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$$\Delta U = Q - W$$



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**THERMODYNAMICS**





□□ Thermodynamics

*"Thermodynamics is the branch of science which deals with the study of Transformation of heat energy into other forms of energy and vice versa".*

Thermodynamics deals with conversion of heat into mechanical work. It is easy to produce heat by doing mechanical work. For example, if you rub your hands briskly, practically the whole of mechanical work done is converted into heat. Thus the conversion from mechanical energy to heat can be almost 100%. However, the opposite process (i.e., continuous conversion of heat into mechanical work) is far less than 100%. In fact, the most efficient heat engine (i.e., a device which converts heat into mechanical work) has an efficiency less than 50%. In other words, not more than 50% of heat can be converted into mechanical work. The reason for this lies in the laws of thermodynamics.

□ •Terms used in thermodynamics

□ [1] Thermodynamical system: "A collection of an extremely large no. of atoms or molecules confined within boundaries such that it has a certain value of pressure (P), Volume (V) and temperature (T), is called a thermodynamical System".

- Thermodynamical system may exist in the form of a solid, liquid or gas or a combination of two or more states.

□ [2] Surrounding: "Anything outside the thermodynamical system to which energy or matter is exchange is called ,its surroundings".

Ex: A gas enclosed in a cylinder fitted with a piston, the gas form thermodynamical system. And, the atmospheric air are the around the cylinder, movable piston, burner for heating the gas, all are the surrounding.

- **Boundary wall of the gaseous system may of two types** -- 1] *Diathermic (through which heat can be transmitted).*  
-- 2] *Adiabatic Wall (through which no heat can be transmitted).*

- Taking into consideration, the interaction between a system and its surroundings, a system may be divided into three class:-

[a] Open system: "A system is said to be an open system if it can exchange both energy and matter with its surrounding".

[b] Closed system: "A system is said to be a closed system if it can exchange only energy with its surrounding".

[c] Isolated system: "A system is said to be an isolated system if it can neither exchange energy nor matter with its surrounding".

□ Thermodynamical behavior: A thermodynamic system can be described by specifying its pressure, Volume, temperature, Heat content, no. of mole. these parameter (or variables) are called thermodynamical behavior. i.e.,

**"The variables which are required to specify the state of thermodynamic system are called thermodynamical behavior".**

- Thermodynamical Variables of a gaseous system: Pressure (P), Temperature(T), Volume(V), heat content(Q).
- Thermodynamical Variables of a Liquid system: Density( $\rho$ ), Temperature (T), Surface tension (S.T) etc
- Thermodynamical Variables of a solid system: Area, Volume, Temperature, Elasticity etc.

□ Equation of state: The relation between the thermodynamic variable (P,V,T) of the system is called equation of state. The equation of state for an ideal gas having 'n' moles is,

$$PV = nRT$$

□ Specific heat capacity ( Specific heat ): "The specific heat capacity of a substance is the amount of heat required to raise the temperature of a unit mass of the substance through 1K or 1C<sup>0</sup>".

Explanation :-- When a body is heated, its temperature increases While, temperature of a body decreased when it is cooled.

- It is found that Gain or loss of heat is directly proportional to ----
- 1] the mass of the body i.e.,  $Q \propto m$
- 2] rise or fall of the temperature of the body i.e.,  $Q \propto \Delta T$

Combining these two, we get

$$Q \propto m \Delta T$$

$$Q = m c \Delta T$$

----- [1] where, C = Constant called Specific heat of the body.

i.e., Heat transferred = mass  $\times$  Sp. heat  $\times$  Change in temperature.

If  $m = 1, \Delta T = 1$  then from [1],

$$Q = 1 \times C \times 1$$

i.e.,  $C = Q$

thus, "Specific heat of a substance is the amount of heat required to raise the temperature of unit mass of the substance through unit degree".

•-- **Unit** : (cgs)  $C = \frac{Q}{m \Delta T} = \frac{\text{Cal.}}{\text{g}^{\circ}\text{C}} = \text{Cal} / \text{g}^{\circ}\text{C}$

(SI)  $C = \frac{Q}{m \Delta T} = \frac{\text{J}}{\text{Kg}^{\circ}\text{C}} = \text{J/K g}^{\circ}\text{C}$

•-- **Dimension formula** :  $C = \frac{Q}{m \Delta T} = \frac{ML^2T^{-2}}{MK} = [M^0 L^2 T^{-2} K]$

•• 1 Cal. / g /K = 4.18 J/ g /<sup>0</sup>C  
= 4180 J/K g /<sup>0</sup>C

- If the substance undergoes the change of state at constant temperature then,  $\Delta T = T_2 - T_1 = 0$

$C = \frac{Q}{m \Delta T} = \frac{Q}{0} = \text{Infinity}$  i.e., **Specific heat of a substance when it meet or boil at constant temperature is infinite.**

- If the temperature of the substance changes without transfer of heat (i.e.,  $Q = 0$ ), then  

$$C = \frac{Q}{m \Delta T} = 0$$

Example:-- When liquid in a thermo-flask is shaken, its temperature increases without the transfer of heat & hence the specific heat of liquid in thermo-flask is zero.

- **Maximum specific heat** ----- [1] Hydrogen = 3.6 cal / g/ °C .  
 [2] Water = 1 Cal / g/ °C.
- **Minimum specific heat** ----- Radon & Actinium = 0.022 Cal / g/ °C.

**MOLAR SPECIFIC HEAT ( Molar heat Capacity ):**

"Molar specific heat of a substance is defined as the amount of heat required to raise the temperature of 1 mole (1g mol) of the substance by a unit degree ( 1K or 1 °C )."

- **Calculation** of no. of moles,  $n = \frac{m}{M}$  → Mass of material  
 → Molecular mass.

From sp. heat ,

$$m = n M$$

$$c = \frac{Q}{m \Delta T}$$

$$c = \frac{Q}{n M \Delta T}$$

$$c M = \frac{Q}{n \Delta T}$$

By definition ,  $cM = C$  → **Capital C**

$$C = \frac{Q}{n \Delta T}$$

, Where C (Capital) = c M is the molar heat capacity.

- **UNIT::** --- (cgs) = Cal / mol / °C  
 --- (SI) = J / mol / °C

- **Dimension formula ::**  $C = \frac{Q}{n \Delta T} = [ M L^2 T^{-2} K^{-1} mol^{-1} ]$

**Def<sup>n</sup> Of r m s :** " It is defined as the square root of the mean squares of the random velocities of the individual molecules of a gas".

**DULONG AND PETIT LAW :**— {French scientist}

Dulong and petit observed that the "Average molar heat of all metal at room temperature is constant being nearly equal to 6 Cal / mol / k = 25 J / mol / k".

--- This statement is known as **Dulong & Petit law**.

**Significance :** The significance of the law lies in the fact that amount of heat energy required to raise the temperature of metal depends upon **Total no. of atoms contained in the sample and not in the mass of individual atoms**. As one mole of each metal contain same no. of atoms{  $N_A$  }, therefore, **MOLAR SPECIFIC HEAT** of all the metals (at room temperature) is nearly constant.

i.e., **Atomic weight × Specific heat = constant**

**SPECIFIC HEAT OF GASES :**

"Specific heat of gases is the amount of heat energy required to raise the temperature of 1 gram of a gas to raise the temperature of 1 gram of gas through 1°C".

- The above definition is based on the assumption that heat supplied to the substance is spent only in raising the temperature the substance . But a substance generally expands on heating,therefore, SOME of the heat supplied is spent in expansion against atmospheric pressure.
- **In case of Solid & Liquid** , the coefficient of expansion is generally very small . And, therefore , amount of heat spent in their expansion is **negligible**.
- **In case of Gases** , theCoefficient of expansion is very large. Therefore , heat energy supplied to a gas is spent not only in raising the temperature of the gas but also expansion of the gas (Against atmospheric pressure).

- **TWO PRINCIPAL SPECIFIC HEAT OF A GAS :** We know that when heat is supplied to a gas , the rise of 10 temperature is accompanied by either increase in the pressure or volume or both. Thus , a gas can be heated under two condition:
  - [1] At constant volume ,
  - [2] At constant pressure.

- **Specific heat of a gas at constant Volume ( C<sub>v</sub> ) :** "C<sub>v</sub> is defined as the amount of heat required to raise the temperature of 1 gram of gas through 1°C Or 1 K at constant volume".

UNIT :-- Cal / mol / k or J / mol / k

- **Specific heat of a gas at constant pressure ( C<sub>p</sub> ) :** "C<sub>p</sub> is defined as the amount of heat required to raise the temperature of 1 gram of gas through 1°C or 1 K at constant pressure.

**Molar specific heat of a gas at constant volume** :  $C_v$  is defined as the amount of heat required to raise the temperature of 1 gram mole of the gas through  $1^\circ\text{C}$  or 1 K at constant volume .

••UNIT :-- Cal / mol / K

$$C_v = M C_{v \text{ specific heat}}$$

**Molar specific heat of a gas at constant pressure** :  $C_p$  is defined as the amount of heat required to raise the temperature of 1 mole of the gas through  $1^\circ\text{C}$  or 1 K at constant pressure .

$$C_p = M C_p$$

**RATIO OF TWO PRINCIPAL SPECIFIC HEAT OF A GAS** :-- (  $\gamma$  )

$$\gamma = \frac{C_p}{C_v} = \frac{M C_p}{M C_v} = \frac{C_p}{C_v}$$

•• **$C_p$  is greater than  $C_v$** •••••

When a gas is heated at constant volume , no heat is spent in the expansion of the gas . The whole amount is used to increase the temperature of the gas .

Now if the same amount of heat is supplied to the gas at **constant pressure** , it is spent in two ways :--

i.) in expanding the gas & ii.) to increase the temperature of the gas .

Thus , to increase the temperature of the gas to the **same value** as in case of constant volume , more heat is to be supplied at constant pressure .

Hence , Sp. heat at constant pressure  $C_p >$  sp. heat at constant volume  $C_v$  .

Relation between  $C_p$  &  $C_v$

$$C_p - C_v = R$$

### CALORIMETRY

Important Terms:

●1. **Heat capacity( Thermal capacity )**

"Thermal capacity of a body is defined as the amount of heat required to raise the temperature of the body through  $1^\circ\text{C}$  or 1 k."

We KNOW that amount of heat required to raise the temperature of 1g substance through  $1^\circ\text{C}$  is specific heat of the substance. Therefore, Amount of heat required to raise the temp<sup>t</sup> of 'm' g substance through  $1^\circ\text{C}$  is thermal capacity .

$$\text{Thermal capacity} = m \times c$$

•• SI UNIT :-- J/K .

•• Cgs :-- Cal / K .

●2. **Water Equivalent (W)**

"It is defined as the mass of water that requires the same amount of heat to raise its temp<sup>t</sup> through  $1^\circ\text{C}$  as is required by the body under consideration ."

•• UNIT – g (Cgs) and Kg (SI)

$$\text{We know that , } Q = m c (\Delta T)$$

As the same amount of heat i.e. , Q is required to raise the temperature of w gram of water through the same range  $\Delta T$  .

$$\text{Therefore, } Q = w (\Delta T) \times 1 \text{ Cal / g / }^\circ\text{C}.$$

$$Q = w (\Delta T).$$

$$\text{Therefore, } w (\Delta T) = m c (\Delta T)$$

$$\boxed{w = m c}$$

i.e. , Water equivalent is numerically equal to the product of sp. heat and mass.

●3. **LATENT Heat**

Latent heat of a substance is the amount of heat energy required to change the state of unit mass of the substance from solid to liquid or from liquid to gas without any change in temperature."

•• (a) **Latent heat of fusion (of a solid)** :

" The heat supplied to a substance to change its solid to liquid state at a constant temperature is called latent heat of fusion.

Ex-- Latent heat of ice = 80 cal / g at  $0^\circ\text{C}$  .

i.e. , 1 g ice at  $0^\circ\text{C}$  , 80 cal of heat is required .

•• (b) **Latent heat of vapourisation (of liquid)** :

The heat supplied to a substance to change its liquid to vapour at a constant temperature is called latent heat of vapourisation .

Ex-- Latent heat of water = 540 Cal / g at  $100^\circ\text{C}$  .

\*\* **Principle of Calorimetry**

$$\boxed{\text{Heat gained} = \text{Heat lost}}$$

**Thermodynamic Process** :

"A thermodynamical process is said to take place when some changes occur in the state of a thermodynamic system." i.e. , the thermodynamic parameter like P,V,&T etc change with time .

Types thermodynamic process

1.) **Isothermal process:**

Isothermal process is a process in which **pressure and volume** of the system change at **constant temperature** .

In this case

$$\boxed{\Delta T = 0}$$

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- In isothermal process, the exchange of heat between the system and the surroundings is allowed.
- Isothermal process is carried out either supplying heat to substance or by extracting heat from it.

Ex— (i) The temp<sup>t</sup> of a substance remains constant during melting, therefore, melting process is an isothermal process.  
 ---(ii) Boiling process.

**Two essential condition**, For perfect isothermal change -----

- [i] There should be free exchange of heat between the system and its surrounding. All the wall of the container and the piston must be perfectly conducting.
- [ii] The system should be compressed or allowed to expand very slowly so that there is a sufficient time for the exchange of heat between the system and surrounding.
- ♣ A process has to be extremely slow to be isothermal.
- ♣  $PV = \text{constant}$  as  $PV = RT$  ----- constant.
- ♣ In an isothermal change, Sp. Heat,  $C = \frac{Q}{m \Delta T} = \frac{Q}{0} = \text{Infinity}$ .

**2.) Adiabatic process:** "A process in which pressure, Volume and temperature of the system change, but there is no exchange of heat between system and surrounding, is called adiabatic process".

- In this case P, V, & T are not constant but Q = constant.

**Two essential condition**, For perfect isothermal change -----

- [i] There should be not any exchange of heat between the system and its surroundings. All the wall 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.

Ex:- [i] Consider a gas contained in a cylinder having insulating wall and fitted with a n insulating piston. When the gas is Compressed suddenly, Heat is produced which cannot escape to the surroundings through the insulating walls. Thus, The temperature of the gas rises.

[ii] Bursting of tube.

[iii] Expansion of hot gases in internal combustion engine.

- ♣ In an Adiabatic change, Q = constant, therefore, Sp. Heat,  $C = \frac{Q}{m \Delta T} = \frac{0}{m \Delta T} = 0$ .

**Some other process in thermodynamics:-**

- 1. **Isochoric process** : (Iso –volumic process) : "A thermodynamic process that takes place at constant volume is called Isochoric process".  
 •-- In this process,  $dV = 0$   
 Ex: Consider a gas enclosed in a cylinder having rigid wall and fixed piston, when heat is added to the gas, there would be no change in the volume of the gas.
- 2. **Isobaric process** : " A thermodynamic process that takes place at constant pressure is called Isobaric process".  
 •-- In this process,  $dP = 0$ .  
 Ex : Heating of water at atmospheric pressure.
- 3. **Cyclic process**: A thermodynamic process in which the system returns to its initial stage after undergoing a series of Change is called Cyclic process".
- 4. **Non- Cyclic process**: A thermodynamic process in which the system does not returns to its initial stage after undergoing a series of Change is called Non- Cyclic process".
- 5. **Equilibrium process**: A thermodynamic process in which proceeds Extremely slowly such that at every instant of time, the temperature and pressure are the same in all parts of the system".

**Sign convection:**

- [i] **Positive sign** --- [+ ] If the system gained heat energy.
- [ii] **Negative sign** --- [- ] If the system lost heat energy .
- [iii] **Positive sign** --- [+ ] **Work done by the system.**
- [iv] **Negative sign** --- [- ] **Work done on the system.**

**Workdone**

"Work is said to be done if a body or a system moves through a certain distance in the direction of the applied force".

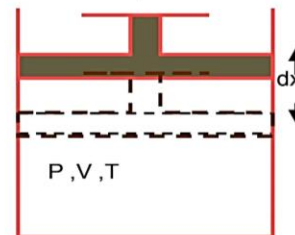
Consider a cylinder fitted with a frictionless piston of area of cross-section 'A'. Let an ideal gas contained in the cylinder. The walls of the cylinder are perfectly conducting one so that the gas in the cylinder is in thermal equilibrium and temperature with 'T' with the surrounding.

If 'P' be the pressure of the gas in the cylinder then the force exerted by the gas on the piston of the cylinder is,

$$F = P A$$

Let the piston move through a small distance 'dx' during the expansion of the gas.

Work done by the gas,  $W = F dx$   
 $W = P A dx = P ( A dx ) = P dV$   
 $W = P dV$



- [a] **Work done in an isothermal expansion** : Consider , 1 mole of an ideal gas enclosed in a cylinder with perfectly conductivity wall and fitted with a perfectly frictionless and conducting piston.

Let  $P_1, V_1, T_1$  = Initial pressure , Volume and temperature.

Let the gas expands to a volume  $V_2$  when pressure reduces to  $P_2$  and temperature remains constant at 'T'.

At any instant during expansion , let the pressure of the gas be 'P'. therefore,

Force exerted by the gas on the piston ,  $F = P A$  ----- [1] {since ,A = Area of the cross-section of the piston}.

- Small Amount of work during expansion ,

$$dW = F dx$$

[Here we assume that pressure of the gas during an infinitesimally small displacement  $dx$  of the piston remains constant ]

$$= P A dx = P dV \xrightarrow{\text{[Small increase in volume , } dV = A dx \text{]}}$$

- Total Work done by the gas in the expansion from initial volume  $V_1$  to final Volume  $V_2$ .

$$W = \int dW = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{RT}{V} dV \quad \{\text{since , } PV = RT\}$$

$$W = RT \int_{V_1}^{V_2} V^{-1} dV \quad \{\text{since , } RT = \text{Constant , because the process is an isothermal}\}$$

$$= RT \left[ \log_e V \right]_{V_1}^{V_2} = RT \left[ \log_e V_2 - \log_e V_1 \right] = RT \log_e \left[ \frac{V_2}{V_1} \right]$$

or,  $W = RT \cdot 2.3026 \log_{10} \frac{V_2}{V_1}$  [ since,  $\log_e = 2.3026$  ]

$$W_{\text{iso.}} = 2.3026 RT \log_{10} \frac{V_2}{V_1}$$

As,  $P_1 V_1 = P_2 V_2$  , therefore,

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

$$W_{\text{iso.}} = 2.3026 RT \log_{10} \frac{P_1}{P_2}$$

- Amount of heat spent in isothermal expansion (in calorie) ,

$$H = \frac{W}{J} = 2.3026 RT \log_{10} \frac{V_2}{V_1}$$

Also, Heat gained or lost by the surrounding

- [b] **Work done in an adiabatic expansion** : Consider , 1 mole of an ideal gas contained in an insulating cylinder with perfectly insulating wall and fitted with a perfectly insulating piston of area of cross-section 'A' .

Let  $P_1, V_1, T_1$  = Initial pressure , Volume and temperature of the gas .

Force exerted by the gas on the piston ,  $F = P A$  Where  $P$  = pressure of the gas during expansion.

$$dW = F dx = P A dx = P dV$$

- Total work done by the gas in adiabatic expansion from initial volume  $V_1$  to final Volume  $V_2$ .

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

the equation of adiabatic change  $PV^\gamma = K$  (constant)  
where,  $\gamma = \frac{C_p}{C_v} = \frac{\text{sp. heat of gas at constant pressure}}{\text{Sp. heat of gas at constant volume}}$

or,  $P = \frac{K}{V^\gamma} = K V^{-\gamma}$

$$W = \int_{V_1}^{V_2} K V^{-\gamma} dV = K \left[ \frac{V^{1-\gamma}}{1-\gamma} \right]_{V_1}^{V_2}$$

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

but,  $P_1 V_1^\gamma = P_2 V_2^\gamma = K$

$$W = \frac{1}{1-\gamma} \left[ P_2 V_2^\gamma V_2^{1-\gamma} - P_1 V_1^\gamma V_1^{1-\gamma} \right]$$

or,  $W = \frac{1}{1-\gamma} \left[ P_2 V_2 - P_1 V_1 \right]$

let the temperature falls to  $T_2$  from  $T_1$  during the expansion , so  $P_1 V_1 = RT_1$  and  $P_2 V_2 = RT_2$

$$W = \frac{1}{1-\gamma} RT_2 - RT_1 = \frac{1}{1-\gamma} R [T_2 - T_1] = \frac{R [T_2 - T_1]}{1-\gamma}$$

or,

$$W = \frac{R [T_1 - T_2]}{\gamma - 1}$$

- When work is done by the system then  $W = +ive$  as  $T_2 < T_1$  i.e., temperature falls when it expands adiabatically.  
□ When work is done on the system then  $W = -ive$  as  $T_2 > T_1$  i.e., temperature of system increases.  
□ Amount of heat spent in adiabatic expansion (in calorie)

$$H = \frac{W}{J} = \frac{R [T_1 - T_2]}{J (\gamma - 1)}$$

□ **Isothermal and adiabatic equation of an ideal gas :-**

- [1] **Isothermal equation of an ideal gas** : For an ideal gas ,  $PV = RT$  , where  $R$  = gas constant = 8.31 j/g/mol .  
In isothermal process ,  $T = \text{Constant}$

or,  $P_1 V_1 = P_2 V_2$  ----- Isothermal equation of ideal gas. **PV = Constant**

[2] **Adiabatic equation of an ideal gas** : Consider 1 mole of an ideal gas enclosed in cylinder fitted with a perfectly frictionless and insulating piston . Let P , V , & T be Initial pressure , Volume and temperature of the gas.

Suppose , a small amount of heat 'dQ' is given to the system . It is spent in two ways-----

---[a] In increasing the temperature of the gas by a small range of 'dT', **at constant volume**.

Portion of heat spent =  $1 \times C_v \times dT$

---[b] In expansion of the gas by a small volume , dV

Portion of heat spent =  $P dV$

$dQ = C_v dT + P dV$  ----- [1]

In an adiabatic change , no heat is supplied from outside ,   $dQ = 0$

from [1] ,  $C_v dT + P dV = 0$  ----- [2]

For an ideal gas ,  $PV = RT$  , on differentiation

$P dV + V dP = R dT$

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

from [2],  $C_v \left\{ \frac{P dV + V dP}{R} \right\} + P dV = 0$

or,  $C_v P dV + C_v V dP + R P dV = 0$   
 $(C_v + R) P dV + C_v V dP = 0$

But,  $C_p - C_v = R$  , or,  $C_p = C_v + R$   
 $C_p P dV + C_v V dP = 0$

Dividing both side by  $C_p PV$ , we get

$\frac{C_p P dV}{C_p PV} + \frac{C_v V dP}{C_p PV} = 0$   
 $\gamma \frac{dV}{V} + \frac{dP}{P} = 0$

Integrating both side , we get

$\gamma \int \frac{dV}{V} + \int \frac{dP}{P} = \text{Constant} = C$   
 $\gamma \log_e V + \log_e P = C$

or,  $\log_e V^\gamma + \log_e P = C$

or,  $\log_e P V^\gamma = C$

or,  $P V^\gamma = \text{antilog } C = K$

Or,  $P V^\gamma = K$

**INTERNAL ENERGY :**

Internal energy of the system is the energy possessed by the system due to molecular motion and molecular configuration.

This simply means that ---

**"The internal energy of a system is the sum of kinetic and potential energy of the molecules of the system".**  
 i.e.,  $U = U_p + U_k$

**In case of ideal gas**, In this particular case , we assume that intermolecular forces are zero . Therefore no work is done in changing the distance of the molecules. therefore,

$U_p = 0$

Thus internal energy of an ideal gas consist of only of internal kinetic energy, which depends only on the temperature of the gas

$U = U_p + U_k$   
 $= 0 + U_k \Rightarrow U = U_k$

**Internal energy (U) of an ideal gas is the function of absolute temperature (T) only** i.e.,  $U = f(T)$

**In case of Real gas**, Intermolecular forces are not zero . Therefore , definite amount of work has to be done in changing the distance between the molecule. Further , the intermolecular forces depends upon intermolecular distance which depends upon the volume of the gas . So, PE of the gas molecules depends upon the volume of the gas .

i.e.,  $U_p = f(V)$

Now, Due to molecular motion , the molecules of real gas possess KE . According to kinetic interpretation of temperature , the KE of the gas depends upon temperature.

i.e.,  $U_k = f(T)$

'U' of a real gas is function of V and T of the gas i.e.,  $U = f(T, V)$

Thus, Internal energy ,  $U = U_p + U_k$

**LAWS OF THERMODYNAMICS**

**1st LAW OF THERMODYNAMICS : [Law of conservation of energy]**

As per 1<sup>st</sup> Law, "When some quantity of heat (say dQ) is supplied to a system capable of doing external work, then the the quantity of heat absorbed by the system (dQ) is equal to the sum of the increase in the internal energy of the system (dU) due to rise in temperature and the energy leaving the system in the form of work done by the system on its surrounding".

i.e.,

$$dQ = dU + dW \quad \text{---- law of conservation of energy}$$

$$dQ = dU + P dV \quad \{ \text{since } dW = P dV \}$$

**Sign convection ::**

- [1] When heat is supplied to a system, 'dQ' is taken as **positive**.
- [2] When heat is drawn Form the system, dQ is taken as **Negative**.
- [3] When a gas expands, Work done by the gas, 'dW' is taken as **Positive**.
- [4] When a gas is compressed, Work is done on the gas, 'dW' is taken as **Negative**.
- [5] When temperature of a gas increases, its internal energy increases, dU is taken as **Positive**.
- [6] When temperature of a gas decreases, its internal energy dU is taken **Negative**.

**Significance of 1<sup>st</sup> law of thermodynamics ::**

- [1] 1<sup>st</sup> law of thermodynamic tells us that it is impossible to get work from any machine without giving it an equivalent amount of energy.
  - [2] 1<sup>st</sup> law of thermodynamic introduce the concept of internal energy.
  - [3] Basically, 1<sup>st</sup> law of thermodynamics, is law of conservation of energy, applies to every process in nature.
- 1<sup>st</sup> law applies equally to all the three phases of matter i.e., solid, liquid or gases.
  - Out of dQ, dW, & dU, dQ & dW are dependent on the path of the system follows in going from initial to final state, while dU does not depends on the path, it depends only on the initial and final state of the system.
  - In applying the 1<sup>st</sup> law of thermodynamics, all the three quantities i.e., dQ, dW, & dU must be expressed in the same units i.e., either in the unit of work or in the unit of heat.

**Application of 1<sup>st</sup> law of thermodynamics**

**[a] Isothermal process ::** In an isothermal process temperature remains constant. If the system is an ideal gas whose internal Energy U depends only on temperature, then the internal energy shall remains constant i.e., dU = 0

$$\square dQ = dU + dW = 0 + dW = dW$$

i.e., during isothermal process, **Heat added (or remove) = Work done by (or on) the system**

- **Heat energy supplied in an isothermal process is used to do work against the external surrounding.**

**[b] Adiabatic process ::** No heat energy enters or leave the system as it is well insulated

$$\begin{aligned} \square dQ &= 0 \\ \text{A/ 1<sup>st</sup> law} \quad dQ &= dU + dW \\ 0 &= dU + dW \\ \square \quad dU &= -dW \end{aligned}$$

- If the work is done by the system adiabatically (expansion), then the internal energy of the system decreases by an equal amount to the work done by it.
- If the work is done on the system, then dW = -ive value. therefore, dU = --(--dW) = +dW
- **Internal energy of the system increases by an amount equal to the work done on it, during adiabatic process.**

**[c] Constant volume process ::** When volume of the system (such as gas) is kept constant then, dW = pdV = P × 0 = 0

$$\begin{aligned} \text{From 1<sup>st</sup> law of thermodynamics,} \quad dQ &= dW + dU \\ \text{or,} \quad dQ &= 0 + dU \\ \text{or,} \quad dQ &= dU \end{aligned}$$

- **if Heat is absorbed by a system at constant volume, its internal energy increases by the same amount and vice versa.**

**[d] Cyclic process ::** In cyclic process, the system is returned to its initial state after any change.

$$\begin{aligned} \text{In this case, } dU &= 0 \\ \text{From 1<sup>st</sup> law law,} \quad dQ &= dW + dU \\ \text{or,} \quad dQ &= dW + 0 \\ \text{or,} \quad dQ &= dW \end{aligned}$$

- **Net work done during a cyclic process must exactly equal to the amount of heat energy transferred.**

**[e] Melting process ::** When a solid melts into a liquid, its internal energy increases.

**Calculation of internal energy ::** Let, mass of solid = m; latent heat of the solid = L,

Amount of heat absorbed (during melting), Q = m × L ----- [1]

When a substance melts, the change in its volume (dV) is very small and hence neglected, therefore dV = 0.

$$\begin{aligned} \square dW &= PdV = 0 \\ \text{From 1<sup>st</sup> law,} \quad dQ &= 0 + dU = dU \\ m \times L &= dU \\ dU &= m \times L \text{ ----- [2]} \end{aligned}$$

- The internal energy during the melting increases by 'm L'.

- **We know that, during melting temperature is constant, therefore, Increase in internal energy during melting must be due to increase in internal potential energy(U<sub>P</sub>). Also, U<sub>K</sub> is also constant.**

**[f] Boiling process ::** In boiling, liquid changes into vapour at constant temperature & pressure.

$$\begin{aligned} \text{let,} \quad \text{mass of liquid at boiling point} &= m \\ \text{Volume of the liquid at boiling point} &= V_1 \\ \text{Constant pressure at which boiling process occurs} &= P \end{aligned}$$



Volume of the same liquid in the vapour form under same pressure =  $V_2$

Latent heat of vapourisation of the liquid =  $L$

□ Heat absorbed by the liquid in the boiling process,  $dQ = mL$

From 1<sup>st</sup> law,  $dQ = dW + dU$

or,  $dU = dQ - dW$

or,  $dU = mL - PdV$

or,  $dU = mL - P\{V_2 - V_1\}$

(Since,  $dV = V_2 - V_1$ )

□ **Increase in the internal energy is again due to increase in internal potential energy.**

**[g] Specific Heat Relation**

**$C_p - C_v = R$**  [Mayer's Formula]

Consider, 1 g mole of an ideal gas enclosed in a cylinder fitted with a piston (frictionless).

Let,  $P, V, T$  be the initial pressure, volume and temperature of the gas.

Let the gas be heated at constant volume through a small range of temperature ' $dT$ '.

□ Amount of heat energy supplied to the gas,

$dQ = C_v \times 1 \times dT$  ----- [1]  
 Molar sp. heat of gas at constant volume

As, the volume remains constant, i.e.,  $dV = 0$ , therefore,

$dW = P dV = 0$

From 1<sup>st</sup> Law,

$dQ = dW + dU$

$C_v dT = 0 + dU$

or,

**$dU = C_v dT$**  ----- [2]

Now, the gas heated at constant pressure through the same range of temperature ' $dT$ ', when its volume increasing by a small amount ' $dV$ '.

□ Amount of heat energy supplied to the gas,  $dQ' = C_p \times 1 \times dT$  ----- [3]  
 where  $C_p$  = Molar sp. heat of gas at constant pressure.

Also,

$dW' = P (dV)$

If the  $dU'$  = increase in internal energy of the gas, then from 1<sup>st</sup> law,

$dQ' = dW' + dU'$

$C_p dT = dU' + P(dV)$  ----- [4]

As rise in temperature of the gas in two cases is the same ( $= dT$ ), therefore,

Increase in internal energy (which depends only on the temperature in case of ideal gas) must be equal in the two cases.

□  $dU' = dU = C_v dT$  [from (2)]

From [4]

$C_p dT = C_v dT + P(dV)$

$(C_p - C_v) dT = P dV$  ----- [5]

now,

$P V = R T$  (ideal gas equation)

differentiating both side, we get,

$P dV = R dT$

[since  $R$  &  $P$  are constant]

From [5],

$(C_p - C_v) dT = R dT$

**$C_p - C_v = R$**

since  $R$  is 'positive', therefore  $C_p > C_v$

□  $C_p - C_v = R$

or,

$\frac{C_p}{M} - \frac{C_v}{M} = \frac{R}{M}$

or,

**$C_p - C_v = r$**

Gas constant for 1 gram.

**Limitation 1st LAW OF THERMODYNAMICS :**

The first law of thermodynamics tells us that heat & mechanical energy are inter convertible. However,

□ [1] **1<sup>st</sup> law does not indicate the direction in which the change can occur, i.e., it does not tell us about the direction of transfer of heat.**

Ex: [a] We know that heat flows from a hot body to cold body, but 1<sup>st</sup> law give no reason as to why heat cannot flow from a cold body to a hot body.

[b] When a bullet strikes a target, KE of the bullet is converted into heat energy. But heat energy developed in the Target cannot be converted back into mechanical energy of the bullet enabling it to fly back.

□ [2] **It does not tell us how much of a given quantity of heat is converted into work.**

EX: No heat engine can convert all the heat energy received from the source into mechanical energy. 1<sup>st</sup> law is silent about all this.

□ [2] **The first law does not tell anything about the condition under which heat can be conserved into work.**

Consider what happens when you drop a stone and it hits the ground. The initial potential energy of the stone changes to kinetic energy as the stone falls. When the stone hits the ground, the kinetic energy is transformed into internal energy of the stone and the ground in the vicinity of the impact; the molecules move faster and the temperature rises slightly. But have you seen the reverse happen—a stone at rest on the ground suddenly rise up in the air because the thermal energy of the molecules is transformed into kinetic energy of the stone as a whole? Energy would be conserved in the process, yet we never see it happen. The first law does not explain why it cannot happen.

**REVERSIBLE AND IRREVERSIBLE PROCESS :**

**REVERSIBLE PROCESS:** "It is the process which can be retraced in the opposite direction so that the system and the surrounding pass through exactly the same state at each stage as in the direct process".

Ex: If some heat has been absorbed from the surrounding in the direct process, the same amount of heat is given out to the surrounding in the reverse process.

□ **At the end of a reversible process, the system and surrounding must return to their initial state.**

● **Basic requirements for a process to be reversible**

- {I} The process should proceed at an extremely slow rate so that :
    - (a) The system remains in mechanical equilibrium i.e., there is no unbalanced force.
    - (b) The system remains in thermal equilibrium i.e., all parts of the system & the surrounding remains at the same temperature
    - (c) The system remains in chemical equilibrium i.e., the internal structure of the system does not change.
  - {II} The system should be free from dissipative forces like friction, viscosity, inelasticity etc.
  - {III} The pressure difference between working substance and surrounding at any stage of the operation of cycle should be very small.
  - {IV} There should be no loss of energy due to conduction connection & radiation during the operation.
- A complete reversible process cannot be realized in actual practical.

□ **IRREVERSIBLE PROCESS :**

**“ It is a process which is not exactly reverse and the system does not pass through the same state in every stage as in direct process.”**

In an irreversible process, there always occurs some loss of energy which are not recovered. Every process in nature is in fact an irreversible process.  
 EX—Rusting of Iron, Decay of organic matter.

□ **SECOND LAW OF THERMODYNAMICS :**

(specifying the condition of transformation of heat into work)

--- **Kelvin's Statement :** **It is impossible to obtain a continuous supplying of work from a body by cooling it to a temp<sup>t</sup> below the coldest of its surrounding.**

EXPLANATION :- **In a heat engine** -- The working substance of a heat engine, cannot convert all the extracted heat into work. It must reject a part of heat to the sink at a lower temperature. So, in order to convert heat into work it is necessary to have both source and sink. Since all the extracted from the source cannot be converted into work. Therefore the efficiency of the engine is never 100% of 1.

--- **Claussius Statement :** **“ It is impossible for a self acting machine, unaided by any external agency to transfer heat from one body at lower temperature to another at a higher temperature .”**

i.e., Heat cannot by itself flow from a body at a lower temperature to a body at a higher temperature.  
 Ex-- No refrigeration can ever work without external supply of electric energy to it.

--- **Planck's Statement :** **“ It is impossible to construct a heat engine that will extract heat from a reservoir and perform on equivalent amount of work.”**

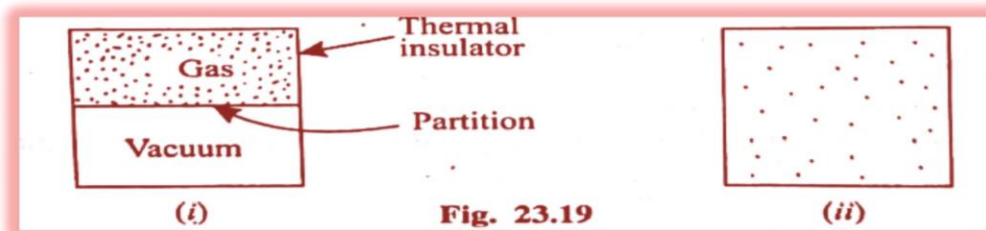
All the statements of the 2<sup>nd</sup> law are equivalent, as one can be obtained from other.

□ **ENTROPY**

**Entropy is a measure of the disorder of a system.**

Explanation: Whenever a physical is allowed to distribute its energy freely, it always does so in a manner That disorder increases i.e., **entropy increases.** (By disorder, means random).

Example : Suppose we have a box with a partition dividing it in two, with a gas on one side of the partition And other side evacuated. With all the molecules of gas in one side, gas has a highly ordered Situation. However, if the partition is removed, the gas molecules will distribute themselves throughout the box and be moving in random direction a less ordered situation. Now we are in the position to say that entropy of gas has increased because the amount of disorder has increased.



**As the disordered of a system increases, its entropy increases.**

- In order to change the disordered system to the ordered one, some work will have to be done. Ex : Water in refrigerator freezes And becomes more ordered because is put into refrigeration cycle

**ENTROPY and 2<sup>ND</sup> LAW OF THERMODYNAMICS**

When the entropy of a system increases, there is decrease in the energy available to do useful work. For example, consider the natural process of heat conduction from a hot body to a cold one. In this process, entropy increases and the order goes to disorder. The fact that disorder has increased as a result of such a process can be explained as follows. Hot and cold objects could serve as high and low temperature regions for a heat engine and thus could be used to obtain useful work. But after the two objects are put in contact and reach the same uniform temperature, no useful work can be obtained from them. With regard to being able to do useful work, order has gone to disorder in the process. Therefore, second law of thermodynamics can also be stated in another useful way.

In any natural (irreversible) process, the entropy increase i.e., some energy becomes unavailable to do Useful work.

- Entropy is a measure of how much energy or heat is available for conversion into useful work.
- When a system at kelvin temperature  $T$  undergoes a reversible process by absorbing an amount of heat  $Q$ , its increase in entropy  $\Delta S$  is....

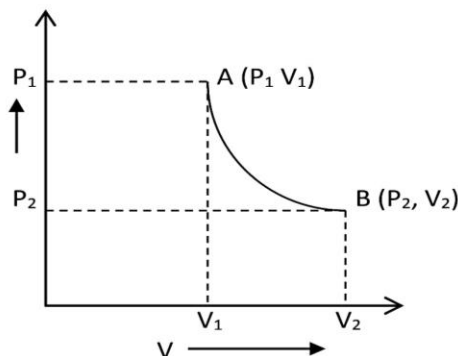
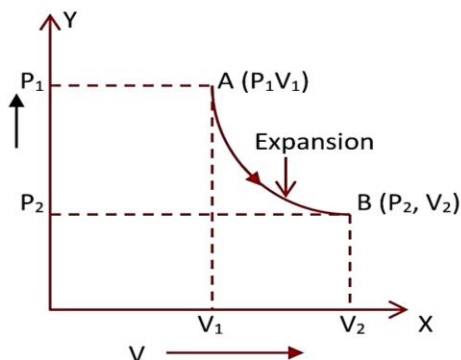
$$\Delta S = \frac{Q}{T}$$

- We are defining Entropy for a reversible process which does not occur in nature and we can use this definition for processes which are approximately reversible.

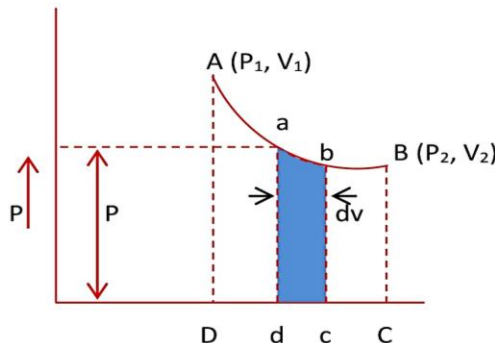
**P-V DIAGRAM**

A graph representing the variation of pressure with the variation of volume is called **P-V diagram**.

'Work done' by the thermodynamical system is equal to the area under P-V diagram.



Consider 1 mole of gas in a cylinder filled with a frictionless piston. Let gas expands from the state A ( $P_1, V_1$ ) to the state B ( $P_2, V_2$ ).



Consider two point 'a' & 'b' on P-V diagram. The point 'a' & 'b' are so closed to each other that the pressure 'P' corresponding to these points is same. Now we have to draw 'ad' & 'bc',  $\perp$  on the volume axis. Here  $dc = dv$  (change in volume).

$\therefore$  Work done by the system against pressure,  
 $dW = PdV = ad \times dc = \text{area of strip 'abcd'}$ .

$\therefore$  Total work done (from A to B)  
 $\int dW = \int PdV = \text{sum of area of all strip within 'ABCD'}$ .

**$\therefore W = \text{Area under P-V diagram}$**

**Comparison of the slopes of an Isothermal and an Adiabatic Curve**

- **For an Isothermal process**,  $PV = \text{constant}$   
 On differentiating,  $PdV + VdP = 0$   
 [Where,  $\frac{dP}{dV}$  represents the slope of an isothermal curve]

$$\therefore \left(\frac{dP}{dV}\right)_{\text{iso}} = \left(-\frac{P}{V}\right) \quad \dots (i)$$

- **For an Adiabatic process**,  $PV^\gamma = \text{constant}$   
 Differentiating,  $P\gamma V^{\gamma-1} dV + V^\gamma dP = 0$   
 ... (ii)

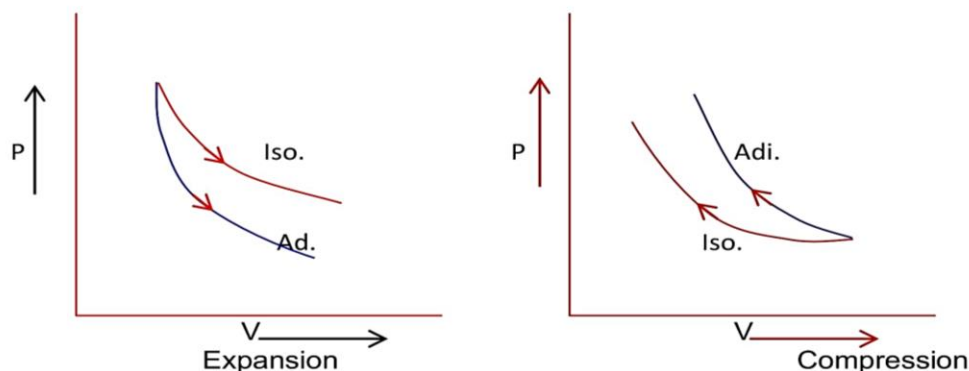
$$\left(\frac{dP}{dV}\right)_{\text{adi}} = -\frac{\gamma P}{V}$$

From (i) & (ii)  $\left(\frac{dP}{dV}\right)_{\text{ad}} = \gamma \left(\frac{dP}{dV}\right)_{\text{iso}}$

$\gamma > 1$

$$\therefore \left(\frac{dP}{dV}\right)_{\text{ad}} > \left(\frac{dP}{dV}\right)_{\text{iso}}$$

I.e., slope of adiabatic curve more steeper than slope of isothermal curve.



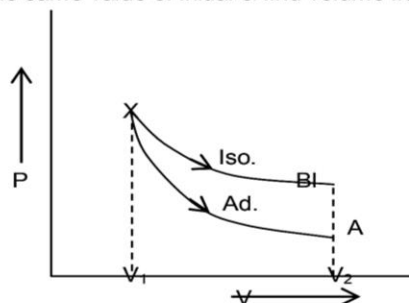
**Comparison of the slopes of an Isothermal and an Adiabatic Curve**

- **1. During Expansion:** Isothermal and Adiabatic expansion between the same value of initial & final volume i.e.  $V_1$  &  $V_2$  (represented by the curve XI and XA).

Work done during isothermal expansion,  
 $W_{\text{iso}} = \int_{V_1}^{V_2} P \, dV$   
 = Area under isothermal curve (XI)  
 = Area of XI  $V_2 V_1$

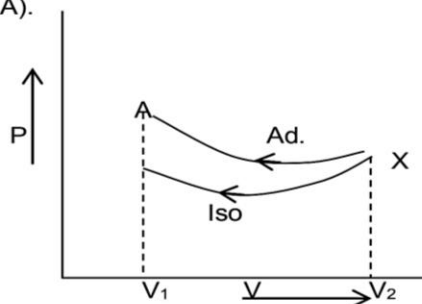
Work done during Adiabatic Expansion  
 $W_{\text{ad}} = \int_{V_1}^{V_2} P \, dV$   
 = Area under Adiabatic curve (XA)  
 = Area  $\times$  AV<sub>2</sub> V<sub>1</sub>

Now As per P-V diagram  
**Area  $V_2 V_1 > \text{Area } XAV_2V_1$**



Work done during isothermal expansion is more than adiabatic expansion between same values of initial & final volumes.

- **2. During compression:** Isothermal and Adiabatic compression between the same value of initial & final vol.  $V_1$  &  $V_2$  (represented by XI and XA).



➤ **Work done during isothermal compression,**

$$W_{iso} = \int_{V_1}^{V_2} P \, dv$$

= Area under isothermal curve XI = Area of XI V<sub>2</sub> V<sub>1</sub>

Also Work done during Adiabatic compression

$$W_{ad} = \int_{V_1}^{V_2} P \, dv$$

= Area under adiabatic curve XA = Area of XA V<sub>1</sub> V<sub>2</sub>

From P-V diagram,

$$\text{Area of XA V}_1 \text{ V}_2 > \text{Area of XI V}_1 \text{ V}_2$$

$$= W_{adi} > W_{iso}$$

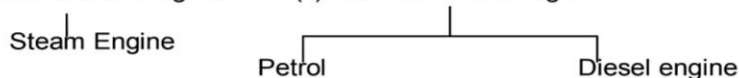
➤ **Work done during adiabatic expansion compression is more than the work done during isothermal compression between the same values of initial & final volumes.**

**Conversion of Heat into Mechanical work [Heat Engine]**

**A heat engine is a device which converts heat energy into mechanical energy.**

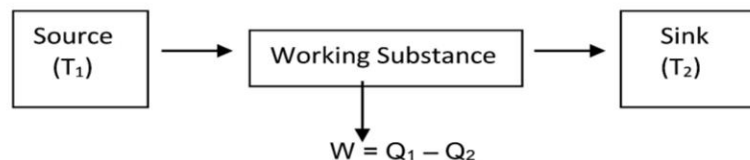
➤ There are two types of Heat Engine:-

- (i) Ext. combustion Engine      (ii) Int. combustion engine



**Construction:** A heat engine in essentially consists of

- (i) **Source:** A body (hot) maintained at very high temperature (T<sub>1</sub>) which supplies Heat energy is called source.
- (ii) **Sink:** A cold body maintained at low temperature (T<sub>2</sub>). Which absorbs the respected heat is called sink.
- (iii) **Working Substance:** A material which absorbs heat energy from the source and converts it into mechanical energy (work) by rejecting some of the Heat to the sink is called Working substance.
- (iv) **Mechanical part:** the mechanical parts of the engine are required for containing and for transfer of mechanical energy to the appropriate parts of the machine.



- **Working and efficiency:** The working substance of the engine absorbs heat energy from the source. A part of this Heat energy is converted into mechanical energy (work) and the remaining heat is rejected to sink. Thus, the temperature of the working substance remains as it was before the absorption of heat energy. Therefore, the working substance is now again ready to absorb the Heat energy from the source and to repeat the process continuous.

- **Efficiency:** Let Q<sub>1</sub> = Amount of Heat absorbs by working substance from the source at (T<sub>1</sub> K)  
 Q<sub>2</sub> = Amount of heat rejected to the sink at T<sub>2</sub> K.  
 W = Mechanical energy or work performed in each cycle.

Since there is no change in the temperature of the working substance at the end of the each cycle,

∴ Change in internal energy of the working substance = 0

i.e.,  $dv = 0$

At 1<sup>st</sup> Case  $dQ = dU + W \Rightarrow dQ = 0 + W$

$$dQ = W$$

or  $W = Q_1 - Q_2$

Thus, "The ratio of net work done per cycle by the engine to the total amount of heat absorbed per cycle by the working substance form the source is called Thermal efficiency of Heat engine." (η)

$$\eta = \frac{\text{Net work done / cycle (w)}}{\text{Total amount of Heat absorbed/cycle}}$$

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

As some, heat is always repeated to the sinks i.e. Q<sub>2</sub> ≠ 0

∴ **efficiency is always less than 1 m other words, thermal efficiency of heat engine is always less than 100%.**

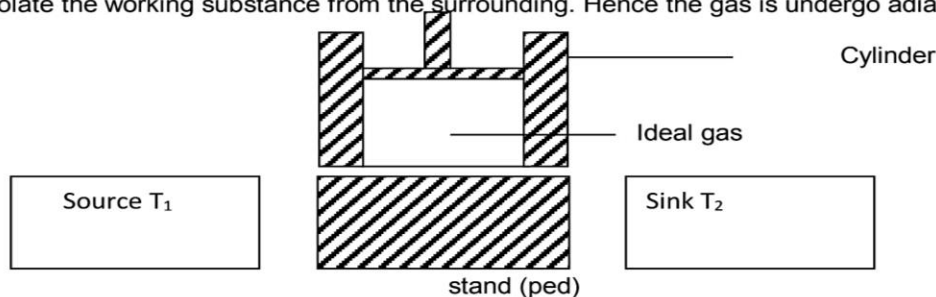
**CARNOT'S IDEAL HEAT ENGINE :**

**Construction:**

- (i) Source of Heat (T<sub>1</sub>)    (ii) Sink (T<sub>2</sub>)    (iii) Working substance

A perfect gas acts as the working substance. It is contained in a cylinder with non-conducting base. This cylinder is fitted with non-conducting and frictionless piston.

There is a perfectly INSULATING pad (stand) on which the cylinder can be placed it would completely isolate the working substance from the surrounding. Hence the gas is undergo adiabatic charge.



**Carnot's cycle (theory):-**

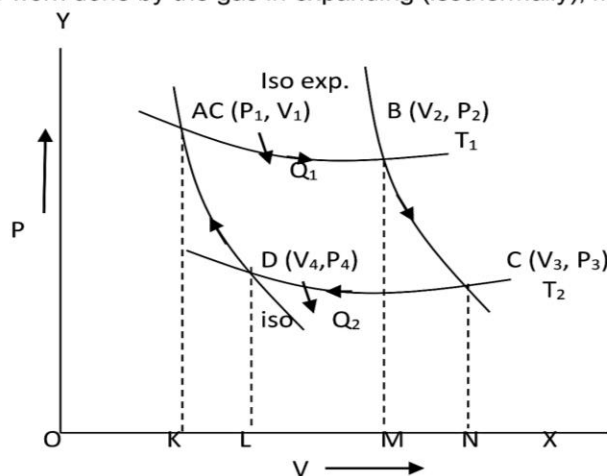
The Carnot's cycle consists of 4 stages:

- (i) Isothermal expansion
- (ii) Adiabatic expansion
- (iii) Isothermal Compression
- (iv) Adiabatic compression

• **Stage (1): Isothermal expansion:** Let the cylinder be placed the source and the gas be allowed to expand by outward motion of the piston . sink absorbs the required amount of heat from the source through the conducting base of the cylinder. Therefore, temperature of the gas remains constant. This operation is called isothermal expansion represented by curve (AB).

Let, Amount of Heat energy absorbed in this process =  $Q_1$

Amount of work done by the gas in expanding (isothermally), from A ( $V_1, P_1$ ) to B ( $P_2, V_2$ ) = kh



$$\therefore Q_1 = W = \int_{V_1}^{V_2} P \cdot dv = RT \cdot \log_e \frac{V_2}{V_1} = \text{Area AB MK.} \quad \dots (i)$$

• **Stage (2): Adiabatic Expansion:** The cylinder is now removed from the source and is placed on the perfectly insulating pad. The gas is allowed to expand further from B ( $V_2, P_2$ ) to C ( $V_3, P_3$ ). Since the gas is thermally insulated from all sides, no heat can be gained from the surrounding temperature of gas falls to  $T_2$ , the expansion is adiabatic (represented by curve BC)

Let  $W_2$  = Work done by the gas in expanding adiabatically from B ( $V_2, P_2$ ) to C ( $V_3, P_3$ )

$$\therefore W_2 = \int_{V_2}^{V_3} PdV = \frac{R}{(\gamma - 1)} (T_1 - T_2) = \text{are BCNB} \quad \dots (ii)$$

• **Stage (3): Isothermal Compression:** The cylinder is non-removed from the insulating pad and is placed on the sink at temperature  $T_2$ . The piston is moved slowly so that the gas is compressed until its pressure is  $P_4$  and volume is  $V_4$ . This state is represented by the point D. Since the base of the cylinder is conducting, Heat produced in compression will pass to C the sink so that the temperature of the gas remains constant at  $T_2$ . Therefore, the process is isothermal (represented by CD).

Let  $Q_2$  = Amount of heat energy rejected to the sink

$W_3$  = Work done on the gas in compressing it (isothermally) from C ( $V_3, P_3$ ) to D ( $V_4, P_4$ ).

$$Q_2 = W_3 = - \int_{V_3}^{V_4} PdV = - RT_2 \log_e \frac{V_4}{V_3} = RT_2 \log_e \frac{V_3}{V_4} = \text{Area CDLN} \quad \dots (iii)$$

(negative sign convention, work done on the system is taken as -ve).

- **Stage (4): Adiabatic Compression:** The cylinder is again placed on the insulating pad. The piston is further moved slowly downward so that the gas is compressed to its initial volume  $V_1$  & pressure  $P_1$ . As the gas is insulated from all sides, Heat produced raises the temperature of the gas  $T_1$  (represented DA).  
 Let  $W_4$  = Work done on the gas in compressing it adiabatically from a state D ( $V_4, P_4$ ) to its initial state A ( $V_1, P_1$ ).

$$\begin{aligned} \therefore W_4 &= \int_{V_4}^{V_1} -PdV = - \frac{R}{\gamma - 1} (T_2 - T_1) = \frac{R}{\gamma - 1} (T_1 - T_2) \\ &= \text{area DAKL} \quad \dots \text{(iv)} \end{aligned}$$

∴ **Work done by the engine per cycle:-**

Total work done by the gas (in stage (1) & (2)) =  $W_1 + W_2$

Total work done on the gas in stage (3) & (4) =  $W_3 + W_4$

Net work done ( $W$ ) by the gas in a complete cycle,

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

$$= W_1 - W_3 + W_2 - W_4$$

$$W = W_1 - W_3$$

as  $[W_2 - W_4 \text{ (mag.)}]$

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

Also,

$$W = Q_1 - Q_2$$

Hence, In Carnot heat engine net work done by the gas per cycle numerically equal to the area of the loop represent the cycle.

### □ Efficiency of Carnot's Cycle

"It is defined as the ratio of net mechanical work done per cycle by the gas ( $W$ ) to the amount of Heat energy absorbed per cycle from the source ( $Q_1$ ).

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

$$\eta = \frac{Q_1 - Q_2}{Q_1} \quad [\text{as } W = Q_1 - Q_2]$$

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

∴ (i)

$$\text{Also, } \eta = \frac{W_1 - W_3}{W_1} = 1 - \frac{W_3}{W_1}$$

Now, A ( $V_1, P_1$ ) and B ( $V_2, P_2$ ) lie on the same isothermal. ∴  $P_1 V_1 = P_2 V_2$  ... (ii)

And, B ( $V_2, P_2$ ) and C ( $V_3, P_3$ ) lie on the same adiabatic ∴  $P_2 V_2^\gamma = P_3 V_3^\gamma$  ... (iii)

Again, C ( $V_3, P_3$ ) and D ( $V_4, P_4$ ) lie on the same isothermal ∴  $P_3 V_3 = P_4 V_4$  ... (iv)

Lastly, D ( $P_4, V_4$ ) & A ( $V_1, P_1$ ) lie on the same adiabatic ∴  $P_4 V_4^\gamma = P_1 V_1^\gamma$  ... (v)

Multiplying (ii), (iii) (iv) & (v)  $(P_1 V_1) (P_2 V_2^\gamma) (P_3 V_3) (P_4 V_4^\gamma) = (P_2 V_2) (P_4 V_4) (P_3 V_3^\gamma) (P_1 V_1^\gamma)$

$$V_1 V_2^\gamma V_3 V_4^\gamma = V_1^\gamma V_2 V_3^\gamma V_4$$

$$V_2^{\gamma-1} V_4^{\gamma-1} = V_1^{\gamma-1} V_3^{\gamma-1}$$

$$(V_2 V_4)^{\gamma-1} = (V_1 V_3)^{\gamma-1}$$

$$\therefore V_2 V_4 = V_1 V_3$$

$$\text{i.e. } \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$\text{Taking log, } \log \frac{V_2}{V_1} = \log \frac{V_3}{V_4} \quad \dots \text{(vi)}$$

$$\begin{aligned} \text{From (i), } \eta &= 1 - \frac{Q_2}{Q_1} = 1 - \frac{W_2}{W_1} \\ &= 1 - \frac{RT_2 \log V_3/V_4}{RT_1 \log V_2/V_1} \end{aligned}$$

$$\eta = 1 - \frac{T_2}{T_1}$$

∴ i.e.,  $\eta$  (efficiency of Carnot's engine) depends on temperature of source  $T_1$  & temperature of sink ( $T_2$ ).

∴  $1 - \frac{T_2}{T_1} < 1$  ∴  $\eta$  is less than 100 %

For  $\eta = 1$  (i.e. 100 %) either  $T_1 = \infty$  or  $T_2 = 0\text{K}$ .

∴ [As source at Infinite temperature or sink at 0K are not attainable, cannot heat engine cannot have 100% efficiency].

∴ If  $T_2 = T_1$  then  $\eta = 1 - \frac{T_2}{T_1} = 1 - 1 = 0$  [i.e., It is not possible to convert heat energy into mechanical work unless source and sink of heat are at different temperature].

∴ Since  $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$  When  $T_2 \neq 0, Q_2 \neq 0$

i.e., some heat must be rejected to the sink. Hence ' $\eta$ ' of even an ideal Heat engine can never be 100 %.

### □ Carnot's Theorem

$$\text{Since, } \eta = 1 - \frac{T_2}{T_1}$$

Carnot showed that "No Heat Engine working between two given temperature of source and sink can be more efficient than a perfectly reversible (Carnot engine) engine working between the same two temperature.

▣ **TYPES of HEAT ENGINES**

- [1] EXTERNAL COMBUSTION ENGINE (STEAM ENGINE)
- [2] INTERNAL COMBUSTION ENGINE (DIESEL AND PETROL ENGINE)

▣ [1] **EXTERNAL COMBUSTION ENGINE (STEAM ENGINE):** In an external combustion engine, the working substance (i.e., steam is produced by the burning of fuel outside the cylinder. The steam engine is an external combustion engine.  
 —Efficiency : about 12 % to 16 %.

▣ [1] **Internal COMBUSTION ENGINE (Petrol and Diesel ENGINE):** In an Internal combustion engine, fuel is burnt inside the cylinder  
 —Efficiency : about 25 % (petrol) and 40% (diesel ).

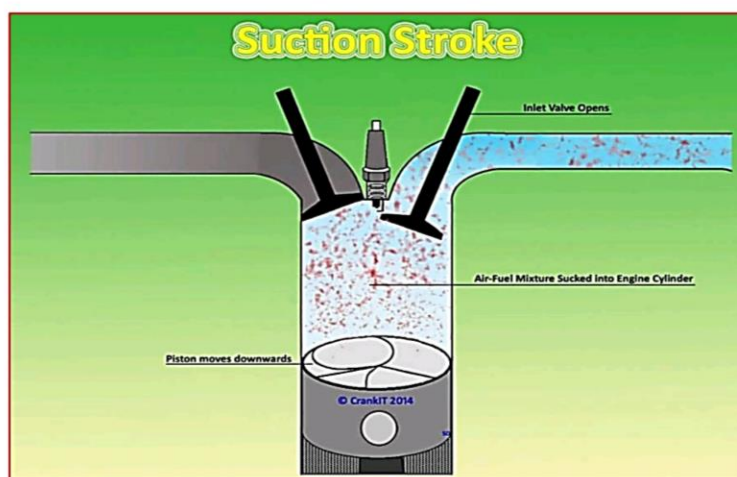
▣ **Petrol engine (Nikolaus otto):**

Otto Cycle is also known as **Four-Stroke Spark-Ignition Cycle**. It was named after German engineer **Nikolaus Otto** who invented, developed and patented first Four-Stroke petrol engine. The Four-Stroke petrol engine works on the following cycle which includes –



●—[1] **INTAKE STROKE (SUCTION STROKE):**

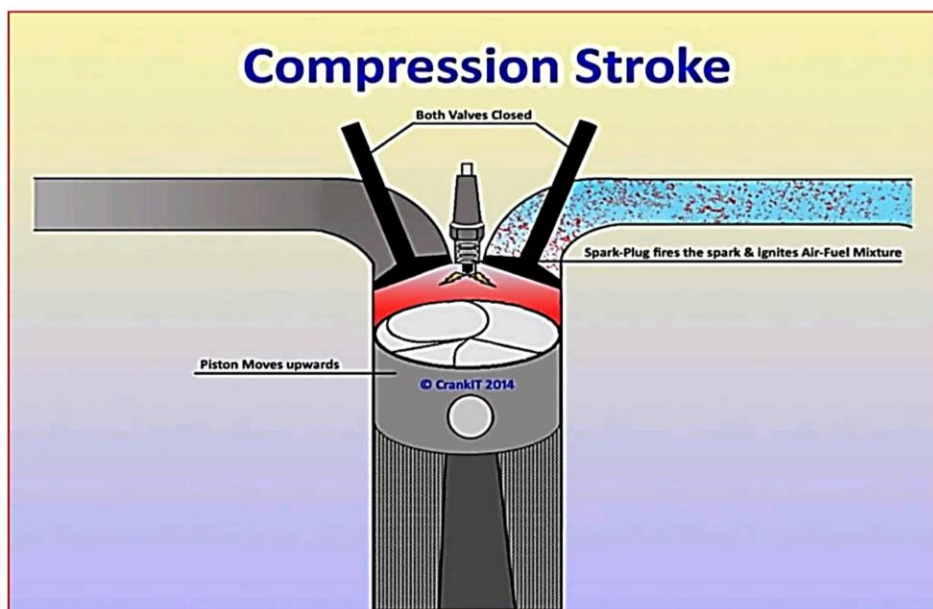
With pistons moving downwards and the opening of the inlet valve creates the suction of air-fuel mixture.



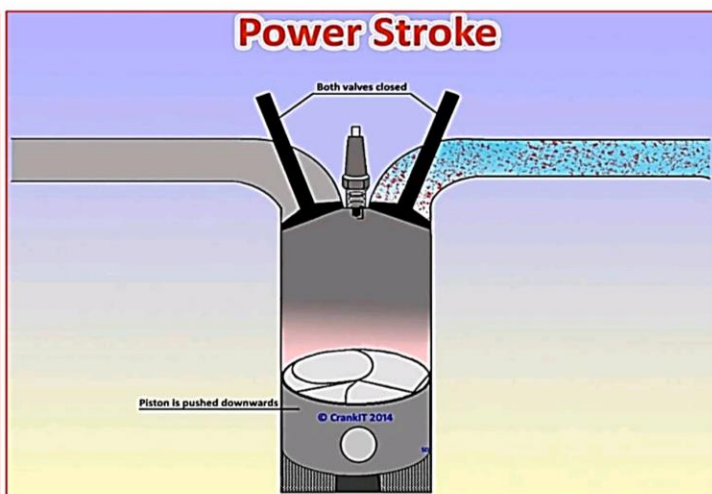
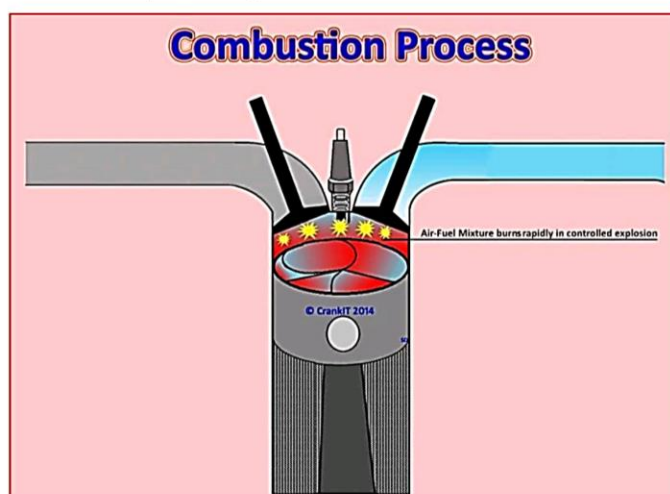
●—[2] **COMPRESSION STROKE** – With the closing of Inlet valve, it closes the area above the piston. The piston moves up resulting in compression of the air-fuel mixture in a confined space.

●● **COMPRESSION IS DONE UPTO 1/8<sup>TH</sup> OF THE ORIGINAL VOLUME.**

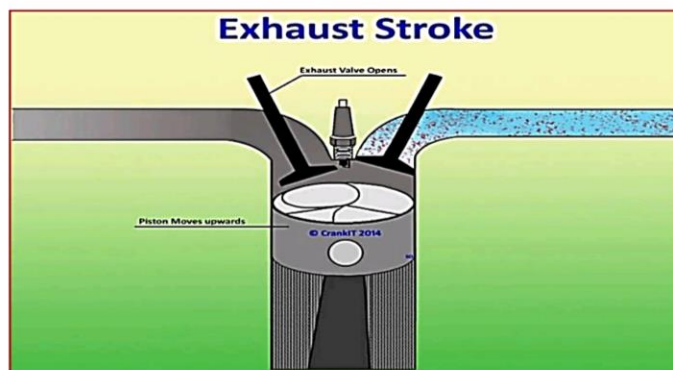




●—[3] **POWER / COMBUSTION STROKE** : At this stage, the spark-plug fires the spark which results in instantaneous burning of petrol causing in an explosion. This causes heat to release which generates expanding forces known as power. Furthermore, these forces again push the pistons downwards resulting in their reciprocating motion.



●—[4] **EXHAUST STROKE** – On their way up, the pistons push the exhaust gases above them thru' the exhaust valve which opens during the exhaust stroke.



Thus, this cycle repeats itself until the engine is turned off, resulting in the continuance of its running. The earlier generation petrol engine used 'Carburettor' to supply petrol to the engine. The newer generation petrol engines use sophisticated 'Fuel-Injection' technology (just like diesel engines) with an 'Engine Management System' for improved performance and lower emissions. However, it still uses the spark-plug for igniting the petrol which was the case in the earlier generation petrol engines.

**❑ Diesel Engine (RUDOLPH DIESEL):**

**Diesel Engine Principle :**

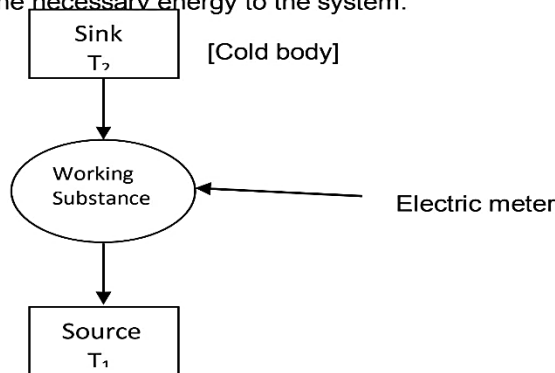
Basically, there are two types of diesel engine types - the Four Stroke and **Two Stroke**. The 'Diesel Cycle' uses higher **Compression-Ratio**. It was named after German engineer Rudolph Diesel, who invented and developed first Four-Stroke **diesel** engine. The four strokes of the diesel cycle are similar to that of a **petrol engine**. However, the 'Diesel Cycle' considerably differs by the way the fuel system supplies the diesel the engine and ignites it.

A conventional internal combustion diesel engine works on 'Diesel Cycle'. In the simple diesel engines, an **injector** injects diesel into the combustion chamber above the piston directly. The 'Compression-Ignition engine' is also another name for the Diesel engine. This is mainly because it burns the **diesel** with hot and compressed air. The temperature of the air inside the combustion chamber rises to above 400°C to 800°C. This, in turn, ignites the **diesel** injected into the combustion chamber. Thus, the 'Diesel Cycle' **does not use** an external mechanism such as a spark-plug to ignite the air-fuel mixture.

**❑❑ Principle of a REFRIGERATOR : [HEAT PUMP]**

A device which is used for cooling things, is called Heat pump or Refrigerator.

- An ideal Refrigerator can be regarded as Carnot's ideal Heat engine working in the reverse direction. 22
- In refrigerator, the working substance would absorb a certain quantity of Heat  $Q_2$  from the sink at lower temperature ( $T_2$ ) and reject longer amount of Heat  $Q_1$  to the source at higher temperature  $T_1$  with the help of external agency supplying the **necessary** energy to the system.



- In actual practice, vapours of ammonia or Freon (dichloro-difluoro methane  $CCl_2F_2$ ) acts as a working substance (refrigerant).
- According to 2<sup>nd</sup> law, it is impossible to have a self acting machine that can transfer heat from a cold body to a hot body. So, to maintain refrigeration process some expenditure of energy is necessary.
- Water and other food stuff to be cooled in the refrigerator act as sink at lower temperature. Heat energy ( $Q_2$ ) is absorbed from the sink. A certain amount of work  $kl$  is performed by the compressor of the refrigerator on the working substance. The compressor is being operated by an electric motor.
- The source is the atmosphere at room temperature  $T_1$  to which heat  $Q_1$  is rejected by the radiator fixed at the back of the refrigerator.
- In the cycle of changes, as the working substances return to its initial state, therefore, there is no change in its internal energy i.e.  $dv = 0$ .

Also,  $dQ = Q_2 - Q_1$  and  $dw = -kl$

According to First law,  $dQ = du + dw = dw$

Or  $Q_2 - Q_1 = -W$  ... (i) [Negative sign with W represents work done on the system]  
 Or  $kl = Q_1 - Q_2$  ... (ii)

**❑ Coefficient of performance of a refrigerator ( $\beta$ )**

" $\beta$  is defined as the ratio of quantity of heat removed per cycle from the contents of the refrigerator ( $Q_2$ ) to the energy spent per cycle ( $W$ ) to remove this Heat." i.e.  $\beta = \frac{\text{Desired output}}{\text{Required input}} = \frac{\text{Heat extracted from cold body}}{\text{Work done on the refrigerant}}$

$\beta = \frac{Q_2}{W}$

Or  $\beta = \frac{Q_2}{Q_1 - Q_2}$  [from (ii),  $W = Q_1 - Q_2$ ]

Or  $\beta = \frac{Q_2/Q_1}{\frac{Q_1 - Q_2}{Q_1}} = \frac{Q_2/Q_1}{1 - \frac{Q_2}{Q_1}} = \frac{Q_2/Q_1}{\frac{Q_1 - Q_2}{Q_1}}$

Or  $\beta = \frac{T_2/T_1}{1 - T_2/T_1}$  (as  $\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$ )

$$\therefore \beta = \frac{T_2/\cancel{W}}{\frac{T_1-T_2}{\cancel{W}}} \Rightarrow \beta = \left( \frac{T_2}{T_1 - T_2} \right)$$

If ' $\eta$ ' is the efficiency of Carnot's cycle, then  $1 - \frac{T_2}{T_1} = \eta$

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

$\therefore \beta = \frac{1-\eta}{\eta}$  as  $\beta = \frac{T_2/T_1}{1 - T_2/T_1} = \frac{1-\eta}{1-\cancel{\eta}-\eta}$

— Higher the value of  $\beta$ , more efficient is the refrigerator.

— Since,  $\beta \propto \frac{1}{T_1 - T_2}$   $\therefore$  greater the value of  $\beta$ , smaller is temperature difference between atmosphere and food stuff.

— As the refrigerator works,  $T_2$  goes on decreasing due to the formation of ice.  $T_1$  is almost constant. Therefore  $\beta$  decreases. In this stage, refrigerator needs to be defrosted.

❖ A refrigerator is a heat engine working backward and hence it is also called Heat pump.

### ❖❖❖❖❖❖❖ CONCEPTUALS ❖❖❖❖❖❖❖❖❖❖❖❖❖

**Q.1. What is the foundation of thermodynamics?**

**Ans.** The foundation of thermodynamics is the law of conservation of energy and the fact that heat flows from a hot body to a cold body and not the other way around.

**Q.2. 100 J of energy is added to a system that does 40 J of external work. By how much the internal energy of the system is raised?**

**Ans.** According to first law of thermodynamics,

$$Q = \Delta U + W$$

or

$$\Delta U = Q - W = 100 - 40 = 60 \text{ J}$$

**Q.3. What would be the ideal efficiency of an engine if its hot reservoir and exhaust were at the same temperature—say 400K?**

**Ans.**  $\eta = 1 - \frac{T_L}{T_H} = 1 - \frac{400}{400} = 1 - 1 = 0$

Therefore, no work output is possible for any heat engine unless a temperature difference exists between the hot reservoir and heat sink.

**Q.4. Give a common example of adiabatic process.**

**Ans.** A common example of adiabatic process is the compression and expansion of gases in the cylinders of an automobile engine. Compression and expansion occur very rapidly so that energy cannot leave the combustion chamber.

**Q.5. Milk is poured into a cup of tea and is mixed with a spoon. Is this an example of reversible process?**

**Ans.** When milk is mixed in tea, certain amount of work is done on the system which appears in the form of heat. The milk cannot be separated from tea with the recovery of same work from heat. Hence this process is not reversible.

**Q.6. Is it possible that there is a change in the temperature of a body without giving/taking heat to/from it?**

**Ans.** Yes in an adiabatic process. During adiabatic change, no heat is given or taken from the system but the temperature changes. In adiabatic compression, the temperature increases while in adiabatic expansion, the temperature falls.

**Q.7. How is Carnot cycle operated?**

**Ans.** A Carnot cycle operates as follows :

(i) Receive thermal energy isothermally from some hot reservoir maintained at a constant high temperature  $T_H$ .

(ii) Reject thermal energy isothermally to a constant low-temperature reservoir ( $T_L$ ).

(iii) Change temperature in reversible adiabatic processes.

Such a cycle, which consists of two isothermal processes bounded by two adiabatic processes, is called Carnot cycle.

Now,  $c = \frac{Q}{m\Delta T}$ . Since in an isothermal change, temperature is constant so  $\Delta T = 0$ .

$$\therefore c = \frac{Q}{m \times 0} = \infty$$

**Q.18. What is the specific heat in an adiabatic change?**

**Ans.** In an adiabatic change, specific heat is zero. Now,  $c = \frac{Q}{m\Delta T}$ . Since in an adiabatic change, no heat can enter or leave the system,  $Q = 0$ .

$$\therefore c = \frac{0}{m\Delta T} = 0$$

**Q.19. What is the slope of an isothermal curve?**

**Ans.** The slope of  $P$ - $V$  curve is  $dP/dV$ . For an isothermal change,

$$PV = \text{constant} = K$$

Differentiating both sides, we get,

$$P.dV + V.dP = 0$$

$$\therefore \text{Slope of curve, } \frac{dP}{dV} = \frac{-P}{V}$$

**Q.20. What is the slope of an adiabatic curve?**

**Ans.** For an adiabatic change,  $PV^\gamma = \text{constant} = K$

Differentiating both sides, we get,

$$\gamma P V^{\gamma-1} dV + V^\gamma dP = 0$$

$$\text{or } V^\gamma dP = -\gamma P V^{\gamma-1} dV$$

$$\therefore \text{Slope of curve, } \frac{dP}{dV} = -\frac{\gamma P V^{\gamma-1}}{V^\gamma} = -\gamma \left( \frac{P}{V} \right)$$

Since  $\gamma > 1$ , the adiabatic curve at any point is steeper than the isothermal curve at that point. For this reason, isothermal curve lies above the adiabatic curve during expansion. Reverse is the case for compression.

**Q.21. Give two practical examples of second law of thermodynamics.**

**Ans.** The first law of thermodynamics is simply law of conservation of energy applied to thermodynamic processes. The second law tells us whether a given thermodynamic process can take place or not.

(i) **Transfer of heat.** When two bodies at different temperatures are put in thermal contact, heat flows from a body at higher temperature to a body at lower temperature till they attain a common intermediate temperature. According to second law of thermodynamics, the entropy of the system increases in the process. Therefore, heat cannot by itself flow from a colder body to a hotter body.

(ii) **Expansion of a gas.** Suppose you have a box with a partition dividing it in two parts with a gas on one side of the partition and other side evacuated. With all the molecules of gas on one side, the gas molecules have highly ordered situation. However, if the partition is removed, the gas molecules will distribute themselves throughout the box and be moving in random directions — a less ordered situation. In other words, the entropy of the gas has increased. The molecules of the gas, on their own, cannot go back into one half of the box. Hence the process is irreversible.

**Q.22. Where do we use petrol and diesel engines?**

**Ans.** Since petrol engine is light in weight and small in size, it is used in cars, aeroplanes, scooters etc. On the other hand, diesel engine is heavy and, therefore, it is used in heavy vehicles e.g. buses, trucks, tractors etc.

**Q.23. Why is defrosting necessary for refrigerators?**

$$\text{Ans. } COP = \frac{T_L}{T_H - T_L}$$

As the refrigerator operates,  $T_L$  goes on decreasing due to the formation of ice. However,  $T_H$  is almost constant. As a result,  $COP$  decreases. When the refrigerator is defrosted,  $T_L$  increases and hence  $COP$  increases.

### Thermodynamics: In-Depth Theory

Thermodynamics is the branch of physics that deals with the study of heat, work, and energy.

It is a fundamental topic in physics and plays a crucial role in understanding how energy is transformed and transferred in various systems.

### Key Concepts of Thermodynamics

#### 1. System and Surroundings:

- **System:** The portion of the universe under study, which can be a mixture of substances, a reaction vessel, or any defined space.
- **Surroundings:** Everything outside the system that can exchange energy or matter with it.
- **Boundary:** The imaginary or real line that separates the system from the surroundings.

#### 2. Types of Systems:

- **Open System:** Exchanges both energy and matter with the surroundings (e.g., an open pot of boiling water).
- **Closed System:** Exchanges only energy, not matter, with the surroundings (e.g., a sealed container).
- **Isolated System:** Does not exchange energy or matter with the surroundings (e.g., a thermos flask).

### Laws of Thermodynamics

#### Zeroth Law of Thermodynamics

- States that if two systems are in thermal equilibrium with a third system, they are in thermal equilibrium with each other.
- **Mathematical Representation:** If  $T_A = T_C$  and  $T_B = T_C$  then  $T_A = T_B$ .
- Establishes the concept of temperature.

#### First Law of Thermodynamics

The First Law, also known as the Law of Energy Conservation, states that energy cannot be created or destroyed, only transferred or converted from one form to another.

**Mathematical Expression:**  $\Delta U = Q - W$

Where:

- $\Delta U$  is the change in internal energy of the system.
- $Q$  is the heat added to the system.
- $W$  is the work done by the system.
- **Example:** Heating a gas in a closed container. The heat added increases the internal energy, causing the temperature to rise.

#### Second Law of Thermodynamics

The Second Law states that the total entropy of an isolated system can never decrease over time. Entropy is a measure of disorder or randomness in a system.

**Mathematical Expression:**  $\Delta S \geq \frac{Q}{T}$

Where:

- $\Delta S$  is the change in entropy.
- $Q$  is the heat added to the system.
- $T$  is the absolute temperature.
- Introduces the concept of entropy as a measure of disorder or randomness.

#### Third Law of Thermodynamics

● States that as the temperature of a system approaches absolute zero, the entropy of a perfect crystal approaches a minimum constant value.

\* **Implication:** It is impossible to reach absolute zero in a finite number of steps.

### Thermodynamic Processes

#### 1. Isothermal Process:

- A process that occurs at a constant temperature.
- In an isothermal process, the change in internal energy ( $\Delta U$ ) is zero because temperature is constant.
- **Expression:**  $\Delta U = 0$  and  $Q = W$  (Heat added = Work done).

#### 1. Isothermal Process:

- Temperature remains constant ( $\Delta T = 0$ ).
- $Q = W$  (since  $\Delta U = 0$ ).

**2. Adiabatic Process:**

- A process where no heat is exchanged with the surroundings.
- In an adiabatic process, the entire change in internal energy ( $\Delta U$ ) is due to work done.
- **Expression:**  $Q=0$  and  $\Delta U=-W$

**2. Adiabatic Process:**

- No heat is exchanged ( $Q = 0$ ).
- $\Delta U = -W$ .

**3. Isochoric Process:**

- A process that occurs at a constant volume.
- In an isochoric process, no work is done since the volume doesn't change.
- **Expression:**  $W=0$  and  $\Delta U=Q$

**4. Isobaric Process:**

- Pressure remains constant ( $\Delta P = 0$ ).
- Work done is  $W = P\Delta V$ .

**4. Isobaric Process:**

- A process that occurs at constant pressure.
- Work done in an isobaric process is given by the expression  $W=P\Delta V$ .
- **Expression:**  $Q=\Delta U+W$

**3. Isochoric Process:**

- Volume remains constant ( $\Delta V = 0$ ).
- $W = 0$  (since no work is done).

**Thermodynamic Diagrams**

**PV Diagram (Pressure-Volume)**

- A graphical representation of the relationship between the pressure and volume of a system.
- **Example:** The area under the curve in a PV diagram represents the work done by the system.

**TS Diagram (Temperature-Entropy)**

- A graphical representation of the relationship between the temperature and entropy of a system.
- **Example:** The area under the curve in a TS diagram represents the heat added to the system.

**Applications of Thermodynamics**

**1. Heat Engines:**

- Devices that convert heat energy into mechanical work (e.g., internal combustion engines).
- **Carnot Cycle:** A theoretical model that defines the maximum possible efficiency of a heat engine.
- **Efficiency Formula:**

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

**2. Refrigerators and Heat Pumps:**

- Devices that transfer heat from a colder region to a hotter region using work.
- **Coefficient of Performance (COP):**

$$\text{COP}_{\text{refrigerator}} = \frac{Q_C}{W}$$

$$\text{COP}_{\text{heat pump}} = \frac{Q_H}{W}$$

Where  $Q_C$  and  $Q_H$  are the heat extracted from the cold region and delivered to the hot region, respectively.

**3. Biological Systems:**

- Thermodynamics helps in understanding metabolic processes and energy transfer in living organisms.