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Isothermal process

It is the process in which other physical quantities might change but the temperature of the system remains or is forced to remain constant. For example, the constant temperature of human body.

Under constant temperature, the volume of a gas system is inversely proportional to the pressure applied, the phenomena being called Boyle's Law, written in symbols as

$$V \propto \frac{1}{P}$$

Or, $V = K_B \times \frac{1}{P}$ where K_B is a constant quantity.

Or, $PV = K_B$ .... (i)

This means whatever be the values of volume and pressure, their product will be constant. So,

$$P_1V_1 = K_B, \qquad P_2V_2 = K_B, \qquad P_3V_3 = K_B, \text{ etc,}$$

Or, $P_1V_1 = P_2V_2 = P_3V_3$, etc.

The requirements for an isothermal process are as follows:

1. The process should be carried very slowly so that there is an ample time for compensation of heat in case of any loss or addition.

2. The boundaries of the system should be highly conducting so that there is a path for heat to flow into or flow away from a closed space in case of any energy loss or oversupply.

3. The boundaries should be made very thin because the resistance of the substance for heat conduction will be less for thin boundaries.

Since in an isothermal change, the temperature remains constant, the internal energy also does not change, i.e. dU = 0. So if dQ amount of heat is given to a system which undergoes isothermal change, the relation for the first law of thermodynamics would be

$$dQ = dU + dW$$

Or, $dQ = 0 + PdV$

Or, $dQ = PdV$

This means all the heat supplied will be utilized for performing external work and consequently its value will be very high compared to other processes.

Expression for work done in an isothermal process

Let 1 mole of an ideal gas is assumed to undergo isothermal expansion from a volume V_1 to V_2. Then the amount of work done can be determined by adding up all the small works done in small steps from V_1 to V_2.

i.e. $W = \int dW = \int_{V_1}^{V_2} PdV$

For 1 mole of gas,

$$PV = RT, \qquad \text{or, } P = \frac{RT}{V}$$

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Therefore, $\quad$ W $\quad = \int_{V_1}^{V_2} \frac{RT}{V} dV \quad = RT \int_{V_1}^{V_2} \frac{dV}{V} \quad = RT\left[\ln V\right]_{V_1}^{V_2} \quad = RT\left[\ln V_2 - \ln V_1\right]$

Or, $\quad$ W $= RT \ln \frac{V_2}{V_1}$

Since the temperature is constant,

$$P_1 V_1 = P_2 V_2$$

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

Therefore,

$$W = RT \ln \frac{P_1}{P_2}$$

Multiple Specific Heat Capacities of Gases

In case of solids and liquids, certain amount of heat energy produces proportional rise in temperature. So the specific heat capacity is constant on all occasions.

However, in cases of gases, the rise of temperature can be manipulated because the overall structure of gases allows them to be highly compressible and expansible. If heat energy is given but expansion of the gas is limited by some means, the temperature rises very much. So according to the relation,

$c = \frac{Q}{m\theta}$, the value of the specific heat capacity (SHC) will be small.

But on certain occasions, if generous expansion is allowed, the rise of temperature will be small, therefore according to the same relationship, the value of the specific heat capacity (SHC) will be large.

Since the rise of temperature can be manipulated in many ways, constant value of SHC is not possible.

Specific Heat Capacity at constant pressure
It is the amount of heat required to raise unit mass of gas by unit degree keeping the pressure constant. It is denoted by c_p. Mathematically,

$$c_p = \left(\frac{Q}{m\theta}\right)_{constant\_pressure}$$

Specific Heat Capacity at constant volume
It is the amount of heat required to raise unit mass of gas by unit degree keeping the volume constant. It is denoted by c_v. Mathematically,

$$c_v = \left(\frac{Q}{m\theta}\right)_{constant\_volume}$$

Molar Heat Capacity at constant pressure
It is the amount of heat required to raise unit mole of gas by unit degree keeping the pressure constant. It is denoted by C_p. Mathematically,

$$C_p = \left(\frac{Q}{n\theta}\right)_{constant\_pressure}$$ where 'n' is the no. of moles.

Molar Heat Capacity at constant volume

It is the amount of heat required to raise unit mole of gas by unit degree keeping the volume constant. It is denoted by C_v. Mathematically,

$$C_v = \left(\frac{Q}{n\theta}\right)_{constant\_volume}$$ where 'n' is the no. of moles.

Relationship between specific and molar heat capacities

The relation for molar heat capacity at constant volume is $C_v = \left(\frac{Q}{n\theta}\right)_{constant\_volume}$

If n = no. of moles, m = mass of the gas and M = molecular mass,

$$n = \frac{m}{M}$$

Therefore,

$$C_v = \left(\frac{Q}{\frac{m}{M}\theta}\right)_{constant\_volume}$$

$$C_v = M\left(\frac{Q}{m\theta}\right)_{constant\_volume}$$

The relation for specific heat capacity at constant volume is $c_v = \left(\frac{Q}{m\theta}\right)_{constant\_volume}$ **,which gives,**

$$\boxed{C_v = Mc_v}$$

Same approach can be applied for the relationship of specific and molar heat capacities at constant pressure, which gives,

$$\boxed{C_p = Mc_p}$$

Relationship between C_p and C_v prove: $C_p = C_v + R$

The relationship between C_p and C_v can be established by considering 1 mole of a gas which has been heated to raise its temperature by a small range dT.

The process is first carried in such a way that the volume remains constant. The small amount of heat energy input required for the purpose is given by

$$(dQ)_v = (dU)_v + (PdV)_v \ldots\ldots\ldots\ldots \quad (i)$$

Since the volume remains constant, dV is equal to zero, which makes the whole quantity $(PdV)_v$ equal to zero. Then,

$$(dQ)_v = (dU)_v \quad .... \quad (ii)$$

According to the heat equations $Q = mc\theta$ (when mass is expressed in terms of grams of kg) and $Q = nC\theta$ (when mass is expressed in terms of no. of moles of gas), the amount of heat energy is given by

$$(dQ)_v = 1 \times C_v dT \quad .... (iii)$$ (Here n = 1 because 1 mole of gas has been used and C_v is used instead of C because the volume has been made constant.)

Comparison of relations (ii) and (iii) gives

$$(dU)_v = C_v dT \quad .... \quad (iv)$$

Then from the same initial conditions, the same amount of gas is heated through same temperature range, but this time at constant pressure. The heat energy required for this purpose would be certainly different and is given by

$$(dQ)_p = (dU)_p + (PdV)_p \quad .... \quad (v)$$

The value of $(dQ)_p$ would be given by

$$(dQ)_p = 1 \times C_p dT$$ (because the pressure has been made constant.)

Or, $\quad (dQ)_p = C_p dT$

The internal energy of a gas system is the sum total of kinetic energy and potential energy. The kinetic energy has its direct dependence on the temperature of the system (as depicted by the relation $\frac{1}{2}m\overline{c}^2 = \frac{3}{2}kT$). So if the change of temperature is the same, the change of kinetic energy would also be the same. Here in both the cases, the change of temperature has been dT, so change of KE should be the same. Similarly the potential energy also has the same dependence. So a change of temperature by dT should give the same amount of rise of potential energy. Overall, change of temperature by dT should bring equal amount of rise of internal energy, whatever the conditions be. Then

$$(dU)_p = (dU)_v = C_v dT$$

Using the values of $(dQ)_p$ and $(dU)_p$ in relation (v) gives,

$$C_p dT = C_v dT + (PdV)_p \quad .... \quad (vi)$$

The term that remains to be changed is $(PdV)_p$ which would require some form of differentiation of volume V. This is achieved by differentiating the ideal gas equation for 1 mole of gas,

i.e. PV = RT

When differentiated with respect to T gives,

$$\frac{d(PV)}{dT} = \frac{d(RT)}{dT}$$

Since the pressure has been allowed to be constant and R is a universal constant,

$$P\frac{dV}{dT} = R\frac{dT}{dT} \qquad \text{Or,} \qquad P\frac{dV}{dT} = R$$

Or, $\quad PdV = RdT$

Using this value of PdV in relation (vi) gives,

$$C_pdT = C_vdT + RdT$$

Or, $\quad \boxed{C_p = C_v + R}$

This relation gives an equation that depicts the relationship between the molar heat capacities measured at constant pressure and constant volume. It shows that their values differ only by a quantity equivalent to the universal gas constant 'R'. It also shows that C_p is greater than C_v.

Adiabatic process

It is the process in which several quantities change within a system but no heat enters or escapes the system. For example, a fast operating petrol engine, a rubber tyre which has just developed a leak or an air pump which is forcing air at a high speed, etc. for a process to be adiabatic, it has to fulfill several requirements

1. The process should be conducted at a high speed so that it is completed before heat energy leaks into or out of the system.
2. Since there should be no exchange of heat, the walls should be nonconducting (insulating) and thick.

Since the heat energy entering or leaving a system is zero in such process, dQ = 0.

So the first law of thermodynamics for an adiabatic process would be

$$dQ = dU + dW$$
Or, $\quad 0 = dU + PdV$
Or, $\quad dU = -PdV$

This means that if a system undergoes sudden compression (adiabatic), the term dV will be negative which makes – PdV positive. So there will rise in internal energy and so increase in temperature. This can also be explained in other way. When compression was done suddenly, work was done on the system. Since no energy can escape (adiabatic), it should be utilized inside by the molecules. When they do, theinternal energy increases and so temperature rises.

However if the system undergoes sudden expansion, the term dV wioll be positive, making –PdV negative. The internal energy therefore decreases causing a reduction in temperature. In other

words, when expansion is performed suddenly, the system does work, for which it needs heat from outside. Since no heat can enter from inside, it has to use internal resources, i.e. the internal energy. The total internal energy then decreases causing a reduction in the temperature.

Equation for adiabatic process

Consider one mole of a gas, which has undergone adiabatic change.

The first law of thermodynamics for 1 mole of ideal gas is,

$$dQ = dU + dW$$

or, $$dQ = dU + PdV$$

In an adiabatic process, no heat enters the system and no heat escapes as well, therefore,

$$dQ = 0$$

It gives,

$$dU + PdV = 0$$

Or, $$C_v dT + PdV = 0 \text{ (since } dU = C_v dT \text{ for 1 mole of an ideal gas) ......Eqn (1)}$$

For one mole of gas,

$$PV = RT$$

Differentiating with respect to T gives,

$$\frac{d(PV)}{dT} = \frac{d(RT)}{dT} \qquad \text{Or,} \qquad P\frac{dV}{dT} + V\frac{dP}{dT} = R\frac{dT}{dT}$$

Or, $$P\frac{dV}{dT} + V\frac{dP}{dT} = R \qquad \text{Or,} \qquad \frac{PdV + VdP}{dT} = R$$

Or, $$\frac{PdV + VdP}{R} = dT \text{ .... (2)}$$

Using the value of dT from eqn (2) in eqn (1) gives,

$$C_v\left[\frac{PdV + VdP}{R}\right] + PdV = 0 \qquad \text{Or,} \qquad \frac{C_v PdV + C_v VdP}{R} + PdV = 0$$

Or, $$C_v PdV + C_v VdP + RPdV = 0 \qquad \text{Or,} \qquad C_v PdV + RPdV + C_v VdP = 0$$

Or, $$(C_v + R)PdV + C_v VdP = 0$$

Or, $$C_p PdV + C_v VdP = 0 \text{ (since } C_p = C_v + R)$$

Dividing the relation in both sides by $C_v PV$ gives,

$$\frac{C_p P dV}{C_v PV} + \frac{C_v V dP}{C_v PV} = 0, \qquad \text{Or,} \quad \frac{C_p dV}{C_v V} + \frac{dP}{P} = 0,$$

The ratio of C_p/C_v is a constant quantity; so let it be denoted by γ (called as adiabatic constant).

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

Integrating the equation gives,

$$\gamma \ln V + \ln P = c \text{ [where c is a constant quantity]}$$

Or, $\ln V^\gamma + \ln P = c$ Or, $\ln (V^\gamma P) = c$

Taking exponential coefficient of both sides gives,

$$\exp[\ln(V^\gamma P)] = \exp(c)$$

or, $V^\gamma P = K$ where K is a constant quantity and is equal to exp (c)

or, $PV^\gamma = K = $ constant ………………… (3)

This is the equation showing the relationship between pressure and volume in an adiabatic change. The equation tells that for adiabatic change, the product of pressure and V^γ is constant.

It means if P_1 and V_1 are the pressures and volumes of a gas at a time which expands adiabatically so that the pressure and volume changes to P_2 and V_2, then

$$P_1 V_1^\gamma = K, \quad \text{and} \quad P_2 V_2^\gamma = K, \text{ and so on.}$$

This gives $\quad P_1 V_1^\gamma = P_2 V_2^\gamma = P_3 V_3^\gamma$ and so on.

Relationship between temperature and volume of the gas

From ideal gas equation,

$$PV = RT \qquad \text{Or,} \quad P = RT/V$$

Using this value of P in equation (3) gives,

$$\frac{RT}{V} V^\gamma = K, \qquad \text{Or,} \quad RTV^\gamma V^{-1} = K$$

Or, $TV^{\gamma-1} = \dfrac{K}{R}$ Or, $TV^{\gamma-1} = K_R$ (where K_R = a constant quantity)

Or, $TV^{\gamma-1} = $ constant.

So if T_1, V_1 are the temperature and volume of the gases at a moment and they undergo adiabatic change so that their temperature and volume changes to T_2 and V_2, then

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

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

Relationship between pressure and temperature of the gas

From ideal gas equation,

$$PV = RT \qquad \text{Or,} \quad V = RT/P$$

Using this value of V in the equation of adiabatic change,

$$P\left[\frac{RT}{P}\right] = K \qquad \text{Or,} \quad \frac{PR^{\gamma}T^{\gamma}}{P^{\gamma}} = K$$

$$\text{Or,} \quad \frac{R^{\gamma}T^{\gamma}}{P^{(\gamma-1)}} = K \qquad \text{Or,} \quad \frac{T^{\gamma}}{P^{(\gamma-1)}} = \frac{K}{R^{\gamma}}$$

$$\text{Or,} \quad \frac{T^{\gamma}}{P^{(\gamma-1)}} = K_{R\gamma} \text{ (a constant quantity)}$$

So if T_1, P_1 be the temperature and pressure of the gas at a moment which changes to T_2, P_2 after an adiabatic expansion, then

$$\frac{T_1^{\gamma}}{P_1^{(\gamma-1)}} = K_{R\gamma} \qquad \text{and} \quad \frac{T_2^{\gamma}}{P_2^{(\gamma-1)}} = K_{R\gamma}$$

This means $\quad \dfrac{T_1^{\gamma}}{P_1^{(\gamma-1)}} = \dfrac{T_2^{\gamma}}{P_2^{(\gamma-1)}}.$

Work done during adiabatic expansion

Let one mole of an ideal gas is considered which is undergoing adiabatic expansion from its initial volume V_1 to final volume V_2. Then the work done by the gas will be given by:

$$W = \int_{V_1}^{V_2} PdV \quad \ldots\ldots\ldots\ldots\ldots \text{ Eqn. (i).}$$

Here P is dependent of V as is depicted by the relation for adiabatic change

$$PV^{\gamma} = K \text{ (a constant quantity)}$$

$$\text{Or, } P = \frac{K}{V^{\gamma}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{ Eqn. (ii)}$$

Using the value of P from eqn, (ii) in eqn. (i) gives,

$$W = \int_{V_1}^{V_2} \frac{K}{V^{\gamma}} dV \qquad = K \int_{V_1}^{V_2} \frac{1}{V^{\gamma}} dV \qquad = K \int_{V_1}^{V_2} V^{-\gamma} dV$$

$$= K \left[\frac{V^{-\gamma+1}}{-\gamma+1} \right]_{V_1}^{V_2} \qquad = \frac{K}{1-\gamma} \left[V_2^{-\gamma+1} - V_1^{-\gamma+1} \right]$$

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

In an adiabatic process, $PV^{\gamma} = K$, therefore whatever be the value of pressure and volume, P_1, P_2, V_1, V_2, ….. etc, the product of pressure and volume powered by γ will be equal to K.

$$\text{ie} \quad P_1V_1^{\gamma} = K, \qquad \& \qquad P_2V_2^{\gamma} = K$$

$$\text{Or} \quad P_1V_1^{\gamma} = P_2V_2^{\gamma} = K$$

Using the two values of K gives,

$$W = \frac{1}{1-\gamma} \left[\frac{P_2V_2^{\gamma}}{V_2^{\gamma-1}} - \frac{P_1V_1^{\gamma}}{V_1^{\gamma-1}} \right] \qquad = \frac{1}{1-\gamma} \left[P_2V_2 - P_1V_1 \right]$$

The ideal gas equation for 1 mole of a gas gives PV = RT. So, $P_1V_1 = RT_1$, $P_2V_2 = RT_2$, and so on. Therefore,

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

Therefore the work done during adiabatic expansion depends only on the initial and final temperatures of the system.

Development of Heat Engine

According to 1st law of thermodynamics, when heat is supplied to a system, some portion is used to increase the internal energy whereas some portion is used to work. Work means it will produce some movement. For example, when the trigger is pulled in a gun, it starts chemical reaction behind the bullet. The resulting substance expands and pushes the bullet out of the nozzle. Similarly, when water is boiled, the steam will push out the lid, producing movement. So, considering this phenomenon there was an effort to develop such an instrument, which would produce maximum movement out of certain energy provided. This instrument was called **Heat engine**.

But, to produce continuous movement several aspects are to be taken care of. In the previous examples, the movement used to stop at some distance and was uncontrollable. But, heat engines should be designed in such a way that movement could be produced whenever required and stopped whenever unnecessary. Joule developed such type of heat engine. For such engines several requirements were to be fulfilled. They are:

- Source of energy: For any work, there should be external supply of heat the heat can be provided by chemical reactions, electricity or other factors.

- Working substance: It is the substance, which accepts heat, expands and causes movement of other substances. Working substances can be some gas, air, gaseous state of some liquids (water, petrol, diesel, spirit, alcohol, etc.).

- Sink: It is the substance in contact with the working substance, which accepts the heat wasted from the working substance. The presence of a sink is inevitable. The only thing that can be done is the control of energy loss. Sink can be the air or outer environment or the walls of the container active.

When Q_1 energy is given to the system, some work W is performed. The remaining work Q_2 is lost by the system to the sink.

Then,

$$W = Q_1 - Q_2$$

The efficiency of such machine (or any machine) will be equal to the ratio of work done and the input energy. So,
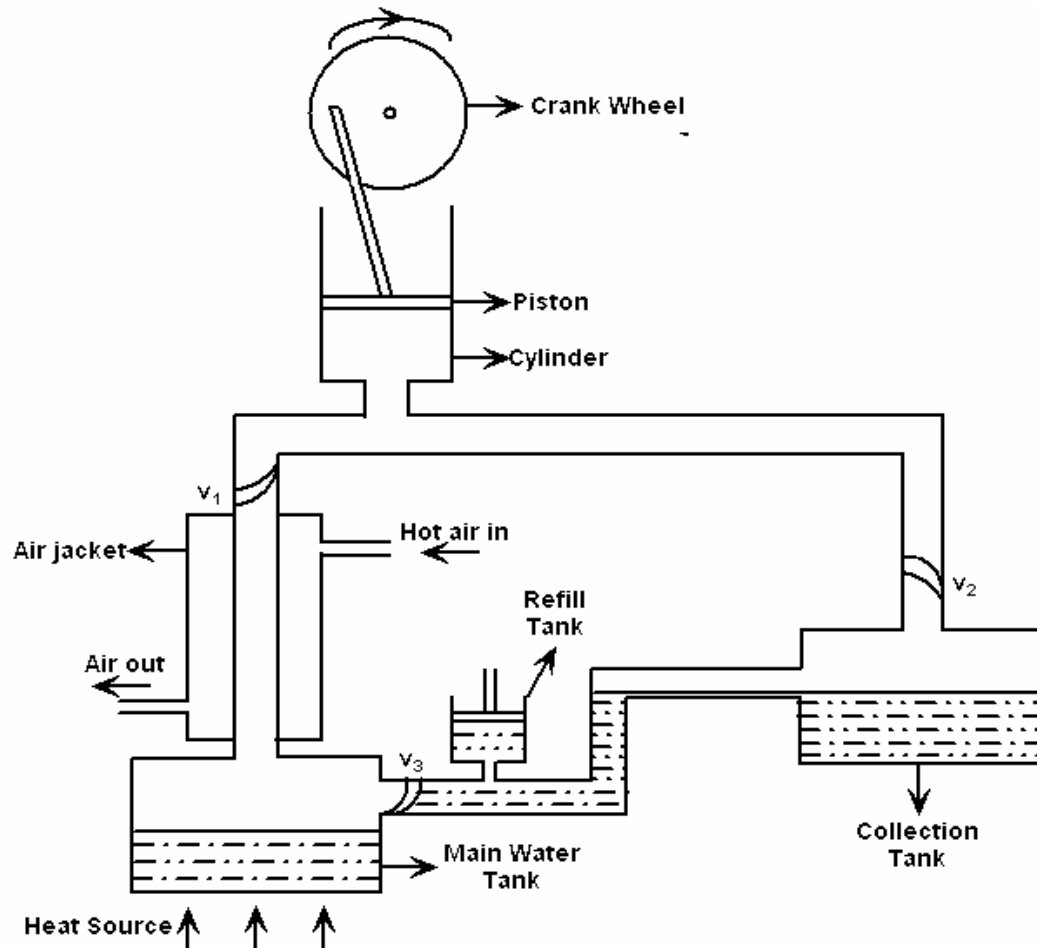
$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

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

In nature, Q_2 can never be equal to zero because there always is some energy loss in some form. Therefore η is always less than 1. In addition, Q1 can not be equal to infinity. Similarly, Q_2 is never greater than Q_1 also because loss of energy can never be greater than the input energy. So η is never less than zero also. Therefore the value of η is always in between zero and 1.

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Steam Engine

The steam engine is an instrument, which does mechanical work from heat by using steam only. It mainly consists of a chamber in which water is heated by means of a dry source, most commonly coal. This water gives out vapor at 100 ^{0}C. It is then led to a piping arrangement surrounded by a hot air jacket. The jacket consists of a controlled flow of air heated to a temperature greater than 500 ^{0}C, which then transforms the vapor into superheated steam. During this process, its temperature rises, and so does pressure by many times.

As the pressure rises, it will force valve v_1 to open suddenly, forcing steam out. Its first impact will be in the cylinder housing the piston because of its proximity. The piston is then pushed out at a high speed causing adiabatic expansion of the air in it. Because of the outward push, the crank wheel rotates, clockwise in this case, resulting in the movement of the wheels connected to the crank.

The sudden expansion also results in the sudden cooling of the steam in the cylinder. So the temperature of the steam decreases, resulting in its partial condensation. This gives a mixture of vapor and some water after full expansion. After the piston reaches its maximum range, it does not stop there. Because of the inertia of rotation of the crank wheel, it continues its motion to the other half. So the piston starts moving inwards. This will try to increase the pressure slightly, which in turn

will close valve v_1 and opens up v_2. Then the vapor and condensed water are forced to the collection tank.

After the piston has reached the minimum range of movement and the wheel has moved through one complete rotation, another burst of hot air is let through, producing another dose of steam and pushing the piston once again. The process continues indefinitely till the engine is being operated. The collection tank gradually gets its input of condensed water. When it fills up, the water goes to the piping arrangement and is periodically let into the main tank for re-heating.

Since, steam engine is a high pressure instrument, some steam leak through in spite of precautions. The lost matter is compensated by letting in water through the refill tank.

Questions for further thought
1. What is "Deadlock" of a steam engine, and hence define "dead centers".
2. Why do people in a train powered by steam engine sway to and fro?
3. Why are steam engines very inefficient?
4. Why is the steam engine called external combustion engine?

Petrol Engine

A petrol engine works with air and petrol vapor as a fuel, which repeatedly undergoes expansion, compression and exhaustion and ignition. The figure shows the operation of a petrol engine. Let the piston be moving downwards and valve v_1 be open. At that time air and petrol vapor will enter the chamber. This is shown by line XA in the graph. The pressure during this whole process is equal to the atmospheric pressure itself. This action is called as **Suction Stroke**.
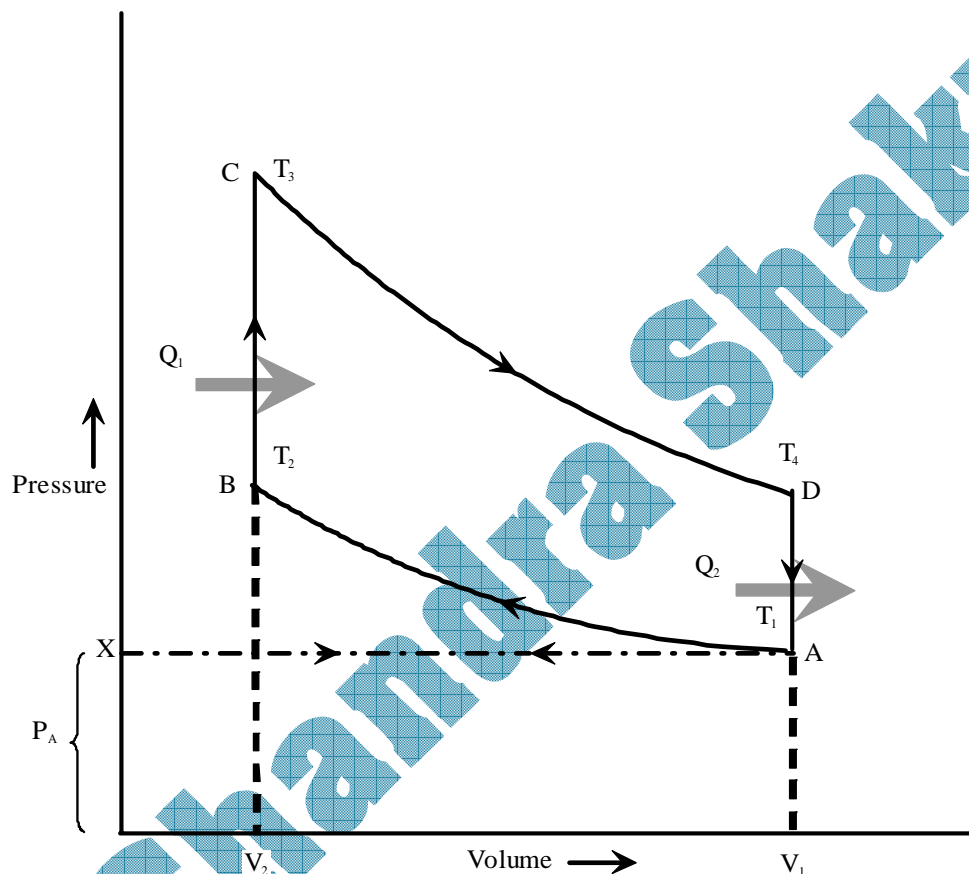
After the piston reaches its lowest point, it rises up. But, at that time both the valves are kept closed. So, the substance inside will undergo adiabatic compression. So, the volume will decrease and both pressure and temperature will increase. This is shown by the curve AB in the graph. The temperature T_2 at this moment is about 500 ^{0}C and is called as **Compression Stroke**.

After the piston reaches maximum height, and is just about to descend, the spark plug is set off. It will initiate vigorous reaction between petrol and oxygen resulting in immense amount of heat. The process is so fast that the pressure will increase suddenly along with temperature (T_3 = 2000 - 2500 ^{0}C). The line BC in the graph shows this phenomenon. This process is called **Ignition Stroke**. The immense pressure put on the piston will forcefully push the piston down resulting in its adiabatic expansion which will reduce its pressure and temperature (T_4). This phenomenon is represented by CD in the graph and is called as the **Working Stroke**.

When the piston is at the lowest point, valve v_2 is opened. This will suddenly release the remaining compressed air and so decrease the pressure abruptly to the level of atmospheric pressure. When

the piston again rises, the exhaust gases will be driven away through v_2 (line AX). The process is called as **Exhaust Stroke** and during the process; the pressure inside the cylinder remains constant equal to the atmospheric pressure (because of the open valve).

Now the cylinder becomes ready for the fresh cycle of strokes.

Efficiency of Petrol Engine:

Let Q_1 be the heat absorbed by the gas in order to run the engine and Q_2 be the amount of heat lost.

Then, for heat engines, efficiency is given by,

$$\eta = 1 - \frac{Q_2}{Q_1} \quad \text{.....................} \quad (1)$$

The gas gets heat only during ignition i.e., when the spark plug goes off. During that process, its temperature rises from T_2 to T_3 at constant volume. So,

$$Q_1 = nC_v(T_3 - T_2) \quad \text{...............} \quad (2)$$

where n is the number of moles.

Similarly, when valve v_2 is opened, the gas loses heat, changing its temperature from T_4 to T_1 at constant volume V_1. Therefore,

$$Q_2 = nC_v(T_4 - T_1) \quad \text{.................} \quad (3)$$

Therefore, using these values in equation (1) gives

$$\eta = 1 - \frac{nC_v(T_4 - T_1)}{nC_v(T_3 - T_2)}$$

$$\eta = 1 - \frac{(T_4 - T_1)}{(T_3 - T_2)} \quad \text{.................} \quad (4)$$

Here, the change of temperature is so rapid that measurement of any one of these quantities is difficult. So, the equation has to be changed to some measurable form.

During adiabatic expansion, the gas at volume V_2 and temperature T_3 changes to V_1 and T_4. So,

$$T_3 V_2{}^{\gamma-1} = T_4 V_1{}^{\gamma-1} \quad \text{.....................} \quad (5)$$

Similarly, during adiabatic compression, the gas at V_1 and T_1 changes to V_2 and T_2. So,

$$T_2 V_2{}^{\gamma-1} = T_1 V_1{}^{\gamma-1} \quad \text{.....................} \quad (6)$$

Subtracting equation (6) from (5)

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

Or, $\qquad \dfrac{V_2^{\gamma-1}}{V_1^{\gamma-1}} = \dfrac{(T_4 - T_1)}{(T_3 - T_2)}$

Using this value in equation (4) gives,

$$\eta = 1 - \dfrac{V_2^{\gamma-1}}{V_1^{\gamma-1}} = 1 - \left[\dfrac{V_2}{V_1}\right]^{\gamma-1}$$

Or, $\qquad \eta = 1 - \left[\dfrac{1}{V_1/V_2}\right]^{\gamma-1}$

Here the ratio of V_1/V_2 tells how much a gas can be compressed inside the cylinder. It also gives idea about the range of movement the gas can perform. This ratio is therefore called compression ratio of the engine and is denoted by ρ.

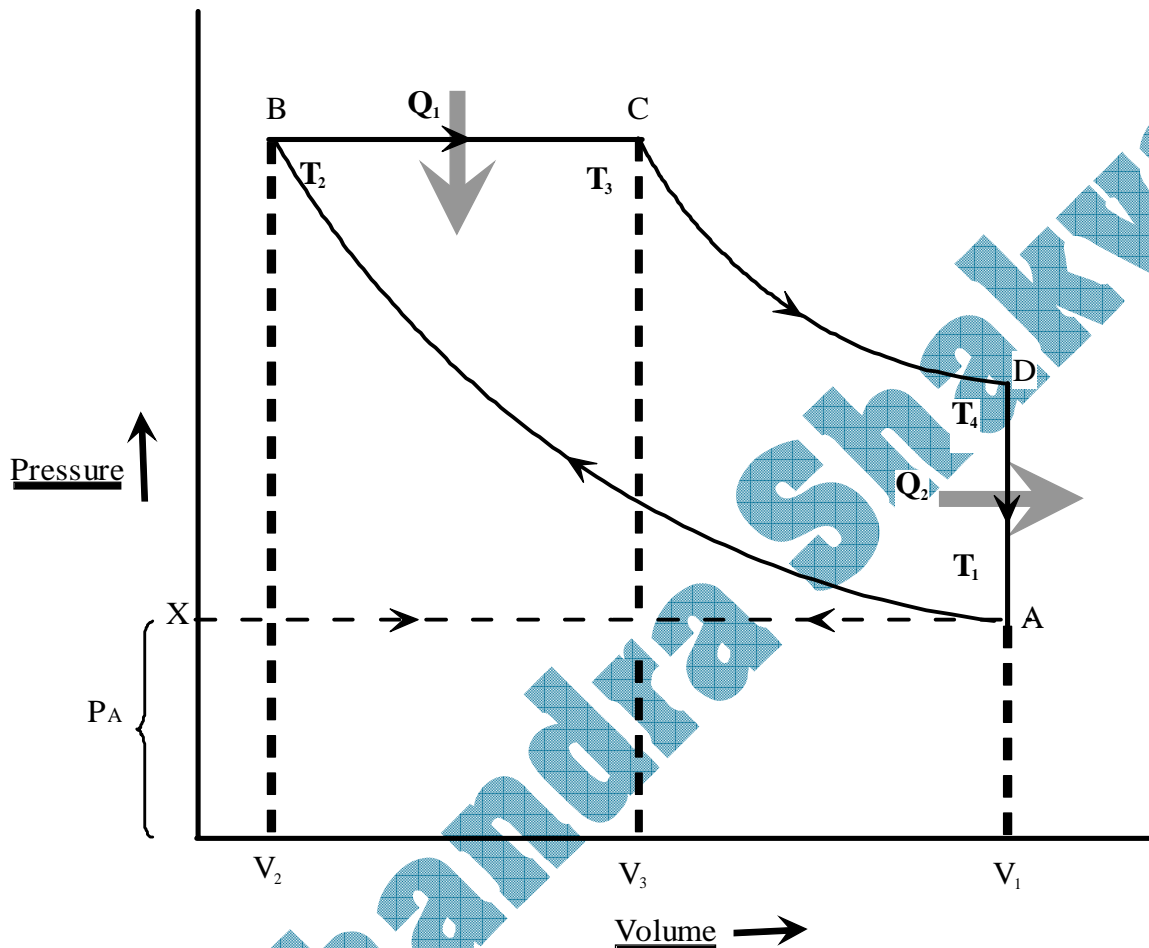$$\eta = 1 - \left[\dfrac{1}{\rho}\right]^{\gamma-1}$$

In modern petrol engines, the maximum compression ratio obtainable in general is around '6' times.

Therefore, maximum efficiency possible (considering $\gamma = 1.4$) is,

$$\eta_{max} = 1 - \left[\dfrac{1}{6}\right]^{1.4-1} = 0.51.$$

However, due to several constraints, such efficiency is impossible to achieve.

Diesel Engine

The diesel engine works with the combustion of diesel inside a compressed chamber. Here, there is no use of electrical sparking device. Instead a mechanical spray jet is used. When the piston of the engine moves downwards, air enters the chamber through open valve v_1. During this process, volume increases under a constant pressure. It is shown by line XA in the graph and is the **Suction Stroke**.

After the piston reaches the least height, it raises valves v_1 and at the same time v_2 is also deliberately closed. So, the air undergoes adiabatic compression. This increases pressure as well as temperature (nearly equal to 1000 ^{0}C) but volume decreases. This is shown by curve AB in the graph and is called as **Compression Stroke**.

After the piston has reached the maximum height, it starts to fall. This tries to decrease the pressure inside the chamber. Right at that moment, some diesel is sprayed into the chamber. Because of high temperature there, diesel ignites and explodes. This raises the pressure slightly, bringing it to the previous maximum pressure state. After diesel is finished, pressure again starts to drop but is reversed by further spraying of diesel, which brings further increase in pressure. This process continues till the quota of diesel for one cycle is finished. During this process, the pressure therefore remains fairly constant (because as soon as the pressure tries to decrease, there will be explosion.

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But volume as well as temperature rises because of repeated explosions. The temperature at that time reaches around 2000 ^{0}C. This is shown by line BC in the graph, the process being called **Ignition Stroke**.

After the supply of oil is stopped, the gas undergoes adiabatic expansion because of the tremendous heat and pressure. But as the gas starts to expand, the pressure and temperature start to decrease whereas volume will increase. It is demonstrated in the graph by curve CD and called as **Working Stroke**.

As the piston reaches the lowest point, valve v_2 is opened which releases any extra gases; which did not undergo combustion; to relieve the pressure. This change occurs almost at constant volume and is shown by the line DA. Then, the piston rises again with v_2 open. This will force away all the substances into the outer atmosphere. Due to opened valve v_2, the pressure however remains constant. It is shown by line AX in the graph and named as **Exhaust Stroke**. The cylinder now becomes ready for fresh intake of air for fresh cycle of operation.

**<u>Efficiency of Diesel Engine</u>** (derivation is not required)
In diesel engines, the efficiency is slightly larger than petrol engines. This is because of higher amount of expansion and contractions that can be achieved. This is made possible by the structure of the engine itself, because such engines do not require spark plugs. So there is less risk of catching fire. That's why nothing will happen to the cylinder even if the expansions and contractions are large and varied. Its efficiency is around 0.62.

Carnot Engine

Concerning lower efficiencies of petrol and diesel engine, Sadi Carnot developed the concept of a hypothetical engine which could work without depending upon the status of the materials used in it but only on the temperature of the substances and the environment. Such engines have not been developed yet but they act as reference for other engines developed later.

Such engines consist of the following items:

1. **Source of Heat**   (at temperature T_1 which can give infinite amount of heat.)
2. **Working substance**   (which is a perfect gas.)
3. **Sink**   (at temperature T_2 which can absorb infinite amount of heat.)
4. **Piston**   (Frictionless.)
5. **Insulating stand**   (which is perfect.)
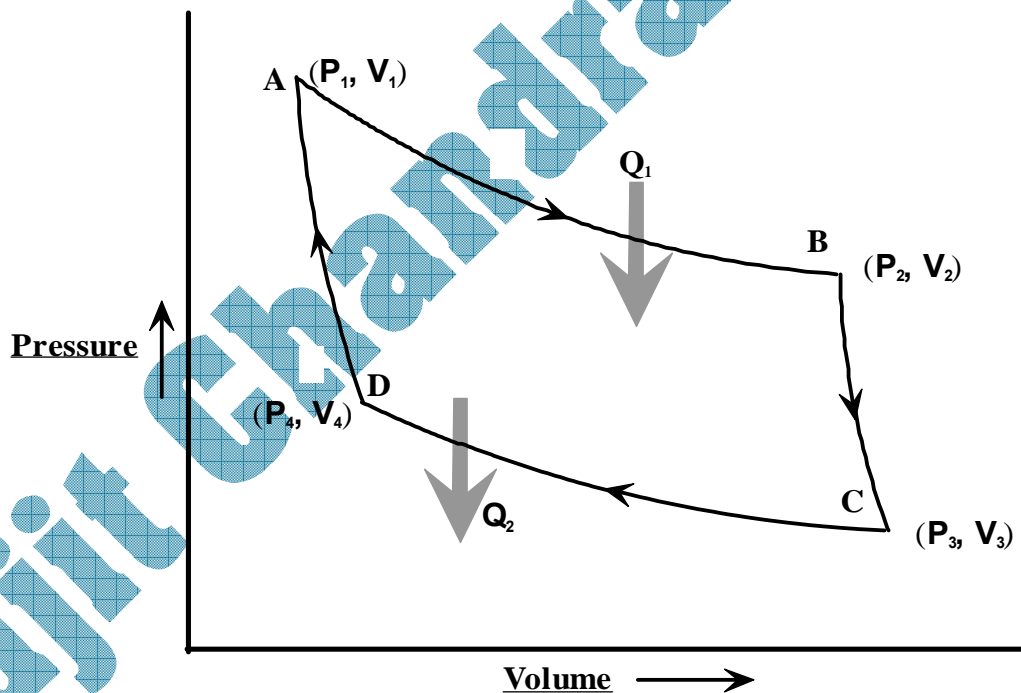
PV diagram of the working of a Carnot engine

The engine has four cycles of operation.

Operation 1:
The cylinder is placed on the source (which is at temperature T_1). Then the load on the piston is slowly decreased. This results in the expansion of the working substance inside and subsequent

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decrease in temperature. But since the source is at higher temperature and it acts as an infinite source of heat, the heat flows in to the working substance giving a constant temperature (i.e. isothermal expansion) of T_1 to the working substance. Let the amount of heat absorbed be Q_1. This is helped by the conducting face of the cylinder as well as the source. This operation is represented by the curve AB in the graph. Since the change is isothermal, the external work done by the gas when it goes from P_1V_1 to P_2V_2 at constant temperature (and which is equal to Q_1) and given by

$$Q_1 = W_1 = \int_{V_1}^{V_2} PdV = RT_1 \ln\left(\frac{V_2}{V_1}\right) \ldots\ldots\ldots\ldots\ldots\text{Eqn. 1}$$

Operation 2:

The cylinder is now removed from the source and placed on the perfectly insulated stand. Because of the inertia, the cylinder is still moving upwards but this time no heat can enter the working substance. So the expansion is totally adiabatic. So it does work spending some of its internal energy and so the temperature falls. The fall of temperature is continued up to T_2 which is the temperature of the sink. The pressure and volume of the gas also changes, this time to P_3V_3. This is represented in the graph by curve BC and is given by

$$W_2 = \int_{V_2}^{V_3} PdV = \frac{R(T_1 - T_2)}{\gamma - 1} \ldots\ldots\ldots\ldots\ldots\text{Eqn. 2}$$

Operation 3:

The cylinder is then removed from the insulating stand and placed on the sink. Then the gas is compressed slowly by adding loads. The heat developed by the compression slowly passes through the conducting faces to the sink keeping the temperature inside the cylinder constant at T_2. The temperature of the sink does not change however because of its infinite heat absorbing capacity. The process is purely isothermal and is represented by curve CD. Since the gas is compressed but is maintained at constant temperature, heat should be lost from it. The work done by the gas (whose value will come out to be negative) is given by

$$W_3 = \int_{V_3}^{V_4} PdV = RT_2 \ln\left(\frac{V_4}{V_3}\right) \ldots\ldots\ldots\ldots\ldots\text{Eqn. 3}$$

Operation 4:

The cylinder is then again placed on the insulating stand with the increase of load still continuing. But this time, due to the presence of the insulating stand, heat cannot escape. So the compression now will be adiabatic. This compression is continued till the temperature rises to T_1 once again. The pressure and volume also becomes equal to P_1V_1. Thus the gas reaches the initial stage. This process can be represented in the graph by curve DA. The work done by the gas (which comes out to be negative) will be given by

$$W_4 = \int_{V_4}^{V_1} PdV = \frac{R(T_2 - T_1)}{\gamma - 1} \ldots\ldots\ldots\ldots\ldots\text{Eqn. 4}$$

Work done by the gas in one cycle

The total work done by the gas will be given by the sum of all the works done by the gas in each operation, i.e.

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$$W = W_1 + W_2 + W_3 + W_4$$

$$= RT_1\ln\left(\frac{V_2}{V_1}\right) + \frac{R(T_1 - T_2)}{\gamma - 1} + RT_2\ln\left(\frac{V_4}{V_3}\right) + \frac{R(T_2 - T_1)}{\gamma - 1}$$

$$= RT_1\ln\left(\frac{V_2}{V_1}\right) + RT_2\ln\left(\frac{V_4}{V_3}\right)$$

$$\text{Or } W = RT_1\ln\left(\frac{V_2}{V_1}\right) - RT_2\ln\left(\frac{V_3}{V_4}\right) \quad\text{.......................... Eqn. 6}$$

The relation is to be changed to some simple form by finding a relationship between $\left(\frac{V_2}{V_1}\right)$ and $\left(\frac{V_3}{V_4}\right)$.

During the adiabatic change of the gas from state B to C, the parameters change from P_2, V_2, T_1 to P_3, V_3, and T_2. So,

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

$$\text{Or, } \left(\frac{T_1}{T_2}\right) = \left(\frac{V_3}{V_2}\right)^{\gamma-1} \quad\text{.................. Eqn 7}$$

Similarly during the adiabatic change of the gas from state D to A, the parameters change from P_4, V_4, T_2 to P_1, V_2, and T_1. So,

$$T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$$

$$\text{Or, } \left(\frac{T_1}{T_2}\right) = \left(\frac{V_4}{V_1}\right)^{\gamma-1} \quad\text{.................. Eqn 8}$$

This gives

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

$$\text{Or } \left(\frac{V_3}{V_2}\right) = \left(\frac{V_4}{V_1}\right)$$

$$\text{Or } \left(\frac{V_3}{V_4}\right) = \left(\frac{V_2}{V_1}\right)$$

Using this value of $\left(\frac{V_3}{V_4}\right)$ in Eqn. 6 gives

$$W = RT_1 \ln\left(\frac{V_2}{V_1}\right) - RT_2 \ln\left(\frac{V_2}{V_1}\right)$$

$$\text{Or } W = R(T_1 - T_2)\ln\left(\frac{V_2}{V_1}\right) \quad \ldots\ldots\ldots\ldots \text{ Eqn 9}$$

So the efficiency of the Carnot Heat Engine is

$$\eta = \frac{W}{Q_1} = \frac{R(T_1 - T_2)\ln\left(\frac{V_2}{V_1}\right)}{RT_1\ln\left(\frac{V_2}{V_1}\right)} = \frac{T_1 - T_2}{T_1}$$

$$\text{i.e. } \eta = 1 - \frac{T_2}{T_1}$$

So the efficiency of a Carnot Engine depends on nothing but only on the temperature of the source and sink.

So the Carnot engine shows several properties as described below:

1. The efficiency of a Carnot Engine can solely controlled by altering the temperatures of the source and sink.
2. The operation of a Carnot engine does not depend upon the nature of the working substance. The only requirement is that it should be a perfect gas.
3. The Carnot engine will give an efficiency of 1 only when the temperature of the sink (i.e. T_2) becomes zero or the temperature of the source (i.e. T_1) becomes infinite. Both of these situations are impossible. So Carnot Engine can have any amount of efficiency, but not equal to 1.

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Second Law of Thermodynamics

The second law of thermodynamics came as an attempt to realize and describe certain phenomena that arose from devices which was constructed based on the first law, especially the heat engines. Work and energy had been defined to be equivalent to each other and each of them could be derived from the other. So it was wondered whether the same could be possible in a heat engine!!

A heat engine, for example a vehicle absorbs heat energy (Q_1) from a region of higher temperature (T_1) and throws some (Q_2) into a region of lower temperature (T_2) after performing some work (W). In layman's term it travels some distance. The questions which arose were:

1. If the thrown amount of heat (Q_2) is somehow stored and then later given to the vehicle engine, will it do the reverse work by itself?
2. And will it add up with the work (W) to store as Q_1 inside the engine?

While doing so, the heat energy would go from lower to higher temperature and also does work, albeit in a reverse direction. The dilemma is frequently encountered and such a possibility (or impossibility) is explained by the famous equation for the efficiency of a Carnot Heat Engine

$$\text{i.e. } \eta = 1 - \frac{T_2}{T_1} = \frac{W}{Q_1}$$

According to the relation, three special conditions arise:

Condition No. 1
If $T_2 = T_1$, $\eta = 0$ and W (the work done) will be zero,

Condition No. 2
If $T_2 < T_1$, $\eta = + ve$, and W will be positive, which means the engine will do some work.

It means that for an engine to perform work, there should be a difference of temperature between two regions, one from where heat energy is to be drawn in (source) and the other where heat is to be thrown into (sink), the former region has to be at a higher temperature for work to be performed. Or in other words, if two regions are at a different temperature, heat energy will flow from the region of higher temperature to the lower and also performs some work (by itself) on the way (no work has to be done from outside). This phenomenon forms one way of expressing a universal truth named as the **Second Law of Thermodynamics**. It states that "for any engine or device to perform work, there is no other way than allowing heat energy to flow from a region of higher temperature to the lower, the ultimate result being the cooling of the former and heating of the latter". This statement was first recorded by Kelvin and Planck and so named as **Kelvin-Planck statement of Second Law**.

Condition No. 3
If $T_2 > T_1$, $\eta = - ve$, and W will be negative, which means that the engine or the device is not going to do work, in fact work has to be done on it to make it possible.

This means that if heat energy is to be carried from a zone of lower temperature to higher temperature, work has to be done on the device or the machine, or the device is not going to do work as in the previous case. Heat energy can itself never ascend from the former to the later. This principle forms the basis of the construction of a refrigerator and was first state by Clausius. He stated that "there is no way heat energy can flow on its own from low temperature region to high

temperature region other than providing some work on it." So this statement is also called as **Clausius statement of Second Law**.

If these statements are applied on the example depicted above, it is evident that when the vehicle engine is operated, it gets energy from the fuel, does some work and throws the rest to environment, the net flow being from inside (high temperature region) to outside (low temperature). If somebody expects that when the thrown heat is again given to the device and it does work in reverse direction, adds up to change to higher amount of that and stores inside the device is a folly. Because heat can not go by itself from low temperature to higher temperature. If this is to be made possible, work has to be done from outside on the device from outside by external agencies.

The phenomenon described by the Second Law of Thermodynamics extends to all the physical phenomena. For example, a positively charge particle when freed around the region of a cluster of positively charged particle immediately flies away and distances itself. In due process it has gone from high energy zone (nearby the cluster) to low energy zone (far away) and also does some work. However, it can not reverse back by itself and again do work, in fact work has to be done from outside to reverse it.

Similarly, any substance raised to a height will fall by itself (comes from high energy region to low energy zone) and also performs some work on the way. However, it can not reverse by itself and provide some work. In fact, work has to be done on it to make it possible.

Again, perfume vapors come out by themselves from their bottles to the outside when the cap of the bottle is left pressed for a moment, and the drops also perform some work on the way. However if the bottles are to be filled up by perfume (as done in the manufacturing plants), work has to be done from outside.

The most striking example is the case of evolution, which says that the structure of the organisms in the world become more and more complex over time. But this did not happen naturally; the organisms had to do work for that. Those who did not do work and let nature take its course got extinct (which is the simplest form and lowest energy category possible). Similarly a living body is itself a concentration of energy. If left unattended, the organism dies and disintegrates, which is the case of flow of energy from higher level to lower. If this is to be prevented or the organism has to live, work should be performed.