# THERMODYNAMICS

**INTRODUCTION:** Thermodynamic is a branch of science that deals with conversion of heat energy into mechanical energy and the reverse process. The two important aspects in study of thermodynamics are (i) energy relations and ii) direction along which the energy changes takes place. These two aspects are covered by I and II Law of thermodynamics.

**DEFINATION OF KEY TERMS IN THE STUDY OF THERMODYNAMICS**:

- **SYSTEM:** A definite quantity of matter enclosed by either a real or an imaginary boundary is called a **system.**
- **ENVIRONMENT** : The region or matter outside the given system is called **environment**
- **OPEN SYSTEM**: A system which can exchange both the matter and energy with the surrounding is known as an **open system**.
- **CLOSED SYSTEM:** A system which can exchange only energy (not matter) with the surroundings is known as **closed system**.
- **ISOLATED SYSTEM:** A system which does not exchange both matter and energy with the surroundings is said to be an isolated **system.**
- **THERMODYYNAMIC STATE**: It is the conditions of the system specified by thermodynamic coordinates such as pressure, volume and temperature of the system.
- **EQUATION OF STATE**: It is the mathematical equation which relates the thermodynamic coordinates of a given system.

  Eg: 1) The perfect gas equation $PV = RT$ is an equation of state.

  2) $(P+a/v^2)(V-b) = RT$ Vander waals equation.

**THERMODYNAMIC EQUILIBRIUM**: a system is said to be in thermodynamic equilibrium, when it is in a state of thermal, mechanical and chemical equilibrium.A system is said to be in thermal equilibrium, if the temperature of every part of the system is same as its surroundings.

A system is said to be in mechanical equilibrium, if there is no unbalanced force in the interior of the system or between system and its surroundings.

A system is said to be in chemical equilibrium, if the chemical composition is same throughout the system.

When the system is in thermodynamic equilibrium, its conditions can be specified by a few variables (such as pressure, volume and temperature) called thermodynamic coordinates or variables of state.

**THERMODYNAMIC PROCESS**: Any change in the thermodynamic variables leads to a change of state. A change from one state to another state of a system is called a T**hermodynamic process** or simply **process.** The process may be Isothermal. Adiabatic, Isochoric and Isobaric.

**ISOTHERMAL:** The thermodynamic process during which the temperature remains constant is known as **isothermal process.**

**ADIABATIC:** A process in which there is no transfer of heat between the system and the surroundings is termed as **adiabatic process**.

**ISOCHORIC:** a thermodynamic process that occurs at constant volume is called **isochoric process.**

**ISOBARIC:** A thermodynamic process that occurs at constant pressure is called **isobaric process.**

**REERSIBLE PROCESS**: Any process that can be made to go in its reverse direction with work and heat effects being equal and opposite to that in the direct process is called **reversible process**.

Eg: A slow isothermal expansion or compression of a gas, a slow adiabatic expansion or compression of a gas, a slow compression of a spring etc is all **reversible process.**

**IRREVERSIBLE PROCESS**: Any process that can't be made to go in the reverse direction is called an **Irreversible process.** Eg: All changes which occurs suddenly, (explosion) or which involves friction and electric resistance. (Heat produced in an electrical resistance)

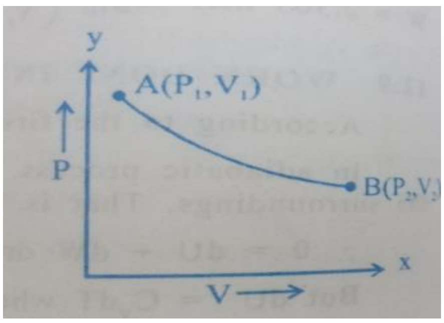
**CYCLIC PROCESS**: A process in which a body or a system under goes a series of change and finally returns to its original state is called a **cyclic process**.

**INTERNAL ENERGY AND WORK**: Internal energy of a ideal gas in the energy due to random motion of the particles and corresponding to Kinetic energy of the particles. In case of real gas internal energy includes the work done to overcome the intermolecular attraction. [The motion of molecules gives rise to K.E. and position and force of attraction of molecules give rise to P.E. The sum of K.E. and P.E. is called **Internal energy].** In an ideal gas P.E. =O. Internal energy is due to K.E. of the molecules of a gas. It is denoted by U. and dU represents increase in internal energy dU includes increase in K.E, dE and external work done dI to overcome the inter molecular attraction.

i.e. $\mathbf{dU = dE + dI}$

Work done by the system or on the system is called **external work** done and is denoted by W work done by the system is taken as **positive** and work done on the system is taken as **negative**. In thermodynamic, heat given to a system or given out by a system is represented by Q. The heat given to a system is taken as **positive** and heat given out by a system is taken as negative. dU, dW and dQ represents small changes.

**INDICATOR DIAGRAM: Work** done in a thermo dynamical process can be easily obtained with the help of diagrams known as **indicator diagram.** In case of gases these are the P –V curves.




In the figure (1). Curve AB is a indicator diagram for a gas which Under goes a process from a state A to state. B. When gas is enclosed in a cylinder fitted with a pistion, during process the gas expands, by moving the piston through a small distance dx, Then change in volume dV = a.dx

Where 'a' in the area of the piston. If P is the pressure of the gas
Then work done dW = Pa.dx = P dV.

This is represented by the shaded area in the fig (1) Total work done by the gas during the process is given by the area under the curve AB. In case of cyclic process area under the loop represents the work done. (Figure (2))

**ZEROTH LAW OF THERMODYNAMICS:**

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

Consider two systems A and B are in thermal equilibrium, separately with a third system C. The physical quantity which has the same value for both the system thermal equilibrium is the temperature 'T'. Thus, the two system A and B in thermal equilibrium with C separately. Then $T_A = T_C$ And $T_B = T_C$. This implies that $\mathbf{T_A = T_B}$. That is systems A and B are also in thermal equilibrium.

**FIRST LAW OF THERMODYNAMIC**:

Statement: **When an amount of heat energy is supplied to the system, part of it increases internal energy of the system and remaining is utilized by the system to do work".**

**Explanation:** If ΔQ is heat supplied to the system by the surrounding, Δu is change in internal energy of the system and Δw is work done by the system on the surrounding.

Then according to first law of thermodynamics $\Delta Q = \Delta u + \Delta w$

* It is the principle of the conservation of energy.

Mathematically first law can also be written as **$dQ = dU + dW$**

In general, the first law of thermodynamics states that **"When heat is transferred into any other forms of energy or when other forms of energy are converted in to heat, the total energy remains constant."** This law is the special case of law of conservation of energy.

is converted in to work. The work done is represented by area under P –V diagram.

**HEAT ENGINES:** A heat engine is a thermo dynamical device which continuously converts thermal energy in to other useful from of energy, like mechanical energy, electrical energy etc. The substance which absorbs heat and does work in a heat engine is called the **working** substance. A heat engine provides a continuous supply of work, because the working substance is taken through a cycle of operation. This can be repeated.

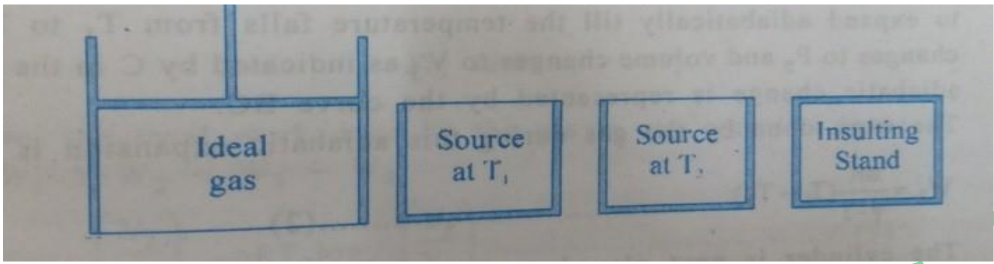
**CARNOT HEAT ENGINE:** In 1824 a French engineer Sadi Carnot describes an ideal heat engine called carnot heat engine. This engine is free from friction and other o imperfections of actual engines. In this engine, heat is absorbed at a constant high temperature and heat is rejected at a constant low temperature. This engine works in a perfectly reversible cycle of operations. Its efficiency is maximum and is an ideal heat engine.

1) **A cylinder** with a perfectly non conducting walls and a perfectly conducting bottom, containing perfect gas as a working substance and fitted with a non conducting frictionless piston.

2) **A source** of heat of infinite thermal capacity. It is maintained at a constant high temperature $T_1$ and supplies any amount of heat.

3) **A sink** of infinite thermal capacity maintained at a constant lower temperature $T_2$ and absorbs any amount of heat.

4) A perfectly **non conducting stand** for the cylinder




$\eta = 1 - \frac{T_2}{T_1}$ is the expression for efficiency of carnot engine.

***Note :*** (i) The interesting aspect of 'η'of Carnot engine is that it is independent of the nature of the working substance. But Carnot used an ideal gas operation which is not strictly followed by real gases or fuels.

(ii) Theoretically 'η'can be 100%.

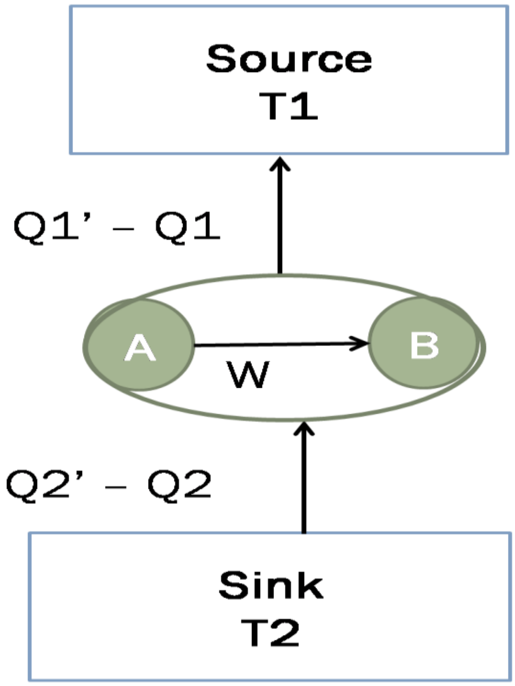
(iii) The efficiency of Carnot's ideal engine depends only on the temperatures of the source and the sink.

(iv) Efficiency of any reversible engine working between same two temperatures is same.

**CARNOT'S THEOREM:**

1. All the reversible engines working between the same temperature limits have the same efficiency.

2. No engine can be more efficient than a carnot's reversible engine working between the same two temperatures.




**Proof** : Consider two reversible engines A and B working between the temperature limits $T_1$ and $T_2$. A and B are coupled. Suppose A is more efficient than B . The engine A works as a heat engine and B as a refrigerator.

The engine A absorbs an amount of heat $Q_1$ from the source at a temperature $T_1$. It does external work W and transfers it to B. The heat rejected to the sink is $Q_2$ at a temperature $T_2$. The engine B absorbs heat $Q_2^{1}$ from the sink at temperature $T_2$ and W amount of work is done on the working substnace. The heat given to the source at temperature $T_1$ Suppose engine A is more efficient than B. Efficiency of the engine A is

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

Efficiency of the engine B is

$$\eta_B = \frac{Q_1^1 - Q_2^1}{Q_1^1} = \frac{W}{Q_1^1}$$

Since $\eta_A > \eta_B \therefore \frac{W}{Q_1} > \frac{W}{Q_1^1} \Rightarrow Q_1^1 > Q_1$

Also , W= $Q_1$ - $Q_2$ = $Q_1^1 - Q_2^1$

$$\therefore Q_2^1 > Q_1^1$$

Thus for two engines A and B working as a coupled system, $Q_2^1 - Q_2$ is quantity of heat taken from sink at a temperature $T_2$ and $Q_1^1 - Q_1$ is the quantity of heat given to the source at a temperature $T_1$. Both $Q_2^1 - Q_2$ and $Q_1^1 - Q_1$ are positive quantitics. It means that heat flows from the sink at a temperature $T_2$ (lower temperature) to the source at a temperature $T_1$ ( higher temperature) i.e, heat flows from a body at a low temperature work has been done on the system. This is contrary to thsecond law of thermodynamics. Thus efficiency $\eta_A$ can not be greater than $\eta_B$. The two engine's working in the same two temperature limits have the same efficiency.

Moreover in the case of a Carnot's engine, there is no loss of heat due to friction, conduction or radiation. Thus carnot's engine has the maximum efficiency. Thus η depends only upon the two temperature limits.

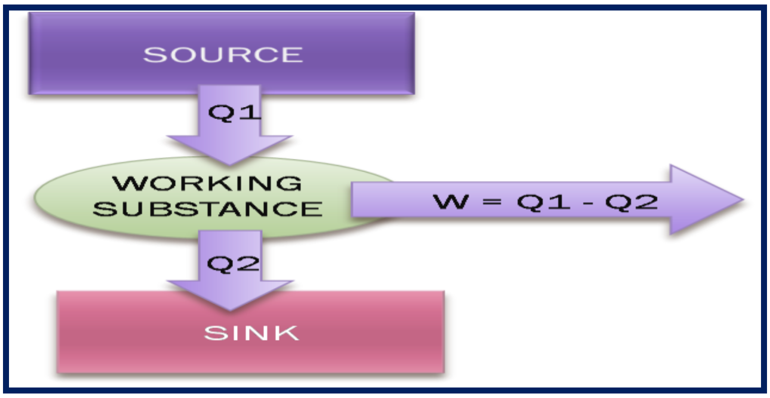
**II LAW OF THERMODYNAMICS**: **KELVIN'S STATEMENT: It is impossible to drive a continuous supply of work by cooling a body below the coldest of its surrounding.**

**CLAUSIUS STATEMENT: It is impossible for any self acting machine unaided by an external agency to transfer heat from body at lower temperature to body at higher temperature. OR. Heat cannot of its own accord flow from a cold body to a hot body.**

**Heat Engines :** A heat engine is a device which converts heat into work.

Any heat engine should have three parts:

i. a hot body or source from which the engine gets heat at a higher temperature.
ii. Cold body or sink to which the engine rejects heat at a lower temperature.
iii. A working substance, which can absorb heat from the source, convert some of it into external work by its expansion and reject the rest to the cold body.



**Block diagram of Heat engine.**

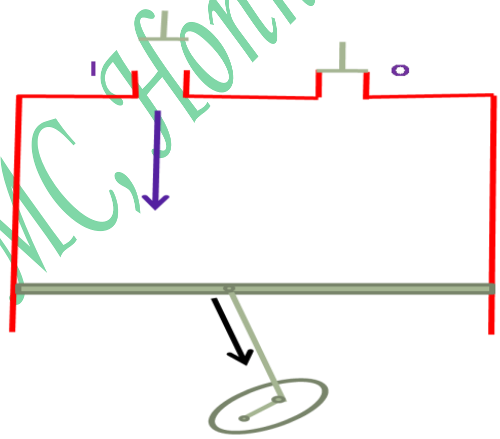
The heat engines can be classified into three

1) External combustion engine, in which heat is supplied by the working substance by burning the fuel outside the cylinder.
2) Internal combustion engine, in which heat is produced by combustion taking place inside the cylinder itself. There are two types of internal combustion engines i) Otto engine ii) Diesel engine
3) Gas turbine

## OTTO ENGINE :

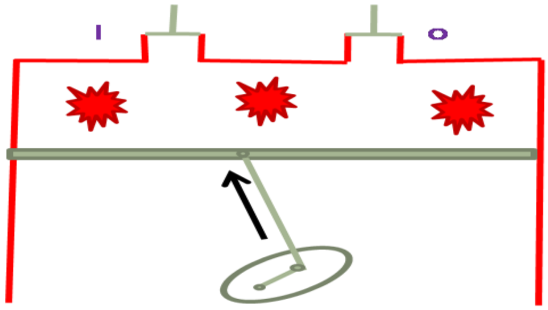
It was realised in practice by Otto the German engineer in 1876. In this engine heat is absorbed by the working substance at aconstant volume.

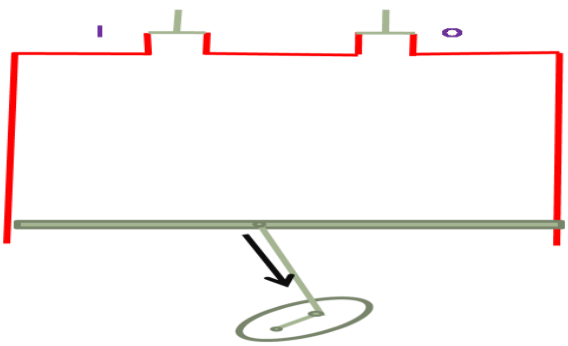
**Construction :** It consists of the usual cylinder and piston, the cylinder being provided with inlet valves 'I' for air & petrol vapour and exhaust valve 'O'. The operations of these valves are controlled by the motion of the piston. The working substance is air and petrol vapour acts as fuel.



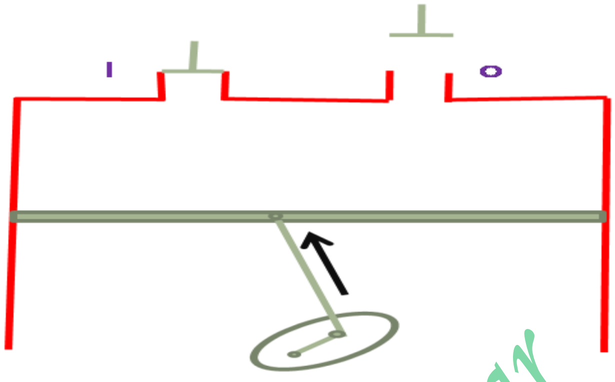

**Working :**

1. **The suction stroke (charing stroke)** :- The outlet valve 'O' is closed and the inlet valve 'I' is opened and a mixture of about 98% of air and 2% of petrol vapour is sucked into the cylinder by the forward motion of the piston at an atmospheric pressure.
2. **The compression Stroke** :- All the valves are closed and the mixture is compressed adiabatically to about $\frac{1}{5}$ th of its original volume by the backward motion of the piston. The temperature of the mixture is here by raised to about 600°C. The process is called pre-heating. At the end of the compression stroke,the mixture is fired by a series of sparks from a sparking plug. The combustion causes a large amount of heat to be developed which raises the temperature of the gas to about 2000°C and a corresponding high pressure (about 15 atmosphere) is produced instantaneously.



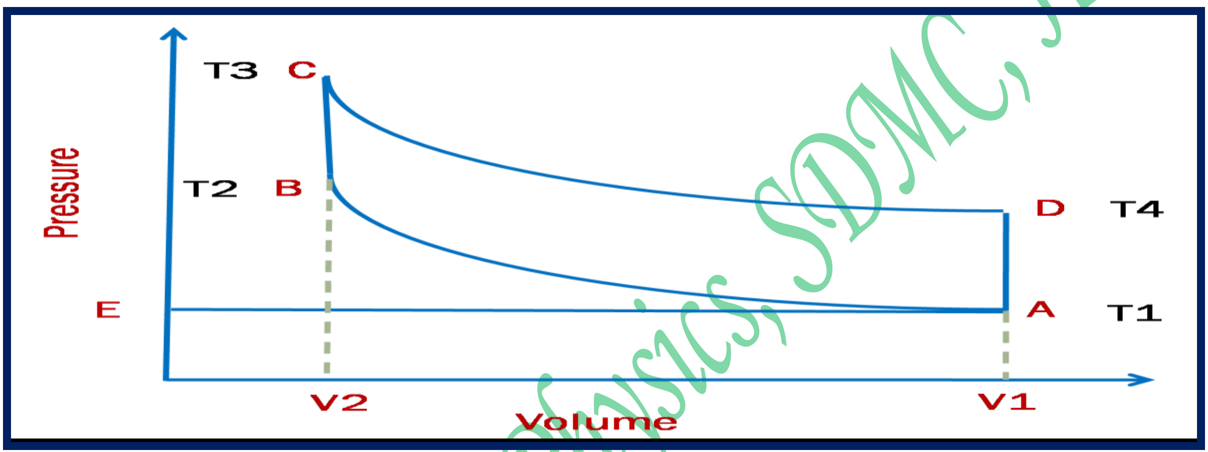




3. **The working stroke**:- The piston is now driven forward with great force owing to the high pressure of the gas, and the gas expands adiabatically to the original volume with a corresponding drop of temperature.




4. **The exhaust stroke**:- At the end of the third stroke, the cylinder is filled with a mixture of gases which is useless for further work. The exhaust valves are then opened and the spent up mixture is ejected out of the cylinder, the piston moving backward. After this scavenging of useless gases is completed, a fresh charge of air and petrol vapour is sucked in and a new cycle starts.

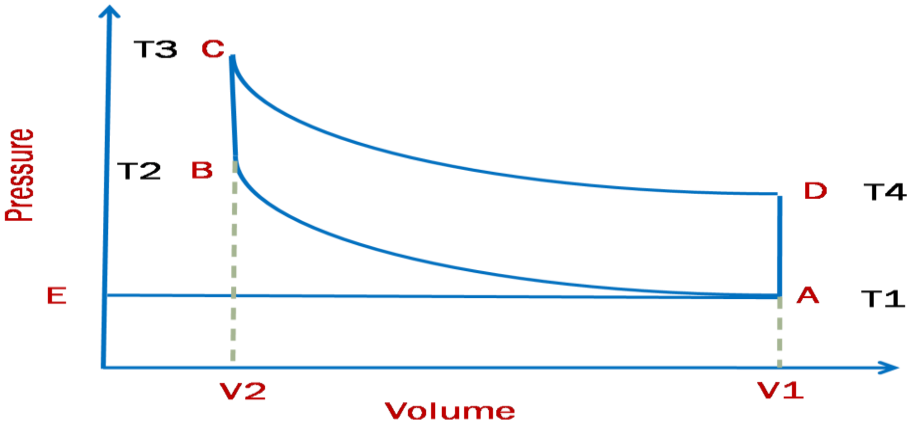
## OTTO CYCLE




1. **<u>E to A</u>** : Represents charging stroke. The mixture of air and petrol vapour is allowed to enter at atmospheric pressure. The final volume is $V_1$ at temperature $\boldsymbol{T_1}$.
2. **<u>A to B</u> :** Represents adiabatic compression. There is no friction and no flow of heat through the walls of the cylinder. The volume changes from $\boldsymbol{V_1\ to\ V_2}$ and temperature changes from $\boldsymbol{T_1\ to\ T_2}$ There is change in pressure also.
3. **<u>B to C</u> :** Represents the combustion stage. A spark is produced and the mixture of air and petrol vapour is ignited. The pressure increases and the temperature changes from $\boldsymbol{T_2\ to\ T_3}$
4. **<u>C to D</u> :** Represents the working stroke. The gas expands adiabatically and the engine works. The volume changes from $\boldsymbol{V_2\ to\ V_1}$ The pressure and temperature decreases.
5. **<u>D to A</u> :** As the point D is reached, the exhaust value opens. D to A represents the change of pressure to atmospheric pressure and the temperature changes from $\boldsymbol{T_4\ to\ T_1}$
6. **<u>A to E</u> :** Represents the exhaust stroke. The exhaust gases are completely discharged from the cylinder. Thus, the initial condition of the engine is restored.

**EXPRESSION FOR EFFICIENCY OF OTTO ENGINE**

Let the mass of the working substance be 1 kg. Let $T_1$ , $T_2$ , $T_3$ and $T_4$ be the absolute temperatures corresponding to the points A, B, C and D respectively $V_1$ , $V_2$ be volume of gas at A and B.




Let $C_v$ be the specific heat of air at a constant volume.

Let $Q_1$ be the amount of heat taken in during the process $B \to C$. Then

$$\boldsymbol{Q_1 = C_v(T_3 - T_2)}$$

Let $Q_2$ be the amount of heat rejected during the process $D \to A$. Then

$$\boldsymbol{Q_2 = C_v(T_4 - T_1)}$$

The efficiency of the engine is given by

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

$$\boldsymbol{\eta = 1 - \frac{T_4 - T_1}{T_3 - T_2}} \quad \dots\dots\dots\dots\dots\dots(1)$$

Now the points A and B lie on the same adiabatic

$$\boldsymbol{T_1 {V_1}^{\nu-1} = T_2 {V_2}^{\nu-1}}$$

Similarly, the points C and D lie on the same adiabatic

$$\boldsymbol{T_4 {V_1}^{\nu-1} = T_3 {V_2}^{\nu-1}}$$

Substracting we get

$$\boldsymbol{(T_4 - T_1){V_1}^{\nu-1} = (T_3 - T_2){V_2}^{\nu-1}}$$

$$\boldsymbol{\frac{(T_4 - T_1)}{(T_3 - T_2)} = \left(\frac{V_2}{V_1}\right)^{\nu-1}}$$

Substituting this value in equation (1), we get

$$\boldsymbol{\eta = 1 - \left(\frac{V_2}{V_1}\right)^{\nu-1}}$$

$$\boldsymbol{\eta = 1 - \left(\frac{1}{\rho}\right)^{\nu-1}}$$ Where $\frac{V_1}{V_2} = \rho$ is called adiabatic compression ratio.

In an actual petrol engine, ρ can not be made greater than 10. If ρ is more than 10, the mixture gets ignited by itself due to compression much before the sparking takes place.

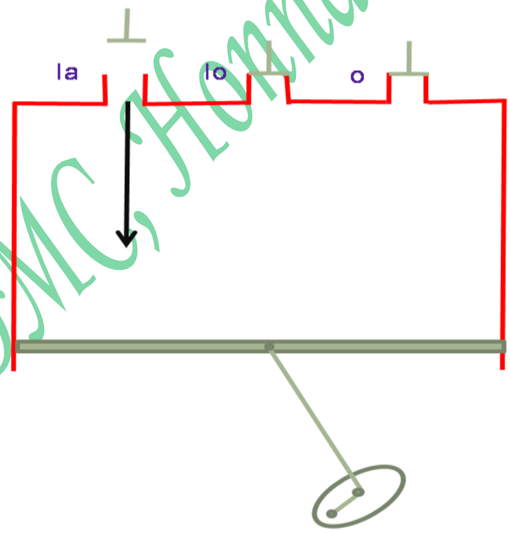
$$\boldsymbol{\eta = 1 - \left(\frac{1}{\rho}\right)^{\nu - 1}}$$

If ρ=6 and $\nu$ =1.4

$$\boldsymbol{\eta = 1 - \left(\frac{1}{6}\right)^{1.4-1}} \qquad \boldsymbol{\eta = 1 - \left(\frac{1}{6}\right)^{0.4}} \qquad \boldsymbol{\eta = 0.5116} \qquad \boldsymbol{\eta = 51.16\ \%}$$

**DIESEL ENGINE:**

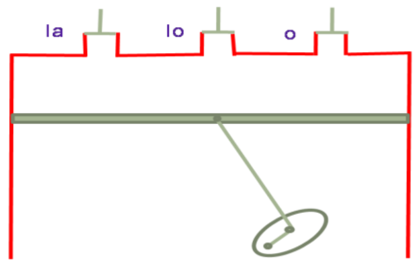
The outline of this engine was proposed by another German engineer Diesel in 1890. In this engine heat is absorbed by the working substance at a constant pressure.




**Construction** : It consists of a cylinder more Robust than that of Otto engine.The cylinder is fitted with frictionless piston and three valves. The valves are air inlet valve $I_a$ , oil inlet valve $I_0$ and exhaust (outlet valve) O. The valves are opened and closed by the movement of piston.

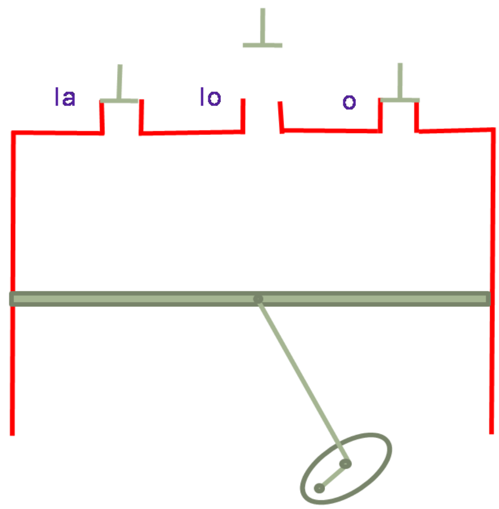
**Working**

1) **The suction stroke ( charging stroke) :-** The oil inlet valve $I_0$ and outlet valve O are closed and air inlet valve $I_a$ is opened. The piston moves down and the pure air is sucked inside the cylinder.



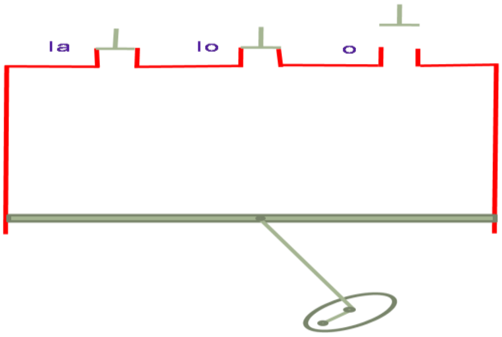

**(2) Compression stroke :-** All valves are closed. The piston moves up. The air is compressed to about $\frac{1}{17}$th of its orignal value and the temperature rises to about 1000°C along with the increase in pressure.

3) **Working Stroke :-** At the end of the compression stroke the oil inlet valve $I_0$ is opened, a heavy oil is injected into the cylinder through $I_0$. The temperature is so high that it ignites the oil. The rate of supply of oil is so adjusted that combustion takes place at a constant pressure, the piston moves down during combustion.

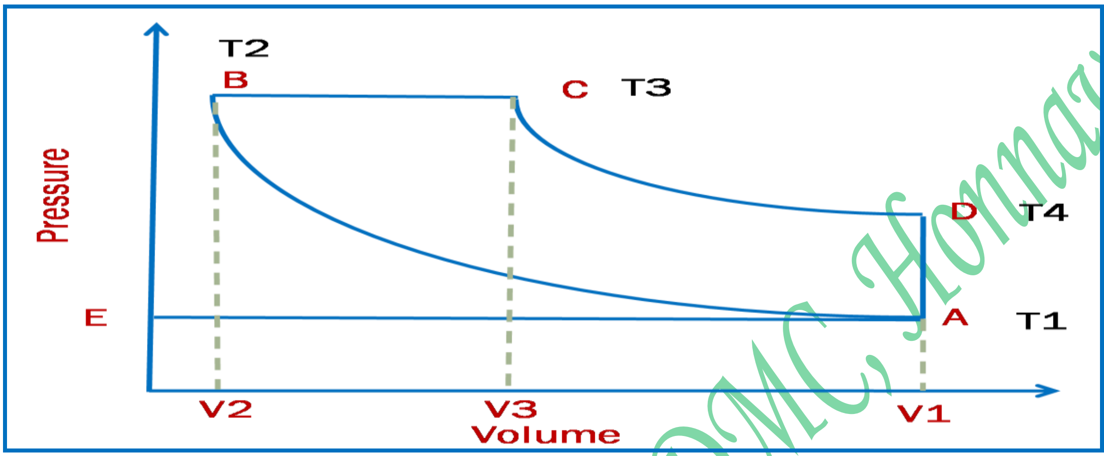



At this point,the temperature rises to about 2000°C and the supply of oil is cut off. During the remaining stroke adiabatic expansion takes place accompained by fall in temperature.

4) **Exhaust stroke :-** Outlet valve O opens, pressure falls to atmospheric pressure, heat is rejected at a constant volume and temperatuer falls down. The piston moves up, the burnt gases escape through O.




**DIESEL CYCLE**




1) **<u>E to A :</u>** Represents the intake of air and its volume changes to $V_1$. This is the charging stroke.

2) **<u>A to B :</u>** Represents the compression stroke. Air is compressed adiabatically. The temperature changes from $T_1$ to $T_2$ and the volume changes from $V_1$ to $V_2$ .The temperature rises to about 1000°C and the pressure to about 40 atmospheres.

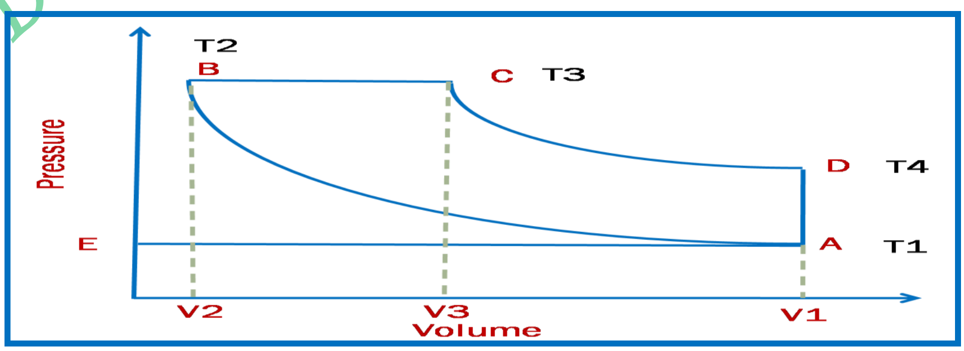
3) **<u>B to C :</u>** Represents the stage when the oil is sprayed into the cylinder. The oil burns immediately. The pressure is maintained constant. The temperature changes from $T_2$ to $T_3$ ( to 2000°C ) and the volume changes from $V_2$ to $V_3$.

4) **<u>C to D :</u>** Represents the working stroke. The mixture of air and diesel oil vapour expand adiabatically.

5) **<u>D to A :</u>** As the point D is reached the exhaust valve opens and the pressure drops to the point A. The volume remains constant, but temperature and pressure decrease.

6) **<u>A to E :</u>** Represents the exhaust stroke. The unburnt vapour of the oil and mixture of gases in the cylinders are exhausted out of the cylinder.

## EXPRESSION FOR EFFICIENCY OF DIESEL ENGINE



Consider the mass of the working substance to be 1kg. Let $T_1$, $T_2$, $T_3$ and $T_4$ be the temperatures and, $V_1$, $V_2$ and $V_3$ be the volumes at these points as shown in the figure.

Let $Q_1$ be the amount of heat absorbed during the process BC at constant pressure, then

$$Q_1 = C_p(T_3 - T_2)$$

$C_P$ is specific heat at constant pressure.

Let $Q_2$ be the amount of heat rejected during the process DA at constant volume,

$$Q_2 = C_V(T_4 - T_1)$$

$C_V$ specific heat at constant volume.

Efficiency

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{C_V(T_4 - T_1)}{C_p(T_3 - T_2)}$$

$$\eta = 1 - \frac{1}{\gamma}\frac{(T_4 - T_1)}{(T_3 - T_2)} - - - - - - - - (1) \qquad \because \gamma = \frac{C_p}{C_V}$$

To evaluate $\frac{(T_4 - T_1)}{(T_3 - T_2)}$ all temperatures are expressed in terms of $T_2$

Let the points A and B lie on the same adiabatic

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

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

$$T_1 = T_2\ .\left(\frac{1}{\rho}\right)^{\gamma-1} - - - - - - - - - - - - - - (2)$$

$$where \quad \frac{V_1}{V_2} = \rho \text{ the adiabatic compression ratio}$$

Let the points B and C are at same pressure ,hence charle's law holds good

$$\frac{T_2}{V_2} = \frac{T_3}{V_3} \qquad \therefore\ T_3 = T_2\ \left(\frac{V_3}{V_2}\right)$$

$$But\ \frac{V_3}{V_2} = \sigma \text{ is called combution expansion ratio or fuel cut off ratio}$$

$$\therefore\ T_3 = T_2\ .\sigma \qquad - - - - - - - - - - - - - - - - - - (3)$$

The points C and D lie on the same adiabatic

$$T_4 {V_4}^{\gamma-1} = T_3 {V_3}^{\gamma-1}$$

$$But\ V_4 = V_1$$

$$T_4 {V_1}^{\gamma-1} = T_3 {V_3}^{\gamma-1}$$

$$\therefore\ T_4 = T_3 \left(\frac{V_3}{V_1}\right)\gamma - 1.$$

$$T_4 = T_3\,(\frac{V_3}{V_2})\gamma - 1.\,(\frac{V_2}{V_1})\gamma - 1$$

$$T_4 = T_2\,.\,\sigma.\,\sigma^{\gamma-1}\,.\,(\frac{1}{\rho})^{\gamma-1}$$

$$T_4 = T_2\,.\,(\sigma^{\gamma}).\,(\frac{1}{\rho})^{\gamma-1} ---------- (4)$$

Substitute the values of $T_1$, $T_3$ and $T_4$ in equation (1)

$$\eta = 1 - \frac{1}{\gamma}\,[\frac{T_2\,.\,(\sigma^{\gamma}).\,(\frac{1}{\rho})^{\gamma-1} - T_2\,\,.\,(\frac{1}{\rho})^{\gamma-1}}{T_2\,.\,\sigma - \,T_2}]$$

$$\eta = 1 - \frac{1}{\gamma}\,\,(\frac{1}{\rho})^{\gamma-1}\,\,[\frac{\sigma^{\gamma} - 1}{\sigma - 1}\,]$$

$$\textit{Assumining}\ \ \rho = 15\ \textit{and}\ \ \sigma = 5\ \textit{then}$$

$$\eta = 0.65$$

$$\eta = 65\%$$

Thus the efficiency of the diesel engine is 64%. But it is less for the reasons explained in the case of Otto cycle.

**<u>Note :</u>** In diesel engine, only air is compressed so on danger of explosion. Hence the compression ratio can be increased more than that of Otto engine. The efficiency of diesel engine is more than that of Otto engine. But to withstand the high pressure, the cylinder of the diesel engine must be made Robust. Crude oil may be used in diesel engine and its consumption is less.