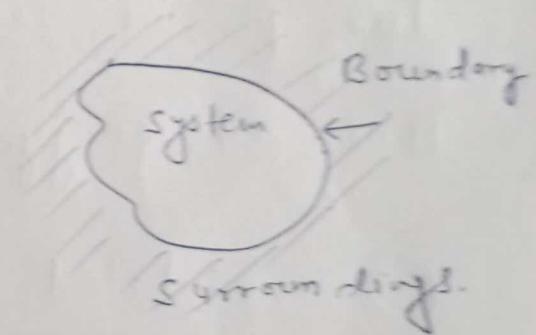
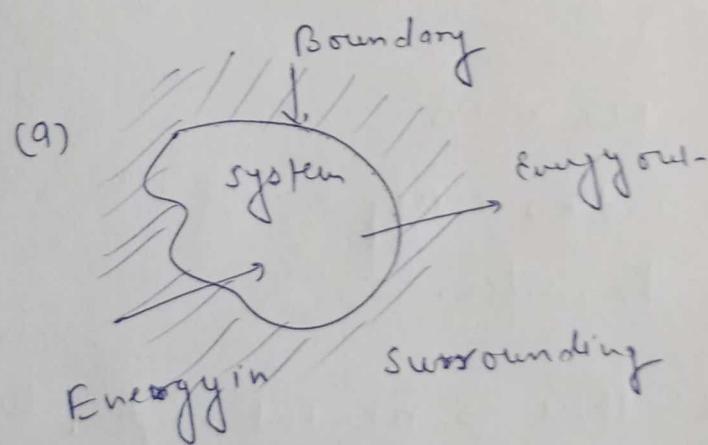


①

Thermodynamics. It is the science of energy transfer and its effect on the physical properties of substances. It is concerned with the relationship between heat and all other kinds of energy such as chemical, electrical etc.

There are certain terms in thermodynamics which are used with specific connotation.

System:- A thermodynamic system is defined as the quantity of matter or a region in space upon which attention is concentrated in the analysis of ~~pb~~ problem.



Closed system

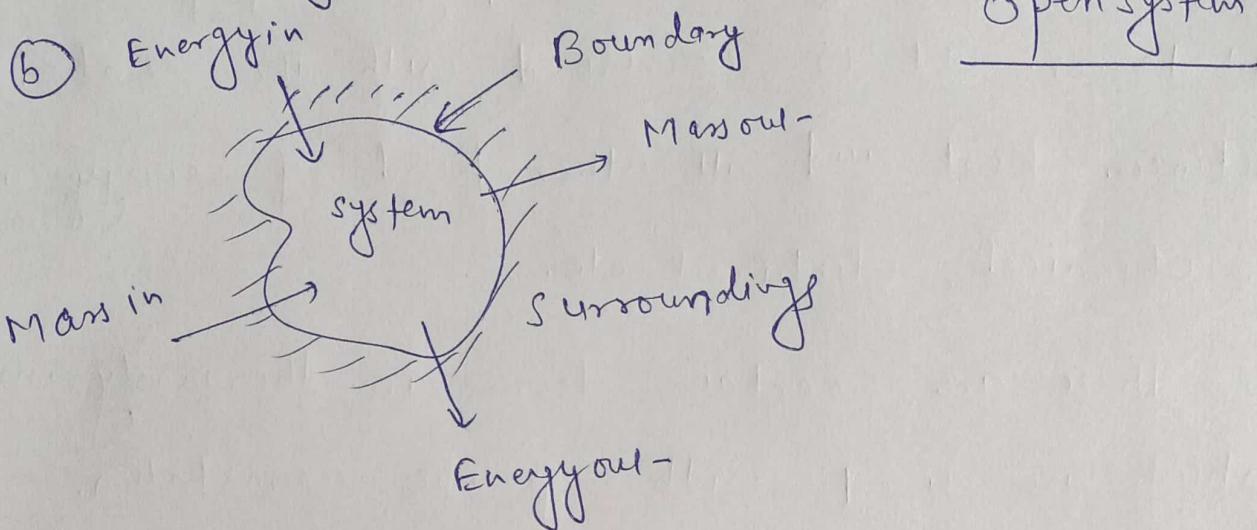
(also termed as  
control mass)

(No mass transfer.)

\*. Ex. A quantity of gas enclosed in a cylinder fitted with a movable piston (fig.)

(a) Closed system is a system of fixed mass. There is no mass transfer across the system boundary. There may be energy transfer into or out-of the system.

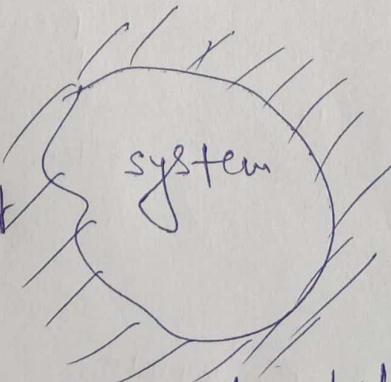
Ex. A certain quantity of fluid in a cylinder bounded by a piston.



In open system; there may be energy transfer.

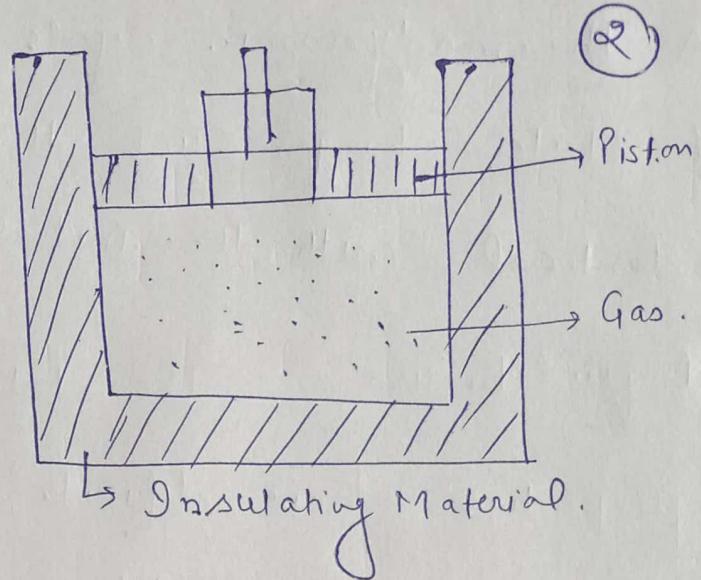
Ex. Air compressor in which air enters at low pressure and leaves at high pressure and there are energy transfers across the system boundary

c) Isolated. :- No mass and no energy transfer.



In isolated system, there is no interaction between the system and the surroundings. It is of fixed mass and energy, and there is no mass or energy transfer across the system boundary

Note:- boundary may be  
fixed or movable.



(fig 9)

State:- Every system has certain characteristics by which its physical conditions may be described. e.g. volume, temperature, pressure etc., such characteristics are called "properties of the system." When all the properties of a system have definite values, the system is said to exist at a definite state.

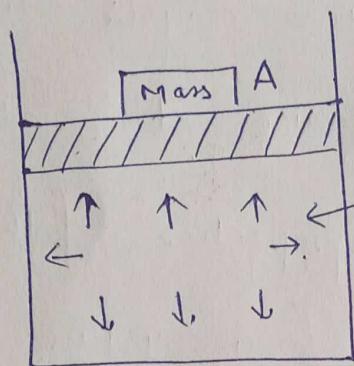
Any operation in which one or more of the properties of a system changes is called a change of state.

Path:- The succession of states passed through during a change of state is called path of the change state.

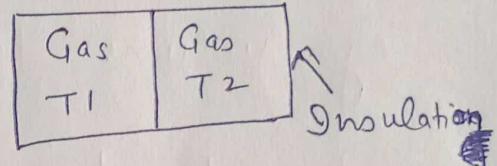
Process:- When the path is completely specified the change of state is called a process.

A thermodynamic cycle is defined as a series of state changes such that the final state is identical with the initial state.

Equilibrium:- The state of a system in which properties have definite, unchanged values as long as external conditions are unchanged is called an equilibrium state.



Gas at  
pressure,  
 $p$ .



(Thermal  
equilibrium)

(Mechanical equilibrium)

If a system is simultaneously in state of mechanical equilibrium (no unbalance forces), thermal equilibrium (no temperature difference) and chemical equilibrium, then system is said to be in thermodynamics equilibrium.

Thermodynamic Equilibrium:-

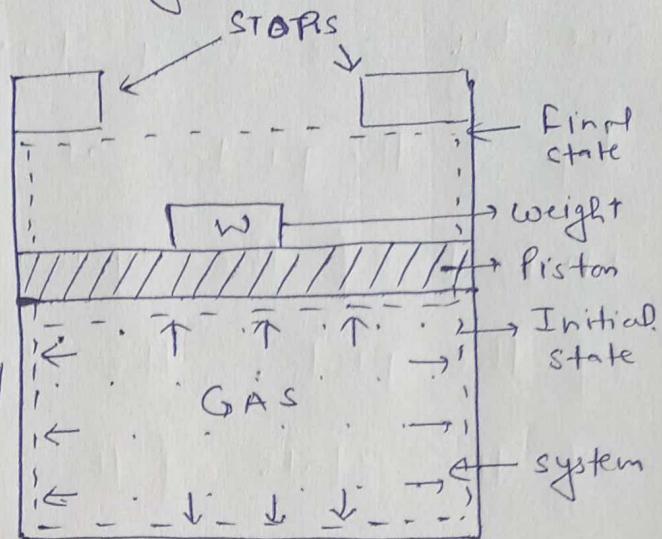
A system is said to be thermodynamic equilibrium if none of the thermodynamic variables determining its state changes with time.

## Quasi-static process:-

(3)

If the state of a system changes, then it is undergoing a process.

Let us consider a system of gas contained in a cylinder. The system initially is in equilibrium state represented by  $(P_1, V_1, T_1)$ .



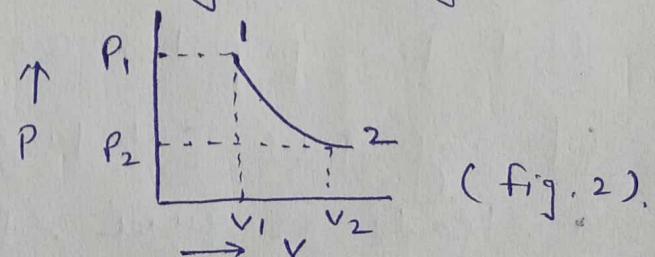
$P_1, V_1, T_1$  (fig-1)

The weight on the piston just balances the upward force exerted by the gas. If the weight is removed, there will be an unbalanced force between the system and surroundings, and under gas pressure the piston will move up till hits the stops. The system again comes to an equilibrium state being described by the properties  $P_2, V_2, T_2$ .

But the intermediate states passed through by the system are ~~not~~ non equilibrium states which cannot be described by thermodynamic co-ordinates.

Fig.-2 shows point 1 and 2 as the initial and final equilibrium states joined by a dotted line.

Now if the single weight  $P$  on the system piston is



(fig. 2).

made up of many very small pieces of weights.

and these weights are removed one by one very slowly from

top of the piston at any instant of the upward travel of the piston, the departure of the state of the system

from the thermodynamic

equilibrium state will be infinitesimally small,

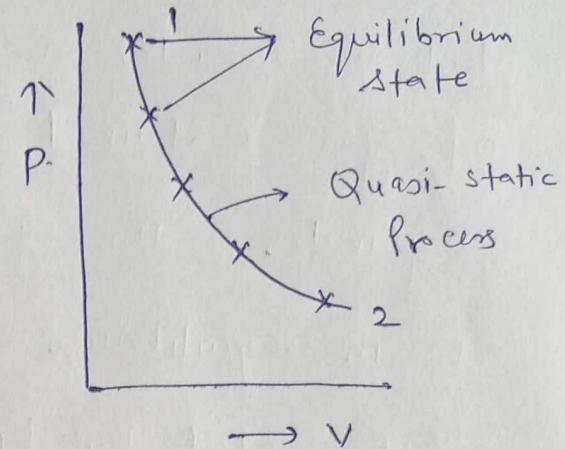
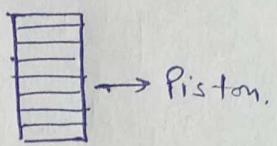
so every state passed through by the system will be an equilibrium state. Such a process, which is a locus of all the equilibrium points passed through by the system, is known as quasi-static process.

→ A quasi-static process is thus a succession of equilibrium states.

→ A quasi-static process is also called a reversible process.

Equation of state:- It is an experimental fact-

that two properties are needed to define the state of any pure substance in equilibrium or undergoing a steady or quasi-steady process.



In other words if we know  $v$  &  $T$ , we (4) know  $P$ . Any of these is equivalent to an  $(P, v T)$  equation of  $f(P, v, T) = 0$ , which is known as an equation of state.

The equation of state for an ideal gas, which is very good approximation to real gases at conditions that are typically is

$$Pv = RT.$$

where  $v$  — volume per mole of gas.

$R$  — Universal gas Constant

$$= 8.31 \text{ J} \cdot \text{K}^{-1} \text{mol}^{-1}$$

( Joules/Kelvin)

Temperature:- The quantity that characterizes the degree of heat.

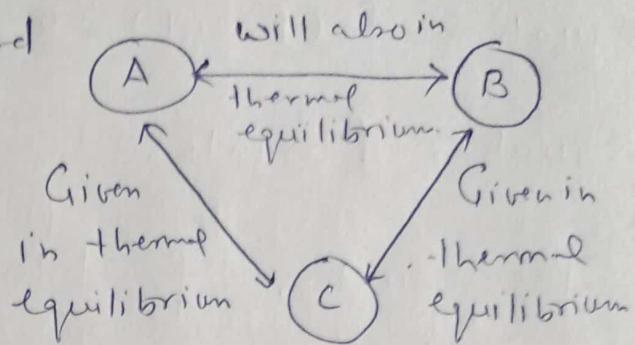
When a body is placed to contact with a cold body, their temp<sup>r</sup> change. The body with high temp<sup>r</sup> gets cool. and body with low temp<sup>r</sup> gets hot.

⇒ Energy exchange takes place between two bodies, called heat exchange, and bodies are said to be in thermal equilibrium.

If temp<sup>r</sup> of two bodies are equal, no heat-exchange take place.

## Zeroth Law of Thermodynamics:-

If two systems A and B are in thermal equilibrium with a third system C, then they (all A, B & C) are in thermal equilibrium with each other.



Heat and work :- Heat is a form of energy. Heat can, therefore be converted into mechanical work and vice-versa.

Ex. Liquids get heated by compression of a gas; make it hot, heat is produced by rubbing of hands and sparks are produced when a stone is hammered.

⇒ work is the energy exchanged between system and surroundings due to change in volume of the system.

Any device which converts heat energy into mechanical ~~energy~~ work is known as a Heat Engine.

Ex. Steam engine, diesel engine and petrol engine etc.

Joule established a relation between work done produced (5) and heat  $Q$ .

$$W \propto Q.$$

$$\boxed{W = TQ}$$

$T \rightarrow$  constant

Known as Joule's

mechanical equivalent  
of heat.

If  $Q = 1$ ,

$$\boxed{W = T}$$

If  $Q$  is in Calories, and  $W =$  Joule

then  $T = 4.18 \text{ J/cal}$ .

### Work Done by a Thermodynamic System:

If a force  $F$  produces an infinitesimal displacement  $dx$ , then the work done by the force is

$$dW = F \cdot dx \quad \dots \quad (1)$$

• If a force is exerted by the system as a whole on its surrounding, the work done either by the system or on the system is called external work.

• If the work done by one part of the system on the another part of the same system is called internal work.

Ex. (1) A gas contained in a cylinder at a uniform pressure while expanding pushes the piston out does external work.

(ii) In an actual gas there exist intermolecular attraction and when such a gas expands, the work is done against these mutual attractions between the molecules, is the internal work.

Now we compute the work done for a specific thermodynamic process,

Consider a constant mass of a gas in a cylindrical container with movable piston and cylinder as the surroundings.

Initially the system be in equilibrium and has  $p_i$ , pressure and  $V_i$  volume. Heat can flow into the system

The force exerted by the gas on the piston.

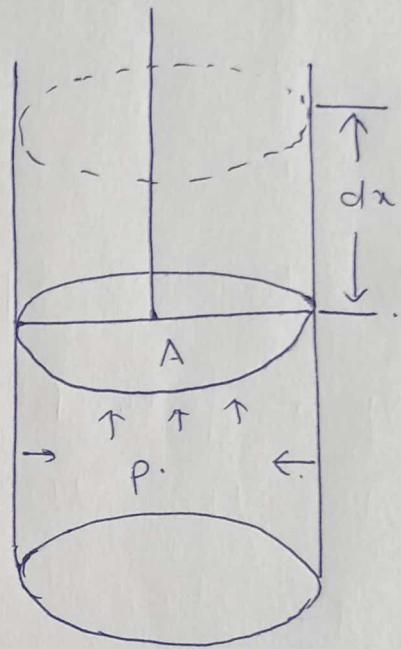
$$F = PA \quad \text{--- (1)} \quad A \rightarrow \text{Area of the piston}$$

Now the gas expands quasistatically.

Piston moves up a distance  $dx$ , the work done by the gas on the piston

$$\begin{aligned} dw &= F dx \\ &= PA dx \\ &= P dV \end{aligned}$$

$$\therefore Adx = dV$$



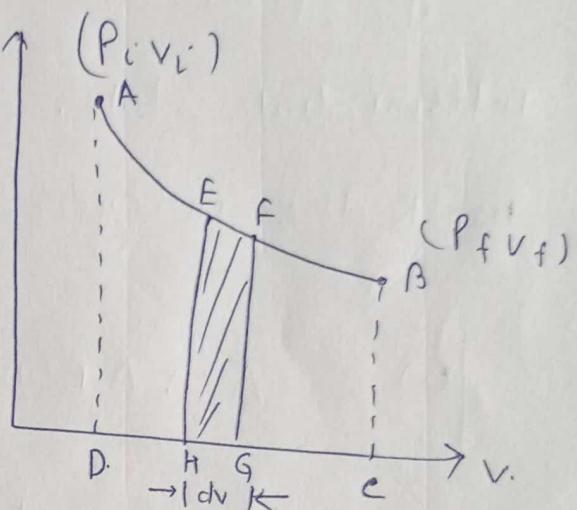
(6)

Total work done by the gas as its volume changes from  $V_i$  to  $V_f$

$$W = \int dw = \int_{V_i}^{V_f} P dV$$

Indicator diagrams:- They help in calculating the work done in the processes in which a direct mathematical relation does not exist b/w  $P$  &  $V$ .

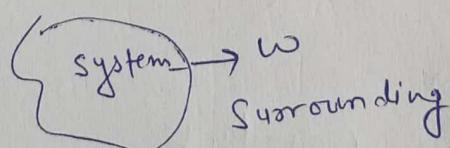
In such cases the work done  $P$  is equal to the area enclosed by the  $P-V$  diagram and the volume axis



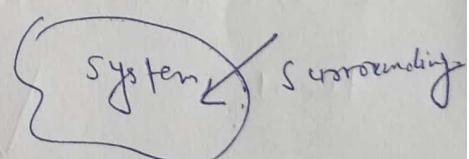
$$\therefore W = \int_{V_i}^{V_f} P dV$$

$W = \text{Area of } Pv\text{-graph}$

→ Work is not a point function but a path function.



work is +ve  
(work done by the system)



work is -ve  
(work done on the system)

→  $dw$  is an inexact or imperfect differential  
 $\therefore dw \neq w_2 - w_1$

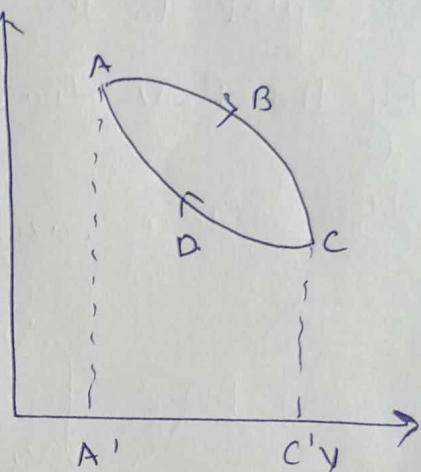
- Thermodynamic properties like pressure, volume, temperature and entropy are point functions.
- Heat is also a path function.

$$W = \int_1^2 dw = Q_2 - Q_1$$

The amount of heat transferred when a system changes from state 1 to state 2 depends on the intermediate state.

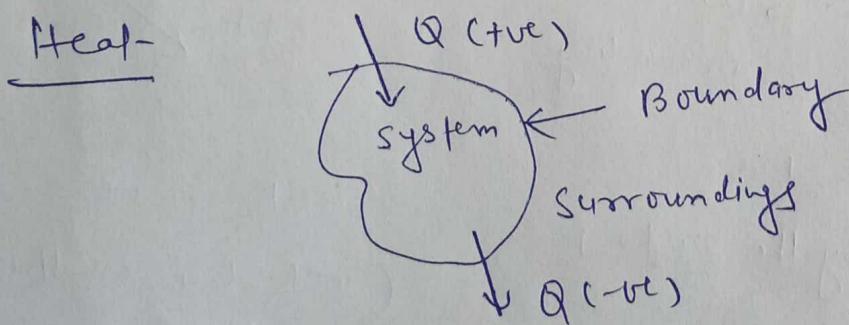
work done in cyclic process

$$W = \text{Area A B C D A}$$



→ If P-V graph is traced in the clockwise direction, the net amount of work done is +ve

→ If the curve is traced in anticlockwise direction, the net work done is -ve.



- Heat flow into a system is taken to be +ve
- Heat flow out of a system is taken to be -ve.

work done in certain process:-

(7)

(i) Isothermal process :- The temp<sup>r</sup> of the system remains constant throughout the change.

$$dW = P dV$$

$$W = \int_{V_1}^{V_2} P dV$$

$$\therefore PV = RT \Rightarrow P = \frac{RT}{V}$$

$$W = RT \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$= RT \log_e \frac{V_2}{V_1}$$

$$W = 2.303 RT \log_{10} \frac{V_2}{V_1}$$

(ii) Adiabatic process :- In this process, the change (No heat is absorbed or ejected)  
of state is not allowed to exchange heat with surroundings. This is done either by thermally insulating the system from the surroundings by the use of insulating materials or by performing the process so rapidly that gas does not find time to exchange heat. In the adiabatic process, the thermal energy remains constant.

$$\therefore W = \int_{V_1}^{V_2} P dV = \text{Area of ABCD.}$$

$$\therefore \text{During an adiabatic process } PV^\gamma = K \text{ (constant)}$$

$$\rho = \frac{K}{\sqrt{\gamma}}$$

$$\therefore \omega = \int_{v_1}^{v_2} K \frac{dv}{\sqrt{\gamma}} = K \int_{v_1}^{v_2} v^{-\gamma} dv$$

$$= K \left[ \frac{v^{-\gamma+1}}{-\gamma+1} \right]_{v_1}^{v_2}$$

$$\therefore \rho_1 v_1^\gamma = \rho_2 v_2^\gamma \quad \because K$$

$$= \frac{K}{1-\gamma} \left[ v_2^{1-\gamma} - v_1^{1-\gamma} \right] = \frac{K}{1-\gamma} \left[ \frac{1}{v_2^{\gamma-1}} - \frac{1}{v_1^{\gamma-1}} \right]$$

$$= \frac{1}{1-\gamma} \left[ \frac{\rho_2 v_2^\gamma}{v_2^{\gamma-1}} - \frac{\rho_1 v_1^\gamma}{v_1^{\gamma-1}} \right]$$

$$\left\{ \begin{array}{l} v_2^{\gamma-\gamma+1} \\ = v_2 \end{array} \right.$$

$$\boxed{\omega = \frac{1}{1-\gamma} \left[ \rho_2 v_2^\gamma - \rho_1 v_1^\gamma \right]}$$

Isobaric process :- If pressure remains constant (8)

The process is called an isobaric process

$$\therefore dW = P dV$$

$$W = \int_{V_1}^{V_2} P dV$$

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

Isochoric Process :- The state of gas changes

in such a manner that its volume remain constant. Obviously, there is a change in the pressure of the gas when heat is given to it or taken from it, no external work is done.

$$\therefore dV = 0$$

$$W = \int_{V_1}^{V_2} P dV$$

$$W = 0$$

Internal Energy:- The energy possessed by a

body or a system by virtue of its molecular arrangement and motion of molecules is called

internal energy or intrinsic energy or microscopic

energy. This energy is associated with thermodynamic state of the system.

for perfect gases, internal energy depends only on the temperature of the system as it is assumed

that the molecular forces of attraction and repulsion are absent. For non-permanent gas, vapour or liquid, internal energy strongly depends on temperature and weakly on pressure.

$$\text{for all gases } U = U(T, P)$$

$$\text{for ideal gas } U = U(T)$$

→ It is a point function.

→ It depends upon the mass of the system.

→ As per Joule's law

$$dU = m C_V dT$$

$$U_2 - U_1 = m \int_{T_1}^{T_2} C_V dT$$

$$U_2 - U_1 = m C_V (T_2 - T_1)$$

for ideal gas  $C_V = \frac{dU}{dT}$

### first law of Thermodynamics :-

"Heat is a form of energy, and energy is conserved."

The first law of thermodynamics is the statement of the principle of conservation of energy.

Consider quantity  $dQ$  of heat supplied to a system

This heat energy is, in general, spent in 3 ways -

→ Partially, it is spent in raising the temperature of the body, which is equivalent of increasing its

internal Kinetic energy.

(9)

(II) A part of it is spent in doing internal work against molecular attractions which is equivalent of increasing the internal Potential energy of the system.

(III) The remaining heat energy is spent in expanding the system against external pressure i.e. in doing external work.

If  $dU_K$  → change in K.E.  
 $dU_p$  → " " P.E.  
 $dW$  → external work done

$$dQ = dU_K + dU_p + dW$$

$$\boxed{dQ = dU + dW}$$

$dU$  → Increase in total internal energy of the system.

→ This is the differential form of first law of thermodynamics.

"The quantity of heat supplied to system will be equal to the sum of work performed by the system and the change in the internal energy of the system."

→ As  $U$  is a state function (depends only on the ends (initial and final) states and not at all on the process. so in a cyclic process.

$$dU = 0$$

$$\therefore \boxed{dQ = dW}$$

→ In an isothermal process, there will be no change in internal energy as temp<sup>r</sup>, internal energy is constant.  $dU = 0$

$$\therefore \boxed{dQ = dW}$$

→ In an adiabatic process, there will be no exchange of heat,  $dQ = 0$

$$\boxed{dW = -dU}$$

⇒ work is done by the system at the expense of its own internal energy.

→ In isolated system, there is no heat flow and work done is zero.

$$dU = 0$$

$$U_2 - U_1 = 0$$

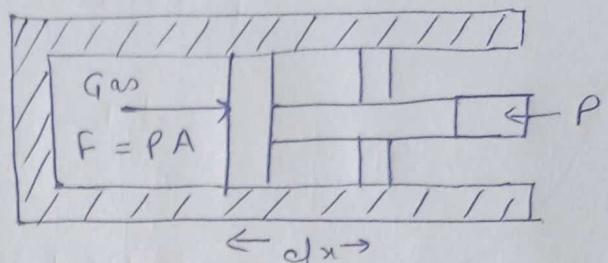
$$\boxed{U_2 = U_1}$$

⇒ Internal energy remains Constant

Adiabatic Equation of state: Consider one (10)

gram molecule a perfect gas contained in a perfectly non-conducting cylinder fitted with a non-conducting piston as shown in fig.

Suppose a gas is compressed adiabatically, so that the piston moves inward through a distance  $dx$ .



If  $A \rightarrow$  area of cross-section of the piston, then

$$\text{total force applied} = P \times A$$

$$\begin{aligned}\text{and work done by the piston} &= \text{force} \times \text{distance} \\ &= P \times A \times dx\end{aligned}$$

$$dx = P dV \quad \text{--- (1)}$$

Heat generated due to compression causes a rise of temp<sup>r</sup>  $dT$  is given by  $= C_v dT \quad \text{--- (2)}$

Where  $C_v$  — gram molecular specific heat at constant volume.

$$dQ = dU + dW$$

$$= dU + P dV$$

for adiabatic change  $dQ = 0$

$$dU + P dV = 0 \quad \text{--- (3)}$$

$$\therefore C_v = \frac{dU}{dT}$$

$$dU = C_v dT \quad \text{--- (4)}$$

from eqn. (III)

$$C_V dT + P dV = 0 \quad \text{--- (V)}$$

$$\therefore PV = RT \quad \text{--- (VI)}$$

Differentiate this eqn.

$$P dV + V dP = R dT$$

$$dT = \frac{P dV + V dP}{R}$$

$$C_V \frac{P dV + V dP}{R} + P dV = 0$$

$$C_V P dV + C_V V dP + R P dV = 0 \quad \text{--- (VII)}$$

$$\text{But } C_P - C_V = R \quad \text{--- (VIII)}$$

$$C_V + R = C_P \quad \text{--- (IX)}$$

where  $C_P$  = gram molecular specific heat at constant pressure.

from eqn. (VII)

$$(C_V + R) P dV + C_V V dP = 0$$

$$C_P P dV + C_V V dP = 0$$

Divided by  $C_V P V$ .

$$\frac{C_P}{C_V} \cdot \frac{dV}{V} + \frac{dP}{P} = 0$$

$$\therefore C_P/C_V = \gamma$$

$$\gamma \cdot \frac{dV}{V} + \frac{dP}{P} = 0$$

On integrate, we have

$$\gamma \log_e V + \log_e P = C$$

$$\log_e PV^\gamma = K$$

11

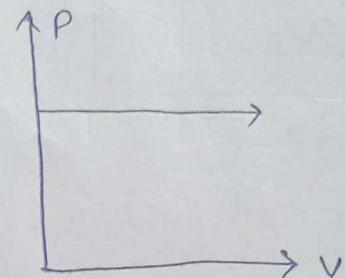
$$PV^\gamma = K$$

$$\text{or } P_1 V_1^\gamma = P_2 V_2^\gamma$$

→ In Isobaric Process pressure is constant.

$$\therefore dQ = dU + dW$$

$$dW = PdV.$$

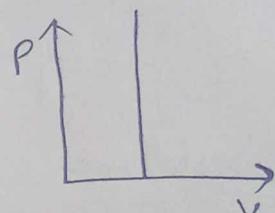


→ In Isochoric Process volume remains constant.

$$\therefore dV = 0$$

$$dW = PdV = 0$$

$$\therefore dQ = dU$$



⇒ Whole of the heat supplied to the system is used to increase its internal energy only.

### Limitations of first Law of Thermodynamics

- This law does not consider the direction of energy transformation.
- This law does not consider the grade of the energy or energy reservoirs. It assumes all energy reservoirs are identical.
- This law tells us whether energy consideration permit-permit a particular process to take a system from one equilibrium state to another. But it does not tell us whether this process will actually occur or not.

## Reversible and Irreversible Process:-

Reversible process is that which can be retraced in opposite direction, so that the working substance passes through exactly the same condition as it does in the direct process.

In other words, if heat is absorbed in the direct process, it is given out in the reverse process and vice versa.

Conditions:- (i) for reversibility Complete absence of dissipative effects such as friction, electrical resistance, magnetic hysteresis etc. is a must. (There must not lose heat by conduction, convection or radiation).

(ii) The change in the pressure and volume of the working substance must take place at an infinitely slow rate.

Any process which does not satisfy the condition of reversible process is known as irreversible process.

→ A thermodynamic process is reversible if the system passes from the initial state to final state. It can be represented by a line on Pv-diagram.

On the other hand an irreversible process passes through from initial to final state through a series of non-equilibrium states. In this case only the initial and final equilibrium states can be represented on PV diagram. Hence, an irreversible process cannot be represented by a line on a P-V diagram.

Ex. for Reversible — ① Ice melt when a amount of heat is absorbed by it. The water so formed can be converted into ice if the same amount of heat is removed.

② All isothermal and adiabatic changes are performed slowly, then they are reversible.

for Irreversible — ① Work done against friction { because in reversing the direction of motion again work has to be done against friction.

② Resting of iron

③ Heat produced by the passage of a current through a resistance

Ex. 1 If in an isothermal expansion the volume of 1 g mole of a gas at 27°C is doubled, calculate the work done in the process. ( $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$ )

Solu.

$$W = 2.303 RT \log_{10} \frac{V_2}{V_1}, \quad T = 300 \text{ K}$$

$$= 2.303 \times 8.3 \times 300 \times \log_{10} \frac{2V_1}{V_1} \quad V_2 = 2V_1$$

$$\text{or } V_1 = V \quad V_2 = 2V$$

$$= 2.303 \times 8.3 \times 300 \times 0.3010$$

$$W = 1725.8 \text{ J}$$

Ex. 2. A definite mass of a perfect gas is compressed adiabatically to half of its original volume. Determine the resultant pressure if the initial pressure was 1 atmosphere [ $\gamma = 1.4$  and  $2^{1.4} = 2.64$ ]

Solu.  $P_1 V_1^\gamma = P_2 V_2^\gamma$

$$P_2 = P_1 \left[ \frac{V_1}{V_2} \right]^\gamma$$

$$= 1 \times \left[ \frac{V_1}{V_1/2} \right]^{1.4} = [2]^{1.4}$$

$$= 2.64 \text{ atmosphere.}$$

Ex. 3. 1 gm of water ( $1 \text{ cm}^3$ ) becomes  $1671 \text{ cm}^3$  of steam when boiled at a constant pressure of 1 atm ( $1.013 \times 10^5 \text{ Pa}$ ). The heat of vaporization of this process is  $L_v = 2.256 \times 10^6 \text{ J/kg, cal.}$

(a) The work done by the water when it is vaporized

(b) Its internal energy change

Solu.  $\therefore dW = P \cdot dV = P(V_2 - V_1) = (1.013 \times 10^5) \times (1671 \times 10^{-6} - 1 \times 10^{-6})$

Heat added to the water to vapourise  $= 169 \text{ J}$

(b)  $\therefore dQ = mL_v = 10^{-3} \times (2.256 \times 10^6) = 2256 \text{ J}$

$dQ = dU + dW \Rightarrow dU = dQ - dW = 2256 - 169 = 2087 \text{ J Ans.}$

# HEAT ENGINE AND THERMAL EFFICIENCY

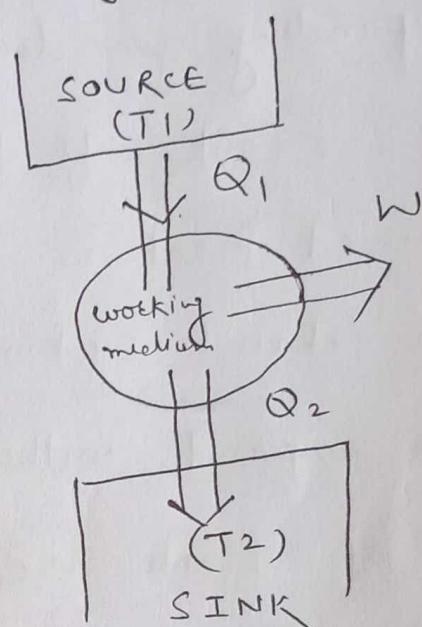
(13)

A heat engine is a device that converts heat energy to work.

Ex. Automobile engines, steam engines etc.

The Schematic diagram for heat engine is shown in figure.. It consists of 3 main parts.

- (I) Source A body at temp<sup>r</sup>  $T_1$ , from which working medium receives a certain quantity of heat  $Q_1$ .



- (II) Sink A low temp<sup>r</sup> body at  $(T_2)$ , to which any amount of heat can be rejected is called sink.

(figure).

- (III) Working Medium It is some gas (or steam) which receives heat  $Q_1$  from source, some of which is used to do useful work  $W$  and.

remaining heat-  $Q_2$  is transferred to sink.  
There are two types of Heat Engine - and returns to its initial state

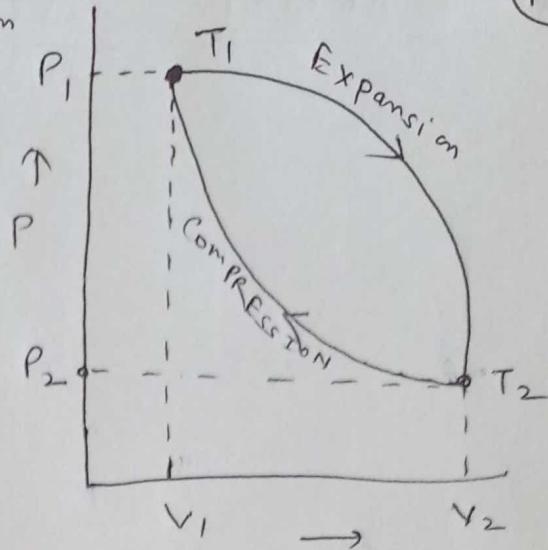
- The external Combustion engine where Combustion of fuel take place outside the sink. e.g. - steam engine
- The internal Combustion engine where Combustion

of fuel takes places inside the sinks. eg- Petrol  
diesel engine etc.

In an actual engine the energy produced in the combustion of fuel is transmitted by heat exchange to some gas. As a result the gas expands and expanding gas does work on a piston that is coupled to a crankshaft to produce useful work output. The unused heat is ejected to the surroundings through an exhaust system. However the gas cannot continue to expand without any limit because the engine is of finite size. Secondly, in practical applications we want an engine to deliver work continuously. For these reasons, the gas must be compressed after expansion, so that the gas and all the parts of the engine return to their initial state. Again the expansion and compression can be repeated, i.e. heat engine must operate in cycles so we have work output during each cycle.

Necessity of Sinks:- In this, it is necessary that the work done in expansion by gas must be greater than the work required to compress the gas. Then only we obtain more mechanical energy.

from PV diagram, it is seen that the work in expansion > work in compression (only if pressure is low in compression) This is possible only when the temp of gas is lower in compression than expansion.



Therefore, an engine will do useful work if the temperature of the gas is lower in compression than in expansion.

### Thermal Efficiency:-

Mechanical efficiency =  $\frac{\text{work output}}{\text{work input}}$

It is a measure of how ~~mechanical~~ economical an engine is.

$$\therefore \Delta Q = \Delta W + \Delta U$$

$$\therefore \Delta U = 0$$

for cyclic processes internal energy remains unchanged

$$\therefore \Delta Q = \Delta W$$

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

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

$$\therefore Q_1 = W + Q_2$$

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

for ideal engine

In practice, the useful work delivered by an engine is < the work W owing to friction losses.

$$\therefore \boxed{\eta < 1 - \frac{Q_2}{Q_1}} \text{ for Real engine.}$$

\* A good automobile engine works at an efficiency of about 20%. and diesel engines have 35% - 40%.

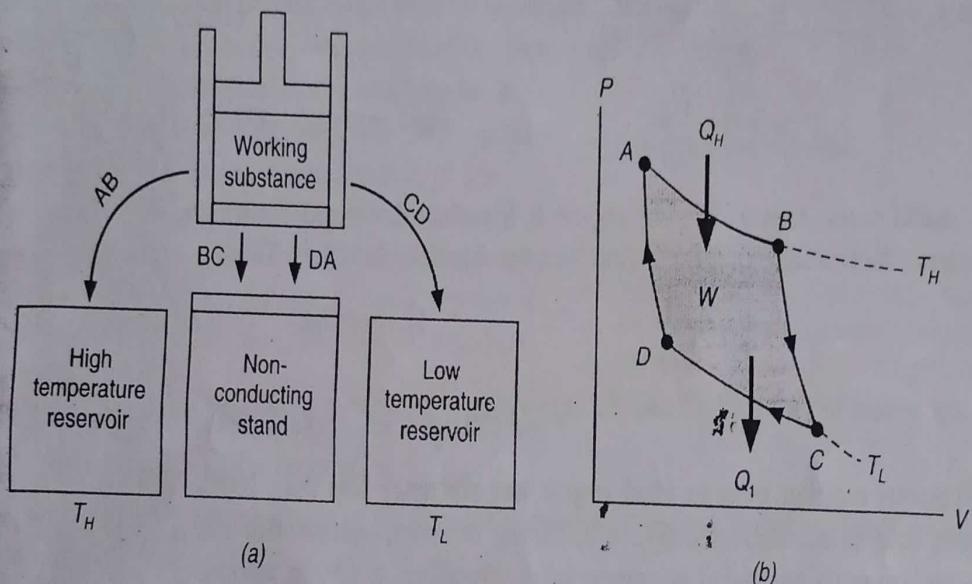
## 16.14 THE CARNOT CYCLE

If the efficiency of all heat engines is less than 100%, what is the most efficient cycle we can have? Let us consider the case of a heat engine that receives heat from a high-temperature reservoir and rejects heat to a lower temperature reservoir. In 1824 a French engineer, Sadi Carnot (1796-1832) showed that a heat engine operating in a reversible cycle between the two heat reservoirs would be the most efficient engine possible. Such an ideal heat engine operates in a cycle in which every process is reversible. If every process is reversible, the cycle is also reversible and if the cycle is reversed, the heat engine becomes a refrigerator. Such a cycle is now called a **Carnot cycle**. The ideal engine is called the **Carnot Engine** which establishes an upper limit on the efficiencies of all engines. That is, the net work done by working substance taken through the Carnot cycle is the largest possible for given amount of heat supplied to the substance.

The Carnot cycle is an idealization of the cycle of a real heat engine. It is assumed that there are no losses of energy by heat exchange with the environment, that there is no friction in the machine and that processes of gas expansion and compression are quasistatic and therefore reversible.

To describe the Carnot cycle, we shall assume that the working substance is an ideal gas contained in a cylinder with a movable piston at one end. Fig. 16.17 (a) is a schematic diagram of a Carnot engine and Fig. 16.17 (b) shows the plot for a Carnot cycle.

1. The cycle begins at the equilibrium state  $A$  [Fig. 16.17(b)] with the cylinder in contact with high-temperature reservoir at a temperature  $T_H$  (Fig. 16.17. a). We assume that the base of the cylinder is **diathermic** (*i.e.* perfectly conducting) and that the walls and the piston are ideally nonconducting. The working substance (the ideal gas) undergoes a slow quasistatic isothermal expansion to state  $B$ . During this part of the cycle  $A \rightarrow B$ , the temperature and hence the internal energy of the gas are constant. Let the total amount of heat absorbed by the gas from the reservoir during the process be  $Q_H$ . This heat energy input is converted directly to the work  $W_{AB}$  done in moving the piston.



**Fig. 16.17:** The Carnot cycle (a) In process  $A \rightarrow B$  the gas expands isothermally while in contact with a heat reservoir  $T_H$ . In process  $B \rightarrow C$ , the gas expands adiabatically. In process  $C \rightarrow D$ , the gas is compressed isothermally while in contact with a reservoir at  $T_L$ . In process  $D \rightarrow A$ , the gas is compressed adiabatically. (b) The PV diagram for the Carnot Cycle. The net work  $W$  done equals the net heat received in one cycle.

2. With the system at  $B$ , the cylinder is removed from contact with the high temperature reservoir and placed on the nonconducting stand. The gas expands adiabatically along the path  $B \rightarrow C$  to the state  $C$ . During this part of the cycle  $B \rightarrow C$  no heat enters or leaves the system. However, work  $W_{BC}$  is done at the expense of reducing the internal energy. Consequently, the temperature falls from  $T_H$  to  $T_L$ .
3. Next the cylinder is placed in contact with the low temperature reservoir at a temperature  $T_L$ . The gas is now slowly compressed (by an external agency) isothermally to a predetermined volume  $V_D$  at point  $D$ . During this part of cycle  $C \rightarrow D$ , the temperature and hence the internal energy of the working substance are constant. During this process  $C \rightarrow D$ , the gas expels heat to the reservoir and the work done on the gas by the external agent is  $W_{CD}$ .
4. In the final part  $D \rightarrow A$ , the cylinder is removed from contact with the low-temperature reservoir and again placed on the non-conducting stand. The gas is compressed adiabatically and brought to the initial state  $A$ . The adiabatic compression is also the result of work  $W_{DA}$  done on the gas by an external energy. Consequent to the adiabatic compression, the system temperature increases from  $T_L$  to  $T_H$ .

This step completes the Carnot cycle and returns the system to its initial condition.

The net work done in this reversible cyclic process is equal to the area enclosed by the path ABCDA of the PV-diagram (Fig.16.17b). In a reversible cycle, the change in internal energy is zero. It follows from first law that the net work done in one cycle equals the net heat transferred into the system. For a system that undergoes a Carnot cycle, no heat is supplied to or rejected by the system during the adiabatic paths, BC and DA (Fig.16.17b). An amount of heat  $Q_H$  is supplied to the system during the isothermal expansion AB, and an amount  $Q_L$  is rejected during the isothermal compression CD. Thus, the first law can be written as

$$W = Q_H - Q_L \quad \text{All heat engines} \quad (16.24)$$

Equ.(16.24) is applicable for a complete cycle of any heat engine. The thermal efficiency is given by equ.(16. 22).

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

#### 16.14.1 Efficiency

For a Carnot engine, the heat exchanges take place during the isothermal processes. During the isothermal expansion  $A \rightarrow B$ , the heat absorbed from the high temperature reservoir is given by

$$Q_H = W_{AB} = nRT_L \ln \frac{V_B}{V_A} \quad (16.25)$$

In a similar manner, the heat rejected to the low temperature reservoir during the isothermal compression  $C \rightarrow D$  is given by

$$Q_L = W_{CD} = nRT_L \ln \frac{V_C}{V_D} \quad (16.26)$$

Dividing these expressions, we get

$$\frac{Q_L}{Q_H} = \frac{T_L \ln(V_C/V_D)}{T_H \ln(V_B/V_A)} \quad (16.27)$$

This can be further simplified by use of the temperature-volume relation for an adiabatic process. For an adiabatic process, the pressure and volume are related by

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

During any reversible process, the ideal gas must also obey the equation of state,

$$PV = nRT \quad (16.28)$$

Eliminating pressure between the above equations, we get

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

Applying this result to the adiabatic processes  $B \rightarrow C$  and  $D \rightarrow A$ , we get

$$T_H V_B^{\gamma-1} = T_L V_C^{\gamma-1} \quad (16.30)$$

$$\text{and} \quad T_H V_A^{\gamma-1} = T_L V_D^{\gamma-1} \quad (16.31)$$

Dividing equ.(16.30) by equ.(16.31) we get

$$\left( \frac{V_B}{V_A} \right)^{\gamma-1} = \left( \frac{V_C}{V_D} \right)^{\gamma-1}$$

$$\left( \frac{V_B}{V_A} \right) = \left( \frac{V_C}{V_D} \right) \quad (16.32)$$

Substituting equ. (16.32) into equ.(16.27) , we obtain

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H} \quad \text{Carnot Engine} \quad (16.33)$$

Using the result equ.(16.33) into equ.(16.23) we obtain the thermal efficiency of the Carnot engine as

$$\eta = 1 - \frac{T_L}{T_H} = \frac{T_H - T_L}{T_H} \quad \text{Carnot Engine} \quad (16.34)$$

This surprisingly simple result says that the efficiency of a Carnot engine depends only on the temperatures of the two reservoirs. When ( $T_H >> T_L$ ) the difference of the two temperatures is large, the efficiency is nearly unity; when the difference is small the efficiency is less than unity. Thus, the greater the temperature difference  $T_H - T_L$ , the greater will be the efficiency of a Carnot engine.

We see from equ. (16.34) that all Carnot engines operating between the same two temperatures in a reversible manner have the same efficiency.

It brings us to the important difference in principle between heat engines and mechanical or electrical machines. In improving the design of mechanical or electrical machines we try to make their efficiency as near as possible to the theoretical limiting value of 100%. Though this limit is unattainable under real conditions, we can approach it by reducing losses. When we improve heat engines, we do not try to bring their efficiency to 100%, but to that of a Carnot engine operating in the same temperature interval. Naturally, the reduction of all kinds of losses also raises the efficiency of a heat engine but the most effective measure is to increase the temperature difference between the high temperature reservoir and low temperature reservoir.

### 16.14.2 Carnot's Theorem

The most important aspect of the Carnot engine is that it is the most efficient heat engine operating between the two heat reservoirs. This is summarized in the **Carnot's theorem** as follows:

*No heat engine operating between two heat reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.*

The Carnot's theorem reveals a fundamental limitation on the conversion of heat into work.

$K (= -15^\circ C)$  which give a typical value of 5.6 for  $K_f$

## 16.16 SECOND LAW OF THERMODYNAMICS

There are two classical statements of the second law of thermodynamics. They are known as the Kelvin-Planck statement and the Clausius statement.

An analysis of operation of heat engines led William Thomson (later Lord Kelvin) and Planck to arrive at the following conclusion:

*It is impossible to construct a heat engine that will operate in a cycle and which will receive a given amount of heat from a high-temperature reservoir and does an equal amount of work. The only alternative is that some heat must be transferred from the working fluid to a low temperature reservoir. Therefore, work can be done by the transfer of heat only if there are two temperature levels involved.*

The analysis of operation of heat pumps led Rudolf Clausius to conclude as follows:

*It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a cold body to a hot body. In effect, it is impossible to construct a refrigerator that operates without an input of work.*

The first law of thermodynamics is concerned with conservation of energy. As long as the energy is conserved in a process, the first law is satisfied. A cycle in which a given amount of heat is transferred from the system and an equal amount of work is done on the system satisfies the first law but it does not ensure that the cycle will actually occur. The second law emphasizes the fact that processes proceed in a certain direction but not in the opposite direction. For instance, a hot cup of coffee cools by virtue of heat transfer to the surroundings but heat will not flow from the cooler surroundings to the hot cup of coffee. Thus, real processes proceed only in one direction. It is important to take note of the fact that a cycle will occur only if both the first and the second laws of thermodynamics are satisfied.

The first law of thermodynamics is a general statement of the conservation of energy. It makes no distinction between the different forms of energy. The second law of thermodynamics asserts that thermal energy is different from all other forms of energy. Various forms of energy can be converted into thermal energy spontaneously and completely, whereas the reverse transformation is never complete. The impossibility of converting heat completely into mechanical energy forms the basis of Kelvin-Planck statement of second law. The fact that work may be dissipated completely into heat whereas heat may not be converted entirely into work expresses the essential one sidedness of nature.

The basis of second law lies in the difference between the nature of mechanical energy and the nature of internal energy. Mechanical energy is the energy of ordered motion of a body. Internal energy is the energy of random motion of molecules within the body. When the body moves, the motion is due to the ordered motion of molecules within it as a whole in the direction of velocity of the body. The energy associated with this ordered motion of molecules is the kinetic energy. The kinetic and potential energies associated with the random motion is the internal energy. When a moving body comes to rest due to friction, the ordered portion of the kinetic energy becomes converted into energy of random molecular motion. It is impossible to reconvert the energy of random motion completely to the energy of ordered motion, since we cannot control the motions of individual molecules. We can convert only a portion of it. That is what a heat engine does.

### 16.17 ENTROPY

The differential form of the first law of thermodynamics is written as

$$dQ = dU + dW$$

The work  $dW$  done depends on the path of process and therefore it is not a function of the state. The same is the case with  $dQ$ , the quantity of heat supplied or taken away. The work  $dW$  can be expressed in terms of thermodynamic variables and their changes. For instance, we have expressed  $dW$  in equ.(16.2) as

$$dW = P dV$$

It is found that  $dQ$  can also be expressed in a similar fashion, in case of reversible processes. We write

$$dQ = T dS \quad (16.37)$$

where  $dS$  is called the **change in entropy** and  $T$  is the temperature. Now, we define the change in entropy as

$$dS = \frac{dQ}{T} \quad \text{Reversible process} \quad (16.38)$$

The change in entropy  $dS$  in the course of an infinitesimal change is equal to the quantity of heat  $dQ$  divided by the absolute temperature  $T$ , where  $dQ$  is the heat absorbed (or rejected) when the change is carried out in a reversible manner.

The total entropy change in a reversible process may be obtained by integrating equ. (16.38). Thus,

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{dQ}{T} \quad (16.39)$$

where  $S_1$  and  $S_2$  are the entropies of the initial and final states of the system.

The importance of the entropy  $S$  is that it is a function of state like the internal energy  $U$ . Both these parameters depend only on the initial and final states of the system and not on the path of the process that takes the system from the initial state to final state. Equation (16.39) assumes a simpler form when the process is an isothermal process. As  $T$  is constant in isothermal process, equ.(16.39) may be written as

$$\Delta S = \int_1^2 \frac{dQ}{T} = \frac{1}{T} \int_1^2 dQ = \frac{Q}{T}$$

Thus,

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

The units of entropy and entropy change are  $J/K$ .

In practice, the value of entropy  $S$  is not of much interest. We have to know the change in entropy when the system changes from one state to another.

### 16.17.1 Entropy, Disorder and Second Law

When processes occur, in general, they are irreversible and the degree of disorder increases as a result of these processes. As an example, let us take the case of isothermal expansion of an ideal gas (Fig. 16.10). As the gas absorbs heat, it slowly expands. At the end of the process the gas occupies a greater volume than at the beginning. The gas molecules are more disordered now. The gas will not, by its own accord, give up its thermal energy and segregate itself to confine to the initial volume. We, thus, observe that the flow of heat takes place in the direction that increases the amount of disorder. The same type of order to disorder change occurs when free expansion of gas occurs, when one gas diffuses into another, and in similar other spontaneous processes.

Rudolf Clausius (1822-1888), the German physicist, introduced the quantity entropy which is regarded as a measure of disorder in a system. An increase in disorder is equivalent to an increase in entropy. Irreversible processes are processes for which entropy increases.

These considerations led Clausius to reformulate the second law of thermodynamics in terms of entropy. According to it, the entropy of an isolate system always tends to increase. Mathematically, it is expressed as

$$\Delta S_{\text{isolated system}} \geq 0 \quad (16.41)$$

### 16.17.2 Some Interesting Points

1. The net change in entropy in any reversible cycle is zero.

Let us take the case of Carnot cycle as an example. There is no change in entropy of the working substance during the two adiabatic paths. Either during adiabatic expansion or compression,  $Q = 0$ . Therefore,  $\Delta S = 0$ . However, there is an increase in entropy during isothermal expansion, as heat  $Q_H$  is added at a constant temperature  $T_H$ . The consequent

increase in entropy  $\Delta S_1 = \frac{Q_H}{T_H}$ . There is a decrease in entropy during the isothermal

compression in which heat  $Q_L$  is rejected at a temperature  $T_L$ . Thus,  $\Delta S_2 = -\frac{Q_L}{T_L}$ .

$\therefore$  The net change in entropy is given by

$$\Delta S = \Delta S_1 + \Delta S_2 = \frac{Q_H}{T_H} - \frac{Q_L}{T_L}$$

But

$$\frac{Q_H}{T_H} = \frac{Q_L}{T_L}$$

$$\therefore \Delta S = 0$$

Reversible Cycle (16.42)

### 2. Entropy increases in all irreversible processes.

It is proved that there is a net increase in the entropy during irreversible processes. Since all real processes taking place in the universe are irreversible, there is a continuous increase

*of its entropy. For this reason, entropy is not conserved. In this respect entropy differs from energy.*

We can illustrate this by taking a simple example. Suppose a small quantity of heat  $dQ$  is radiated away from a hot body A, at a temperature  $T_H$ , to a cold body B at a temperature  $T_C$ . Let  $dQ$  be so small that  $T_H$  and  $T_C$  are not altered appreciably, due to the exchange of heat. However, the entropy of A decreases by  $-dQ/T_H$  whereas that of B increases by  $dQ/T_C$  in this process.

$$\Delta S = \frac{dQ}{T_C} - \frac{dQ}{T_H}$$

$$\text{As } T_H > T_C \quad \Delta S > 0 \quad (16.43)$$

### 3. Entropy indicates the direction in which processes proceed in nature.

All natural processes are irreversible. They proceed in the direction of increasing entropy.

### 4. Entropy represents the unavailability of energy.

In the thermodynamic sense, entropy is a measure of the capability to do work or transfer heat. A system at a higher temperature will tend to do work on and/or transfer heat to its lower temperature surroundings. In the process, the entropy of the system increases and the greater the entropy the less available is the energy.

Let us consider the example of Carnot engine. The efficiency of Carnot engine is given by

$$\eta = 1 - \frac{T_L}{T_H}$$

As  $Q_H$  is the heat input, heat converted into work =  $Q_H \left(1 - \frac{T_L}{T_H}\right)$

∴ Heat unavailable for work =  $Q_H = T_L$

But  $Q_H / T_H$  represents the increase in entropy  $\Delta S$  during isothermal expansion.

$$\therefore \text{Energy wasted} = T_L \Delta S \quad (16.44)$$

If  $T_L$  is constant, the amount of energy wasted is proportional to the increase in entropy.

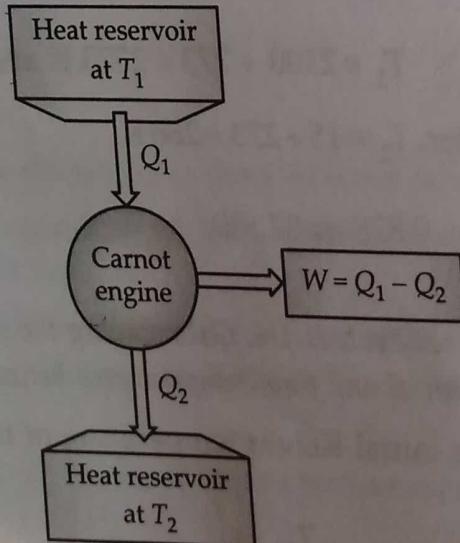
## 16.18 THIRD LAW OF THERMODYNAMICS

With a decrease in temperature, a greater degree of order prevails in any system. If we could cool a system to 0K, the maximum conceivable order would be established in the system and the minimum entropy would correspond to this state. Now, suppose we apply a pressure on the system at 0K. What does happen to the entropy of the system? On the basis of experiments conducted at low temperatures, W.Nernst concluded that "at 0K, any change in the state of a system takes place without a change in the entropy". This is called **Nernst's theorem**. It is also called the **third law of thermodynamics**. Third law of thermodynamics is sometimes known as the principle of unattainability of absolute zero. It is stated as follows:

**It is impossible to attain a temperature of 0K.**

## 1.16 CARNOT'S ENGINE AND CARNOT'S REFRIGERATOR

Any heat engine operating in a Carnot cycle is called a *Carnot's engine* and may be represented schematically as shown in Fig. 1.19.



**Fig. 1.19** A Carnot's engine.

A Carnot's engine may be defined as a reversible engine operating between two reservoirs.

If a Carnot cycle is performed in opposite direction as discussed above, it becomes a Carnot's refrigerator.

Consider a Carnot's cycle of a fluid as shown in Fig. 1.20.

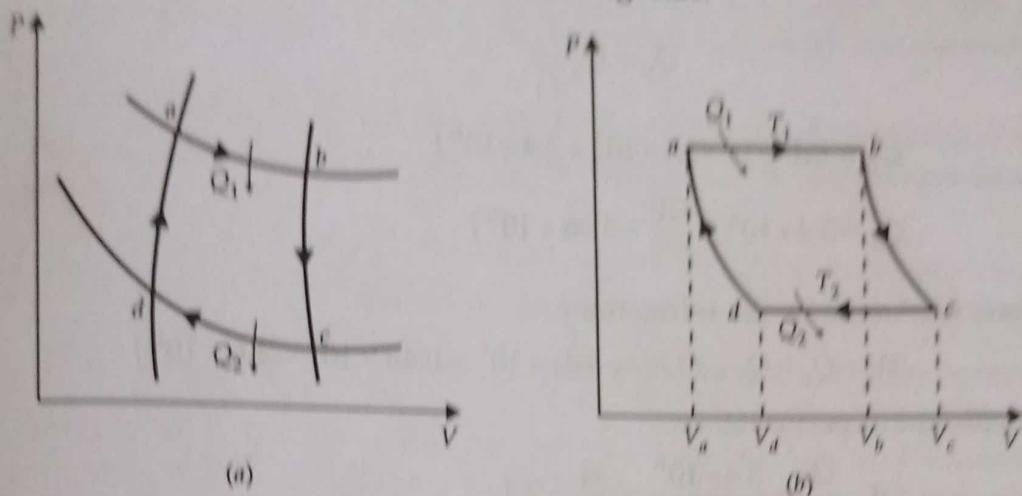


Fig. 1.20 Carnot cycle a gas (a) P-V diagram, (b) T-V diagram.

If the directions of the arrows are reversed cycle becomes  $adcba$  instead of  $abcd$ . Then the cycles are reversible because each process is reversible, the magnitudes of the quantities  $Q_1$ ,  $Q_2$  and  $W$  remain the same but their signs are reversed. Thus, heat  $Q_2$  is absorbed by the system from the lower temperature reservoir and heat  $Q_1$  is rejected to the higher temperature reservoir while work  $W$  in the cycle represents workdone on the system as shown in Fig. 1.21.

The features common to all refrigeration cycles are absorption of heat at a low temperature, rejection of amount of workdone on the system. In a domestic refrigerator heat is pumped out of the interior of the refrigerator, which is at a temperature lower than that of the surroundings, a larger quantity of heat is rejected to the surroundings and workdone by the motor driving the refrigerator.

In this case the input is the workdone on the system  $W$ , and output is the heat  $Q_2$  removed from the lower temperature reservoir. A refrigerator is therefore rated by its coefficient of performance ( $\beta$ ), defined as

$$\beta = \frac{\text{Heat output}}{\text{Work input}} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$

The definition of coefficient of performance applies to any refrigerator whether it operates in Carnot cycle or not.

**Example 1.7** A Carnot's refrigerator absorbs heat from water at  $0^\circ\text{C}$  and rejects it at the room temperature  $37^\circ\text{C}$ . Calculate the amount of work required to convert 10 kg water at  $0^\circ\text{C}$  into ice at same temperature [Latent heat of ice =  $3.4 \times 10^5 \text{ J kg}^{-1}$ ]. Also find the coefficient of performance of the refrigerator.

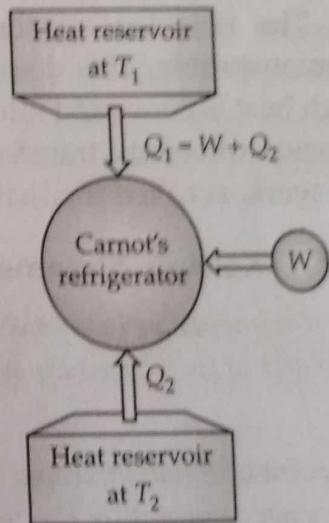


Fig. 1.21 A Carnot's refrigerator.

which is mathematical form of second law.

### 1.18 CARNOT'S THEOREM

**STATEMENT :** A reversible engine operating between two given reservoirs i.e., Carnot's engine is most efficient that can operate between those reservoirs.

Or

No engine operating between two given temperature is more efficient than Carnot's engine.

**Proof.** Operate a Carnot's engine C and an arbitrary engine X (not necessarily reversible) between two reservoirs at temperature  $T_1$  and  $T_2$  with ( $T_1 > T_2$ ). By first law of thermodynamics, the workdone by the engines (see Fig. 1.22).

$$(W)_C = (Q_1)_C - (Q_2)_C \quad \dots(1.63)$$

and

$$(Q)_x = (Q_1)_x - (Q_2)_x \quad \dots(1.64)$$

Let  $\frac{(Q_1)_C}{(Q_1)_X} = \frac{N}{M}$ , where  $N, M$  are two integers (can be

satisfied to any desired accuracy).

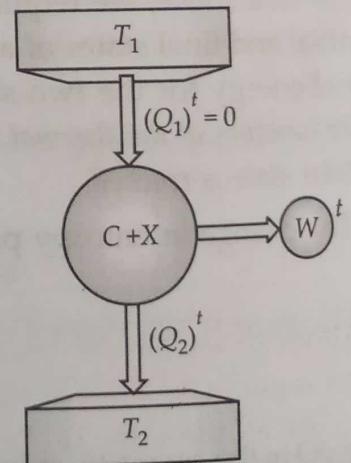


Fig. 1.22 Illustration for Carnot's theorem.

Now operate engine C, M cycles in reverse (as Carnot engines are reversible) and engine X, N cycles in forward direction. Consider (C + X) as an engine total, then

$$(W)_{\text{Total}} = N(W)_X - M(W)_C \quad \dots(1.65)$$

But

$$(Q_1)_{\text{Total}} = N(Q_1)_X - M(Q_1)_C = 0 \quad \dots(1.66)$$

and

$$(Q_2)_{\text{Total}} = N(Q_2)_X - M(Q_2)_C \quad \dots(1.67)$$

Hence

$$(W)_{\text{Total}} = -(Q_2)_{\text{Total}} = -[N(Q_2)_X - M(Q_2)_C]$$

This is shown in Fig. 1.22.

However, Kelvin's statement says we cannot convert heat entirely to work – here we have extracted no heat from  $T_1$ . Thus Kelvin's statement is broken unless  $(W)_{\text{Total}} \leq 0$  or  $(Q_2)_{\text{Total}} \geq 0$  i.e.,

$$N(Q_2)_X - M(Q_2) \geq 0$$

or

$$\frac{N}{M} \geq \frac{(Q_2)_C}{(Q_2)_X} \quad \dots(1.68)$$

Therefore

$$\frac{(Q_1)_C}{(Q_2)_X} \geq \frac{(Q_2)_C}{(Q_2)_X}$$

or

$$\frac{(Q_2)_C}{(Q_1)_C} \leq \frac{(Q_2)_X}{(Q_2)_X} \quad \dots(1.69)$$

and

$$\eta_{CE} \left( = 1 - \frac{(Q_2)_C}{(Q_1)_C} \right) \geq \eta_X \left( = 1 - \frac{(Q_2)_C}{(Q_1)_C} \right)$$

$$\eta_{CE} \geq \eta_X \quad \dots(1.70)$$

This equality holds if X engine is also reversible. We therefore have the following corollary.

**COROLLARY.** All reversible engine (Carnot's engines) working between the same two heat reservoirs have identical efficiency.

This is a remarkable result. It means for reservoirs at temperature  $T_1$  and  $T_2$ ,  $\eta_{CE} = \eta_X(T_1 - T_2)$  only independent of working substance, for example, the working substance could be an ideal gas, real (non-ideal) gas, a paramagnet etc. We can evaluate for any one, and other will be same. So we prefer an ideal gas.