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CHAP: 4 : THERMODYNAMICS

Thermodynamics :- It is the branch of physics that deals with the concept of heat and temp. & the inter-conversion of heat and other forms of energy.

Thermal Equilibrium :- When the two substances are at diff. temps; the heat is transferred from a substance at higher temp. to that at lower temp. untill both the substances are at the same temp, then they are in thermal equilibrium.

Q. state and Explain Zeroth law of thermodynamics.

⇒ Zeroth law of thermodynamics:-

If two systems are each in thermal equilibrium with a third system, they are also in thermal equilibrium with each other.

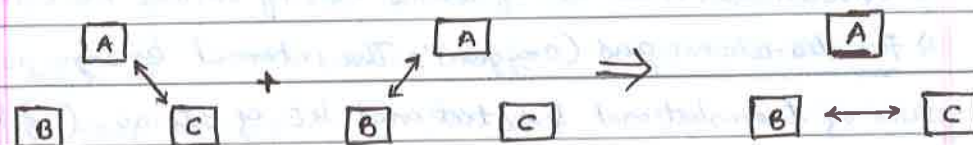
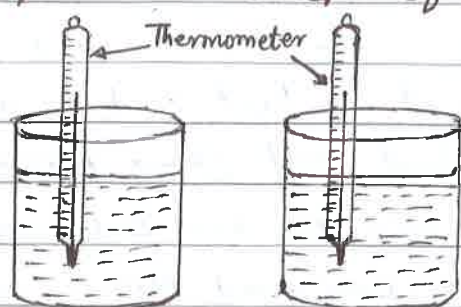


Fig. shows representation of the Zeroth law of thermodynamics. The double arrow represents thermal equilibrium betⁿ systems. If system A & C are in thermal equilibrium & system A & B are in thermal equilibrium, then systems B & C must be in thermal equilibrium. Then systems A, B & C are at the same temp.



Q. Explain the concept of temp. measurement.



Thermometer is used to measure temp of an object. When thermometer and object are in thermal equilibrium, the thermometer indicates the temp of object.

The zeroth law enables to use a thermometer to compare the temp. of diff. objects. It is shown in figs.

The science of measuring temps. is called thermometry.

* Internal Energy:- It is defined as the energy associated with the random, disordered motion of the molecules of a system.

1) For ideal monoatomic gas (Argon) - The internal energy is only translational KE of atoms having linear motion ($\frac{3}{2}kT$)

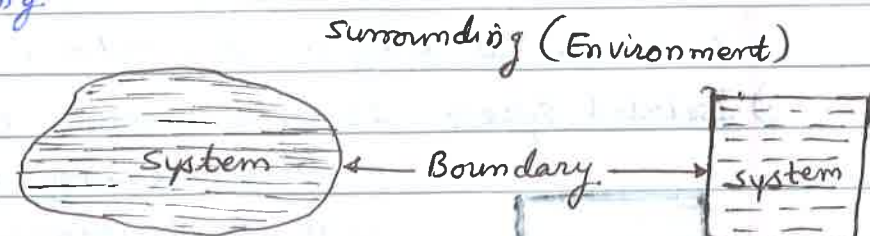
2) For di-atomic gas (Oxygen):- The internal energy is the sum of translational & rotational KE of atoms. ($\frac{5}{2}kT$)

3) For polyatomic gas (Carbon-di-oxide):- The internal energy is the sum of translational, rotational & vibrational KE of atoms ($\frac{7}{2}kT$)

* Thermodynamic system, Surrounding and process:

Thermodynamic System:- It is a collection or a group of objects form a unit which exchange energy with its surrounding.

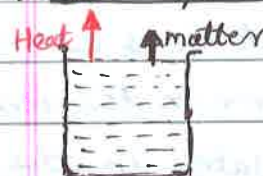
Thermodynamic Surrounding: Anything outside the system which exchange energy with system is called as surrounding.



Water kept in a vessel is a system, the vessel is its boundary & the atmosphere around it is its surrounding.

Thermodynamic system can be classified on the basis of possible transfer of heat and matter to environment so there are three types of thermodynamic systems.

1) Open system: It is a system that freely allows exchange of energy and matter with its environment.



eq. water boiling in a kettle.

Heat escapes into the air, this is exchange of energy with the surrounding, at the same time steam also escapes into the air, this is exchange of matter with the surrounding.

2) Closed system:- It is a system that can allow only exchange of energy but not matter with its environment.



eq. water boiling in a boiler is a closed system. It allows only energy (Heat) to be transferred



From the source of energy (Heat) to the system (water) inside. Similarly heat is also transferred to the surrounding. matter (steam) is not allowed to escape as long as the valve is kept closed

3) Isolated system It is a system that cannot exchange energy as well as matter with its environment.



eg. A thermos flask is an isolated system.

* Thermodynamic process: It is a process in which the thermodynamic state of a system is changed.

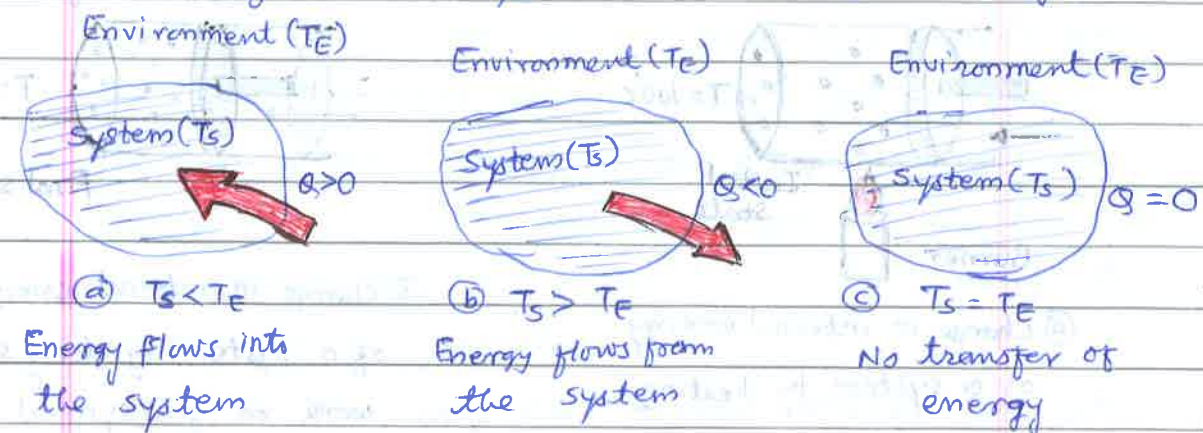
eg. water contained in a vessel with a lid on it is an open system. When the pot is heated externally, water starts boiling after some time & steam is produced which exerts pressure on the walls of the vessel. i.e. the state of water in the container is changed; means temp, volume & pressure of water inside the vessel change when it starts boiling.

* Heat (Relation betⁿ Heat and internal energy of system)

To show the relation betⁿ Heat & internal energy of a system. Consider a glass filled with water on a table. The glass along with water is the system, let its temp. be T_s . The table & other relevant parts of the room be its surrounding (environment), its

temp. is T_E . T_s & T_E are not the same. So T_s will change until both the temps are equal & a thermal equilibrium will be reached. If the surrounding is very large, the change in T_E is very small but not zero. such change in temp is caused by the transfer of internal energy betⁿ the system & its surrounding.

- When the energy is transfer to system from its surrounding, it is positive. i.e. system gains (absorbs) energy.
- When the energy is transfer from system to surrounding, it is negative. i.e. system losses (releases) energy.

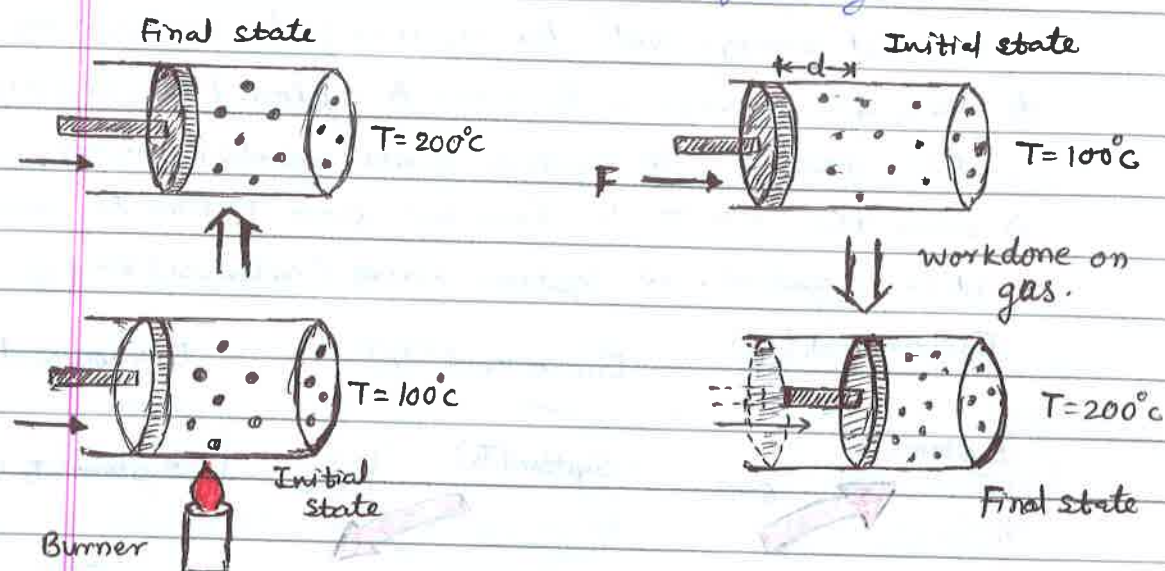


- As shown in fig (a) $T_s < T_E$, so energy is transferred from surrounding to system, so system gains energy (Q) & it is positive.
- As shown in fig (b) $T_s > T_E$, so energy is transferred from system to surrounding, so system loses energy (Q) & it is negative.
- As shown in fig (c) $T_s = T_E$, so there is no transfer of energy betⁿ system & surrounding. so $Q = 0$, due to no temp diff betⁿ system & surrounding.

Q. Explain the change in internal energy of a system with suitable experiment.

⇒ The internal energy of a system can be change (gained or released) due to exchange with its environment.

To explain it consider the following experiment



(a) Change in internal energy of a system by heating the system.

(b) change in internal energy of a system by doing some work on gas(system).

* As shown in figs (a) & (b) a cylinder filled with gas. It is provided with movable, massless & frictionless piston at one end. The gas inside the cylinder is system & the rest is its environment. T_s & T_E be their respective temps.

Internal energy of the system can be changed in two ways.

i) As shown in fig (a) gas in a cylinder is in contact with source of heat. Due to temp. diff. betⁿ the source of heat (environment) and the system (gas) will cause a flow of energy (heat) from environment to system. This is because $T_E > T_s$. Thus there will be an increase in the internal energy of system (gas). It can be possible if $T_s > T_E$, the gas will lose energy to its environment & cool down.

ii) To increase the internal energy of the gas is to quickly push the piston inside the cylinder, so that the gas is compressed as shown in fig (b), here piston does some work on the gas in moving some distance d . The gas gains energy, so its temp. increases. If the piston is pushed out by the gas, i.e. gas expands, some work is done by the gas, so it loses some of its energy & gas cools down.

In this way the internal energy of a system can be changed in two diff. ways (a) by heating it or (b) by doing work on it. It shows that the energy transferred to or by the system & the heat is involved in the process. This leads to the First law of thermodynamics.

$$W = J \times H$$

W = Mechanical work

H = Heat produced

J = Mechanical equivalent of heat (const.)

Q. State first law of thermodynamics. Describe it with suitable experiment.

⇒ First law of thermodynamics:-

The energy supplied to the system goes in partly to increase the internal energy of the system and the rest in work on the environment.

$$Q = \Delta U + W$$

Q = Heat supplied to system by surrounding

ΔU = change in internal energy of system

W = workdone by the system on the surrounding.

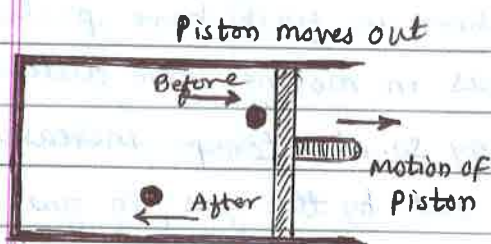


fig (a) positive workdone by a system.

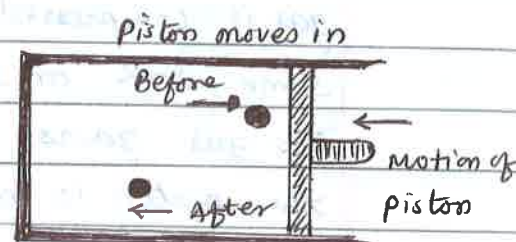


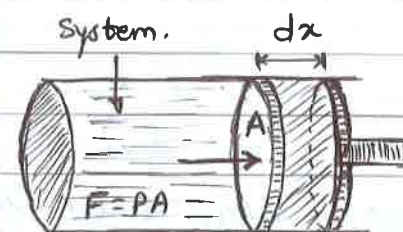
fig (b) Negative workdone by a system.

Consider some quantity of an ideal gas enclosed in a cylinder with a movable, massless & frictionless piston. The gas is system & the cylinder along with the piston is its environment.

1) As shown in fig (a) consider the workdone by the system in increasing the volume of gas. During expansion the gas molecules strike the piston lose their momentum to it, & exert a pressure on it, so piston moves out through a finite distance. The gas does a positive work

on the piston.

2) when the piston is pushed in so that the volume of the gas decreases as shown in fig (b), the gas molecules striking it, gain momentum from the piston. The gas does a negative work on the piston.



(c) A system enclosed in a cylinder (force exerted on piston by system)

consider a system enclosed in a cylinder with a movable, massless & frictionless piston so that its volume can change. 'A' be the area of crosssection of cylinder as well as piston. 'P' is the pressure exerted by system on piston, so force

exerted on piston by the system is

$$F = PA \quad \text{--- (1)}$$

As the piston moves through very small distance dx , the workdone by this force is

$$dW = F \cdot dx \quad \text{--- (2)}$$

put (1) in (2)

$$dW = PA \cdot dx \quad \text{--- (A} \cdot dx = dV = \text{change in vol}^m)$$

$$\therefore dW = P dV \quad \text{--- (3)}$$

If V_i & V_f be the initial & final volume of system (cylinder) The total workdone in changing the volume of cylinder is

$$W = \int_{V_i}^{V_f} P dV \quad \Rightarrow \quad W = P [V]_{V_i}^{V_f}$$

$$\therefore W = P [V_f - V_i] \quad \text{--- (4)}$$

This change in volume is very small. The internal energy of a system can be changed either by providing some heat to it or by removing heat from it; also by doing some work on it or extracting work from it.

When the amount of heat Q is added to the system & the system does not do any work during the process, its internal energy increases by the amount $\Delta U = Q$. On the other hand, when the system does some work to increase its volume, & no heat is added to it while expanding, the system loses energy to its surrounding & its internal energy decreases. So W is +ve & ΔU is -ve & vice versa. $\therefore \Delta U = -W$

The internal energy can change both the ways. So consider the effect of both together & write the total change in the internal energy as

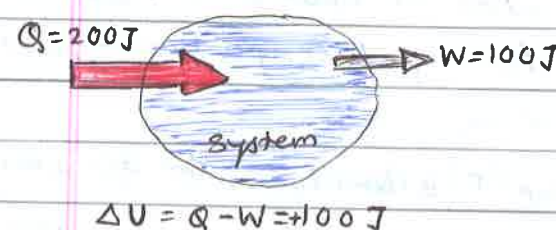
$$\Delta U = Q - W \quad \text{--- (5) from eq (5)}$$

$$\text{or } \Delta U = Q + W \quad \therefore [Q = \Delta U + W] \text{ --- (6)}$$

Eq (5) & (6) shows that when the amount of heat Q is added to a system, its internal energy is increased by an amount ΔU & the remaining is lost in the form of workdone W on the surrounding.

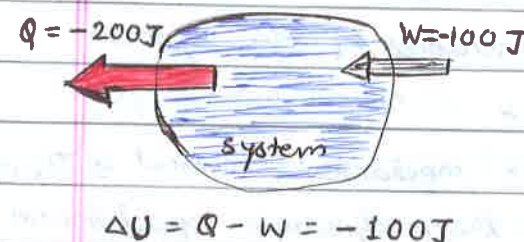
The quantities Q & W can be positive, negative or zero. So ΔU can be positive, negative or zero.

1) Increase in internal energy ($\Delta U > 0$)



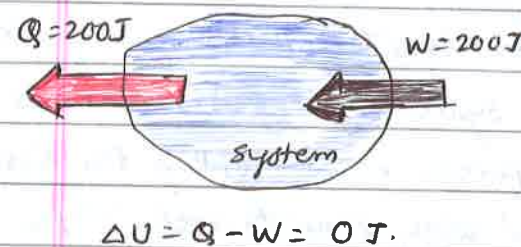
When more heat is added to the system than the workdone by it. The internal energy of the system increases ($\Delta U > 0$)

2) Decrease in internal energy ($\Delta U < 0$)



When more work is done by the system than the heat added to it. In this case internal energy decreases ($\Delta U < 0$)

3) No change in internal energy ($\Delta U = 0$)



When heat added to the system & the workdone by it are the same. The internal energy of the system remains unchanged ($\Delta U = 0$)

Thermodynamic state variables (System Variables)

Pressure, Volume, Temperature, density & mass of a system are macroscopic variables of a system.

* Intensive and Extensive variables

Intensive variables do not depend on the size of the system. Extensive variables depend on the size of the system.

Consider a system in equilibrium. Let this system be divided into two equal compartments, each with half the original volume.

Pressure (P), temp (T) & density (ρ) are the same in both compartments, are known as intensive variables.

The total mass (M) & the internal energy (U) of the system are equally divided in the two compartments are known as extensive variables of the system.

* Thermodynamic Equilibrium:-

If the system is in mechanical, chemical & Thermal equilibrium then it is in thermodynamic equilibrium.

1) Mechanical equilibrium:- when there are no unbalanced forces within the system and betⁿ the system & its surrounding then the system is said to be in mechanical equilibrium. Or when the pressure throughout the system and betⁿ the system & its surrounding is the same, even unbalanced forces exist within the system, they will get neutralized with time to attain the condition of equilibrium. i.e. pressure remains same throughout & does not change with time.

2) Chemical Equilibrium:- When there are no chemical reactions going on within the system or there is no transfer of matter from one part to the other part of system due to diffusion, then the system is said to be in chemical equilibrium. The chemical composition of system remains same throughout & does not change with time.

3) Thermal Equilibrium:- When the temp. of a system is uniform throughout & does not change with time, the system is said to be in thermal equilibrium.

* Thermodynamic state variables & Equation of state:-

Pressure (p), volume (V), temp (T) and mass (m) be the thermodynamic state variables.

Every equilibrium state of a thermodynamic system is completely described by specific values of some macroscopic variables, are the state variables.

The mathematical relation betⁿ the state variables is called as equation of state.

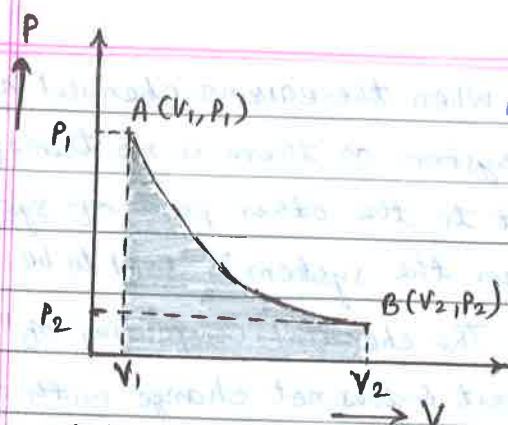
For an ideal gas, the eqⁿ of state is

$$PV = nRT$$
 $n = \text{No. of moles of gas}$

$R = \text{Universal gas constant}$

For fixed amount of gas (given n) there are only two independent variables i.e. p & V , p & T or V & T .

The graphical representation of equation of state of a system is called as p - V diagram or p - V curve or indicator diagram.



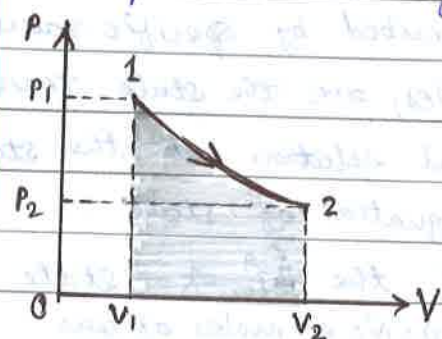
P-V diagram (Indicator diag).

The eqⁿ of state of a system (gas in a cylinder with movable, massless & frictionless piston) & its P-V diagram are useful in studying its behaviour (workdone).

We have the eqⁿ of workdone:

$$W = \int_{V_1}^{V_2} P dV; \text{ This eqⁿ can be represented graphically.}$$

1) Gas expanded with varying pressure (positive workdone)



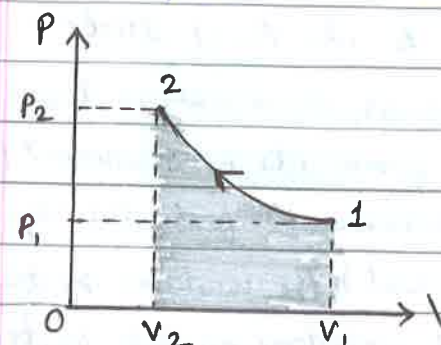
$$\text{Work} = \text{Area}$$

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

$$W = P(V_2 - V_1) > 0$$

The area under the P-V curve in increasing the volume of gas represents workdone as shown in graph $V_2 > V_1$, so workdone is positive. Its volume changes due to outward displacement of the piston & pressure of gas decreases, the workdone by the gas is positive because volume of gas increased.

2) Gas Compressed with varying pressure (Negative workdone)



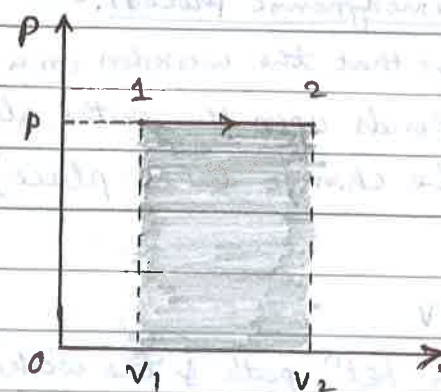
$$\text{Work} = \text{Area}$$

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

$$W = P(V_2 - V_1) < 0$$

When the volume of gas changes from V_1 to V_2 at constant pressure with increase in pressure from P_1 to P_2 , due to inward displacement of the piston, the workdone on the gas is negative.

3) Positive work at constant pressure



$$\text{Work} = \text{Area}$$

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

$$W = P(V_2 - V_1) > 0$$

When the volume of changes from V_1 to V_2 at constant pressure. The curve is a line parallel to the volume axis; the workdone during this process is constant.

When the volume is constant with change in pressure, the workdone on gas is zero because there is no displacement of piston.

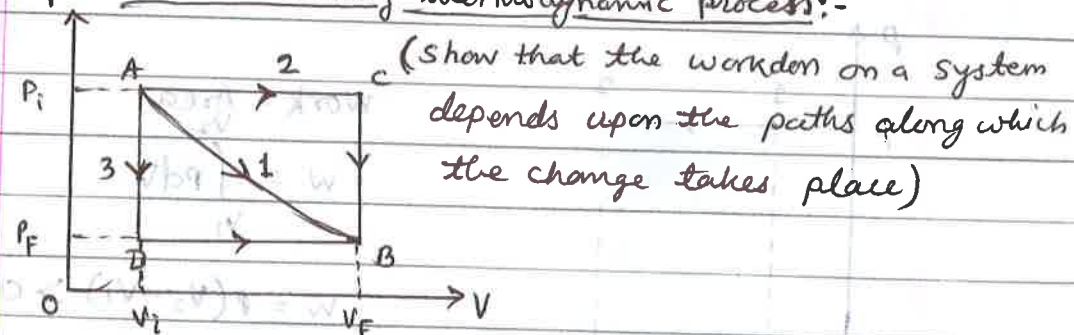
* Thermodynamic process:

It is a procedure in which the initial state of system changes to its final state.

During this process there may be transfer of heat into the system from its environment (positive heat) or heat is transferred (released) from the system to its environment (negative heat). The workdone by the system is positive workdone while workdone on the system is negative workdone. When the piston in a cylinder is pushed in, there is workdone on the system.

During thermodynamic system changes from its initial state to its final state there are diff paths as shown in the following graphs. (P-V diagrams)

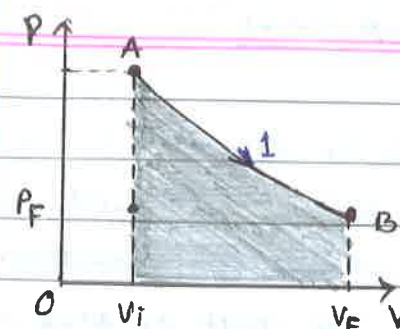
Workdone during thermodynamic process:-



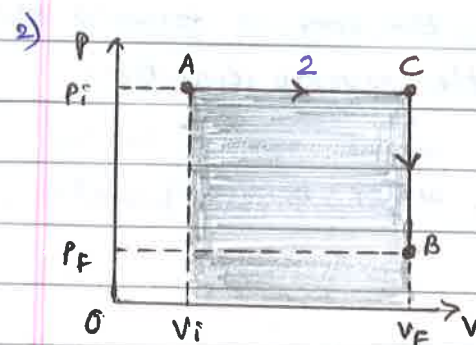
To find the relation betⁿ path & the workdone along the path consider three diff paths in the change of state in thermodynamic system.

1) A is the initial state on the P-V diagram where P_i is pressure & V_i is the volume.

Consider path (1) (curve 1). from A to B, both pressure and volume changes from P_i, V_i to P_f, V_f .

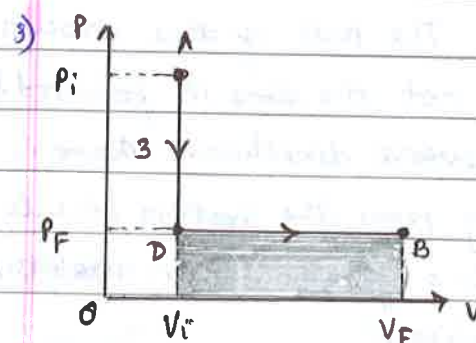


The pressure decreases while volume increases. The workdone by the system is positive (vol^m increases) & it is given by the area under the curve 1 as shown in graph.



The state changes from A to B along path 2. In this case the volume increases from V_i to V_f at constant pressure P_i upto point C. Then pressure decreases from P_i to P_f from point C to B with constant vol^m V_f .

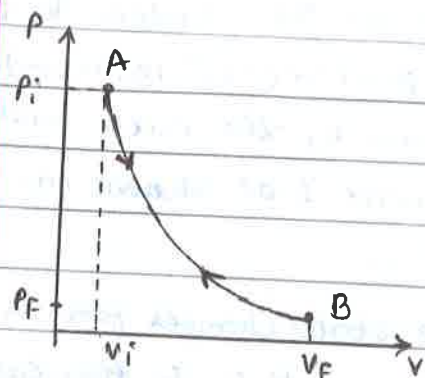
The workdone in this process is represented by the shaded area under the curve 2.



The state changes from A to B along path 3. In this case the pressure decreases from P_i to P_f at constant volume V_i upto point D. From A. Then volume increases from V_i to V_f from point D to B at constant pressure P_f . The workdone in this process is represented by the shaded area under the curve 3. It shows that workdone by a system depends not only on the initial & the final states, but also on the intermediate states i.e. on the paths along which the change takes place.

* Reversible and Irreversible processes

1) Reversible process:

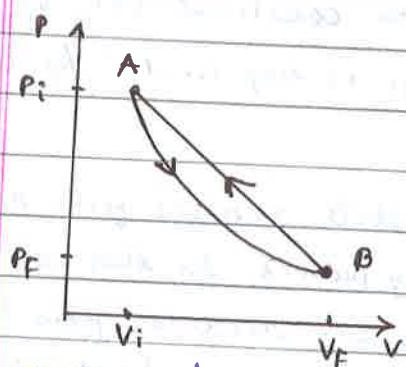


Reversible process is a change that can be retraced in reverse (opposite) direction.

The path of this process is the same in forward and the reverse direction.

eg. melting of ice, Freezing of water, boiling of water, condensation of steam.

2) Irreversible process:



Irreversible process is a change that cannot be retraced in reverse (opposite) direction.

The path of this process is not the same in forward & reverse direction. There is

permanent loss of energy from the system due to friction or other dissipative forces in an irreversible process. This shows a hysteresis.

eg. Puncturing an inflated balloon or a tyre, Rubbing our palms together, burning a candle.

* Causes of Irreversibility:-

- 1) many processes such as a free expansion or an explosive chemical reaction take the system to non-equilibrium states.

- 2) most processes involve friction, viscosity & some other dissipative forces.

Q. state the assumptions for discussion of thermodynamic processes.

- ⇒
- 1) majority of the thermodynamic processes are in reversible processes. They are quasistatic in nature, which are extremely slow & system undergoes infinitesimal change at every stage except the adiabatic processes i.e. system is in thermodynamic equilibrium during all the changes.
 - 2) The system is an ideal gas enclosed in a cylinder having a movable, frictional & massless piston. Depending on the requirements of the process, the walls of the cylinder can be good thermal conductors (for isothermal process).
 - 3) The ideal gas equation is applicable to the system.

* Isothermal process:- It is a process in which change in pressure & volume takes place at a constant temperature. eg. melting of ice, it takes place at constant temp.

Q. Explain thermodynamics of Isothermal process to find the equation of workdone & plot P-V diagram.

⇒ During isothermal change, Boyle's law is applied to study the changes in pressure & volume of a system, & use the equation of state.

$$PV = \text{Constant} \quad \text{--- (1)}$$

If P_i, V_i & P_f, V_f be the initial & final pressure & volume.

of a system respectively for an isothermal change.

$$P_i V_i = P_F V_F = \text{Constant}$$

Consider the isothermal expansion of an ideal gas. The workdone during this small isothermal expansion is given by

$$dw = p dv \quad \text{--- (2)}$$

The total workdone for the expansion of gas from initial vol^m V_i to final vol^m V_F is

$$W = \int_{V_i}^{V_F} P dv \quad \text{--- (3)}$$

The ideal gas eqⁿ is $PV = nRT$

$$P = \frac{nRT}{V} \quad \text{--- (4)}$$

put (4) in (3)

$$W = nRT \int_{V_i}^{V_F} \frac{dv}{v}$$

$$W = nRT \ln \frac{V_F}{V_i} \quad \text{--- (5)}$$

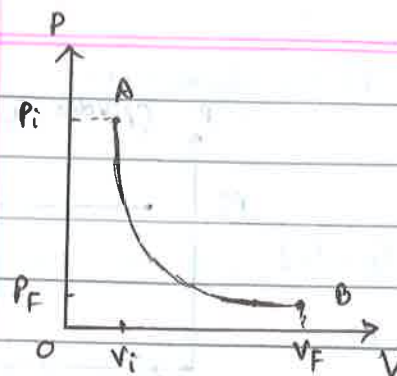
For an ideal gas, its internal energy depends on its temp. $\therefore$ during isothermal process, the internal energy of an ideal gas remains constant ($\Delta U = 0$) as $\Delta T = 0$

According to first law of thermodynamics:

$$Q = W$$

$$Q = W = nRT \ln \frac{V_F}{V_i} \quad \text{--- (6)}$$

It shows that, the heat transferred to the gas is completely converted into the workdone for expansion of gas.



p-V diagram of an isothermal process.

When gas absorbed heat, it does positive work & its vol^m increases during expansion. When the gas is compressed, it releases heat & it does negative work due to decrease in volume.

* Isobaric process:- It is a process of workdone at const pressure.

eg - The Boiling of water at constant pressure.

Q. Explain thermodynamics of isobaric process to find the eqⁿ of workdone & change in internal energy of system in terms of specific heats & plot p-V diagrams of an isobaric process.

$\Rightarrow$ During isobaric process the pressure of system remains constant ($\Delta P = 0$). Consider an ideal gas undergoing expansion of vol^m at constant pressure. Let V_i & T_i be the initial vol^m & temp of a system (gas), V_F & T_F be its final vol^m & temp of system. The workdone during the expansion is given by.

$$W = P dV$$

$$= P(V_F - V_i) = nR(T_F - T_i) \quad \text{--- (1)}$$

Also the change in the internal energy of system is

$$\Delta U = nC_v \Delta T$$

$$\Delta U = nC_v (T_F - T_i) \quad \text{--- (2)}$$

Where C_v is the specific heat at constant vol^m

According to first law of thermodynamics.

$$Q = \Delta U + W \quad \text{--- (3)}$$

put ① & ② in ③

$$Q = nC_v(T_f - T_i) + nR(T_f - T_i)$$

$$Q = (nC_v + nR)(T_f - T_i)$$

$$Q = n(C_v + R)(T_f - T_i) \quad \text{--- (C}_p = C_v + R\text{)}$$

$$\boxed{Q = nC_p(T_f - T_i)} \quad \text{--- (4)}$$

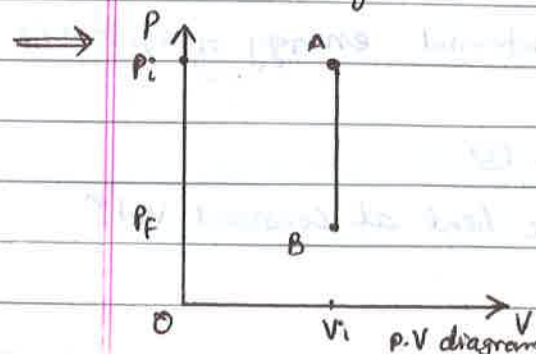
where C_p = sp. heat of gas at constant pressure.

From eqⁿ ④ it shows that the temp. of a system changes in an isobaric process therefore its internal energy also changes.

So heat exchanged is partly used for increasing temp & partly to do some work. The change in temp depends upon C_p .

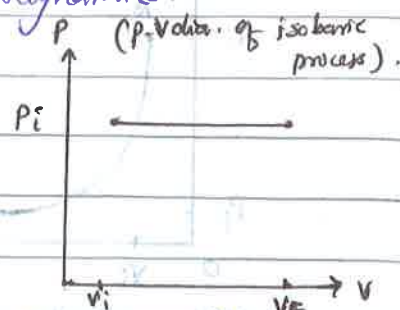
* Isochoric process: - It is a process at constant ~~temp~~ volume in which no work is done on its environment.

Q. Explain thermodynamics of isochoric process to find the heat exchanged in a system.



In this process the state of system changes from A to B; during this change pressure changes from P_i to P_f at constant volume V_i .

P-V diagram for isochoric process



ie change in volume is $\Delta V = 0$. The system does not do any work & all the energy supplied to the system is converted into its internal energy. So According to first law of thermodynamics for isochoric process

$$Q = \Delta U \quad \text{--- (1)}$$

but $\Delta U = nC_v\Delta T$ --- (change in internal energy)

The workdone is given by

$$W = p\Delta V = 0 \quad \text{--- } (\Delta V = 0)$$

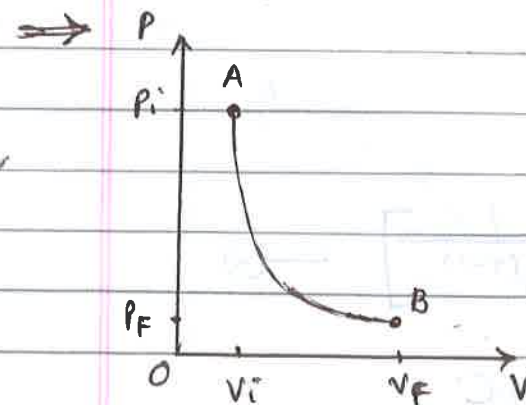
$$\therefore Q = \Delta U + W$$

$$\boxed{Q = \Delta U = nC_v\Delta T} \quad \text{--- (2)}$$

* Adiabatic process: It is a process in the work is done on a system in which there is no transfer of heat from or to the system. ($Q = 0$)

eg. Puncturing an inflated balloon or a tyre.

Q. Explain thermodynamics of adiabatic process to find the equation of temp workdone & state the value of ratio of specific heats (γ) for diff. gases.



P-V diagram of adiabatic process.

In this process when gas(system) is compressed, the workdone is negative

$$\Delta U = -W \quad \text{--- (3) [internal energy } \Delta U \text{ increases]}$$

When the gas expands adiabatically then workdone is positive & ΔU is negative i.e. internal energy decreases.

In adiabatic process internal ^{energy} increases.

For this process

$$pV^\gamma = \text{constant} = C \quad \text{--- (1)}$$

Where $\gamma = \frac{C_p}{C_v} \rightarrow$ Ratio of sp. heat at constant pressure to the sp. heat at constant volume.

So γ is called as adiabatic ratio.

For monoatomic gas $\Rightarrow \gamma = \frac{5}{3}$,

For diatomic gas $\Rightarrow \gamma = \frac{7}{5}$,

For Polyatomic gas $\Rightarrow \gamma = \frac{8}{6} = \frac{4}{3}$.

An adiabatic system is thermally isolated from its environment, so it cannot exchange heat with it. During this process temp & internal energy both changes.

The change in internal energy is

$$\Delta U = C_v \Delta T \quad \text{--- (2)}$$

The workdone is given by

$$W = \int_{V_i}^{V_F} P dV \quad \text{--- (3)} \quad \left(P = \frac{C}{V^\gamma} \text{ from eq (1)} \right)$$

$$\therefore W = C \int_{V_i}^{V_F} \frac{dV}{V^\gamma}$$

$$\therefore W = C \left[\frac{V^{-(\gamma-1)}}{1-\gamma} \right]_{V_i}^{V_F}$$

$$\therefore W = \frac{C}{1-\gamma} \left[\frac{1}{V_F^{(\gamma-1)}} - \frac{1}{V_i^{(\gamma-1)}} \right] \quad \text{--- (4)}$$

From eq (1) $P_i V_i^\gamma = P_F V_F^\gamma = C$

$\therefore$ Eq (4) becomes.

$$W = \frac{1}{(1-\gamma)} \left[\frac{P_F V_F^\gamma}{V_F^{(\gamma-1)}} - \frac{P_i V_i^\gamma}{V_i^{(\gamma-1)}} \right]$$

$$W = \frac{1}{1-\gamma} (P_F V_F - P_i V_i) \quad \text{--- (5)}$$

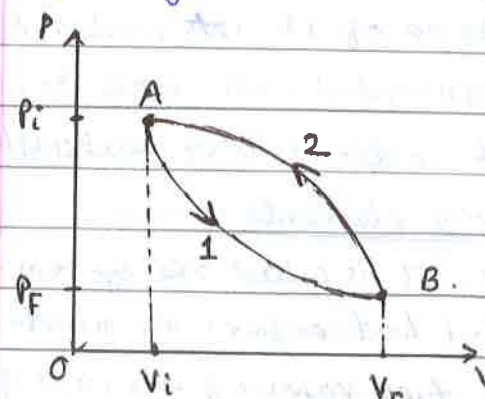
$$W = \frac{nR(T_i - T_F)}{(1-\gamma)} = \frac{(P_F V_F - P_i V_i)}{(1-\gamma)} \quad \text{--- (6)}$$

Eq (6) shows that when work is done by the gas (expands) $W > 0$ & $T_i > T_F$. It means that gas will cool down.

Similarly, if the work is done on the gas (compressed) $W < 0$ & $T_i < T_F$. It means that the gas will warm up.

* Cyclic Process: It is a thermodynamic process that returns a system to its initial state.

In this process initial state & final state is the same & total change in the internal energy of a system is zero ($\Delta U = 0$).



According to first law of thermodynamics in cyclic process

$$Q = W$$

P-V diagram of a cyclic process

* Free Expansion:- These expansions are adiabatic & there is no exchange of heat bet. system & its environment. Also there is no work done on the system or by the system $\therefore Q = W = 0$ & also by first law of thermodynamics $\Delta U = 0$. Free expansion is diff. than other thermodynamic processes. It is an uncontrolled change. It is an instantaneous change & the system is not in thermodynamic equilibrium. Free expansion cannot be plotted on a P-V diagram. Only initial & final state can be plotted.

eg. when a balloon is ruptured suddenly or a tyre is suddenly punctured, the air inside rushes out rapidly but there is no displacement of piston or any other surface.

* Heat Engine: It is a device which transforms heat partly into work or mechanical energy.

It works by using cyclic processes & involve thermodynamic changes.

eg. Automobile engines.

Heat engine receives heat from a source called reservoir & converts some of it into work. All heat absorbed is not converted into work by a heat engine. Some heat is lost in the form of exhaust.

Heat engine has following elements:

- i) A working substance:- It is called the system. Ideal gas is used for ideal heat engine. For practical heat engine mixture of fuel vapour & air in a gasoline (petrol)

or diesel engine or steam in a steam engine.

This working substance that absorbs heat & does work.

2) Hot and cold reservoir:- The working substance interacts with the reservoirs. The hot reservoir is the source of heat. It is at very high temp. & is capable of providing large amount of heat at constant higher temp (T_H). It is also called as the source. The cold reservoir absorbs large amount of heat from the working substance at constant lower temp. (T_C). It is also called as the sink.

3) Cylinder:- The system (working substance) is enclosed in a cylinder with moving, frictionless & massless piston. The system does some work by displacing the piston in the cylinder; this work is transferred by some arrangement (crank shaft) to mechanical energy to the wheels of a vehicle.

Types of Heat engine:-

- 1) External combustion engine - In which working substance is heated externally (steam engine)
- 2) Internal combustion engine - In which working substance is heated internally. (Automobile engine)

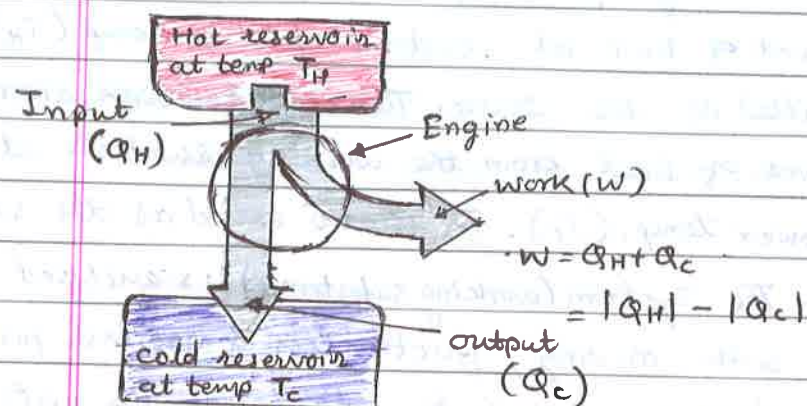
Q - State the basic steps of working in heat engine.

- ⇒
- 1) The working substance absorbs heat from a hot reservoir at higher temp.
 - 2) Part of heat absorbed by the working substance is converted into work.

3) The remaining heat is transferred to a cold reservoir at lower temp.

Q. Draw energy flow diagram of heat engine & find the eqns of thermal efficiency of heat engine.

⇒



The heat engines are diagrammatically represented by an energy flow diagram as shown in fig.

Energy exchange takes place during various stages of working of heat engines.

Let Q_H be the heat absorbed by working substance at the source, & Q_c be the heat rejected by it at the sink. (Q_H is positive & Q_c is negative) & W be the workdone by the working substance. The circle

represents the engine. The heat pipelines represents the heat absorbed, rejected & converted into work.

The width of heat pipeline indicated by Q_H is proportional to the amount of heat absorbed at the source, Q_c heat rejected at sink & W proportional to part of heat

converted into mechanical work.

Here a single step of one operating cycle of the engine, several such cycles are repeated when a heat engine operates.

The net heat Q absorbed per operating cycle is

$$Q = Q_H + Q_c = |Q_H| - |Q_c| \quad \text{--- (1)}$$

Ideally all heat Q_H is converted into work, but practically there is some heat lost i.e. $Q_c \neq 0$.

∴ The thermal efficiency η of heat engine is defined as the ratio of the workdone by the working substance to the amount of heat absorbed by it or it is the ratio of the output in the form of workdone W by the engine to the input in the form of heat supplied Q_H . It is also defined as the fraction of the heat absorbed that is converted into work.

$$\eta = \frac{W}{Q_H} \quad \text{--- (2)}$$

There is a fundamental limit on the efficiency of a heat engine set by the second law of thermodynamics.

From eqns (1) & (2)

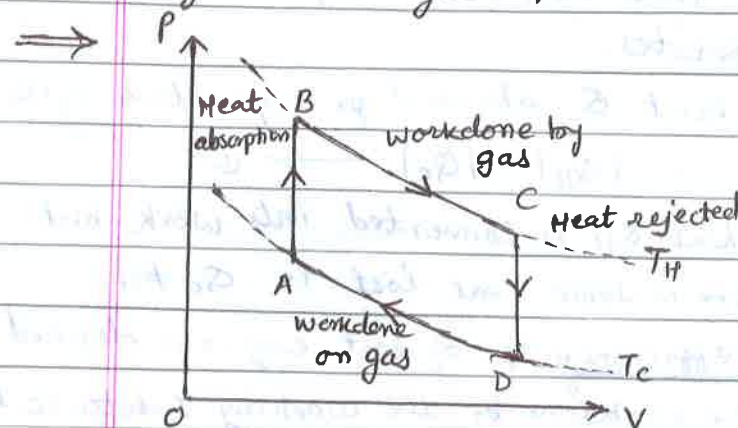
$$\eta = \frac{W}{Q_H} = 1 + \frac{Q_c}{Q_H} = 1 - \frac{|Q_c|}{|Q_H|} \quad \text{--- (3)}$$

Eqn (3) gives the thermal efficiency of a heat engine.

It is no unit as it is a ratio of quantities represents energy.

Describe

Q. (Explain) the working of typical heat engine with the help of p - V diagram to show the operation of heat engine is a cyclic process.



Typical p - V diagram of a typical heat engine.

The working substance of a heat engine is a well defined sequence of operation in a cyclic thermodynamic process. It is represented by p - V diagram.

The heat engine uses energy absorbed in the form of heat to do work & reject the remaining heat which cannot be used to do work. Heat is absorbed in one part of cycle, work is done in another part, & unused heat is rejected in other part of the cycle.

The operating cycle begins at A. The working substance (gas) absorbs heat at constant volume & no work is done by the gas or on the gas, but pressure increases till point B is reached. The temp of gas also increases & its internal energy increases.

From point B the gas starts expanding by pushing the piston away with increasing volume from point B to C; the pressure reduces due to expansion of gas; the work is done by the gas.

At point C, the excess heat which is not utilised in doing work by the gas is rejected. So gas cools down & its internal energy decreases. This process is again at constant volume. The pressure of the gas is reduced & point D is reached.

The gas is now compressed. From D to A, its volume decreases & pressure increases; during this work is done on the gas; the cycle is complete & the system is ready for the next cycle.

The p - V diagram gives to understand the behavior of the three state variables of a gas throughout the operational cycle. The area of loop represents the work done during one complete cycle.

Q. Explain the concept of transferring heat from cold region to a hot region used in refrigerators or air conditioners.

⇒ According to second law of thermodynamics heat can not flow from a region of lower temp. to a region of higher temp. on its own; but by doing work on the system we can force heat to flow from the region of lower temp to a region of higher temp. The Refrigerators, air conditioners & heat pumps in which heat to be transferred from a cold region to a hot region, which is due to phase change of fluid, called as refrigerant. The refrigerant is forced to evaporate & then condense by decreasing & increasing pressure. The pump extracts the heat of

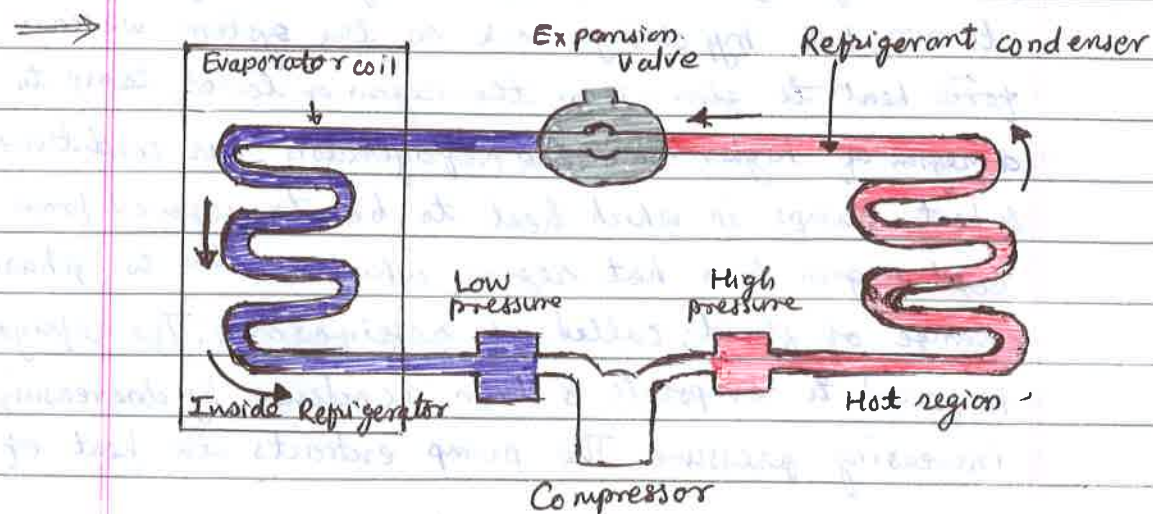
Vaporisation of the refrigerant from the cold region & rejects it to the hotter region outside the refrigerator. The heat of evaporation of the refrigerant thus absorbed is rejected by compressing & condensing it into liquid at a higher temp.

All this process is carried out in a mechanism involving the compressor & closed tubing such as seen at the back of a household refrigerator.

Workdone = Compression & forced condensation (Heat rejection). Expansion and forced Vaporisation (Heat absorption)



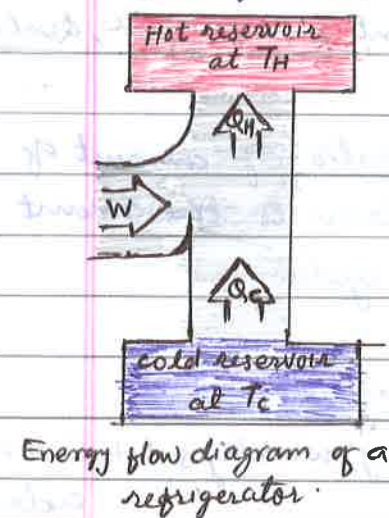
Q. Draw neat labelled diagram of refrigerator & describe the diff. steps of its working.



Refrigeration is an artificial cooling process in which cooling a space or substance of a system and to maintain its temp. below its ambient temp.

A refrigerator extracts heat from a cold region & delivers it to the surrounding, thus further cooling the cold region. So outer region of refrigerator is hot (warm) & interior is cold. An air conditioner also works on same principles.

It consists of a compressor, an expansion valve, closed tube which carries the refrigerant. Part of tube called the cooling coil, is in the region which is to be cooled at lower temp. & lower pressure. The other part which is exposed to the surrounding (atmosphere) is at higher temp. & higher pressure. A fluid such as (Fluorinated hydrocarbons) is used as refrigerant. The cold & hot part of the coil contain the refrigerant as a mixture of liquid & vapour phase in equilibrium.



As shown in energy flow diagram heat extracted from a cold reservoir is supplemented by the mechanical workdone by the compressor & the total energy is rejected at the hot reservoir.

The refrigerant goes through the following steps in one complete cycle of refrigeration.

step-1: The fluid passes through a nozzle & expands into a low pressure area. Similarly carbon dioxide comes out of a fire extinguisher & cools down, the fluid turns into a gas & cools down (adiabatic expansion)

step-2: The cool gas is in thermal contact with the inner compartment of the ~~fridge~~ ^{fridge}. It heats up as heat is transferred to it from the contents of the fridge.

~~adiabatic~~ (Isobaric expansion) at constant pressure

step-3: The gas is transferred to a compressor, which does most of the work in this process. The gas is compressed adiabatically, heating it and turning it back to a liquid.

step-4: The hot liquid passes through coils on the outside of the fridge & heat is transferred to the atmosphere. (Isobaric compression).

The compressor is driven by an external energy source and it does the work (W) on the working substance during each cycle.

* Performance of refrigerator [Coefficient of performance, Quality factor or Q value of refrigerator]

It is defined as the ratio of amount of heat absorbed by the working substance to the amount of work done in one operating cycle.

$$K = \frac{|Q_c|}{|W|} \quad \text{--- (1)}$$

where Q_c = Amount of heat absorbed by working substance in one cycle.
& W = work done in one cycle.

As Q_c is heat absorbed at lower temp. & Q_H is rejected at high temp. $\therefore Q_c > 0$ (positive), $Q_H < 0$ (negative)
 $W < 0$ (negative) $\therefore |Q_H| = -Q_H$.

$$\therefore Q_H + Q_c = W \quad \text{or} \quad Q_H + Q_c - W = 0$$

$$\therefore -Q_H = Q_c - W \quad \text{or} \quad |W| = |Q_c| - |Q_H|$$

$\therefore$ From eqⁿ (1)

$$K = \frac{|Q_c|}{|W|} = \frac{|Q_c|}{|Q_c| - |Q_H|} \quad \text{--- (2)}$$

where K is dimensionless; has no unit.

for typical household refrigerator $K \approx 5$

* Air conditioner:

The air conditioner & refrigerator are working exactly similar. For air conditioner the evaporator coils are inside the room that is to be cooled, & the condenser is outside the room. The air cooled by the evaporator coils inside the room is circulated by a fan placed inside the air conditioning unit. The performance of an air conditioner is defined by coefficient of performance ($K = \frac{|Q_c|}{|W|}$) --- (1) It is consider the rate of heat removed (H) & the power (P) required for removing the heat.

The rate of heat removed as heat current

$$H = \frac{|Q_c|}{t} \quad \text{--- (2) where } t = \text{time in which heat } |Q_c| \text{ removed.}$$

$\therefore$ The coefficient of performance of an air conditioner is

$$K = \frac{|Q_c|}{|W|} = \frac{Ht}{Pt} = \frac{H}{P} \quad \text{--- (3)} \quad \left[K = 2.5 \text{ to } 3.0 \text{ for room air conditioner} \right]$$

- * Heat pump: The working of heat pump is similar to refrigerator. It is used to heat a building or larger structure by cooling the air outside it.

In heat pump the evaporator coils are outside & absorb heat from the cold air from outside. The condenser coils are inside the building. They release the absorbed heat to the air inside & thus warming the building.

Q. What are the limitations of the First law of thermodynamics?

⇒ According to First law of thermodynamics heat can be converted into work & work can also be converted into heat; but there are some limitations.

1) According to First law heat may on its own flow from an object at higher temp to one at lower temp. & it can also on its own flow from an object at lower temp to one at higher temp, but practically heat cannot flow from an object at lower temp to another at higher temp.

2) According to First law we could convert 100% of heat available to us into work. Similarly all the work could be converted into heat. but practically this is not possible.

Hence the First law of thermodynamics does not prevent us from converting heat entirely into work or work entirely into heat.

- * Engine law (Engine statement) of the second law of thermodynamics

It is impossible to extract an amount of heat (Q_H) from a hot reservoir & use it all to do work (W). Some amount of heat (Q_C) must be exhausted to a cold reservoir. This prohibits the possibility of a perfect heat engine.

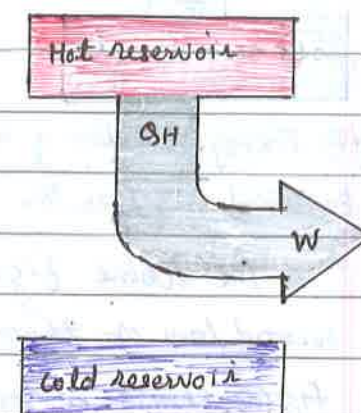
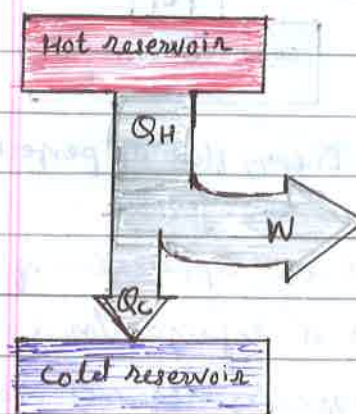


Fig 6 Second law of thermodynamics

Fig 6 Energy flow dia. of Engine

As shown in fig 6 all heat engines ^{statement} lose some heat to the environment of a perfect heat engine. All the heat extracted (Q_H) can not be used to do work. Fig 6 shows the energy flow diagram for such a situation.

This is first form of the second law of thermodynamics also called as Kelvin - Planck statement.

Heat engine is one form of heat-work conversion. & Refrigerator is other form of work-heat conversion.

The second form of the second law of thermodynamics is the Clausius statement, it is also called as Refrigerator law or Refrigerator statement of second law of thermodynamics.



fig (a) Energy flow dia. of a practical refrigerator

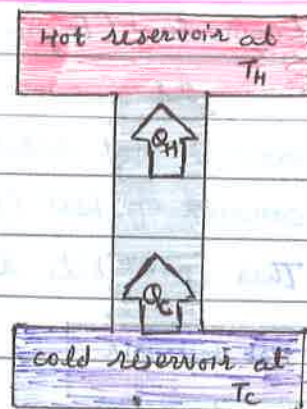


fig (b) Energy flow of perfect refrigerator

The above figures represent the application of the second law of thermodynamics to a refrigerator.

fig (a) shows a practical refrigerator requires work (W) to be done to extract heat Q_H from a cold reservoir & reject it to hot reservoir. i.e. the spontaneous flow of heat from an object at cold temp is not possible as shown in fig (b).

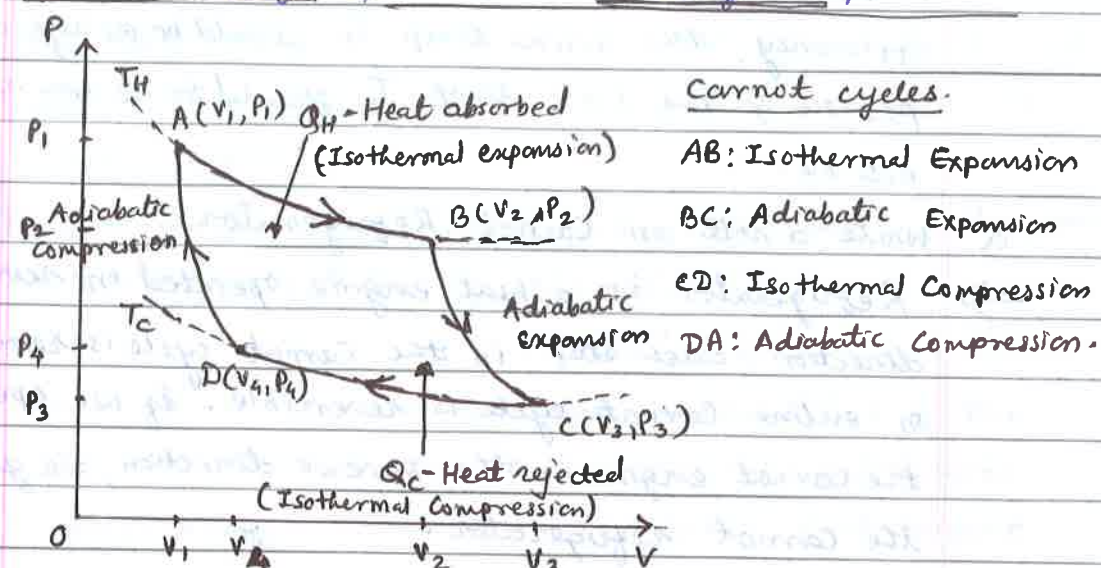
It shows that, it is not possible for heat to flow from a colder body to a warmer body without any work having been done to accomplish this flow.

Q. Explain about the max^m efficiency of a heat engine & Carnot's cycle with the help of p - V diagram.

→ We know that in refrigerator conversion of work to heat is an irreversible process & in heat engine it would convert max^m heat into work, if all irreversible

processes could be avoided; so the efficiency of heat engine is max^m. Sadi Carnot (French) proposed a hypothetical ideal engine (1824) which has the max^m efficiency.

In Carnot engine, there are basically two processes.



1) Exchange of heat (step A to B & C to D)

For this to be reversible the heat exchange must be isothermal. This is possible if the working substance is at the temp T_H of the source while absorbing heat. The working substance should be at temp T_C of the cold reservoir, while rejecting the heat.

2) Workdone (step B to C & D to A):

For workdone to be reversible, the process should be adiabatic.

Thus the cycle includes two isothermal & two adiabatic processes for max^m efficiency.

The efficiency of Carnot engine/cycle is as

$$\eta = \frac{W}{Q_H} = 1 - \frac{|Q_C|}{|Q_H|} = 1 - \frac{T_C}{T_H} \quad \text{--- (1)}$$

Thus while designing the heat engine for max^m efficiency, the source temp T_H should be as high as possible & the sink temp T_C should be as low as possible.

Q Write a note on Carnot Refrigerator.

⇒ Refrigerator is a heat engine operated in reverse direction. Each step in the Carnot cycle is reversible, so entire Carnot cycle is reversible. If we operate the Carnot engine in the reverse direction, we get the Carnot refrigerator.

The coefficient of performance of a Carnot refrigerator is given by

$$K = \frac{|Q_C|}{|Q_C| - |Q_H|} = \frac{\frac{|Q_C|}{|Q_H|}}{1 - \frac{|Q_C|}{|Q_H|}} \quad \text{--- (1)}$$

$$\text{but } \frac{|Q_C|}{|Q_H|} = \frac{T_C}{T_H} \quad \text{--- (2)}$$

$$\therefore K = \frac{T_C}{T_H - T_C} \quad \text{--- (3)}$$

Eqⁿ (3) gives the coefficient of performance of an ideal refrigerator or the Carnot refrigerator; it also shows that K depends not only the temp. diff. of hot & cold

reservoir. When the temp diff is very small, K is very large, so large quantity of heat can be removed from the lower temp. to the higher temp. by doing very small amount of work. K is very small when the temp. diff. is large. i.e. a small quantity of heat will be removed even when a large amount of work is done.

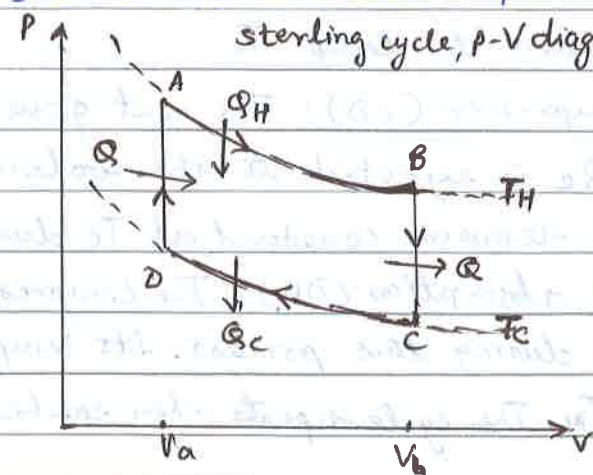
Q Describe sterling cycle (Carnot cycle) with neat p-V diagram according to second law of thermodynamics.

⇒ All the Carnot engines operating betⁿ the same two temp. have the same efficiency, irrespective of the nature of the working substance, for Carnot engine.

- 1) Carnot engine is the most efficient heat engine
- 2) Efficiency of a Carnot engine is independent of its working substance.

A Carnot refrigerator has a greater coefficient of performance among all the refrigerators working betⁿ the same two temps.

sterling cycle, p-V diagram.



sterling cycle is a closed thermodynamic cycle.

The sterling engine is based on this cycle.

The working substance in it is air, helium, hydrogen, nitrogen etc.

All the processes in this cycle are reversible. When the gas is heated, the sterling engine produce useful work. When work is done on the gas, it works as a refrigerator. This is reverse working of a sterling cycle; this reversed process is used in the field of cryogenics to produce extremely low temps. or to liquefy air or gases.

The ideal sterling cycle has two isothermal processes AB & CD & two isobaric processes BC & DA connect the two isothermal processes. Heat is absorbed at constant temp T_H & rejected at constant temp T_C , as follows.

- 1) Isothermal expansion (AB): The gas is heated by supplying heat Q_H at constant temp T_H . Useful work is done by the gas.
- 2) Isochoric process (BC): The heat Q_H absorbed by the gas in part AB is released by the gas to the refrigerator. This heat Q is used in the next part. The gas cools down to temp T_C .
- 3) Isothermal compression (CD): The heat generated in this part Q_C is rejected to the coolant (sink). The temp of gas remains constant at T_C during CD.
- 4) Iso baric heat absorption (DA): The compressed gas absorbs heat Q during this process. Its temp is increased to T_H . The cycle repeats when reaches at A.

Examples

- 1) A gas enclosed in a cylinder is expanded to double its initial volume at a constant pressure of 1 atmosphere. How much work is done in this process?

⇒ Given

$$1 \text{ atm pressure} = 1.01 \times 10^5 \text{ Pa.}$$

$$V_f - V_i = 0.5$$

$$W = P(V_f - V_i)$$

$$= 1.01 \times 10^5 (0.5)$$

$$W = 0.505 \times 10^5 \text{ J}$$

- 2) 1.0 kg of liquid water is boiled at 100°C & all of it is converted to steam. If the change of state takes place at the atmospheric pressure ($1.01 \times 10^5 \text{ Pa}$), calculate
- a) The energy transferred to the system.
 - b) The workdone by the system during this change
 - c) The change in the internal energy of the system.

Given the volume of water changes from $1.0 \times 10^{-3} \text{ m}^3$ in liquid form to 1.671 m^3 when in the form of steam.

⇒ a) Liquid water changes to steam by absorbing the heat of vaporisation,

$$Q = L \cdot m$$

$$Q = 2256 \frac{\text{kJ}}{\text{kg}} \times 1.0 \text{ kg} = \underline{2256 \text{ J}}$$

b) workdone

$$W = P \Delta V$$

$$= 1.01 \times 10^5 [1.671 - 1.0 \times 10^{-3}] = \underline{1.69 \times 10^5 \text{ J}}$$



c) change in internal energy

$$\Delta U = Q - W$$

$$= 2265 \text{ kJ} - 169 \text{ kJ}$$

$$\Delta U = 2096 \text{ kJ}$$

As energy is positive i.e. there is increase in internal energy of water when it boils.

3) 104 kJ of work is done on certain volume of a gas. If the gas releases 125 kJ of heat, calculate the change in internal energy (in kJ) of the gas.

⇒ Given

$W = 104 \text{ kJ}$, This work is done on the gas.

$$\therefore W = -104 \text{ kJ}.$$

Similarly, the heat is released by the gas.

$$\therefore Q = -125 \text{ kJ}.$$

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

$$\Delta U = 125 - 104$$

$$\Delta U = 21 \text{ kJ}$$

at

4) 0.5 mole of gas at temp 300 K expands isothermally from an initial volume of 2.0 L to final volume of 6.0 L

a) What is the workdone by the gas? ($R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$)

b) How much heat is supplied to the gas?

⇒ Given

$$n = 0.5, \quad V_F = 6 \text{ L}, \quad V_i = 2 \text{ L}.$$



a) workdone

$$W = nRT \ln \left(\frac{V_F}{V_i} \right)$$

$$= 0.5 \times 8.314 \times 300 \ln \left(\frac{6}{2} \right) \quad \left(\ln 3 = 2.303 \log_{10} 3 \right)$$

$$W = 1.369 \text{ kJ}$$

b) Heat supplied to gas

By first law of thermodynamics, the heat supplied in an isothermal process is spent to do work on a system

$$\therefore Q = W = 1.369 \text{ kJ}$$

5) One mole of an ideal gas is initially kept in a cylinder with a movable frictionless & massless piston at pressure of 1.0 mPa, & temp 27°C. It is then expanded till its volume is doubled. How much work is done if the expansion is isobaric?

⇒ Given

$$R = 8.31 \text{ J/mol K}$$

$$V_F = 2V_i, \quad T = 27^\circ\text{C} = 27 + 273 = 300 \text{ K}, \quad n = 1 \text{ mole}$$

$$W = P \Delta V = P (V_F - V_i)$$

$$= P (2V_i - V_i)$$

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

$$P_i V_i = nRT_i$$

$$\therefore V_i = \frac{nRT_i}{P_i} = \frac{1 \times 8.31 \times 300}{1 \times 10^6} = 24.9 \times 10^{-4} \text{ m}^3$$

$$W = 2 \times 10^6 \times 24.9 \times 10^{-4}$$

$$W = 4.9 \text{ kJ}$$

- 6) A Carnot engine receives 2.0 kJ of heat from a reservoir at 500 K. does some work & reject some heat to a reservoir at 350 K.

- (a) How much work does it do?
 (b) How much heat is rejected?
 (c) What is its efficiency?

⇒ Given

$$Q_H = 2 \text{ kJ} = 2000 \text{ J}$$

$$T_H = 500 \text{ K}, \quad T_C = 350 \text{ K}$$

(a) work done

$$W = Q_H + Q_C \quad \text{--- (1)}$$

$$Q_C = -Q_H \frac{T_C}{T_H} = -(2000) \times \frac{350}{500}$$

$$Q_C = -1400 \text{ J} \quad \text{--- (2)}$$

put (2) in (1)

$$W = 2000 + (-1400)$$

$$\boxed{W = 600 \text{ J}}$$

(b) Heat rejected

$$Q = 600 \text{ J} = W$$

(c) Efficiency

$$\eta = 1 - \frac{T_C}{T_H} = 1 - \frac{350}{500} = 0.30 = 30\%$$

- 7) An Ideal gas of volume 1.0 L is adiabatically compressed to $(\frac{1}{5})^{1/4}$ of its initial volume. Its initial pressure & temp is $1.01 \times 10^5 \text{ Pa}$ & 27°C respectively. Given C_V for ideal gas = $20.8 \frac{\text{J}}{\text{mol K}}$, $\gamma = 1.4$ calculate

- (a) Final pressure (b) work done (c) Final temp.
 (d) How would your answers change, if the process were isothermal?

⇒ Given

$$V_i = 1.0 \text{ L} = 10^{-3} \text{ m}^3, \quad V_f = \frac{V_i}{5}, \quad P_i = 1.01 \times 10^5 \text{ Pa}, \quad T_i = 27^\circ\text{C} = 27 + 273 = 300 \text{ K}$$

$$C_V = 20.8 \text{ J/mole K}, \quad \gamma = 1.4$$

(a) Final pressure

$$P_i = P_f \left(\frac{V_i}{V_f} \right)^\gamma$$

$$= 1.01 \times 10^5 \times (5)^{1.4}$$

$$\boxed{P_f = 44.8 \times 10^5 \text{ Pa}}$$

(b) Work done

$$W = \frac{(P_f V_f - P_i V_i)}{(1 - \gamma)}$$

$$W = \frac{[(1.01 \times 10^5 \times 10^{-3}) - (44.8 \times 10^5 \times \frac{10^{-3}}{5})]}{1.4 - 1}$$

$$\boxed{W = -494 \text{ J}}$$

(c) Final temp

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{\gamma-1} = 300 (5)^{0.4}$$

$$\boxed{T_f = 886 \text{ K} = 613^\circ\text{C}}$$

d) i) Pressure in isothermal is

$$P_i V_i = P_F V_F$$

$$P_F = \frac{P_i V_i}{V_F} = \underline{\underline{15 \text{ atm}}}$$

ii) Temp = constant at isothermal process

iii) Workdone

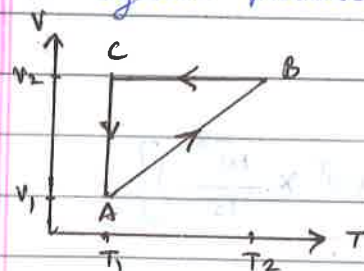
$$W = nRT \ln \left(\frac{V_F}{V_i} \right) \quad (n = 0.405)$$

$$= 0.405 \times 831 \times 300 (-0.270)$$

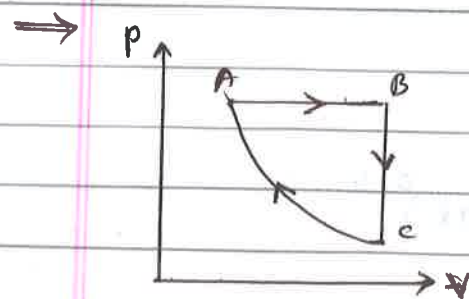
$$W = \underline{\underline{-2726 \text{ J}}}$$

The workdone during adiabatic process is very much less than the workdone during isothermal process.

8) A cyclic process ABCA is shown in V-T diagram



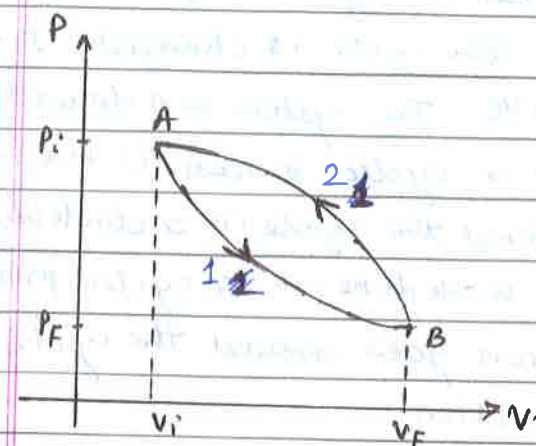
It is performed with a constant mass of ideal gas. How will this transform to a P-V diagram,



Straight line from A to B on the V-T diagram means $V \propto T$, i.e. P is constant; V is constant & temp decreases. Along B-C i.e. P should also decrease

Temp. is constant along CA. i.e. it is an isothermal process. The P-V curve would look as shown in P-V graph

9) The total workdone in the cyclic process as shown in fig is -1000 J .



a) what does the -ve sign mean?

b) what is the change in internal energy & the heat transferred during this process.

c) what will happen when the direction of cycle is changed?

→ a) The workdone from A to B along path 2 is given by the area under this curve. Here volume increases so workdone is +ve.

workdone in the process from B to A along path 1 is given by the area under this curve. Here volⁿ decreases so workdone is -ve.

The total total workdone during the complete cycle from A to B along the path 2 & from B to A along the path 1 is the area enclosed by the closed loop.

This is the diff. betⁿ the area under the curve 1 & that under the curve 2. Since area under the curve 1 is -ve & larger than the area under the curve 2. Then area of the loop is also -ve. So Workdone by the system is -ve



b) This is the cyclic process which means the initial & the final state of the system is the same.

$$\therefore \Delta U = 0, \therefore Q = W = -1000 \text{ J.}$$

i.e. 1000 J of heat must be rejected by the system.

c) If the direction of the cycle is changed, the workdone will be +ve. The system will do work.

$\therefore$ The Σ Total workdone in a cyclic process is +ve if the process is goes around the cycle in a clockwise direction. The total workdone in a cyclic process is -ve if the process goes around the cycle in anticlockwise direction.

