

~~Numerical~~ (6) Second law of Thermodynamics

* Kelvin's statement :- states that "It is impossible to get a continuous supply of work from a body by cooling it to a temp^r lower than the temp^r of ~~some~~ surrounding."

* Clausius statement :- "It is impossible for a self acting machine ~~to be~~ unaided by any external agent to convey heat from one body to another at a higher temperature."

→ That is :- we can't make heat flow from a colder body to a warmer body without doing external work.

• Heat engine :- Any device which converts heat energy continuously into mechanical work is heat engine. The essential parts of heat engine are :-

(i) Source :- The source is a hot reservoir at constant higher temperature from which the heat engine can draw heat.

(ii) Sink :- The sink is a cold reservoir at constant low temperature to which the engine rejects heat.

(iii) Working substance :- The substance which on absorbing heat performs mechanical work is called working substance.

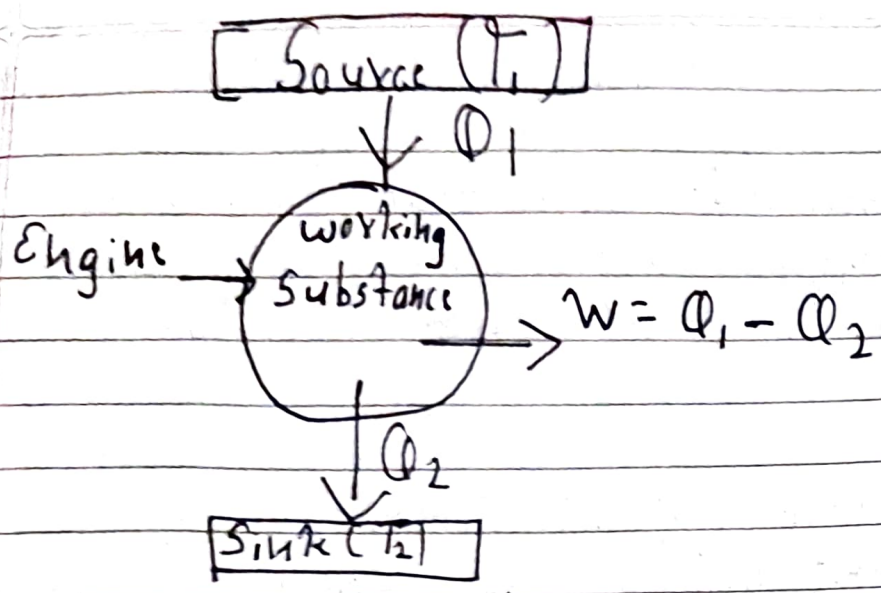


Fig: Block diagram of heat engine

The working substance absorbs Q_1 amount of heat from the source at higher temp^r T_1 , performs mechanical work W & rejects the remaining heat Q_2 to the sink at lower temp^r T_2 . Therefore $Q_1 - Q_2$ amount of heat is converted into mechanical work.

* Efficiency of heat engine (η)

It can be defined as ratio of external work done to the amount of heat absorbed by the working substance from the source.

Efficiency (η) = $\frac{\text{External work done}}{\text{Heat absorbed by the working substance from the source.}}$

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

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

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

Since efficiency is expressed in percentage

$$\eta = \left(1 - \frac{Q_2}{Q_1}\right) \times 100\%$$

$Q_2 \neq 0$. So η cannot be 100%.

Q. Why the efficiency of heat engine cannot be 100%?

The efficiency of heat engine is given by

$$\eta = \left(1 - \frac{Q_2}{Q_1}\right) \times 100\%$$

$\therefore Q_2 \neq 0$. So η cannot be 100%.

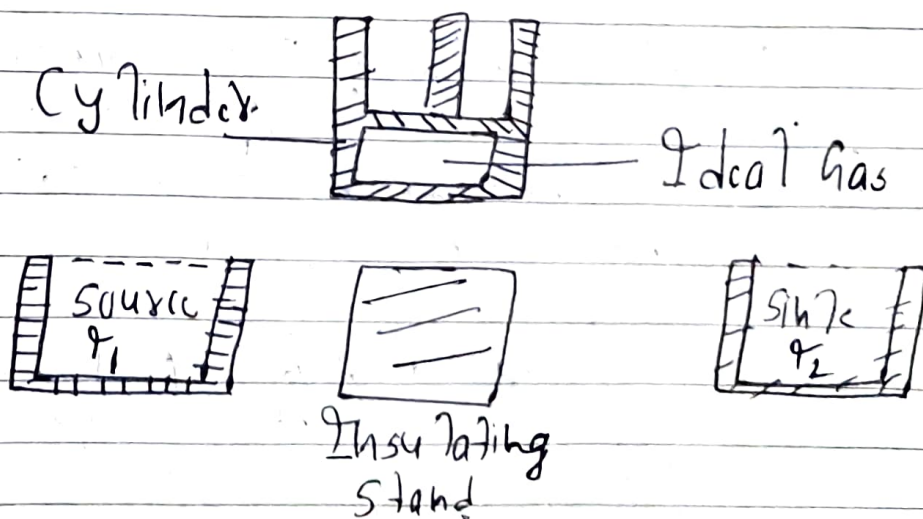
Also,

$$\eta = \left(1 - \frac{T_2}{T_1}\right) \times 100\%$$

\therefore Since $T_2 \neq 0K$ so η cannot be 100%.

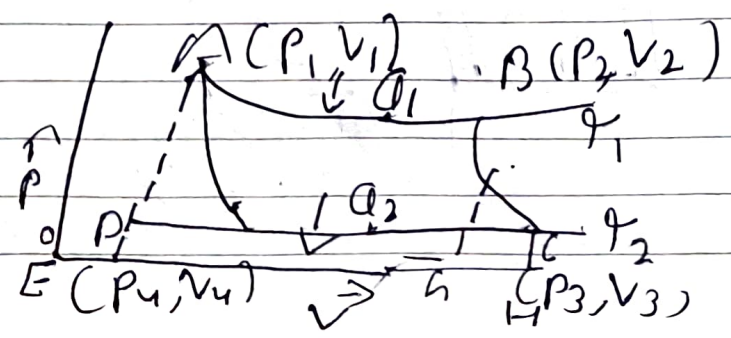
II Carnot engine: Carnot derived an ideal cycle of operation for the heat engine. This cycle is called Carnot cycle. The device used for realizing such cycle of operation is called Carnot engine.

The essential parts of Carnot engine



- (a) **Source:** - A source is a hot body of infinite thermal capacity. It is maintained at constant higher temp T_1 . Any amount of heat can be drawn from the source without changing its temp.
- (b) **Sink:** A sink is a cold body of infinite thermal capacity. It is maintained at constant lower temp T_2 . Any amount of heat can be rejected to the sink without changing its temp.
- (c) **Cylinder:** A cylinder is provided with frictionless & insulating piston enclosing an ideal gas. The walls of the cylinder are perfectly insulating whereas the bottom of the cylinder is perfectly conducting.
- (d) **Insulating stand:** During the operation of Carnot cycle, the working substance undergoes a diabatic expansion & compression for which the cylinder is placed on the insulating stand. The insulating stand separates the working substance from the surrounding.

* **Carnot cycle:** The working substance is taken through a cycle of 4 operations consisting of two isothermal & two adiabatic process called Carnot cycle.



(a) Isothermal Expansion (AB) In this step, the cylinder is placed on the source & gas is allowed to expand isothermally from state A (P_1, V_1) to B (P_2, V_2) at constant temp T_1 . Let Q_1 be the amount of heat gained by working substance. If W_1 is the work done by the gas during this expansion, then

$$Q_1 = W_1 = + \int_{V_1}^{V_2} P dV = nRT_1 \log\left(\frac{V_2}{V_1}\right) \text{--- (i)}$$

Area ABGEA

(b) Adiabatic Expansion (BC): In this step the cylinder is removed from the source & placed on the insulating stand & gas is allowed to expand adiabatically from B (P_2, V_2) to C (P_3, V_3). Temp of the gas falls to T_2 . If W_2 is the work done by the gas during this expansion, then,

$$W_2 = + \int_{V_2}^{V_3} P dV = \frac{nR}{\gamma-1} (T_1 - T_2) \text{--- (ii)}$$

Area BCMB

(c) Isothermal compression (CD): In this step the cylinder is placed on the sink & gas is allowed to compress isothermally from the state C (P_3, V_3) to D (P_4, V_4) at constant temp T_2 . Let Q_2 be the amount of heat rejected by the working substance. If W_3 is the work done on the gas during this compression, then

$$Q_2 = W_3 = - \int_{V_3}^{V_4} P dV = -nRT_2 \ln \left(\frac{V_4}{V_3} \right) - nRT_2 \ln \left(\frac{V_3}{V_4} \right) \quad \text{--- (iii)}$$

Area CDHC

(d) **Adiabatic compression:** In this step the cylinder is placed on the insulating stand & gas is allowed to compress adiabatically from state D (P_4, V_4) to state A (P_1, V_1). Temp of gas rises to T_1 . If W_4 is the work done on the gas during this compression then,

$$W_4 = - \int_{V_4}^{V_1} P dV$$

$$= \frac{-nR}{\gamma - 1} (T_2 - T_1)$$

$$= \frac{nR}{\gamma - 1} (T_1 - T_2) \quad \text{--- (iv)}$$

Area DAEFD

Work done by carnot engine per cycle

→ The net work done by carnot engine per cycle is given by

$$W = (\text{work done by gas}) - (\text{work done on gas})$$

$$\frac{(W_1 + W_2)}{W_1 + W_2} - \frac{(W_3 + W_4)}{W_3 + W_4} \quad \text{--- (v)}$$

From (ii) & (iv)

$$W_2 = W_4$$

So eqn (V) becomes

$$W = W_1 - W_3$$

$$W = Q_1 - Q_2$$

The net work done by Carnot engine per cycle (in terms of area) is

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

$$\text{Area } ABGEA + BCHAB - CDHCD - DAETD$$

$$= \text{Area of closed loop ABCDA}$$

Efficiency of Carnot engine:

→ The efficiency of Carnot engine is given by

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

$$1 - \frac{nRT_2 \ln \left(\frac{V_3}{V_4} \right)}{nRT_1 \ln \left(\frac{V_2}{V_1} \right)}$$

$$1 - \frac{T_2 \ln \left(\frac{V_3}{V_4} \right)}{T_1 \ln \left(\frac{V_2}{V_1} \right)} \quad \text{--- (vi)}$$

For the Adiabatic BC & AD

$$P_1 V_2^{\gamma-1} = P_2 V_3^{\gamma-1} \quad \text{(vii)}$$

$P_1 V_1^{\gamma-1} = P_2 V_4^{\gamma-1}$ (viii)

Dividing (vii) by (viii)

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

Putting this value in (6)

$$\eta = 1 - \frac{T_2 T_4 \left(\frac{V_3}{V_4} \right)}{T_1 T_4 \left(\frac{V_3}{V_4} \right)}$$

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

which is the expression for efficiency of Carnot engine.

(1) The above expression shows us that the efficiency of Carnot engine depends on temp^s of sources & sink only.

(2) Efficiency of Carnot engine is independent on the nature of working substance.

Note:

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

if $T_2 = 0$ Kelvin, $\eta = 100\%$.
Since $T_2 = 0$ Kelvin cannot be achieved so $\eta \neq 100\%$.

(2) if $T_1 = T_2$, $\eta = 0$
(3) we have

$$\frac{Q_2}{T_2} = \frac{Q_1}{T_1}$$

If $T_2 = 0$ then $Q_2 = 0$
Since $T_2 \neq 0$, so $Q_2 \neq 0$

H

(i)

→

(ii)

→

H

Types of heat Engine :-

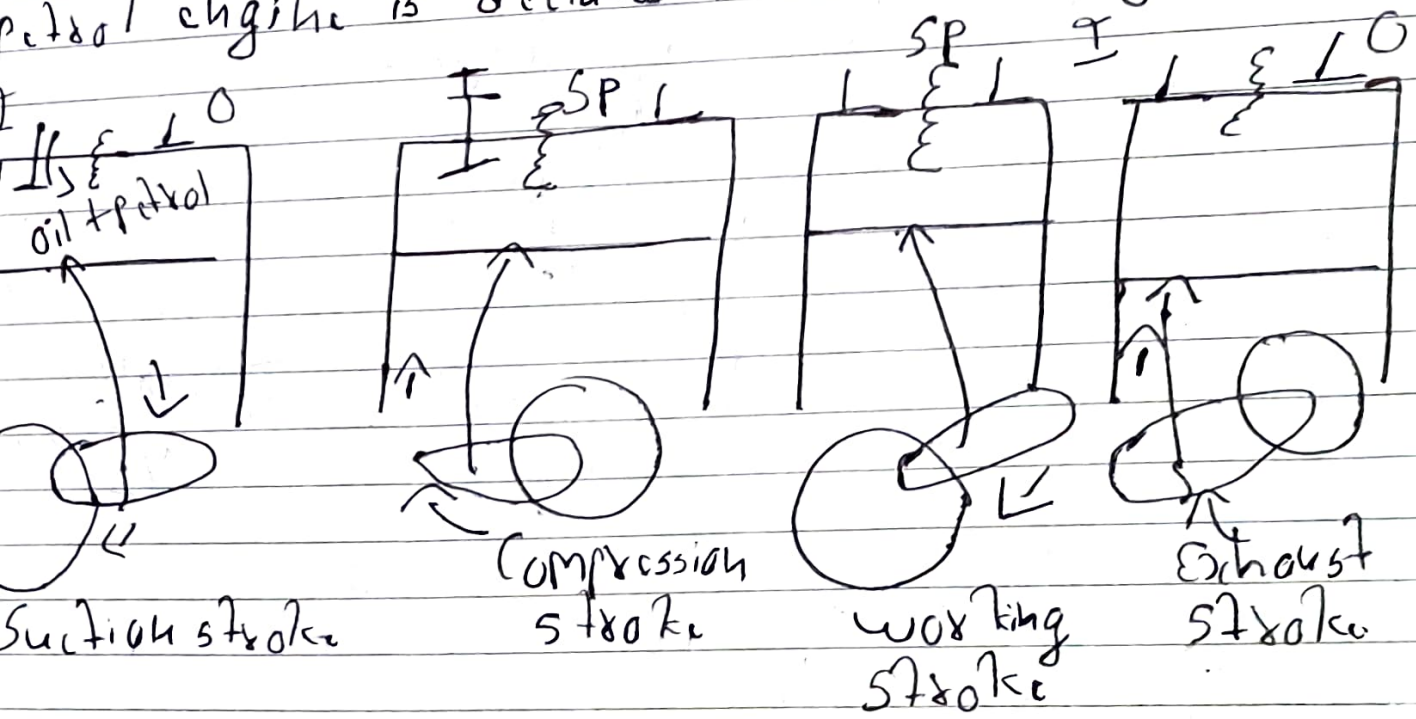
External combustion heat engine

Combustion of fuel takes place outside the engine
 For eg :- Steam engine (used in train for coal burning)

Internal combustion heat engine

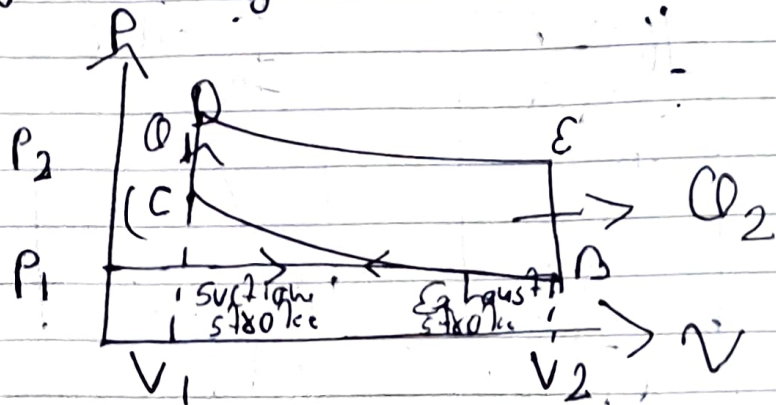
Combustion of fuel takes place inside the engine
 Eg :- Petrol Engine, Diesel engine

Petrol Engine: Petrol engine was developed by otto in 1876 & hence it is also called otto engine. It consists of a cylinder provided with inlet valve (I) & outlet valve (O). A spark plug is also placed inside the cylinder. There are four strokes in a complete cycle & uses a mixture of petrol & air (2% petrol & 98% air) as a working substance. The working of petrol engine is declared in the following steps.



- (a) **Suction stroke:** In this stroke the inlet valve (I) opens & the mixture of air & petrol is pulled inside the cylinder by the outward motion of piston.
- (b) **Compression stroke:** In this stroke both the valves are closed. The mixture is compressed adiabatically to $\frac{1}{5}$ th of its original volume. Temp of the mix rises to about 600°C .
- (c) **Working stroke:** In this stroke both the valves are closed. The compressed mixture is burnt by passing spark through the spark plug - temp & pressure of the mixture increases to 2000°C & 15 atm resp. The piston moves outward & the shaft rotates.
- (d) **Exhaust stroke:** The outlet valve (O) opens & the burnt out gases are exhausted out to the surrounding. The engine is again ready for fresh new cycle.

II otto cycle on PV diagram.



- Portion AB represents suction stroke at constant pressure P_1 .
- Portion BC represents adiabatic compression in which volume of mixture decreases from V_2 to V_1
i.e. $V_1 = \frac{1}{5} V_2$
- ⇒ Temp^r at point C is 600°C at this point spark plug produces spark.
- Portion CD represents explosion of mixture, Both pressure & temp^r of the mixture increases at constant volume V_1 . During this process Q_1 amount of heat is supplied to the engine.
- At point D, temp^r is 2000°C & pressure 15 bar
- Portion DE represents adiabatic expansion in which volume increases from V_1 to V_2 . This is the working stroke
- At point E outlet, valve opens
- Portion EB represents sudden drop in pressure & temp^r. During this process Q_2 amount of heat is rejected by the engine.
- Finally portion BC represents exhaust stroke at constant pressure.

* Efficiency of petrol engine.

The efficiency of petrol engine is given by

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

We have,

$$dQ = m C_V dT$$

So,

$$Q_1 = n C_V (T_D - T_C) \quad \text{--- (ii)}$$

$$Q_2 = n C_V (T_E - T_B) \quad \text{--- (iii)}$$

Dividing iii by ii

From the adiabatic change BC & ED

$$T_B \cdot V_2^{\gamma-1} = T_C \cdot V_1^{\gamma-1} \quad \text{--- (v)}$$

$$T_E \cdot V_2^{\gamma-1} = T_D \cdot V_1^{\gamma-1} \quad \text{--- (vi)}$$

Subtracting (v) & (vi)

$$(T_E - T_B) V_2^{\gamma-1} = (T_D - T_C) V_1^{\gamma-1}$$

$$\frac{T_E - T_B}{T_D - T_C} = \left(\frac{V_1}{V_2} \right)^{\gamma-1} \quad \text{--- (vii)}$$

Equating (iv)

$$\frac{Q_2}{Q_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

Putting this value in eqn (i)

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

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

$$\eta = 1 - \left(\frac{1}{r} \right)^{\gamma-1}$$

where $\frac{V_2}{V_1} = r$ is the compression ratio of petrol engine

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$$S = 5, \gamma = 1.4$$

∴ $\eta = 1 - \left(\frac{1}{5}\right)^{1.4-1}$

$$= 1 - 0.52$$
$$= 0.48$$

48% to 52%

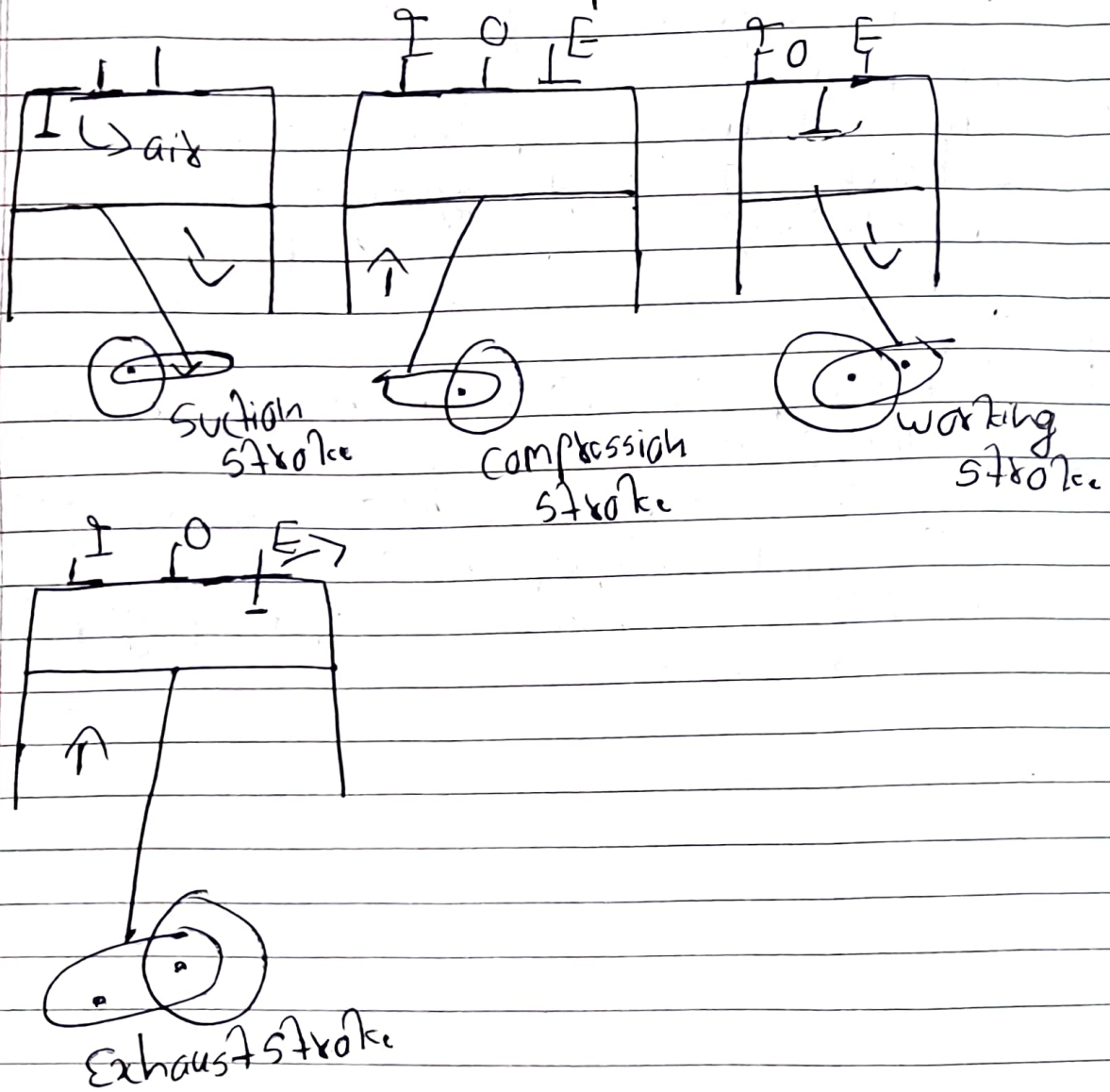
Merits

- ① Petrol engine is small in size & light in weight & is applicable for light vehicle like buses, car, aeroplane etc.
- ② The efficiency of petrol engine is more than the efficiency of steam engines.
- ③ Petrol engine is practically maintenance free.

Demerits

- ① It is expensive to run petrol engine due to the high cost of petrol.
- ② There is a chance of catching fire during the expansion of petrol vapour.
- ③ The occasional failure of spark plug makes petrol engine less reliable.

Diesel Engine: Diesel engine was designed by a German engineer Rudolf Diesel. It overcomes the main drawbacks of petrol engine. Its construction & working is similar to that of petrol engine. In a diesel engine, air is the working substance & diesel is the fuel. There are three valves namely air inlet valve (I), oil supply valve (O) & exhaust valve (E). Spark plug is absent in diesel engine. This engine also works on four stroke principle.



(1)

Suction stroke: In this stroke the air inlet valve (I) opens & pure air from atmosphere is pulled inside the cylinder by the outward motion of piston.

(2)

Compression stroke: In this stroke all the valves are closed. Air is compressed adiabatically to $\frac{1}{17}$ th of its original volume. Temp^r of air rises to about 1000°C .

(3)

Working stroke: In this stroke the oil supply valve (O) opens & oil is forced in under pressure. At high temp^r oil burns spontaneously. The supply of oil is so regulated that during combustion as the piston moves downward pressure remains constant. The temp^r increases to about 2000K & oil supply is cut off. This is the stroke in which useful work is done.

(4)

Exhaust stroke: The exhaust valve (E) opens & the burnt out gases are exhausted out to the surrounding & the engine gets ready for another fresh cycle.

|| Diesel cycle on P-V diagram

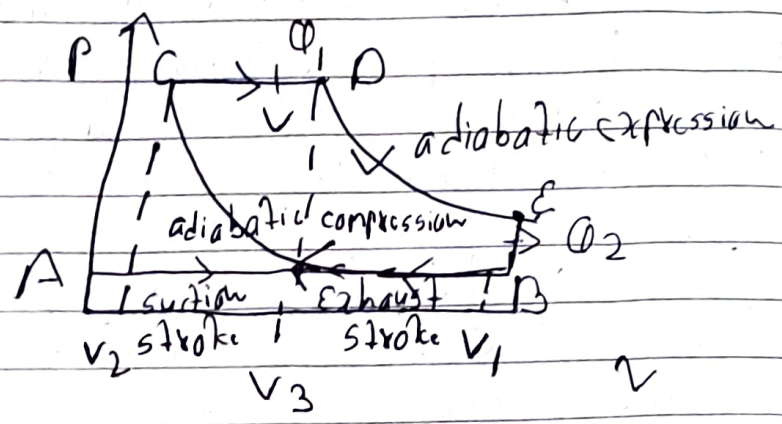
→ Portion AB represents suction stroke at constant pressure,

→ Portion BC represents adiabatic compression in which volume decreases from V_1 to V_2
i.e. $V_2 = \frac{1}{17} V_1$

→ At point C, temp^r is about 1000°C . At this point oil supply valve opens.

→ Portion CD represents combustion of fuel at constant pressure. During this process Q_1 amount

- > At heat is supplied to the engine.
- > At point D, temp is about 200K & the oil supply is cut off
- > Portion DE represents adiabatic expansion in which volume of mixture, increases from V_3 to V_1
- > At point E exhaust valve opens
- > Portion EB represents sudden drop in pressure & temp at constant volume V_1 . During this process Q_2 amount of heat is rejected by the engine.
- > Finally portion BA represents exhaust stroke at constant pressure.



Efficiency of diesel engine (η)

-> The efficiency of diesel engine is given by

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1} \left[1 - \left(\frac{1}{r_c}\right)^{\gamma-1} \right]$$

$$= 1 - \left(\frac{1}{\rho}\right)^{\gamma-1}$$

where $\frac{h}{v_2} = \rho$ is the compression ratio of diesel engine.

For a typical diesel engine.

$$\rho = 17, \gamma = 1.4$$

$$\eta = 1 - \left(\frac{1}{17}\right)^{1.4-1}$$

$$0.68$$

$$68\%$$

Merits

- ① The efficiency of diesel engine is more than that of petrol engine.
- ② Diesel is cheaper.
- ③ Diesel is less inflammable, so there is less chance of catching fire.
- ④ There is no problem of spark plug.

Demerits

- ① It cannot be used in light vehicle.

Diff between petrol & diesel engine.

Petrol engine

It is a light engine.
Spark plug is present.
Its efficiency is less.
Petrol is the fuel.
Petrol engine is cheaper.

diesel engine

It is a heavy engine.
Spark plug is absent.
Its efficiency is more.
Diesel is the fuel.
Diesel engine is costly.

Q Why spark plug is absent in diesel engine?

→ In a diesel engine, air is compressed adiabatically to $\frac{1}{17}$ th of its original volume. Temp of air rises to 100°C which is sufficient to burn the diesel spontaneously.

II Refrigerator

→ A refrigerator is a machine that operates in a manner opposite to that of heat engine.

In a refrigerator, the working substance is absorbed Q_2 amount of heat from the sink at lower temp T_2 . If W is the external work done on the working substance then the amount of heat delivered to the source at higher temp T_1 is

$$Q_1 = Q_2 + W$$

Therefore, a refrigerator transfers heat from a cold body to a hot body when external work is done on the system. Thus cold body becomes colder.

* Coefficient of Performance of a Refrigerator (B)

→ It can be defined as the ratio of amount of heat absorbed from cold body to the work done in running the machine. It is represented by B.

i.e $B = \frac{Q_2}{W}$

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

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

From Carnot cycle,
 $\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$

So,

$$\beta = \frac{T_2}{T_1 - T_2}$$

$$\beta = \frac{\left(\frac{T_2}{T_1}\right)}{\left(\frac{T_1 - T_2}{T_1}\right)} = \frac{T_2}{T_1 - T_2}$$

Smaller the value of $T_1 - T_2$,
 larger the value of β .

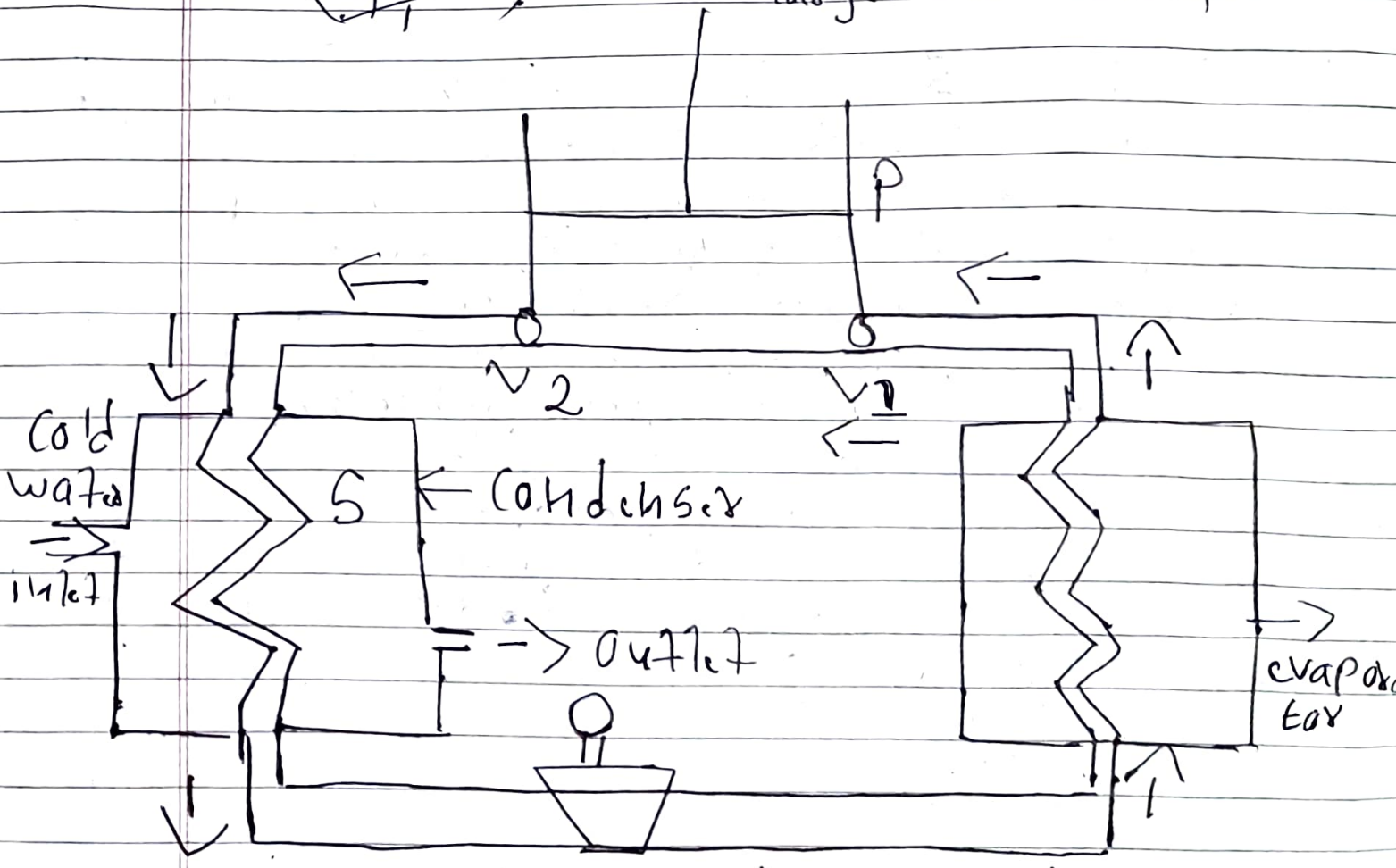


Fig:- Schematic diagram of refrigerator.

→ In the diagram, P is the compressor in which working substance is compressed to a high pressure. The working substance used is called refrigerant. For eg:- Ammonia, Sulphur dioxide.

The hot high pressure gas coming out thru the valve V_2 is cooled by passing it thru a spiral tube in the condenser. The compressed vapour gets liquid. Thru a throttling valve V_3 , the high pressure liquid enters the spiral tube in the evaporator. The necessary heat is taken from the material kept inside the evaporator. The vapour coming out of the evaporator is pulled back into the compressor thru the valve V_1 . The process is repeated & therefore continuous cooling is produced.

Entropy (S):- The quantitative measure of disorderliness of a system is called entropy.

Let us consider an isothermal process. Suppose an amount of heat is added to a gas that expands at constant temp. Then

$$dT = 0 \quad \& \quad dU = nCv dT = 0$$

From 1st law of thermodynamics,

$$dQ = dU + dW$$

$$dQ = 0 + dW$$

$$dQ = dW$$

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

From ideal gas eqn

$$PV = nRT$$

$$\therefore P = \frac{nRT}{V}$$

Putting the value of P in eqn (1)

$$dQ = nRT \frac{dv}{v}$$

~~$$nRT \frac{dv}{v} = nR \times \frac{dQ}{T}$$~~

$$\frac{dv}{v} = \text{constant} \cdot \frac{dQ}{T} \quad (\text{since } nR \text{ is constant})$$

$$\frac{dv}{v} \propto \frac{dQ}{T}$$

So the gas molecules undergoes more disorder state after expansion (i.e. $\frac{dv}{v}$ increases). Therefore the term $\frac{dQ}{T}$ can be introduced v to measure the disorder

of a system. If S is the entropy of a system, then the change in entropy ds at constant temp T is given by

$$\left[ds = \frac{dQ}{T} \right]$$

The SI unit is $J K^{-1}$

If Q amount of heat is added to a system

$$\Delta S = S_2 - S_1 = \frac{Q}{T}$$

For reversible process, the change in entropy between two states A & B is

$$\Delta S = S_2 - S_1 = \int_A^B \frac{dQ}{T}$$

For reversible process,

$$dS = 0$$

$$\left(\frac{T_1}{T_2} \right)$$

For irreversible process,
 $ds > 0$

For adiabatic process, $dQ = 0$.
So S is constant

The second law of thermodynamics can be stated as, "it is impossible to have a process in which entropy of an isolated system is decreased."

Explain 1st law of thermodynamics in terms of entropy.

$$ds = \frac{dQ}{T}$$
$$dQ = T \cdot ds$$

We have,

$$dQ = dU + dW$$
$$T \cdot ds = dU + dW$$

MCQ

① The efficiency of heat engine can be increased by

- (a) Increasing source temp, ~~decreasing~~
- (b) decreasing sink temp,
- (c) Increasing diff between source & sink
- (d) All of the above \equiv

② Which of the following is most efficient?

- (a) Carnot
- (b) Petrol
- (c) diesel
- (d) Steam engine

C > d > P > S

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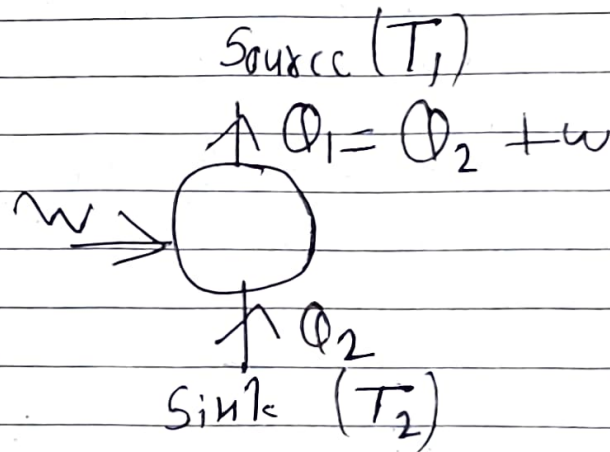
Hint: C > d > P > S

③ When the compression ratio of internal combustion engine increases, η is

- (a) Increases (b) decreases (c) Same (d) None

Hint: If S increases η increases & vice versa
④ The door of a refrigerator is kept open, the temp of room

- (a) Increases (b) decreases (c) Same (d) None



⑤ An ideal refrigerator is working between 0°C and 127°C . The coeff of performance is

- (a) 0.56 (b) 2.15 (c) 3.25 (d) 2.82

$$T_1 = 127^\circ\text{C} = 400\text{K}$$
$$T_2 = 0^\circ\text{C} = 273\text{K}$$

$$\beta = \frac{T_2}{T_1 - T_2} = \frac{273}{400 - 273} = 2.15$$