Chapter- 12

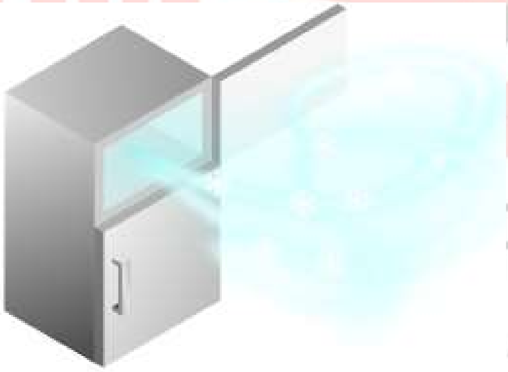
THERMODYNAMICS

12.1 INTRODUCTION:

- Thermodynamics is that branch of physics which deals with concepts of heat and temperature and their relation to energy and work.
- We can also consider it as a macroscopic science which deals with bulk systems and tells us about the system as a whole.
- In this chapter, we will learn about the laws of thermodynamics which describes the system in terms of macroscopic variables, reversible and irreversible processes. Finally, we will also learn what principle heat engines, refrigerators and Carnot engine work.

Examples: - Refrigerator, steam engine

Refrigerator



Thermodynamics vs. Mechanics

- In Thermodynamics we consider only the state of the object which means we will only consider macroscopic variables like pressure, volume and temperature.
- In mechanics, we consider the motion, velocity and acceleration of the object.

For eg: -

- In mechanics, if a bullet is fired from a gun we will consider the motion of bullet and its velocity, acceleration etc.

Bullet getting fired from the gun

Consider a second scenario where a bullet is fired on a wall. When it hits the wall its kinetic energy gets converted to heat. Due to heat generation, there will be a change in temperature and the internal energy of the bullet. These are the macroscopic variables which we will study in Thermodynamics.

Bullet fired from the gun and hitting a wall

Thermal Equilibrium

- Two systems are said to be in thermal equilibrium if the temperatures of the two systems are equal.

- In mechanics, if the net force on a system is zero, the system is in equilibrium.

- In Thermodynamics equilibrium means all the macroscopic variables (pressure, temperature and volume) don’t change with time. They are constant throughout.

For Example: -

- Consider two bodies at different temperatures one is at 30^{0}C and another at 60^{0}C then the heat will flow from the body at a higher temperature to the body at a lower temperature.
- The heat will flow until both bodies acquire the same temperature.
- This state when there is no heat flow between two bodies when they acquire the same temperature is known as thermal equilibrium.

In the above case if consider a hot cup of coffee will become cold after some time if it is kept on the table as there will heat flow between the hot coffee and surroundings. When the cup of coffee attains the same temperature as of room temperature then there will be no flow of heat.

Types of Equilibrium

Thermal Equilibrium: - Two systems are said to be in thermal equilibrium with each other if the temperatures of both the systems do not change with time.

Chemical Equilibrium: - Two systems are said to be in chemical equilibrium with each other if the composition of the system does not change over time.

Mechanical Equilibrium: - Two systems are said to be in mechanical equilibrium with each other if the pressure of the system doesn’t change with time.

A system is said to be in **Thermodynamic equilibrium** when all of its macroscopic variables are constant.

System and Surroundings

System: - System is defined as any part of the universe enclosed by some boundary through which exchange of heat or energy takes place.

Surroundings: - Any part of the universe which is not a system.

- For example: - If we consider a hot coffee in a kettle then the kettle is the system and everything else is the surroundings.
- System and surroundings constitute the Universe.

Kettle with hot coffee constitutes System and everything else around it is surroundings.

A system is in thermal equilibrium or not depends on:-

- Surroundings

For example -A cup of hot coffee after some time becomes cold due to the exchange of heat between the system and surroundings.

- The nature of the wall dividing the system and surroundings.
- If the wall is adiabatic then there will be no flow of heat between the system and surroundings. As it is an insulating wall.

- If the wall is diathermic then the flow of heat will take place between the system and surroundings. As it is a conducting wall.

Types of Systems

1. **Open System: -** In this system, there is an exchange of energy and matter. For Example: - Water boils in a pan without lid, a cup of coffee.

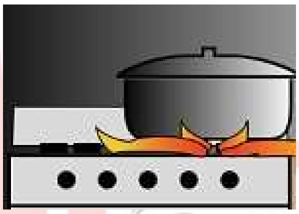
Water is boiling in a pan without lid.

The cup of coffee.

2. **Closed System: -** In this system exchange of matter does not take place but the exchange of energy takes place. For Example:- A balloon filled with gas, A pot with a lid

Gas balloon

- A pot with a lid closed - In this case heat is getting transferred from gas stove to pot and also heat is transferred to surroundings. But steam is not allowed to escape from a pot.



A pot with a lid

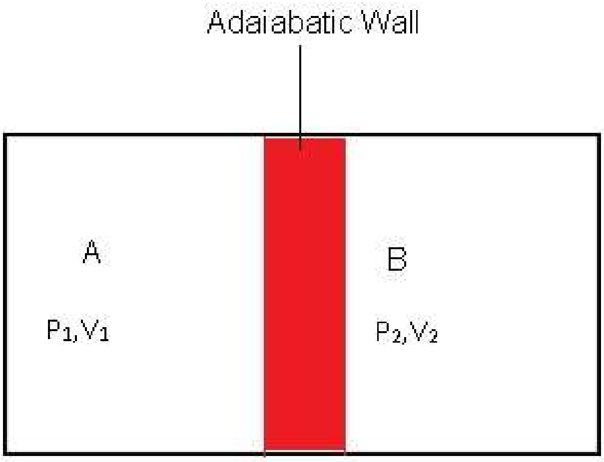
1. **Isolated System: -** In this system, there is neither change in matter nor change in energy. For example: - Any closed insulated vessel like a thermos flask. In thermos, tea can be kept hot for many hours because the walls of thermos are insulated and it does not allow heat to flow out of the flask.

Thermos Flask

Types of Walls

1. **Adiabatic wall**: - It is an insulating wall which doesn't allow heat to flow from one system to another. This means the temperature of both the systems won't change with time.

- Consider 2 systems A and B as shown in the figure, which are separated by an adiabatic wall. Let pressure and volume of A be(P_1, V_1) and B be(P_2, V_2)
  - Both are at the same temperature as there is no change in temperature with time.
  - There is no heat flow between A and B as they are separated by an adiabatic wall.
  - Both these systems are also separated from the surroundings by the adiabatic wall which means there is no flow of heat between A and surroundings and also B and surroundings.



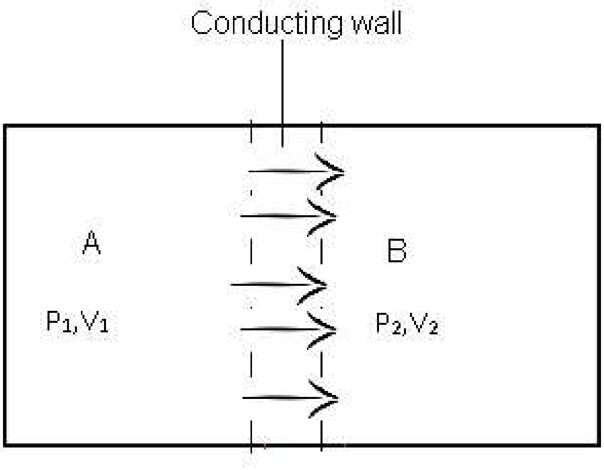
Two systems A and B are separated by an adiabatic wall from each other as well as from surroundings.

For example: - Thermos Flask. In which tea or coffee remains hot for a long time as it is made of insulating walls due to which there is no heat flow between tea and surroundings.

Thermos Flask

1. **Diathermic Wall**: - It is a conducting wall which allows the flow of heat between any 2 systems.

- Consider two systems A and B which are separated by a conducting wall. System A is at higher temperature T_1, pressure P_1 and volume V_1 and System B are at lower temperature T_2, pressure P_2 and volume V_2.
- There is a flow of heat from a system at a higher temperature to the system at a lower temperature until the systems reach thermal equilibrium.
- For Example: - A vessel made up of metals like copper or aluminium has diathermic walls.



Two systems are separated by a conducting wall.

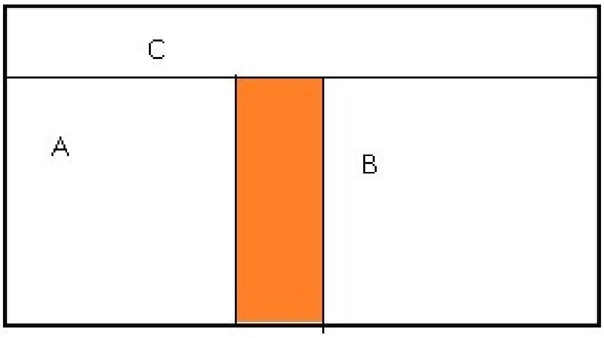
- For example -Hot tea in a cup. It will become cold after some time as there will be a flow of heat between tea and surroundings. And when the temperature of the tea is in thermal equilibrium then there will be no heat flow.

Cup of Tea

Copper vessels

Zeroth Law of Thermodynamics

- Zeroth law of thermodynamics states that when two systems are in thermal equilibrium through a third system separately then they are in thermal equilibrium with each other also.
    - For eg: - Consider two systems A and B which are separated by an adiabatic wall. Heat flow happens between systems A and C, and between B and C, due to which all 3 systems attain thermal equilibrium.



Systems A and B are in thermal equilibrium with C. Then they will be in equilibrium with each other also.

- Zeroth Law of Thermodynamics suggested that there should be some physical quantity which should have the same value for the system to be in thermal equilibrium.

- This physical quantity which determines whether a system is in equilibrium or not is Temperature.

- Temperature is the quantity which determines whether the system is in thermal equilibrium with the neighbouring system.
- When the temperature becomes equal then the flow of heat stops.

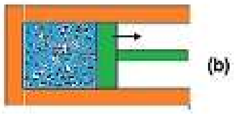
12.2 FIRST LAWS OF THERMODYNAMICS

Thermodynamic state variables

Thermodynamic state variables are the macroscopic quantities which determine the thermodynamic equilibrium state of a system.

- These macroscopic quantities are known as thermodynamics state variables.
- Since these macroscopic quantities describe the behaviour of the thermodynamic system it is known as thermodynamic.
- As they determine the state of the system that is pressure, volume and temperature, at one particular time they are known as thermodynamic state variables.
- Pressures (P), Volume (V), Temperature (T), mass (m), Internal energy (U) are the thermodynamic state variables.
- These variables can tell us the position or the condition of any gas at that particular time.

- A system not in equilibrium cannot be described by state variables. It means the macroscopic variables are changing with time and they are not constant.



(a) The partition in the box is suddenly removed leading to free expansion of the gas. **(b)** A mixture of gases undergoing an explosive chemical reaction. In both situations, the gas is not in equilibrium and cannot be described by state variables.

<u>Types of thermodynamic state variables:-</u>

1. **Extensive variables**: - They indicate the size of the system, which means extensive variables are those that depend on the mass of the system or the number of particles in the system. Example: volume, mass, internal energy. If we consider a system whose mass is greater than the size of that system is greater. All these depend on the size of the system.
2. **Intensive variables**: -

- They don't depend on the size of the system.
- Pressure and Temperature are known as intensive variables.

Equation of State

- Equation of State depicts the relationship between the state variables (pressure, mass, volume, density).
- It describes the state of the matter under the given set of physical conditions.
- Consider an ideal gas the equation of state is

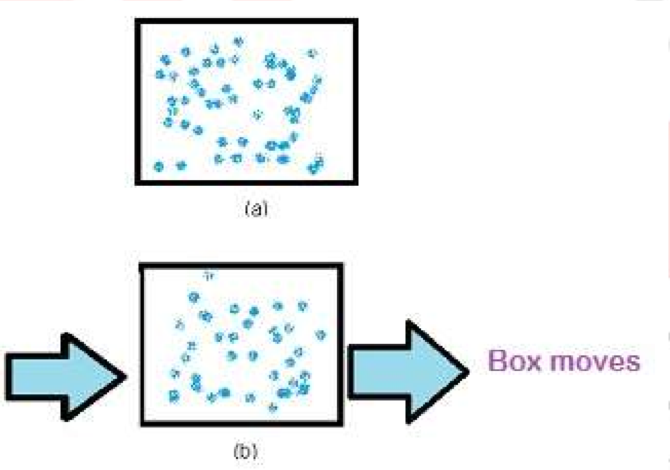
$PV = \mu RT$ where

- P, V and T are state variables and μ = number of moles
- For a fixed amount of gas, we can have two independent variables either volume and temperature or volume and pressure.

- All the variables cannot be independent at the same time.
- This is a known **equation of state for an ideal gas**.

Internal Energy

- It is defined as the sum of kinetic energies and potential energies of the molecules constituting the system as a whole and not of an individual molecule.
- It is a macroscopic variable of the system.
- It is denoted by U.
- It is a thermodynamic state variable.
- It is an extensive variable as it depends on the size of the system.
- It can be specified by values of pressure, volume and temperature at that particular time.
- It only depends on the state of the system at that particular time.
- It does not depend on how the system has reached that state.



In figure(a) shows a box at rest then the Internal energy of ta gas inside the box is some of the kinetic and potential energies of its molecules.

In figure (b) if the same box is pushed and it starts moving as a whole with some velocity, the kinetic energy of the box is not to be included in U.

Two different modes to change Internal energy are:-

1. Heat
2. Work

Heat: - Consider a bottle and a balloon are tied at the neck of the bottle. When we heat the bottle, due to the difference in temperature heat flow takes place, as a result, the balloon blows up. That is due to transfer of heat kinetic energy and potential energy changes from bottle to the balloon. This results in the change of internal energy.

Work: - We can do some work on the system (in this case system is a bottle with a balloon tied) as a result the internal energy of the system changes.

Internal energy increases when the system absorbs heat and some work is done on the system similarly internal energy decreases if we change the conditions.

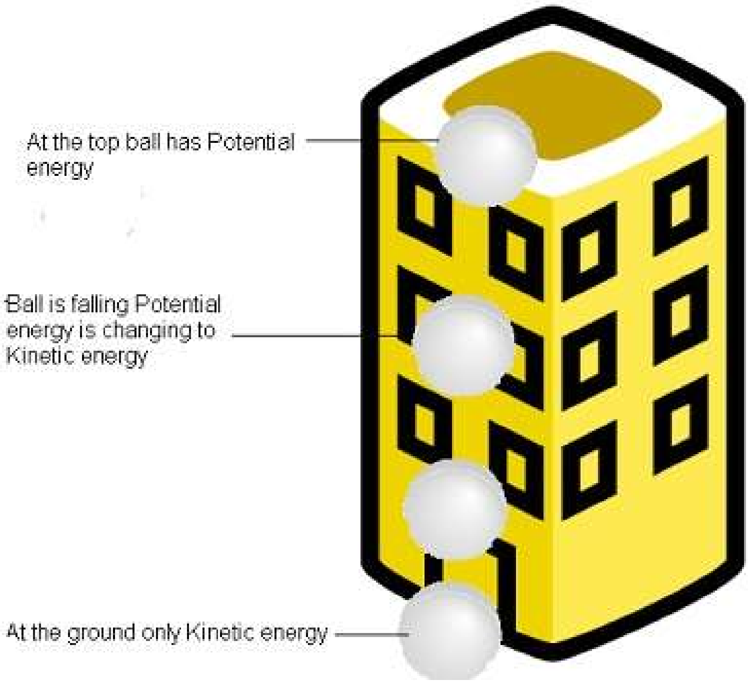
How Internal energy is different from Work and Heat

- Heat and work are not state variables, unlike internal energy.
- They are modes of energy transfer to the system resulting in a change in internal energy.

First Law of Thermodynamics

- The First law of thermodynamics is the same as the law of conservation of energy.

- According to the law of energy conservation: - Energy can neither be created nor be destroyed, only transformed into other forms.
- According to the first law of thermodynamics:- The change in the internal energy of a closed system is equal to the amount of heat supplied to the system, minus the amount of work done by the system on its surroundings.
- Examples:- Consider a ball falling from the roof of the building when at top of the building the ball has only potential energy and when it starts falling potential energy decreases and kinetic energy starts increasing. At the ground, it has only kinetic energy.



A ball falling from the roof of the building

Mathematically:-

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

Where:

- ΔQ is the heat supplied to the system by the surroundings
- ΔW is the work done by the system by the surroundings
- ΔU is the change in internal energy of the system
- Some part of heat supplied gets lost and the remaining part is the work done on the surroundings. This remaining part is used up to increase or change the internal energy of the system.

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

Consider a system whose initial state is (P_1, V_1) and final state (P_2, V_2)

ΔU is the change in the energy of the system to change from initial state to final state.

- Internal energy is a state variable which means it is path independent. It does not depend on how state changes from initial to final.
- But the work is done and heat is path-dependent. It depends on how the path changes from initial to final.
- Consider a system whose initial state is defined as (P_1, V_1) and Final state is defined as (P_2, V_2).
- The internal energy doesn't depend on how the system has changed from the initial state to the final state. It only depends on how it has reached from initial state to final state.

Therefore:-

$\Delta Q - \Delta W = \Delta U$ where

- (ΔQ and ΔW are path-dependent quantities whereas ΔU is path independent quantity)
- This concludes $\Delta Q - \Delta W$ is path independent quantity.

- Case 1:- System undergoes a process such that $\Delta U = 0$ which means internal energy is constant. From the first law of thermodynamics

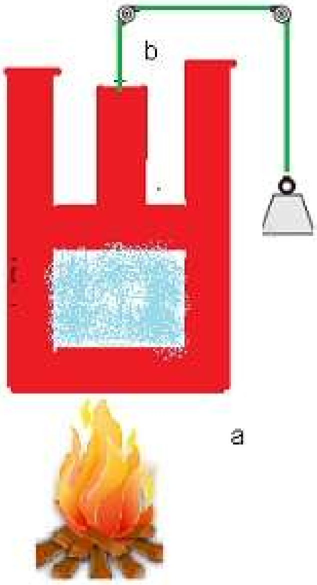
  $\Delta Q = \Delta U + \Delta W$ putting $\Delta U = 0$

- This implies **$\Delta Q = \Delta W$** this means heat supplied by the surroundings is equal to the work done by the system on the surroundings.

- Case 2:- System is a gas in a cylinder with a movable piston, by moving the piston we can change the volume of the gas.
- If we move the piston downwards some work is done and it can be given as:-

- Work done = ΔW
- = Force x displacement
- = P x Area x displacement
- $\Delta W = P\Delta V$ (ΔV= Area x displacement) (Equation 1)
- Therefore by the first law of thermodynamics
- **$\Delta Q = \Delta U + P\Delta V$** where ΔV= change in volume

  (From Equation 1)



Heat and work are two distinct modes of energy transfer to a system that results in a change in its internal energy. (a) Heat is energy transfer due to the temperature difference between the system and the surroundings. (b) Work is energy transfer brought about by means (e.g. moving the piston by raising or lowering some weight connected to it) that do not involve such a temperature difference.

Problem: An electric heater supplies heat to a system at a rate of 100W. If the system performs work at a rate of 75 Joules per second. At what rate is the internal energy increasing?

Answer:

Heat is supplied to the system at a rate of 100 W.

Heat supplied, Q = 100 J/s

The system performs at a rate of 75 J/s.

Work done, W = 75 J/s

From the first law of thermodynamics, we have:

Q = U + W

Where, U = Internal energy

U = Q – W

= 100 – 75

= 25 J/s

= 25 W

Therefore, the internal energy of the given electric heater increases at a rate of 25 W.

Problem: A cylinder filled with gas and fitted with a movable piston. In changing the state of a gas adiabatically from equilibrium state A to another equilibrium state B, an amount of work equal to 22.3 J is done on the system. If the gas is taken from state A to B via a process in which the net heat absorbed by the system is 9.35 cal, how much is the net work done by the system in the latter case? (Take 1 cal = 4.19 J)

Answer:

The work is done (W) on the system while the gas changes from state A to state B is 22.3 J.

This is an adiabatic process. Hence, a change in heat is zero.

$\Delta Q = 0$

$\Delta W = -22.3$ J (Since the work is done on the system)

From the first law of thermodynamics, we have:

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

Where,

ΔU = Change in the internal energy of the gas

$\Delta U = \Delta Q - \Delta W = -(-22.3\text{ J})$

$\Delta U = +22.3$ J

When the gas goes from state A to state B via a process, the net heat absorbed by the system is:

$\Delta Q = 9.35\text{ cal} = 9.35 \times 4.19 = 39.1765$ J

Heat absorbed, $\Delta Q = \Delta U + \Delta Q$

$\Delta W = \Delta Q - \Delta U$

$= 39.1765 - 22.3$

$= 16.8765$ J

Therefore, 16.88 J of work is done by the system.

Problem: Two cylinders A and B of equal capacity are connected to each other via a stopcock. A contains gas at standard temperature and pressure. Bis completely evacuated. The entire system is thermally insulated. The stopcock is suddenly opened. Answer the following:

(a) What is the final pressure of the gas in A and B?

(b) What is the change in internal energy of the gas?

(c) What is the change in the temperature of the gas?

(d) Do the intermediate states of the system (before settling to the final equilibrium state) lie on its P-V-T surface?

Answer:

(a) When the stopcock is suddenly opened, the volume available to the gas at 1 atmospheric pressure will become two times. Therefore, the pressure will decrease to one-half, i.e., 0.5 atmosphere.

(b) There will be no change in the internal energy of the gas as no work is done on/by the gas.

(c) Since no work is being done by the gas during the expansion of the gas, the temperature of the gas will not change at all.

(d) No, because the process called free expansion is rapid and cannot be controlled. the intermediate states are non-equilibrium states and do not satisfy the gas equation. In due course, the gas does return to an equilibrium state.

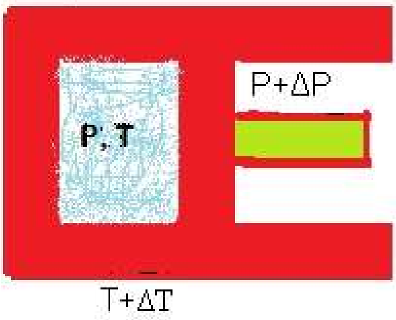
12.3 ISOTHERMAL AND ADIABATIC SYSTEMS

Thermodynamic processes – Quasi-Static Process

- The quasi-static term means semi-static . It is not purely moving.
- It is a hypothetical construct which means it is not in real.
- It is an infinitely slow process which means the change from its original position is not at all significant.

- System changes its variables (P, T, and V) so slowly that it remains in equilibrium with its surroundings throughout.

- Consider a gas initially at Pressure (P) and Temperature (T) changes it to a new state whose Pressure is (P') and Temperature (T').
- If we change the surrounding pressure to P by a very small amount then allow the system to reach that system.
- The characteristics for a system to be Quasi-static process
- Extremely very slow process.
- There should not be any accelerated motion. Not large temperature gradient. Temperature gradient means the difference in temperature (T_1-

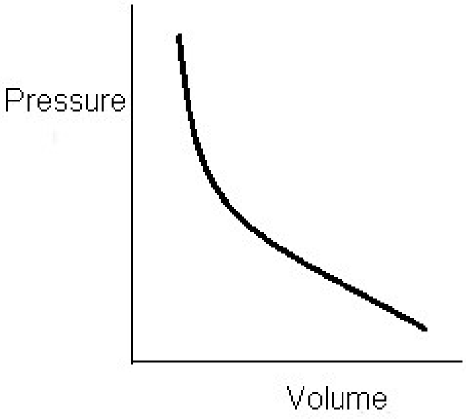


T_2).

In a quasi-static process, the temperature of the surrounding reservoir and the external pressure differ only infinitesimally from the temperature and pressure of the system.

Isothermal Processes

- Isothermal: - Iso means same and thermal related to temperature. In the Isothermal process, the temperature remains constant throughout while all other variables change.
- Temperature is constant throughout.
- For an ideal gas
    - PV = nRT where
    - n=no. of moles (constant), R = universal gas constant, T =constant for isothermal process.
- This implies PV=constant
- Pressure and volume are inversely proportional to each other.
- Graphically if we plot pressure and volume



- We will get a decreasing curve because if we increase pressure-volume decreases and vice versa.
- This curve is known as Isothermal Curve.

Isothermal Expansion of an Ideal gas

- It can be described as an amount of work done during the isothermal expansion of an ideal gas under constant temperature.
- Initially ideal gas is at Pressure P_1 and Volume V_1.
- At constant temperature, the gas will expand from pressure P_1 to P_2 and volume changes from V_1 to V_2.So the final state (P_2, V_2).
- These expansions are QuasiStatic processes.
- Consider any intermediate stage,
  - The pressure is P and volume is $V_1 + \Delta V$ where ΔV increase in volume.
  - $\Delta W = P \Delta V$ where ΔW = small work done
  - By solving and doing calculation the above equation the work done for an ideal gas the work done will be given as:-

$W = RT \ln V_2/V_1$

- In an isothermal expansion, there is no change in the internal energy of an isothermal process. As there is no change in temperature as a result there is no change in internal energy.
- From First law of thermodynamics
- $\Delta Q = \Delta U + \Delta W$ (putting $\Delta U = 0$ as $\Delta T = 0$)
- $\Delta Q = \Delta W$.This means the amount of heat supplied to the gas is equal to the amount of work done by the gas on the surroundings.

Isothermal expansion and contraction

- The expression of an isothermal process for the work done is:
- $W = RT \ln V_2/V_1$
- In the isothermal expansion, the work is done by the gas whereas in isothermal contraction the work is done on the gas.
- Case 1: Isothermal expansion: $V_2>V_1$
- This implies $W>0$, work is positive which means work is done by the gas that is heat is absorbed by the gas.
- Case 2: Isothermal contraction: $V_2<V_1$
- This implies $W<0$, work is negative which means work is done on the gas that is heat is released.

Adiabatic Processes

- Adiabatic is a process in which there is no heat flow takes place between the system and the surroundings.
- These processes are sudden.
- The walls of the container should be adiabatic
- For an adiabatic process of an ideal gas
- From Boyle's law
- PV^{γ} = constant

Where $\gamma = C_p/C_v$ Specific heat ratio

Example: - Hot tea in Thermos flask. It will remain hot as there is no exchange of heat takes place because the walls of the thermos is insulating.

Problem: - A cylinder with a movable piston contains 3 moles of hydrogen at standard temperature and pressure. The walls of the cylinder are made of a heat insulator, and the piston is insulated by having a pile of sand on it. By what factor does the pressure of the gas increase if the gas is compressed to half its original volume?

Answer: The cylinder is completely insulated from its surroundings. As a result, no heat is exchanged between the system (cylinder) and its surroundings. Thus, the process is adiabatic.

Initial pressure inside the cylinder = P_1

Final pressure inside the cylinder = P_2

The initial volume inside the cylinder = V_1

The final volume inside the cylinder = V_2

The ratio of specific heats, $\gamma = 1.4$

For an adiabatic process, we have: $P_1V_1^{\gamma} = P_2V_2^{\gamma}$

The final volume is compressed to half of its initial volume.

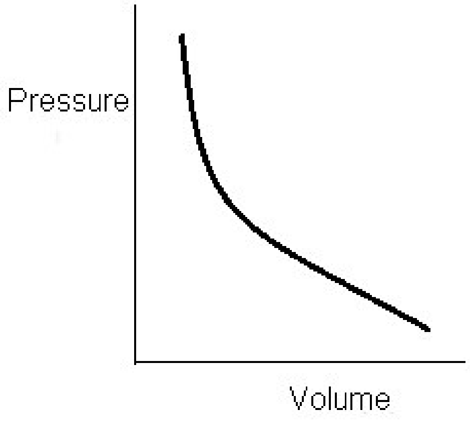
$V_2 = V_1/2$

$P_1V_1^{\gamma} = P_2(V_1/2)^{\gamma}$

$= P_2/P_1 = V_1^{\gamma}/(V_1/2)^{\gamma} = (2)^{\gamma} = (2)^{1.4} = 2.639$

Hence, the pressure increases by a factor of 2.639.

Graphically if we plot pressure and volume.



As pressure and volume are inversely proportional we will have a decreasing curve.

This curve is known as Adiabatic Curve.

Adiabatic change of an ideal gas

- It implies how much work is done during the adiabatic change of an ideal gas.
- Initially ideal gas is at Pressure P_1, Volume V_1 and Temperature T_1 (P_1, V_1, T_1)
- The final state of an ideal gas Pressure P_2, Volume V_2 and Temperature T_2 (P_2, V_2, T_2)
- $P V^{\gamma} = \text{const}$
- $\gamma = Cp/Cv$
- If an ideal gas undergoes a change in its state adiabatically from (P_1, V_1) to (P_2, V_2)
- $P_1V_1^{\gamma} = P_2V_2^{\gamma}$
- The work is done in an adiabatic change of an ideal gas from the

state (P_1, V_1, T_1) to the state (P_2, V_2, T_2).

$W = \int P V dV = P \int V dV$ (Integrating between the limits V_2 and V_1)

For Adiabatic Process

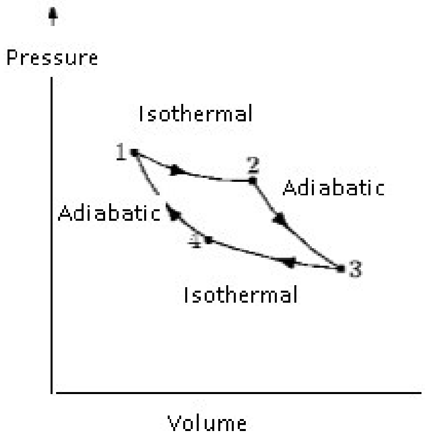
- $P V^{\gamma} = \text{constant}$
- This implies $P = \text{constant} / V^{\gamma}$
- $W = \text{constant} \int dV / V^{\gamma}$
- $\text{constant} [V^{\gamma-1}/-\gamma+1]$
- $\text{constant}/1-\gamma [V_2^{1-\gamma} – V_1^{1-\gamma}]$
- $= \text{constant}/1-\gamma[1/ V_2^{1-\gamma} - 1/ V_1^{1-\gamma}]$
- By solving Work done **$W= R/ (\gamma-1)(T_2-T_1)$,** where
- T_2= final Temperature
- T_1=initial temperature
- R=Universal gas constant
- γ = Specific heat ratio
- This is the work done during adiabatic change.
- Consider $W= R/ (\gamma-1)(T_2-T_1)$

Case 1: W>0 (when T1>T2)

The temperature of the gas decreases.

Case 2:- W< 0 (T1<T2)

The temperature of the gas increases.

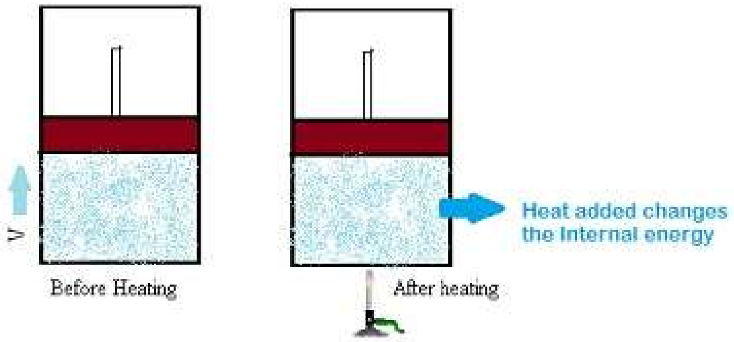


P-V curves for isothermal and adiabatic processes of an ideal gas.

Isochoric Processes

- Isochoric process means volume is constant while all other variables change.
- As volume is kept constant therefore no work is done on or by the gas.
- Heat absorbed by the gas is completely used to change its internal energy and its temperature.
- From First law of Thermodynamics
- $\Delta Q = \Delta U + \Delta W$ ($\Delta W = 0$)
- $\Delta Q = \Delta U$
    - This means whatever heat is supplied to the system that is used up completely to change the internal energy and temperature of the system.
- $C_v = \Delta U / \Delta T$

Example: - If we heat a gas-filled in a closed cylinder fitted with a piston. When we supply heat to this cylinder the piston won't move as there is no volume change. There will be no work is also being done. Whatever the heat is added it will be used to increase the internal energy of the system.



Isobaric Processes

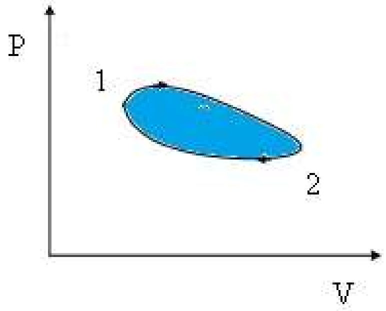
- Iso means same and baric is related to pressure.
- In this process, the pressure is constant while all other variables change.
- Process in which pressure is constant.
- Work done is given as :
  - $W=P(V_2-V_1)$
  - $=\mu R(T_2-T_1)$
- From First law of thermodynamics
- $\Delta Q=\Delta U+\Delta W$
- $\Delta Q=\Delta U+\mu R(T_2-T_1)$
- We can see from the above equation that the heat absorbed goes partly to increase internal energy and partly to do work.

Example: -

- Consider a cylinder filled with gas fitted with a piston. When we heat the cylinder the gas expands but the pressure remains the same because of the piston.
- Boiling water in an open pot which is at atmospheric pressure. When the water boils it changes to steam and this steam expands and since it is not contained, it stays at atmospheric pressure. So the pressure remains constant but energy changes.

Cyclic Processes

- A Process in which the system will come back to its initial state.
- Δ U=0 this means the total heat absorbed equals the work done by the system.

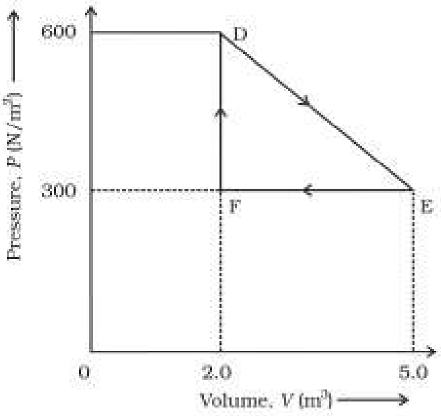


The system started from point 1 it went through a series of processes reached its final position 2 and then it comes back to its initial position 1.

- The total internal energy is 0.
- By applying the First law of thermodynamics:
- $\Delta E = Q + W$ as $(\Delta E=0)$,
- Therefore
- $W=Q$
- The work done by the system in a cyclic process is equal to the heat absorbed by the system.

Example: - Heat Engine, Heat Pump

Problem: - A thermodynamic system is taken from an original state to an intermediate state by the linear process shown in Fig.?



Its volume is then reduced to the original value from E to F by an isobaric process. Calculate the total work done by the gas from D to E to F?

Answer:

Total work is done by the gas from D to E to F = Area of ΔDEF

Area of ΔDEF = ½ x DE x EF

Where,

DF = Change in pressure = 600 N/m^2

– 300 N/m^2

= 300 N/m^2

FE = Change in volume

= 5.0 m^3

– 2.0 m^3

= 3.0 m^3

Area of ΔDEF =1/2x300x3 = 450 J

Therefore, the total work done by the gas from D to E to F is 450 J.

12.4 Second laws of Thermodynamics

There are 2 statements of second law of thermodynamics given by two scientists:

- **Kelvin-Planck [Statement: -** No process is possible whose result is the absorption of heat from a reservoir and the complete conversion of the heat into work.
- **Clausius statement**: - No process is possible whose result is the transfer of heat from a colder object to a hotter object.

Explanation of Kelvin-Planck Statement: It is always impossible that the total amount of heat which is supplied to the system will get converted to work, and there will always be loss of heat. Complete conversion of heat into work is not possible.

Explanation of Clausius statement: - Transfer of heat from a colder body to a hotter body won't take place until some external work is done on the system.

Reversible and Irreversible processes

Reversible Process

- A thermodynamic process is reversible if the process can be turned back such that the system and surroundings return to their original states, with no other change anywhere else in the universe.

- This means in the Reversible processes if a process starts from the initial state then it goes to the final state and then it can be reversed back from the final state to the initial state.
- Examples:- Isothermal expansion and compression, Electrolysis
- A process is reversible if:-

1. It is quasi-static
2. No dissipative forces (that is no loss of heat by friction etc.).
3. Both initial and final states of the system are in thermodynamic equilibrium with each other.

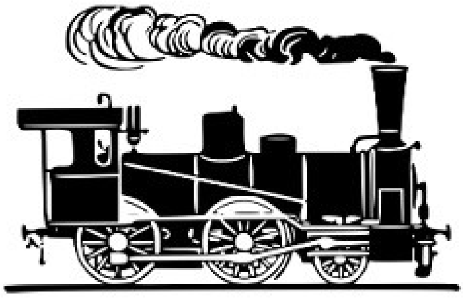
Irreversible Process

- Irreversible processes are those that cannot be reversed.
- Two causes which give rise to irreversible processes
    - Irreversible processes takes place at a very fast rate.

  - Dissipative Effects.
- Examples:-Plastic deformation, Combustion, Diffusion, Falling of water from the hill.

12.5 HEAT ENGINES

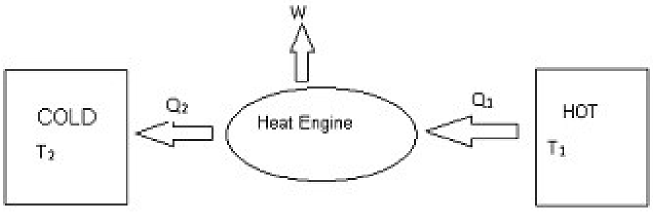
- In a heat engine, a body is configured to do work when placed in alternating contact with hot and cold bodies so that heat can be supplied and absorbed. In simple terms, a heat engine is a device which converts thermal energy to mechanical energy.



Steam Engine

- Basic Components: -
- Working substance For Example: - a mixture of fuel vapour and air in a steam engine.
- External Reservoir which is at a higher temperature.
- External Reservoir which is at a lower temperature.
- The reservoirs are at a different temperature so that there is a flow of energy from the higher level to lower level.
- Consider a hot reservoir having a temperature T_1 and a cold reservoir having a temperature T_2.
- Heat engine takes heat Q_1 from the hot reservoir it does some work Won the surroundings and remaining amount of heat Q2 is returned to the cold reservoir
- Example: - If we consider a steam engine, the work done by the engine on the surroundings is same as the mechanical energy which gets transferred to the wheels of the vehicle and as a result the vehicle moves.

Simple Representation of heat engine



The engine takes heat Q_1 from a hot reservoir at temperature T_1, releases heat

Q_2 , to a cold reservoir at temperature T_2 and delivers work W to the surroundings.

Efficiency of a heat engine:

- Efficiency indicates how much useful work we get as an output by the engine by using the amount of heat energy as input.
- It is denoted by η.
- Mathematically :
- $\eta = W/Q_1$
  - where W= output and Q_1 = input
  - By calculating
- **$\eta = 1 - Q_2/Q_1$**

Where

- Q1=heat input in 1 cycle
- Q2=work done in 1 cycle.
- $\eta = 1 – Q_2/Q_1$
- For 100% efficient $\eta = 1$ (which means $Q_2/Q_1=0$)
  - There is always some heat is lost to the surroundings
- Heat lost (Q_2) = 0

There is no heat engine whose efficiency is 100%. There is always some of the losses associated with the heat engines.

Problem: A steam engine delivers 5.4×10^8 J of work per minute and services 3.6×10^9 J of heat per minute from its boiler. What is the efficiency of the engine? How much heat is wasted per minute?

Answer:

Work done by the steam engine per minute, $W = 5.4 \times 10^8$ J

Heat supplied from the boiler, $H = 3.6 \times 10^9$ J

Efficiency of the engine =Output energy/Input energy

$\eta = W/H = 5.4 \times 10^8 / 3.6 \times 10^9 = 0.15$

Hence, the percentage efficiency of the engine is 15 %.

Amount of heat wasted = $3.6 \times 10^9 - 5.4 \times 10^8$

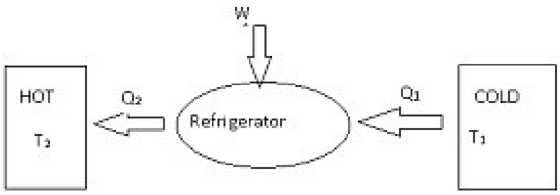
= $30.6 \times 10^8 = 3.06 \times 10^9$ J

Therefore, the amount of heat wasted per minute is 3.06×10^9 J.

Refrigerators

- It works on the principle which is reverse of a heat engine.
- In refrigerators, we have 2 bodies lower temperature (cold) body which is freezer and higher temperature (hot) body which is surroundings.
- It takes heat from the cold reservoir and then some work is done on the refrigerator and then the amount of heat is transferred to the heat reservoir.
- Let Q_2 be the takes from the cold reservoir, W is the work done on the system and then releases Q_1 amount of heat to the hot reservoir.
- Mathematically $Q_2 + W = Q_1$

Simple Representation of Refrigerators



Working of a refrigerator or a heat pump is based on the same principle which is the reverse of a heat engine.

Coefficient of Performance (COP) of the refrigerator

- It is denoted by α.
- Mathematically given as :
    - **$\alpha = Q_2/W$**
    - where Q_2 is the heat extracted from the cold reservoir
    - W is the work done on the system–the refrigerant
- α can be greater than 1

- Using the Law of energy conservation:- $Q_2+W=Q_1$
- This implies $W=Q2-Q1$
- Therefore:-
- $\alpha = Q2/Q1-Q2$
- $W \neq 0$ then $Q1-Q2 \neq 0$
- This implies $\alpha \neq$ infinite

Problem: A refrigerator is to maintain eatables kept inside at 9°C. If the room temperature is 36° C, calculate the coefficient of performance?

Answer:

Temperature inside the refrigerator, T_1 = 9°C = 282 K

Room temperature, T_2 = 36°C = 309 K

Coefficient of performance = $T_1/ T_2 - T_1$

= 282/(309-282) = 10.44

Therefore, the coefficient of performance of the given refrigerator is 10.44.

Heat Pump

In a heat pump heat is supplied into the system when the surroundings are cold.

12.6 HEAT ENGINES (CARNOT)

Carnot engine

- A Carnot engine is named after Carnot scientist.
- It is a reversible heat engine operating between two temperatures.
- It has a maximum efficiency which no other engine can have.

Cycle of processes in a Carnot engine

Basic Function of any heat engine is it will take heat Q_1 from a hot reservoir at temperature T_1 and give heat Q_2 to a cold reservoir at temperature T_2.

- As system is absorbing heat so it is an isothermal expansion. Engine absorbs heat Q_1 at temperature T_1.
- An adiabatic process takes place inside the engine because of which there is an increase in the temperature of the engine from T_1 to T_2 but no flow of heat.
- As system is releasing heat so it is isothermal contraction. Engine releases heat Q_2 at temperature T_2.
- An adiabatic process takes place again which changes the temperature of the system from T_2 to T_1.
- One cycle of Carnot engine will have Isothermal expansion then adiabatic process, and then isothermal contraction followed by an adiabatic process.
- This will keep on repeating.

Details:

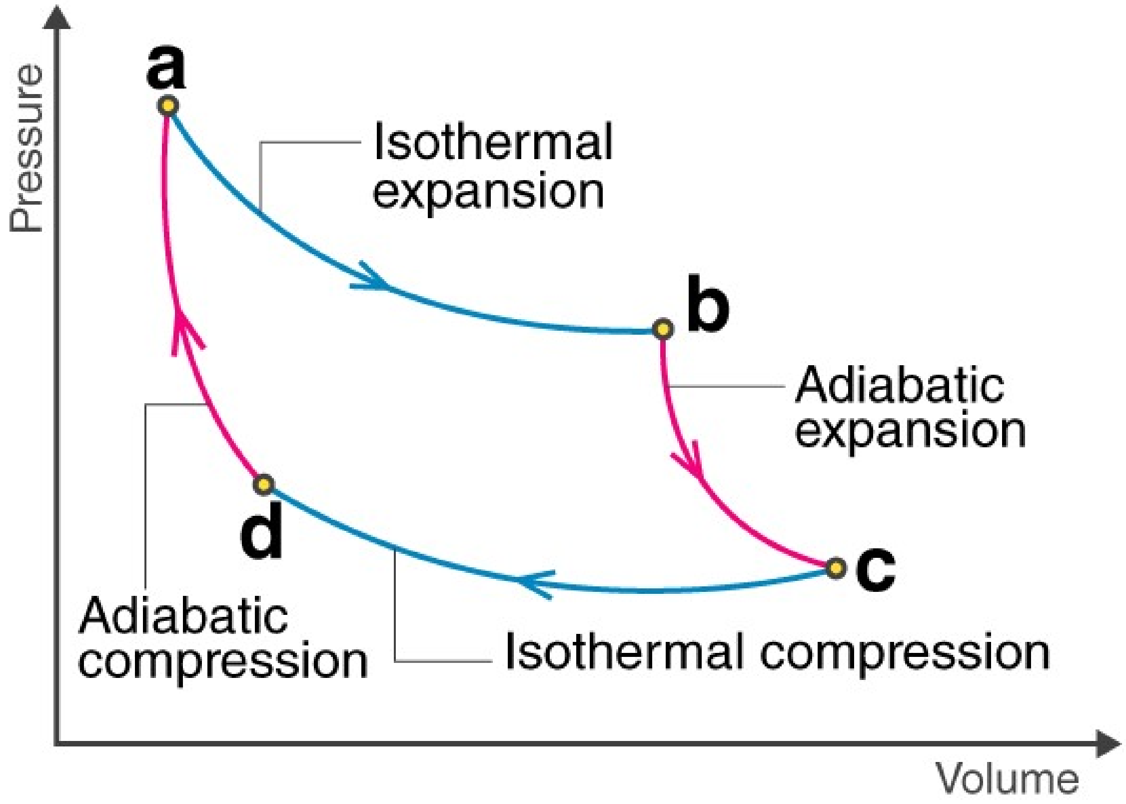
- Suppose we have a hot reservoir at temperatureT1 and a cold reservoir at temperature T2. What is the maximum efficiency possible for a heat engine operating between the two reservoirs and what cycle of processes should be adopted to achieve the maximum efficiency
- Sadi Carnot, a French engineer, first considered this question in 1824. Interestingly, Carnot arrived at the correct answer, even though the basic concepts of heat and thermodynamics had yet to be firmly established.

- We expect the ideal engine operating between two temperatures to be a reversible engine. Irreversibility is associated with dissipative effects, as remarked in the preceding section, and lowers efficiency.
- A process is reversible if it is quasi-static and non-dissipative. We have seen that a process is not quasi-static if it involves a finite temperature difference between the system and the reservoir.
- This implies that in a reversible heat engine operating between two temperatures, heat should be absorbed (from the hot reservoir) isothermally and released (to the cold reservoir) isothermally.
- We thus have identified two steps of the reversible heat engine: isothermal process at temperatureT1 absorbing heat Q1 from the hot reservoir, and another isothermal process at temperature T2releasing heat Q2 to the cold reservoir.
- To complete a cycle, we need to take the system from temperature T1 to T2 and then back from temperature T2 to T1. Which processes should we employ for this purpose that are reversible?
- A little reflection shows that we can only adopt reversible adiabatic processes for these purposes, which involve no heat flow from any reservoir. If we employ any other process that is not adiabatic, say an isochoric process, to take the system from one temperature to another, we shall need a series of reservoirs in the temperature range T2 to T1 to ensure that at each stage the process is quasi-static. (Remember again that for a process to be quasi-static and reversible, there should be no finite temperature difference between the system and the reservoir.)

- But we are considering a reversible engine that operates between only two temperatures. Thus adiabatic processes must bring about the temperature change in the system from T1 to T2and T2 to T1 in this engine.

A reversible heat engine operating between two temperatures is called a Carnot engine. We have just argued that such an engine must have the following sequence of steps constituting one cycle, called the Carnot cycle,

Carnot engine is a theoretical thermodynamic cycle proposed by **Leonard Carnot**. It gives the estimate of the maximum possible efficiency that a heat engine during the conversion process of heat into work and conversely, working between two reservoirs, can possess. In this section, we will learn about the Carnot cycle and Carnot Theorem in detail.



Carnot Theorem:

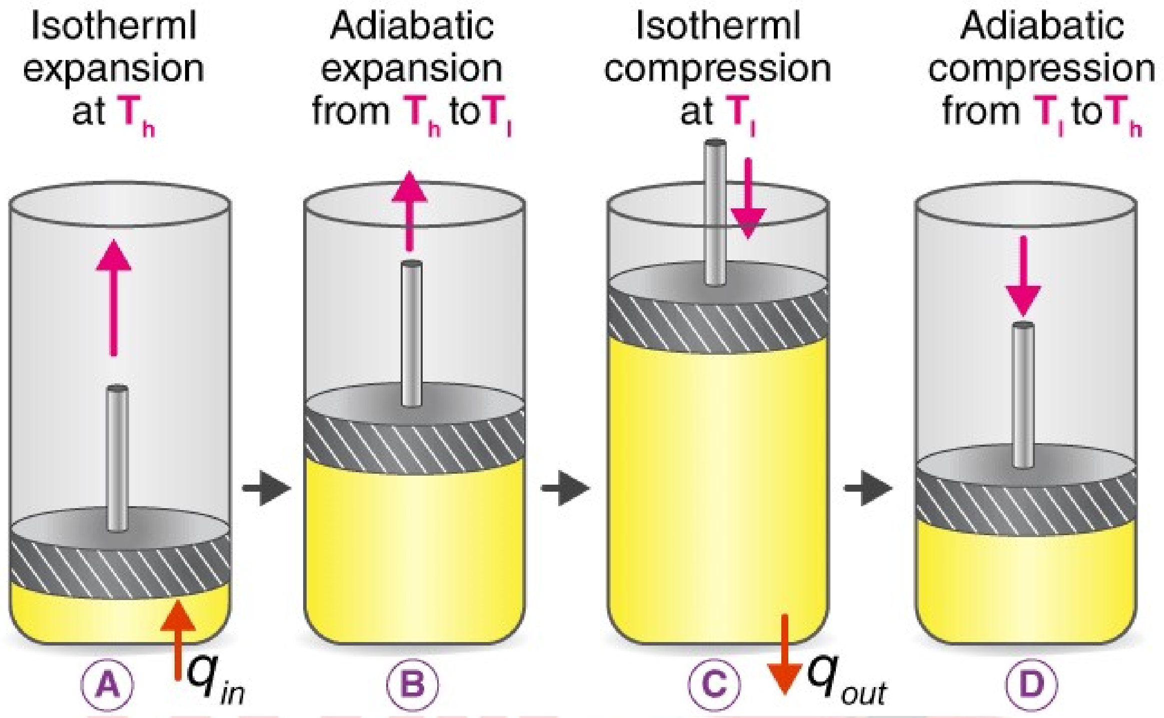
According to Carnot Theorem:

Any system working between two given temperatures T_1 (hot reservoir) and T_2 (cold reservoir), can never have an efficiency more than the Carnot engine working between the same reservoirs respectively.

Also, the efficiency of this type of engine is independent of the nature of the working substance and is only dependent on the temperature of the hot and cold reservoirs.

Carnot Cycle:

A Carnot cycle is defined as an ideal reversible closed thermodynamic cycle in which there are four successive operations involved, and they are isothermal expansion, adiabatic expansion, isothermal compression, and adiabatic compression. During these operations, the expansion and compression of substance can be done up to the desired point and back to the initial state.



Following are the four processes of the Carnot cycle:

- In (a), the process is reversible isothermal gas expansion. In this process, the amount of heat absorbed by the ideal gas is q_{in} from the heat source, which is at a temperature of T_h. The gas expands and does work on the surroundings.
- In (b), the process is reversible adiabatic gas expansion. Here, the system is thermally insulated, and the gas continues to expand and work is done on the surroundings. Now the temperature is lower, T_l.
- In (c), the process is reversible isothermal gas compression process. Here, the heat loss q_{out} occurs when the surroundings do the work at temperature T_l.

- In (d), the process is reversible adiabatic gas compression. Again the system is thermally insulated. The temperature again rises back to T_h as the surrounding continue to do their work on the gas.

Steps involved in a Carnot Cycle

For an ideal gas operating inside a Carnot cycle, the following are the steps involved:

Step 1:

Isothermal expansion: The gas is taken from P_1, V_1, T_1 to P_2, V_2, T_2. Heat Q_1 is absorbed from the reservoir at temperature T_1. Since the expansion is isothermal, the total change in internal energy is zero, and the heat absorbed by the gas is equal to the work done by the gas on the environment, which is given as:

$$W_{1\to 2} = Q1 = \mu \times R \times T_1 \times ln\frac{v_2}{v_1}$$

Step 2:

Adiabatic expansion: The gas expands adiabatically from P_2, V_2, T_1 to P_3, V_3, T_2.

Here work done by the gas is given by:

$$W_{2\to 3} = \frac{\mu R}{\gamma - 1}(T_1 - T_2)$$

Step 3:

Isothermal compression: The gas is compressed isothermally from the state (P_3, V_3, T_2) to (P_4, V_4, T_2).

Here, the work done on the gas by the environment is given by:

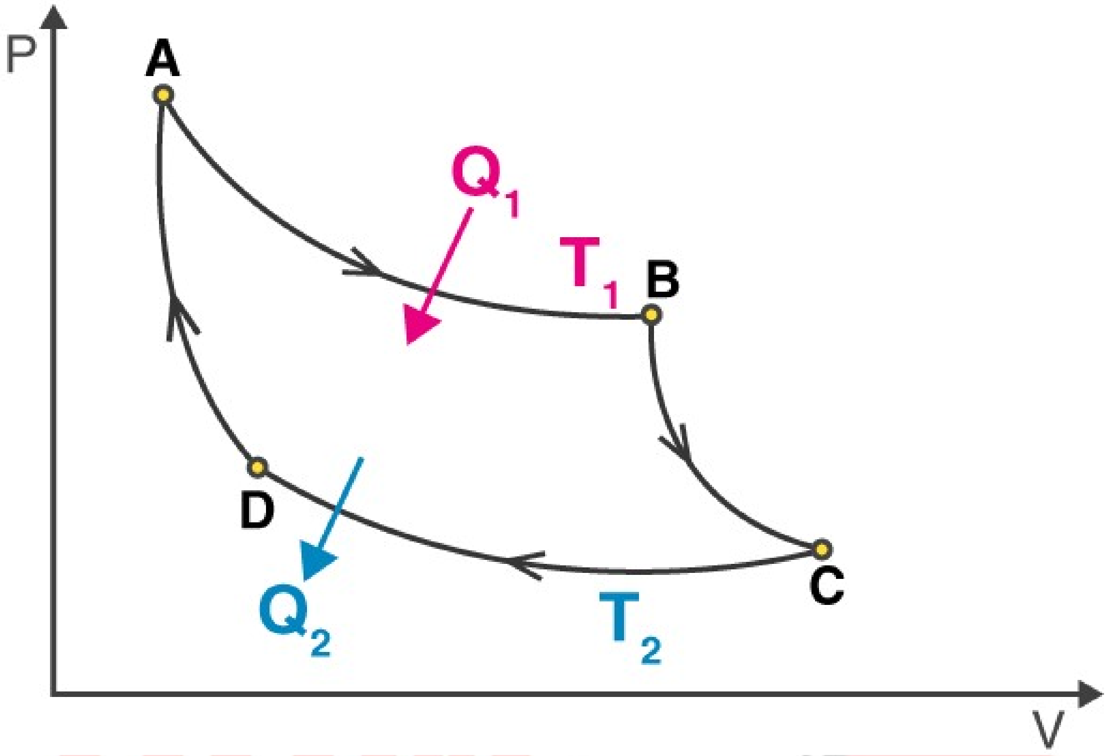
$$W_{3\to4} = \mu R T_2 ln\frac{v_3}{v_4}$$

Step 4:

Adiabatic compression: The gas is compressed adiabatically from the state (P_4, V_4, T_2) to (P_1, V_1, T_1).

Here, the work done on the gas by the environment is given by:

$$W_{4\to1} = \frac{\mu R}{\gamma-1}(T_1 - T_2)$$



Hence, the total work done by the gas on the environment in one complete cycle is given by:

$$W = W_{1\to 2} + W_{2\to 3} + W_{3\to 4} + W_{4\to 1}$$
$$W = \mu\, RT_1\, ln\frac{v_2}{v_1} - \mu\, RT_2\, ln\frac{v_3}{v_4}$$

$$Net\ efficiency = \frac{Net\ workdone\ by\ the\ gas}{Heat\ absorbed\ by\ the\ gas}$$

$$Net\ efficiency = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}\frac{ln\frac{v_3}{v_4}}{ln\frac{v_2}{v_1}}$$

Since step 2–>3 is an adiabatic process, we can write $T_1V_2^{Y-1} = T_2V_3^{Y-1}$

$$\frac{v_2}{v_3} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}}$$

Similarly, for the process 4–>1, we can write

$$\frac{v_1}{v_2} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}}$$

This implies,

$$\frac{v_2}{v_3} = \frac{v_1}{v_2}$$

So, the expression for net efficiency of carnot engine reduces to:

$$Net\ efficiency = 1 - \frac{T_2}{T_1}$$

➢ .