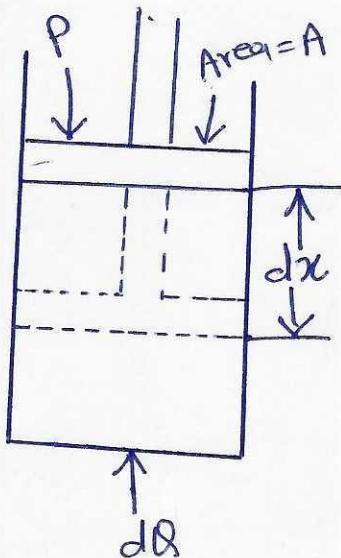
Let the system is a gas contained in a cylinder provided with a movable piston.

Then the gas does work in moving the piston. The work done by the system against a constant pressure  $P$  is

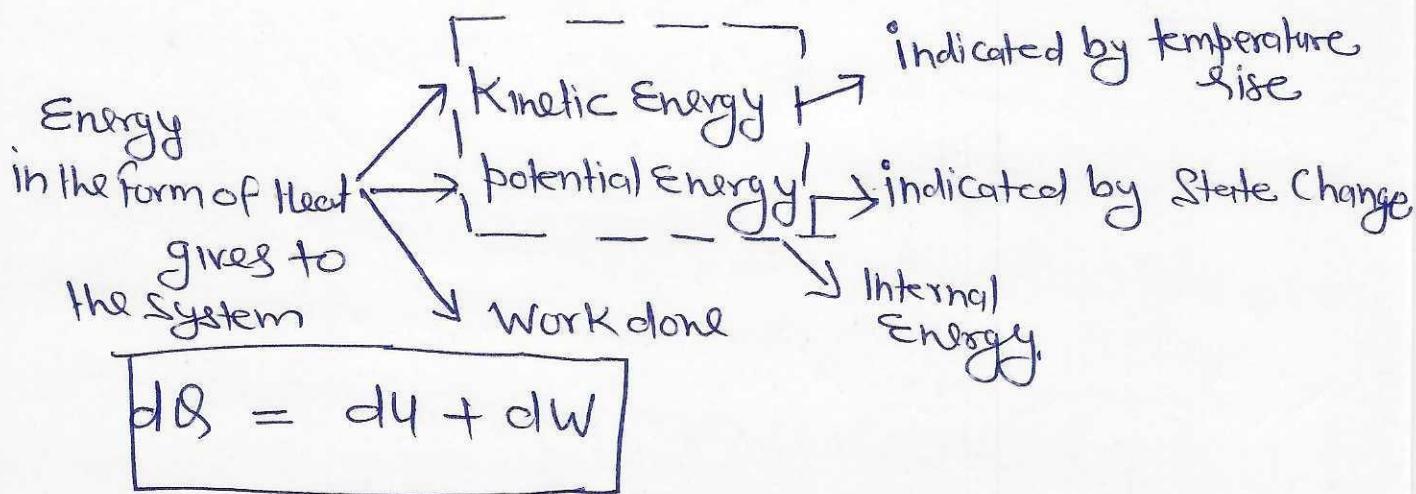
$$\begin{aligned} dw &= \text{Force} \times \text{distance} \\ &= \text{Pressure} \times \text{Area} \times \text{distance} \\ &= PA dx \end{aligned}$$

$$dw = PdV$$

So the first law of thermodynamics takes the form



# Heat, Internal Energy and Work



Heat — Heat is the mode of Energy transfer due to  
( $\delta$ ) temperature difference between System and  
Surroundings

Work — Work is the mode of Energy transfer by applying  
( $W$ ) force on to a body ~~which~~ or system which  
produce motion.

Internal Energy — The Internal Energy of a System is the  
 $\frac{(U)}{(U)}$  Sum of molecular Kinetic Energy and  
molecular potential Energy when the centre of  
mass of the System is at ~~not~~ rest.

The molecules of a gas are always in a state of random motion. As the temperature increases, the average kinetic energy of the gas molecules also increase.

Thus the internal kinetic energy of a gas is a function of its temperature.

The molecules of a real gas exert mutual force of attraction on one another. Hence they possess intermolecular potential energy. If the volume of the gas increases, work is done by the gas against intermolecular attraction so, its potential energy increases. Thus intermolecular potential energy of a real gas is a function of its volume.

[\*\* "For gases internal energy is only kinetic indicated by temperature" ]

### Sign Conventions used—

- 1) Heat absorbed by a system is positive. Heat given out by a system is negative.
- 2) Work done by a system is positive. Work done on a system is negative.
- 3) The increase in internal Energy of a system is positive. The decrease in internal Energy of a system is negative.

# Applications of First Law of Thermodynamics —

## 1 — Isothermal Expansion —

First Law of Thermodynamics

$$dQ = dU + dW$$

In isothermal Expansion, there is no change in temperature.

$$\text{So, } \Delta T = 0 \text{ or } dT = 0$$

Therefore, no change in internal Energy.

$$\Delta U = 0 \text{ or } dU = 0$$

So

$$dQ = dW$$

All given thermal Energy is converted into work alone  
by the System

## 2) Adiabatic Expansion —

First law of Thermodynamics

$$dQ = dU + dW$$

In Adiabatic Expansion, no heat is transferred

$$\text{So, } dQ = 0$$

Therefore

$$0 = dU + dW$$

$$dW = -dU$$

$$PdV = -dU$$

$+dW = +PdV$  gives sudden expansion

and  $-dU$  gives internal energy decreases  
i.e. temperature decreases

OR

$$-dW = dU$$

$$-PdV = dU$$

$-PdV$  gives sudden compression

~~$dU$~~

$+dU$  gives internal energy increases

i.e. temperature increases

3)

Boiling Process —

First Law of Thermodynamics

$$dQ = dU + dW$$

$$dU = dQ - dW$$

or  $dU = dQ - P(dV)$

$$dU = dQ - P(V_2 - V_1)$$

At boiling point Temp. does not change i.e. no change in kinetic energy. only state change.  
Water  $\Rightarrow$  Vapour  
So, only change in Potential Energy.

#### 4. Melting Process —

First law of Thermodynamics

$$dQ = dU + dW$$

In melting process, negligible Change in Volume

$$\text{So } dV = 0$$

Therefore

$$dQ = dU + PdV$$

$$dQ = dU + 0$$

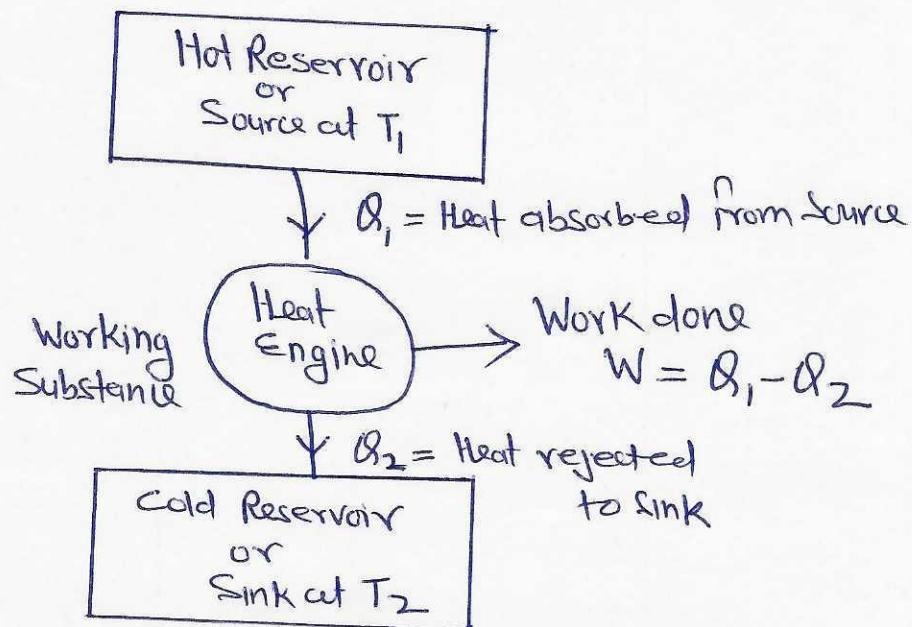
$$\boxed{dQ = dU}$$

## Limitations of the first Law of Thermodynamics

- 1) It does not say anything about the direction of flow of heat:  
Heat always flows from a hot body to a cold body  
first law does not give any reason as to why heat cannot flow from a cold body to a hot body.
- 2) It does not tell whether a process is possible or not:  
First law explains the stopping of a revolving wheel due to conversion of its kinetic energy into heat due to friction. But it fails to explain as to why the heat energy cannot be converted into kinetic energy of rotation of wheel and put it back into rotation.
- 3) It does not tell that how ~~much~~ much work we obtain:  
No heat engine can convert all the heat extracted from the source into mechanical work continuously without rejecting a part of it to the surrounding.

## Heat Engine —

Heat Engine is a device that converts heat energy into work. It takes heat from a reservoir then does some work like moving a piston, and finally discharges some heat energy into the sink.



Source — It is a heat reservoir at high temperature  $T_1$ .

It is supposed to have infinite thermal capacity so that any amount of heat can be drawn from it without changing its temperature.

Sink — It is a heat reservoir at a lower temperature  $T_2$ . It has also infinite thermal capacity so that any amount of heat can be added to it without changing its temperature.

Working Substance — Working Substance is any material (solid, liquid or gas) which performs mechanical work when heat is supplied to it.

Working — In every cycle of operation, the working substance absorbs a definite amount of heat  $Q_1$  from the source at higher temperature  $T_1$ , converts a part of this heat energy into mechanical work  $W$  and rejects the remaining heat  $Q_2$  to the sink at lower temperature  $T_2$ . The work done  $W$  in a cycle is transferred to the environment by some arrangement.

### Efficiency of a heat Engine —

The efficiency of a heat engine is defined as the ratio of the net work done by the engine in one cycle to ~~the~~ the amount of heat absorbed by the working substance from the source.

Net heat absorbed in a cycle = Work done

$$Q_1 - Q_2 = W$$

### The Efficiency of heat Engine

$$\eta = \frac{\text{Work done by engine}}{\text{Heat absorbed from the Source}}$$

$$= \frac{W}{Q_1}$$

$$\eta = \frac{Q_1 - Q_2}{Q_1}$$

$$\eta = 1 - \frac{Q_2}{Q_1}$$

The —

## Second Law of Thermodynamics —

According to Kelvin-Planck Statement —

It is impossible to construct an engine, which will produce no effect other than extracting heat from a reservoir and performing an equivalent amount of work.

This is applicable to a heat engine. It indicates that a working substance, operating in a cycle, cannot convert all the heat extracting from the source into mechanical work. It must reject some heat to the sink at a lower temperature.

According to Clausius Statement —

It is impossible for a self acting machine, to transfer heat from a body to another at higher temperature.

This is applicable to a refrigerator. The working substance can absorb heat from a cold body only if work is done on it. The work is done by an electric compressor. If no external work is done, the refrigerator will not work.

Significance of Second Law —

- 1) According to Second Law of Thermodynamics, the efficiency of a heat engine can never be unity. i.e. the heat released to the cold reservoir can never be made zero.
- 2) The coefficient of performance of a refrigerator can never be infinite i.e. external work can never be zero.

## Reversible and Irreversible Process

### Reversible Process

Any process which can be made to proceed in the reverse direction by variation in its condition such that any change occurring in any part of the direct process is exactly reversed in the corresponding part of the reverse process is called reversible process.  
for example—

- 1) The process of gradual compression and extension of an elastic spring is approximately reversible.
- 2) A working substance taken along the complete Carnot's cycle.

### Irreversible process

Any process which cannot be retraced in the reverse direction exactly is called an irreversible process.

for example—

- 1) Rusting of iron
- 2) Sudden expansion or contraction of gas
- 3) Dissolution of salt in water

Entropy — Entropy measures the degree of disorderliness of the system.

$$\Delta S = \frac{\Delta Q}{T}$$

when  $T$  is constant

or  $dS = \frac{dQ}{T}$

$$\int dS = \int \frac{dQ}{T}$$

$$\Delta S = \int \frac{dQ}{T}$$

when  $T$  is not constant

When heat is given to the system, Change in Entropy is positive.

When heat is taken from the system, Change in Entropy is negative.

Entropy is a state function. it depends on the state of the System and not the path that is followed.

1) Change in Entropy for Spontaneous process

$$\Delta S = S_f - S_i$$

$$\Delta S = +ve$$

$$\Delta S > 0$$

2) For reversible Process —



Change in Entropy  $\Delta S = + \frac{\Delta Q}{T}$   
 $A \rightarrow B$

for B to A Change in entropy

$$\Delta S = - \frac{\Delta Q}{T}$$

$$\Delta S_{\text{reversible}} = + \frac{\Delta Q}{T} - \frac{\Delta Q}{T} \\ = 0$$

3) Isolated System —

In isolated System  $\Delta Q = 0$

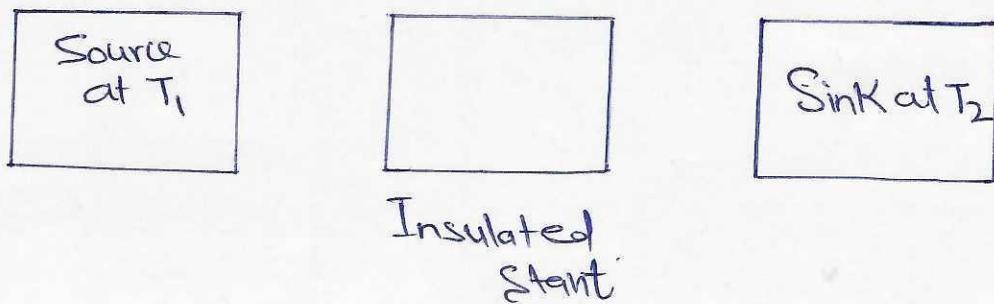
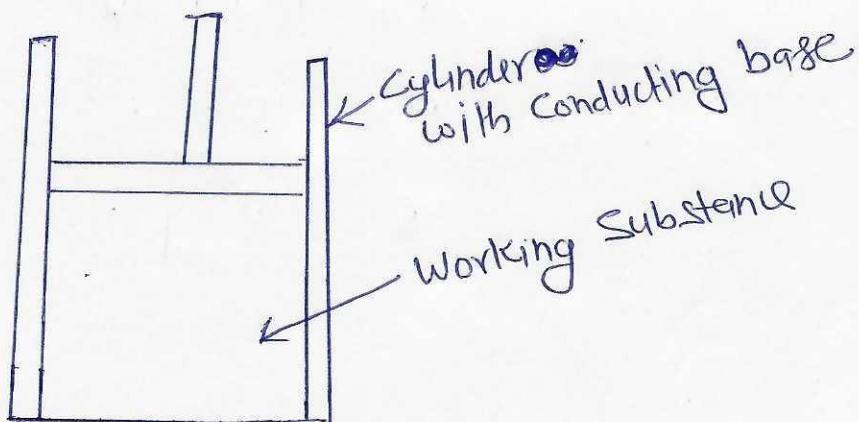
$$\Delta S_{\text{total Entropy}} = \Delta S_{\text{System}} + \Delta S_{\text{surrounding}}$$

~~$\Delta S_{\text{total}}$~~

$$\Delta S_{\text{total Entropy}} = 0$$

\*\* But for Spontaneous process  $\Delta S$  of System  $> 0$

Carnot Engine — It is an ideal reversible heat engine that operates between two temperatures  $T_1$  (Source) and  $T_2$  (Sink). It operates through a series of two isothermal and two adiabatic processes called Carnot Cycle. It is a theoretical heat engine with which the ~~operating~~ efficiency of practical engines is compared.



Carnot Engine has the following main parts

1 — Cylinder — This is the main part of engine has Conducting base and Insulating walls. It is filled with an insulating and frictionless piston.

**Source** — It is a heat reservoir at a higher temperature  $T_1$ , from which the engine draws heat. It is supposed that the source has an infinite thermal capacity and so any amount of heat can be drawn from it without changing its temperature.

**Sink** — It is a heat ~~reservoir~~ reservoir at a lower temperature  $T_2$  to which any amount of heat can be rejected by the engine. It has also infinite thermal capacity and so any amount of heat can be added to it without changing its temperature.

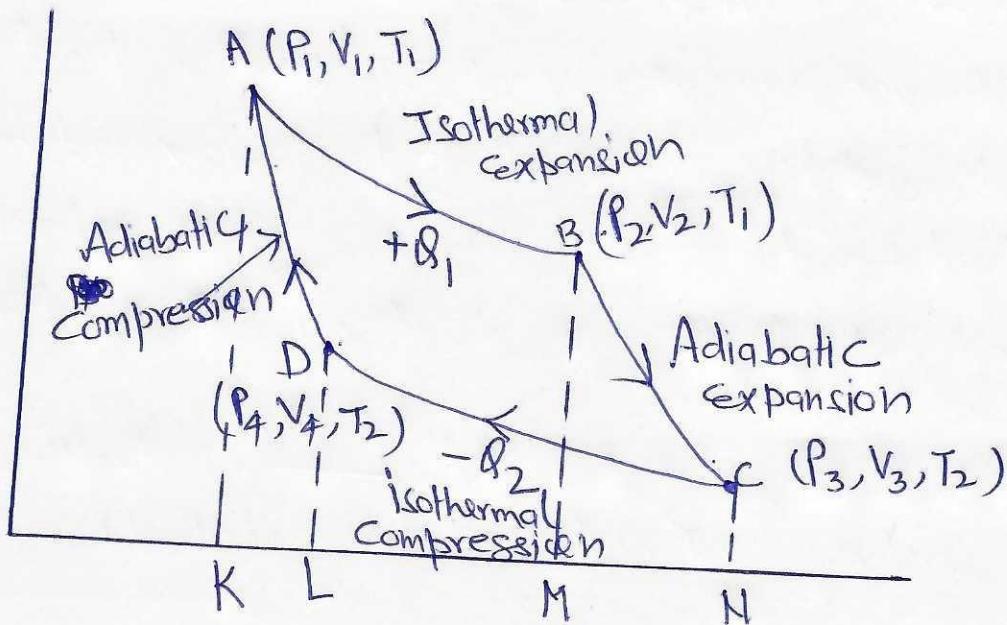
**Working Substance** — The working substance is an ideal gas contained in the cylinder.

**Insulating Stand** — When the base of the cylinder is attached to the insulating stand, the working substance gets isolated from the surroundings.

**Carnot Cycle** — The working substance is carried through a reversible cycle of the following four steps.

## Isothermal Expansion

**Step 1 — Place the Cylinder on the Source So that the gas acquires the temperature  $T_1$  of the source.**  
 The gas is allowed to expand by slow outward motion of the piston. The temperature of the gas falls. As the gas absorbs the required amount of heat from the source, it expands isothermally.



If  $\dot{Q}_1$  heat is absorbed from the source and  $W_1$  work is done by the gas in isothermal expansion which takes its state from  $(P_1, V_1, T_1)$  to  $(P_2, V_2, T_2)$  then

$$W_1 = \dot{Q}_1 = nRT_1 \ln\left(\frac{V_2}{V_1}\right) = \text{Area of ABMKA}$$

**Step 2 — Adiabatic Expansion — The gas is now placed on the insulating stand and allowed to expand slowly till its temperature falls to  $T_2$**

If  $W_2$  Work is done by the gas in the adiabatic expansion which takes its state from  $(P_2, V_2, T_1)$  to  $(P_3, V_3, T_2)$

Then

$$W_2 = \frac{n R (T_1 - T_2)}{r-1} = \text{area BCNMB}$$

Step 3 — Isothermal Compression —

The gas is now placed in thermal contact with the sink at temperature  $T_2$ . The gas is slowly compressed so that as heat is produced it easily ~~is released~~ flows to the sink. The temperature of the gas remains constant at  $T_2$ .

If  $Q_2$  heat is released by the gas to the sink and  $W_3$  work is done on the gas by the surroundings in the isothermal compression which takes its state from  $(P_3, V_3, T_2)$  to  $(P_4, V_4, T_2)$  then

$$W_3 = Q_2 = n R T_2 \ln \left( \frac{V_3}{V_4} \right) = \text{Area CDLNC}$$

Step 4 — Adiabatic Compression — The cylinder is again placed on the insulating stand. The gas is further compressed slowly till its returns to its initial state  $(P_1, V_1, T_1)$  then

$$W_4 = \frac{n R (T_1 - T_2)}{r-1} = \text{area DAKLD}$$

Net Work done by the gas per Cycle —

Total work done by the gas =  $W_1 + W_2$

Total work done on the gas =  $W_3 + W_4$

∴ Net Work done by the gas in one complete cycle,

$$W = W_1 + W_2 - (W_3 + W_4)$$

But  $W_2 = W_4$

$$W = W_1 - W_3 = Q_1 - Q_2$$

Also  $W = \text{area } ABMKA + \text{area } BCNMB$   
- area  $CDLNC$  - area  $DAKLD$

$$W = \text{area } ABCDA$$

Hence in a Carnot Engine, the mechanical work done by the gas per cycle is numerically equal to the area of ~~of~~ the Carnot cycle.

## Efficiency of Carnot Engine —

It is defined as the ratio of the net work done per cycle by the engine to the amount of heat absorbed per cycle by the working substance from the source.

$$\text{Eff} \quad \eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

$$\begin{aligned}\eta &= 1 - \frac{Q_2}{Q_1} \\ &= 1 - \frac{nRT_2 \ln(V_3/V_4)}{nRT_1 \ln(V_2/V_1)}\end{aligned}$$

Step 2 is an adiabatic expansion, therefore

$$T_1 V_2^{V-1} = T_2 V_3^{V-1} \quad \text{--- (A)}$$

Step 4 is an adiabatic compression, therefore

$$T_1 V_1^{V-1} = T_2 V_4^{V-1} \quad \text{--- (B)}$$

On dividing Eqn (A) by Eqn (B)

$$\left(\frac{V_2}{V_1}\right)^{V-1} = \left(\frac{V_3}{V_4}\right)^{V-1}$$

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$