KINETIC THEORY OF GASES AND THERMODYNAMICS
SECTION I
Kinetic theory of gases

Some important terms in kinetic theory of gases
Macroscopic quantities:
Physical quantities like pressure, temperature, volume, internal energy are associated with gases. These quantities are obtained as an average combined effect of the process taking place at the microscopic level in a system known as macroscopic quantities. These quantities can be directly measured or calculated with help of other measurable macroscopic quantities

Macroscopic description:
The description of a system and events associated with it in context to its macroscopic quantities are known as macroscopic description.

Microscopic quantities:
Physical quantities like speed, momentum, kinetic energy etc. associated with the constituent particle at microscopic level, are known as microscopic quantities
Microscopic description:
When the system and events associated with it are described in context to microscopic quantities, this description is known as microscopic description

Postulates of Kinetic theory of gases
(1) A gas consists of a very large number of molecules. Each one is a perfectly identical elastic sphere.
 (2) The molecules of a gas are in a state of continuous and random motion. They move in all directions with all possible velocities.
(3) The size of each molecule is very small as compared to the distance between them. Hence, the volume occupied by the molecule is negligible in comparison to the volume of the gas.
(4) There is no force of attraction or repulsion between the molecules and the walls of the container.
(5) The collisions of the molecules among themselves and with the walls of the container are perfectly elastic. Therefore, momentum and kinetic energy of the molecules are conserved during collisions.

(6) A molecule moves along a straight line between two successive collisions and the average distance travelled between two successive collisions is called the mean free path of the molecules.

(7) The collisions are almost instantaneous (i.e) the time of collision of two molecules is negligible as compared to the time interval between two successive collisions.

Behavior of gases

It has been observed from experiments that for very low densities, the pressure, volume and temperature of gas are interrelated by some simple relations.

Boyle's law

At constant temperature and low enough density, the pressure of a given quantity (mass) of gas is inversely proportional to its volume

Thus at constant mass and constant temperature

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

Or PV = Constant

Charles's law

At constant pressure and low enough density, the volume of a given quantity (mass) of a gas is proportional to its absolute temperature

Thus at constant mass and constant pressure

$$V \propto T$$

Or $\frac{V}{T} = constant$

Gay Lussac's law

For a given volume and low enough density the pressure of a given quantity of gas is proportional to its absolute temperature.

Thus at constant mass and constant volume

$$P \propto T$$

Or $\frac{P}{T} = constant$

Avogadro's Number

"For given constant temperature and pressure, the number of molecules per unit volume is the same for all gases"

At standard temperature (273K) and pressure (1 atm), the mass of 22.4 litres of **any** gas is equal to its molecular mass (in grams). This quantity of gas is called 1 mole.

The number of particles (atoms or molecules) in one mole of substance (gas) is called Aveogadro number, which has a magnitude $N_A = 6.023 \times 10^{23}$ mol^{-1}

If N is the number of gas molecules in a container , then the number of mole of given gas is

$$\mu = \frac{N}{N_A}$$

If M is the total mass of gas in a container, and mass of one mole of gas called molar mass M_O, then the number of moles of gas is

$$\mu = \frac{M}{M_O}$$

Other important laws of an ideal gas
Grahm's law of diffusion states that when two gases at the same pressure and temperature are allowed to diffuse into each other, the rate of diffusion of each gas is inversely proportional to the square root of the density of the gas

$$rate\ of\ diffusion \propto \sqrt{\frac{1}{density\ of\ gas}}$$

Dalton's law of partial pressure states that the pressure exerted by a mixture of several gases equals the sum of the pressure exerted by each gas occupying the same volume as that of the mixture
$P_1, P_2, …, P_n$ are the pressure exerted by individual gases of the mixture, then pressure of the mixture of the gas is
$P = P_1 + P_2 + … + P_n$

Ideal gas-state equation and it different forms
If we combine Boyle's law and Charle's law we get
$$\frac{PV}{T} = constant$$
For a given quantity of gas, which shows that for constant temperature and pressure, if quantity or mass of gas is varies, then volume of the gas is proportional to the quantity of gas.
Thus constant on the right hand side of the equation depends on the quantity of the gas. If quantity is represented in mole then
$$\frac{PV}{T} = \mu R$$
Equation is called an ideal gas-state equation
Here R is universal gas constant = 8.314 J mole^{-1} K^{-1}
If gas completely obeys equation
$$PV = \mu RT \quad --- eq(1)$$
at all values of pressure and temperature, then such a (imaginary) gas is called an ideal gas. By putting
$$\mu = \frac{N}{N_A}$$

In above equation we get

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$$PV = \frac{N}{N_A}RT = N\frac{R}{N_A}T$$

Putting $R/N_A = k_B$ (Boltzmann's constant = 1.38×10^{-23} J K^{-1})

$$PV = Nk_BT$$
$$\therefore P = \frac{N}{V}k_BT$$

If n = N/V number of molecules per unit volume of gas

$$\therefore P = nk_BT \quad --- eq(2)$$

Putting

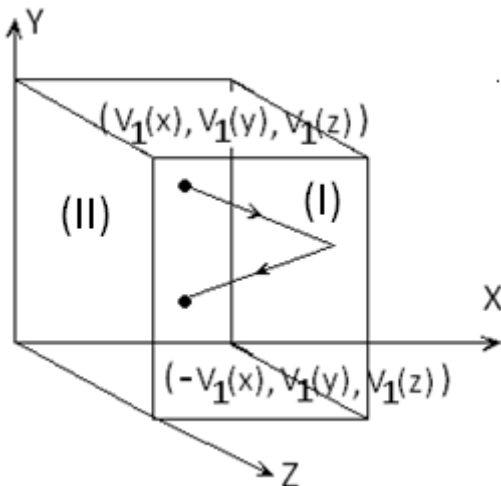$$\mu = \frac{M}{M_O}$$

In equation (1)

$$PV = \frac{M}{M_O}RT$$

$$P = \frac{M}{V}\frac{RT}{M_O}$$

$$P = \frac{\rho RT}{M_O} \quad --- eq(3)$$

ρ is the density of gas

Pressure of an ideal gas and rms speed of gas molecules

The molecules of a gas are in a state of random motion. They continuously collide against the walls of the container. During each collision, momentum is transferred to the walls of the container.

The pressure exerted by the gas is due to the continuous collision of the molecules against the walls of the container. Due to this continuous collision, the walls experience a continuous force which is equal to the total momentum imparted to the walls per second. The force experienced per unit area of the walls of the container determines the pressure exerted by the gas.

Consider a cubic container of side L containing n molecules of perfect gas moving with velocities C_1, C_2, C_3 ... C_n

A molecule moving with a velocity v_1, will have velocities $C_1(x)$, $C_1(y)$ and $C_1(z)$ as components along the x, y and z axes respectively. Similarly $C_2(x)$, $C_2(y)$ and $C_2(z)$ are the velocity components of the second molecule and so on.

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Let a molecule P shown in figure having velocity C_1 collide against the wall marked I perpendicular to the x-axis. Only the x-component of the velocity of the molecule is relevant for the wall . Hence momentum of the molecule before collision is $m\,C_1(x)$ where m is the mass of the molecule.
Since the collision is elastic, the molecule will rebound with the velocity $C_1(x)$ in the opposite direction. Hence momentum of the molecule after collision is $-mC_1(x)$

Change in the momentum of the molecule = Final momentum - Initial momentum
Change in the momentum of the molecule = $- mC_1(x) - mC_1(x) = -2mC_1(x)$
During each successive collision on face I the molecule must travel a distance 2L from face I to face II and back to face I.

Time taken between two successive collisions is = $2L/ C_1(x)$

$$\therefore Rate\ of\ change\ of\ momentum = \frac{change\ in\ momentum}{time\ taken}$$

$$Rate\ of\ change\ of\ momentum = \frac{-2mC_1(x)}{\dfrac{2L}{V_1(x)}} = \frac{-mC_1^2(x)}{L}$$

$$Force\ exerted\ on\ the\ molecule = \frac{-mC_1^2(x)}{L}$$

According to Newton's third law of motion, the force exerted by the molecule =
$$= -\frac{-mC_1^2(x)}{L} = \frac{mC_1^2(x)}{L}$$

Force exerted by all the *n* molecules is
$$F_x = \frac{mC_1^2(x)}{L} + \frac{mC_2^2(x)}{L} + \frac{mC_3^2(x)}{L} + \cdots + \frac{mC_n^2(x)}{L}$$

Pressure exerted by the molecules
$$P_x = \frac{F_x}{A}$$

$$P_x = \frac{1}{L^2}\left(\frac{mC_1^2(x)}{L} + \frac{mC_2^2(x)}{L} + \frac{mC_3^2(x)}{L} + \cdots + \frac{mC_n^2(x)}{L}\right)$$

$$P_x = \frac{m}{L^3}\left(C_1^2(x) + C_2^2(x) + C_3^2(x) + \cdots + C_n^2(x)\right)$$

Similarly, pressure exerted by the molecules along Y and Z axes are

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$$P_y = \frac{m}{L^3}\left(C_1^2(y) + C_2^2(y) + C_3^2(y) + \cdots + C_n^2(y)\right)$$

$$P_z = \frac{m}{L^3}\left(C_1^2(z) + C_2^2(z) + C_3^2(z) + \cdots + C_n^2(z)\right)$$

Since the gas exerts the same pressure on all the walls of the container
$$P_x = P_y = P_z$$

$$P = \frac{P_x + P_y + P_z}{3}$$

$$P = \frac{1}{3}\frac{m}{L^3}\big[\left(C_1^2(x) + C_2^2(x) + C_3^2(x) + \cdots + C_n^2(x)\right) \\ + \left(C_1^2(y) + C_2^2(y) + C_3^2(y) + \cdots + C_n^2(y)\right) \\ + \left(C_1^2(z) + C_2^2(z) + C_3^2(z) + \cdots + C_n^2(z)\right)\big]$$

$$P = \frac{1}{3}\frac{m}{L^3}\big[\left(C_1^2(x) + C_1^2(y) + C_1^2(z)\right) + \left(C_2^2(x) + C_2^2(y) + C_2^2(z)\right) + \cdots \\ + \left(C_n^2(x) + C_n^2(y) + C_n^2(z)\right)\big]$$

$$P = \frac{m}{3V}\left[C_1^2 + C_2^2 + \ldots + C_n^2\right]$$

$$P = \frac{mn}{3V}\left[\frac{C_1^2 + C_2^2 + \ldots + C_n^2}{n}\right]$$

$$P = \frac{mn}{3V} < C^2 >$$

Here V is volume of gas
Where $< C^2 >$ is called the root mean square (RMS) velocity, which is defined as the square root of the mean value of the squares of velocities of individual molecules.
Since mn = mass of gas and density ρ = mass/volume

$$P = \frac{\rho}{3} < C^2 >$$

Relation between the pressure exerted by a gas and the mean kinetic energy of translation per unit volume of the gas

Mean kinetic energy of translation per unit volume of the gas

$$E = \frac{1}{2}\rho < C^2 >$$

Thus

$$\frac{P}{E} = \frac{\frac{\rho}{3} < C^2 >}{\frac{1}{2}\rho < C^2 >} = \frac{2}{3}$$

Or P = (2/3)E

Average kinetic energy per molecule of the gas

Let us consider one mole of gas of mass M and volume V.

$$P = \frac{\rho}{3} < C^2 >$$

$$P = \frac{M}{3V} < C^2 >$$

$$PV = \frac{M}{3} < C^2 >$$

From ideal gas equation for one mole of gas

PV = RT

$$\frac{M}{3} < C^2 > = RT$$

$$M < C^2 > = 3RT$$

$$\frac{1}{2}M < C^2 > = \frac{3}{2}RT$$

Average kinetic energy of one mole of the gas is equal to = (3/2) RT

Since one mole of the gas contains N_A number of atoms where N_A is the Avogadro number we have $M = N_A m$

$$\frac{1}{2}N_A m < C^2 > = \frac{3}{2}RT$$

$$\frac{1}{2}m < C^2 > = \frac{3}{2}\frac{R}{N_A}T$$

$$\frac{1}{2}m < C^2 > = \frac{3}{2}k_B T$$

k_B is Boltzmann constant
Average kinetic energy per molecule of the gas is equal to (3/2) k_BT

Hence, it is clear that the temperature of a gas is the measure of the mean translational kinetic energy per molecule of the gas

Degrees of freedom
The number of degrees of freedom of a dynamical system is defined as the total number of co-ordinates or independent variables required to describe the position and configuration of the system.

(i) A particle moving in a straight line along any one of the axes has one degree of freedom (e.g) Bob of an oscillating simple pendulum.
(ii) A particle moving in a plane (X and Y axes) has two degrees of freedom. (eg) An ant that moves on a floor.
(iii) A particle moving in space (X, Y and Z axes) has three degrees of freedom. (eg) a bird that flies.
A point mass cannot undergo rotation, but only translatory motion. Three degree of freedom
A rigid body with finite mass has both rotatory and translatory motion.
The rotatory motion also can have three co-ordinates in space, like translatory motion ; Therefore a rigid body will have six degrees of freedom ; three due to translatory motion and three due to rotator motion.

Monoatomic molecule
Since a monoatomic molecule consists of only a single atom of point mass it has three degrees of freedom of translatory motion along the three co-ordinate axes
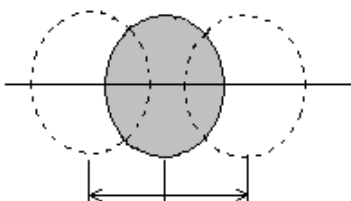Examples : molecules of rare gases like helium, argon, etc.

Diatomic molecule rigid rotator
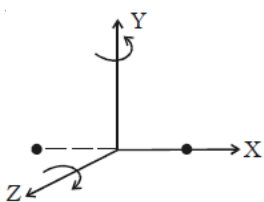
The diatomic molecule can rotate about any axis at right angles to its own axis. Hence it
has two degrees of freedom of rotational motion in addition to three degrees of freedom of translational motion along the three axes. So, a diatomic molecule has five degrees of freedom (Fig.). Examples : molecules of O_2, N_2, Cl_2, etc

Diatomic molecule like CO : Have five freedom as stated in rigid rotator apart from that

they have two more freedoms due to vibration (oscillation) about mean position
Plyatomic molecules posses rotational kinetic energy energy of vibration in addition to their translational energy.
Therefore when heat energy is given to such gases, it is utilized in increasing the translational kinetic energy, rotational kinetic energy and vibrational kinetic energy of the

gas molecules and hence more heat is required. This way polyatomic molecules posses more specific heat

Law of equipartition of energy

Law of equipartition of energy states that for a dynamical system in thermal equilibrium the total energy of the system is shared equally by all the degrees of freedom. The energy associated with each degree of freedom per moelcule is (1/2)kT
where k is the Boltzmann's constant.
Let us consider one mole of a monoatomic gas in thermal equilibrium at temperature T. Each molecule has 3 degrees of freedom due to translatory motion.
According to kinetic theory of gases, the mean kinetic energy of a molecule is (3/2)kT
Let Cx, Cy and Cz be the components of RMS velocity of a molecule along the three axes.
Then the average energy of a gas molecule is given by

$$\frac{1}{2}mC^2 = \frac{1}{2}mC_x^2 + \frac{1}{2}mC_y^2 + \frac{1}{2}mC_z^2$$
$$\frac{1}{2}mC_x^2 + \frac{1}{2}mC_y^2 + \frac{1}{2}mC_z^2 = \frac{3}{2}kT$$

Since molecules move at random, the average kinetic energy corresponding to each degree of freedom is the same.

$$\frac{1}{2}mC_x^2 = \frac{1}{2}mC_y^2 = \frac{1}{2}mC_z^2 = \frac{1}{2}kT$$

∴ Mean kinetic energy per molecule per degree of freedom is (1/2) kT

Mean free path

"The linear distance travelled by a molecule of gas with constant speed between two consecutive collisions (between molecules) is called free path. The average of such free paths travelled by a molecule is called mean free path"
Suppose molecules of gas are spheres of diameter d. If the centre between the two molecules is less or equal to d then they will collide when they come close.
Consider a molecule of diameter d moving with average speed v, and the other molecule is stationary. The molecule under consideration will sweep a cylinder of πd²vt. In time t.
If the number of molecules per unit volume is n, then the number of molecules in this cylinder is nπd²vt. Hence the molecule will under go nπd²vt collisions in time t
The mean free path l is the average distance between two successive collision

$$Mean\ free\ path = \frac{distance\ travelled\ in\ time\ t}{number\ of\ collisions\ in\ time\ t}$$
$$l = \frac{vt}{2\pi d^2 vt}$$
$$l = \frac{1}{2\pi n d^2}$$

In this derivation other molecules are considered stationary. In actual practice all gas molecules are moving and there collision rate is determined by the average relative velocity < V > Hence mean free path formula is $l = \frac{1}{\sqrt{2}\pi n d^2}$

Solved Numerical

Q) Find the mean translational kinetic energy of a molecules of He at 27°

Solution: Since He is mono atomic degree of freedom is 3

Kinetic energy $=(3/2)k_BT$

Here k_B = Boltzmann's constant = 1.38×10^{-23} J K^{-1} Temperature T = 27+273 = 300 K

$$K = \frac{3}{2} \times 1.38 \times 10^{-23} \times 300 = 6.21 \times 10^{-21} J$$

Q) At what temperature rms velocity of O_2 is equal to rms velocity of H_2 ay 27^OC?

Solution

Kinetic energy

$$\frac{1}{2}m < C^2 > = \frac{3}{2}k_BT$$

$$< C^2 > = \frac{3k_BT}{m}$$

But rms velocity of O_2 rms velocity of He

$$\frac{3k_BT}{32} = \frac{3k_B \times 300}{4}$$

$$T = 2400\ K$$

Q) Find rms velocity of hydrogen at 0^OC temperature and 1 atm pressure. Density of hydrogen gas is 8.9×10^{-2} kg m^{-3}

Solution:

From formula

$$P = \frac{\rho}{3} < C^2 >$$

$$< C > = \sqrt{\frac{3P}{\rho}}$$

$$< C > = \sqrt{\frac{3 \times 1.01 \times 10^5}{8.9 \times 10^{-2}}} = 1845\ ms^{-1}$$

Q) If the molecular radius of hydrogen molecule is 0.5Å, find the mean free path of hydrogen molecule at 0^OC temperature and 1 atm pressure

Solution

d = 2×r = 1 Å

From formula P = nK_BT

$$n = \frac{P}{k_BT}$$

$$n = \frac{1.01 \times 10^5}{1.38 \times 10^{-23} \times 273} = 2.68 \times 10^{25}$$

From formula for mean path $l = \frac{1}{\sqrt{2} \times 3.14 \times 2.68 \times 10^{25} \times (1 \times 10^{-10})^2} = 8.4 \times 10^{-7} \, m$

SECTION II
Thermodynamics

Some important terms

Thermodynamic system : It is apart of the universe under thermodynamic study. A system can be one, two or three dimensional. May consists of single or many objects or radiation

Environment : remaining part of universe around the thermodynamic system is Environment. Environment have direct impact on the behavior of the system

Wall: The boundary separating the Stem from the universe is wall

Thermodynamic co-ordinates: The macroscopic quantities having direct effect on the internal state of the system are called thermodynamic coordinates. For example
Take the simple example of a sample of gas with a fixed number of molecules. It need not be ideal. Its temperature, *T*, can be expressed as a function of just two variables, volume, *V*, and pressure, *p*. We can, it turns out, express all gas properties as functions of just two variables (such as *p* and *V* or *p* and *T*). These properties include refractive index, viscosity, internal energy, entropy, enthalpy, the Helmholtz function, the Gibbs function. We call these properties 'functions of state'. The state is determined by the values of just two variables

Thermodynamic system: The system represented by the thermodynamic co-ordinate is called a thermodynamic system

Thermodynamic process: The interaction between a system and its environment is called a thermodynamic process

Isolated system: If a system does not interact with its surrounding then it is called an isolated system. Thermal and mechanical properties of such system is said to be ina definite thermodynamic equilibrium state
Heat (Q) and Work(W): The amount of heat energy exchanged during the interaction of system with environment is called heat (Q) and the mechanical energy exchanged is called work (W).

Thermodynamic variables: Thermodynamic variables describe the momentary condition of a thermodynamic system. Regardless of the path by which a system goes from one state to another — i.e., the sequence of intermediate states — the total changes in any state variable will be the same. This means that the incremental changes in such variables are exact differentials. Examples of state variables include: Density (ρ), Energy (E), Gibbs free energy (G), Enthalpy (H) , Internal energy (U), Mass (m) , Pressure (p) ,Entropy (S) Temperature (T), Volume (V)

Extensive thermodynamic state variable: The variables depending on the dimensions of the system are called extensive variables. For examples mass, volume, internal energy

Intensive thermodynamic state variable: The variables independent on the dimensions of the system are called intensive variables. For examples pressure, temperature, density

Thermal equilibrium: When two system having different temperatures are brought in thermal contact with each other, the heat flows from the system at higher temperature to that at lower temperature. When both the system attains equal temperatures, the net heat exchanged between them becomes zero. In this state they are said to be in thermal equilibrium state with each other.

Zeroth Law of thermodynamics: "If the system A and B are in the thermal equilibrium with a third system C, then A and B are also in thermal equilibrium with each other"

Temperature may be defined as the particular property which determines whether a system is in thermal equilibrium or not with its neighbouring system when they are brought into contact
adiabatic wall – an insulating wall (can be movable) that does not allow flow of energy (heat) from one to another**.**
diathermic wall – a conducting wall that allows energy flow (heat) from one to another

Specific heat capacity
Specific heat capacity of a substance is defined as the quantity of heat required to raise the temperature of 1 kg of the substance through 1K. Its unit is J kg^{-1}K^{-1}.

Molar specific heat capacity of a gas
Molar specific heat capacity of a gas is defined as the quantity of heat required to raise the temperature of 1 mole of the gas through 1K. Its unit is J mol^{-1} K^{-1}.
Let *m* be the mass of a gas and *C* its specific heat capacity. Then $\Delta Q = m \times C \times \Delta T$ where ΔQ is the amount of heat absorbed and ΔT is the corresponding rise in temperature.
Case (i)

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If the gas is insulated from its surroundings and is suddenly compressed, it will be heated up and there is rise in temperature, even though no heat is supplied from outside
(i.e) ΔQ = *0* ∴ *C = 0*

Case (ii)
If the gas is allowed to expand slowly, in order to keep the temperature constant, an amount of heat Δ*Q* is supplied from outside, then

$$C = \frac{\Delta Q}{m\Delta T} = \frac{\Delta Q}{0} = +\infty$$

(∵ ΔQ is +ve as heat is supplied from outside)

Case (iii)
If the gas is compressed gradually and the heat generated Δ*Q* is conducted away so that temperature remains constant, then

$$C = \frac{-\Delta Q}{m\Delta T} = \frac{-\Delta Q}{0} = +\infty$$

(∵ ΔQ is -ve as heat is supplied by the system)

Thus we find that if the external conditions are not controlled, the value of the specific heat capacity of a gas may vary from +∞ to -∞

Hence, *in order to find the value of specific heat capacity of a gas, either the pressure or the volume of the gas should be kept constant.* Consequently a gas has two specific heat capacities

(i)   Specific heat capacity at constant volume
(ii)   Specific heat capacity at constant pressure.

Molar specific heat capacity of a gas at constant volume
Molar specific heat capacity of a gas at constant volume C_V is defined as the quantity of heat required to raise the temperature of one mole of a gas through 1 K, keeping its volume constant

Molar specific heat capacity of a gas at constant pressure
Molar specific heat capacity of a gas at constant pressure C_p is defined as the quantity of heat to raise the temperature of one mole of a gas through 1 K keeping its pressure constant

Specific heat of gas from the law of equipartition of energy
The energy associated with each degree of freedom is $(1/2)K_BT$. It means that, if the degree of freedom of a gas molecule is f then the average heat energy of each molecule of gas is

$$E_{ave} = f \times \frac{1}{2}k_BT$$

If number of moles of an ideal gas is μ , then the number of moles in the gas is μN_A.
Therefore the **internal energy** of μ mole of ideal gas is

U = μN_A $E_{average}$

$$U = \mu N_A f \times \frac{1}{2} k_B T$$

$$U = \frac{f}{2} \mu R T \quad (\because R = N_A k_B)$$

Work in thermodynamics

The amount of mechanical energy exchanged between two bodies during mechanical interaction is called work. Thus work is a quantity related to mechanical interaction. A system can possess mechanical energy, but cannot posses work

In thermodynamics the work done by the system is considered positive and the work done on the system is considered negative.

The reason behind such sign convention is due to the mode of working of heat engine in which the engine absorbs heat from the environment and converts it into work W means the energy of the system is reduced by W

Formula for the work done during the compression of gas at constant temperature
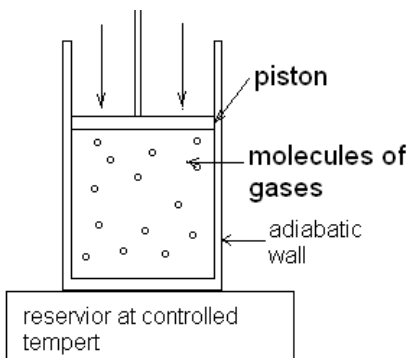
As shown in figure μ molecules of gas are enclosed in a cylindrical container at low pressure, and an air tight piston capable of moving without friction with area A is provide.. the conducting bottom of the cylinder is placed on an arrangement whose temperature can be contolled.
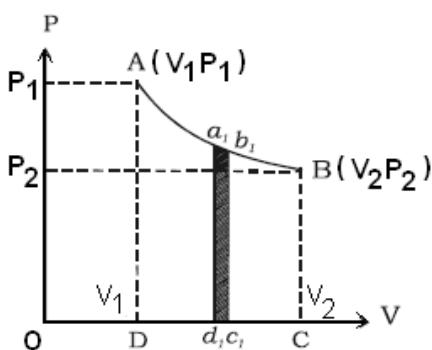
At constant temperature , measuring the volume of the gas for different values of pressure, the graph of P-V can be plotted as shown in figure. These types of process are called isothermal process and curved of P-V is called isotherm.

Suppose initial pressure and volume of the pas is represented by P_1 and V_1 respectively. Keeping the temperature T of the gas to be constant , volume of gas decreases slowly by pushing piston down. Let final pressure and volume of the gas be is P_2 and V_2

During the process, at one moment when pressure of the gas is P and volume V, at that time, let the piston moves inward by Δx. then the volume of the gas decreases by ΔV. this displacement is to small that there is no apparent change in pressure.

Hence work done on the gas

ΔW = FΔx

ΔW = PAΔx

ΔW = PΔV

If the volume of the gas is decreasing from V_1 to V_2 through such small changes, then the total work done on the gas

$$W = \sum_{V_1}^{V_2} P \, \triangle V$$

If this summation is taking the limit as ΔV → 0 the summation results in integration

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

But the ideal gas equation for μ moles of gas is PV=μRT thus

$$W = \int_{V_1}^{V_2} \frac{\mu RT}{V} dV$$

$$W = \mu RT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$W = \mu RT [\ln V]_{V_1}^{V_2}$$

$$W = \mu RT [V_2 - V_1]$$

$$W = \mu RT \ln \left(\frac{V_2}{V_1} \right)$$

$$W = 2.303 \mu RT \log_{10} \left(\frac{V_2}{V_1} \right)$$

Equation does not give the work W by an ideal gas during every thermodynamic process, but it gives the work done only for a process in which the temperature is held constant.

Since $V_2 < V_1$ hence log(V_2/V_1) is negative . Thus we get negative value of work which represents that **during the compression of gas at constant temperature, the work is done on the gas**

If the gas is expanded then Since $V_2 > V_1$ hence log(V_2/V_1) is positive . Thus we get negative value of work which represents that **during the compression of gas at constant temperature, the work is done by the gas**

The P-V, T-V and T-P diagram for isothermal process will be like the curves given below

ISOTHERMAL PROCESS
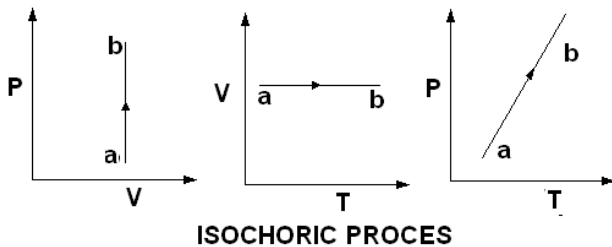
15
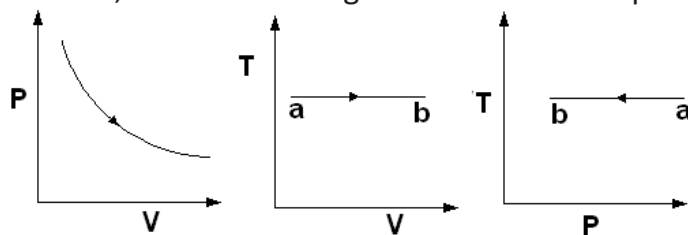
Work done at constant volume and constant pressure

Constant volume : Also called as isochoric process

If the volume is constant then dV = from equation

$$W = \int_{V_1}^{V_2} PdV$$

Work done is zero

The P-V, V-T and P-T diagrams for isochoric process will be like curves given below

ISOCHORIC PROCES

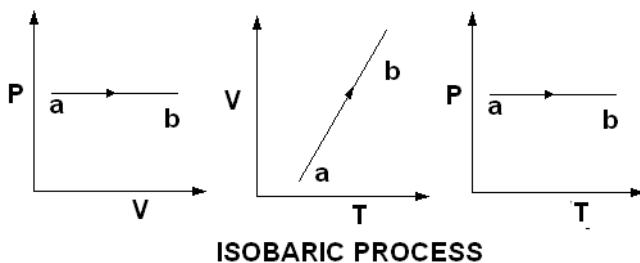**Constant pressure :Also called as Isobaric process**

If the volume is changing while pressure is constant then from equation

$$W = \int_{V_1}^{V_2} PdV = P \int_{V_1}^{V_2} PdV$$
$$W = P[V_2 - V_1]$$

W = PΔV (for constant pressure)

The P-V, V-T and P-T diagrams for isobaric process will be like curves given below

ISOBARIC PROCESS

Work done during adiabatic process

No excahge of heat takes palce between system and it environment in this process. This is possible when (1) walls of a system are thermal insulator or (2) process is very rapid.

The relation between pressure and volume for ideal gas is

$$PV^\gamma = constant$$

Where $\gamma = \frac{c_P}{c_V}$

For an adiabatic process

$$W = \int_{V_1}^{V_2} PdV$$

Let

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$$PV^{\gamma} = A$$

$$W = \int_{V_1}^{V_2} \frac{A}{V^{\gamma}} dV$$

$$W = A \int_{V_1}^{V_2} \frac{dV}{V^{\gamma}}$$

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

$$W = \frac{1}{1 - \gamma} \left[AV_2^{-\gamma+1} - AV_1^{-\gamma+1} \right]$$

But $A = P_2 V_2^{\gamma} = P_1 V_1^{\gamma}$

$$W = \frac{1}{1 - \gamma} \left[P_2 V_2^{\gamma} V_2^{-\gamma+1} - P_1 V_1^{\gamma} V_1^{-\gamma+1} \right]$$
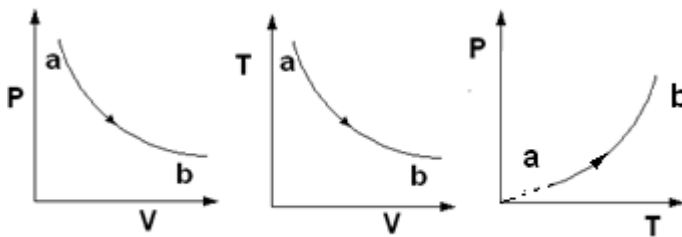
$$W = \frac{1}{1 - \gamma} [P_2 V_2 - P_1 V_1]$$

$$W = \frac{1}{\gamma - 1} [P_1 V_1 - P_2 V_2]$$

From ideal gas equation PV = μRT

$$W = \frac{\mu R}{\gamma - 1} [T_1 - T_2]$$

The P-V, T-V and P-T diagrams for adiabatic process will be lie the curves given below

ADIABATIC PROCESS

Solved Numerical

Q) Calculate work done if one mole of ideal gas is compressed isothermally at a temperature 27° C from volume of 5 litres to 1 litre

Solution:

Formula for work done during iso-thermal process is

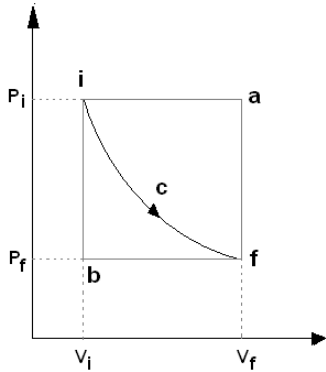$$W = 2.303 \mu RT \log_{10} \left(\frac{V_2}{V_1} \right)$$

$$W = 2.303 \times 1 \times 8.31 \times 300 \times log \left(\frac{1}{5} \right)$$

$$W = 2.303 \times 1 \times 8.31 \times 300 \times [log1 - log5]$$
$$W = 2.303 \times 1 \times 8.31 \times 300 \times [0 - 0.6990]$$

W = -4012.5J

First law of thermodynamics

Suppose a sytem absorbs heat and as a result work is done by it (by the system). We can think of different paths (process) through which the system can be taken from initial stage (i) to final state (f)

For the process iaf, ibf, icf. Suppose the heat absorbed by the system are Q_a, Q_b, Q_c respectively and the values of the work done are respectively W_a, W_b, W_c. Here

$Q_a \neq Q_b \neq Q_c$ and $W_a \neq W_b \neq W_c$, but difference of heat and work done turns out to be same

$Q_a - W_a = Q_b - W_b = Q_c - W_c$

Thus value of Q – W depends only on initial and final state of the system. A thermodynamic state function can be defined such that the difference between any two states is equal to Q – W. Such a function is called internal energy U of system

The system gains energy Q in the form of heat energy and spends energy W to do work. Hence the internal energy of the system changes by Q-W.

If the internal energies of system in initial state is U_i and final state is U_f then

$U_i - U_f = \Delta U = Q - W$ Which is the first law of thermodynamics

The first law is obeyed in all the changes occurring in nature

Isochoric process

Since in this process volume remains constant, the work done in this process is equal to zero. Applying first law of thermodynamics to this process, we get

ΔQ = ΔU + ΔW

ΔQ = ΔW

So heat exchange in this process takes place at the expense of the internal energy of the system.

dQ = dU

$$\left(\frac{dQ}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V$$
$$since \ U = \frac{f}{2}RT$$

$$\left(\frac{dQ}{dT}\right)_V = \frac{f}{2}R$$

Thus above equation is for the energy required to increase temperature by one unit of one of ideal gas it is molar specific heat at constant volume C_V

$$\left(\frac{dQ}{dT}\right)_V = \frac{f}{2}R = C_V$$

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Isobaric process

Applying first law of thermodynamics to isobaric process we get

$$\Delta Q = \Delta U + P(V_2 - V_1)$$

$$\Delta Q = \Delta U + P\Delta V$$

But $PV = RT$ for one mole of gas

$$\therefore P\Delta V = R\Delta T \text{ thus}$$

$$\therefore \Delta Q = \Delta U + R\Delta T$$

$$since \ U = \frac{f}{2}RT$$

$$\therefore \left(\frac{dQ}{dT}\right)_P = \frac{f}{2}R\frac{dT}{dT} + R\frac{dT}{dT}$$

$$\therefore \left(\frac{dQ}{dT}\right)_P = \frac{f}{2}R + R$$

Since dQ/dT is specific heat at constant pressure = C_P

$$\therefore C_P = C_V + R$$

$$OR \ C_P - C_V = R$$

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{f}{2}R + R}{\frac{f}{2}R}$$

$$\gamma = 1 + \frac{2}{f}$$

f is degree of freedom

For monoatomic molecule f = 3

$$C_V = \frac{3R}{2}, \ \ C_P = \frac{5R}{2}, \gamma = \frac{5}{3}$$

For the diatomic molecules (rigid rotator) f = 5

$$C_V = \frac{5R}{2}, \ \ C_P = \frac{7R}{2}, \gamma = \frac{7}{5}$$

For the diatomic molecules (with vibration , molecule like CO) f = 7

$$C_V = \frac{7R}{2}, \ \ C_P = \frac{9R}{2}, \gamma = \frac{9}{7}$$

According to the equipartion theorem the change in internal energy is related to the temperature of the system by

$$\Delta U = mC_V\Delta T$$

Isothermal process

For isothermal process $\Delta U = 0$.

Applying first law of thermodynamics we get

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ΔQ = W

$$\Delta Q = W = 2.303 \mu RT \log_{10}\left(\frac{V_2}{V_1}\right)$$

Adiabatic process
Applying first law of thermodynamics we get
ΔQ = ΔU + ΔW
For adiabatic process ΔQ = 0

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

The reduction in internal energy of the gas (due to which temperature fails) is equal to the work done during an adiabatic expansion. Again during an adiabatic compression the work done on the gas causes its temperature rise. Adiabatic processes are generally very fast.
Example when we use air pump to fill air in bicycle tyre, pump get heated on pumping rapidly

Solved Numerical

Q) At 27°C, two moles of an ideal momoatomic gas occupy a volume V. The gas expands adiabatically to a volume 2V. Calculate (a) final temperature of the gas (b) Change in its internal energy (c) Work done by the gas during the process
Take R = 8.31 J/mole/K
Solution:
For monoatomic gas γ = 5/3.
T = 27+273 =300
(a) Gas expanded adiabatically

$$P_2 V_2^{\gamma} = P_1 V_1^{\gamma}$$

Since PV∝T
P∝ T/V
Thus

$$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$$
$$\therefore T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$
$$\therefore T_2 = 300 \left(\frac{1}{2}\right)^{5/3-1} = 189K$$

(b) For adiabatic process ΔQ = 0

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

$$W = -\Delta U = \frac{\mu R}{\gamma - 1}[T_1 - T_2]$$
$$-\Delta U = \frac{2 \times 8.31}{\frac{5}{3} - 1}[300 - 189] = 2767.23 \, J$$

ΔU = -2767.23 J

(c) $\Delta W = -\Delta U$

$\Delta W = 2767.23$ J

Isothermal and adiabatic curves

The relation between the pressure and volume of gas can be represented graphically. The curve for an isothermal process is called isothermal curve or an isotherm and there are different isotherms for different temperatures for a given gas. A similar curve for an adiabatic process is called an adiabatic curve or adiabatic

Since
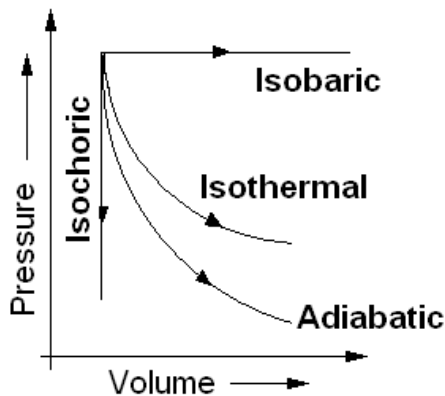
$$\left(\frac{dP}{dV}\right)_{isothermal} = -\frac{P}{V}$$

And

$$\left(\frac{dP}{dV}\right)_{adiabatic} = -\gamma \frac{P}{V}$$

So

$$\left(\frac{dP}{dV}\right)_{adiabatic} = \gamma \left(\frac{dP}{dV}\right)_{isothermal}$$

Since γ > 1, so adiabatic curve is steeper-than the isothermal curve

To permit comparison between isothermal ,adiabatic process, Isochoric and isobaric process an isothermal curve ,an adiabatic curve isochoric and Isobaric curves of gas are drawn on the same pressure-volume diagram starting from the same point.

Solved Numerical

Q)When a system is taken from state a to state b along the path acb it is found that a quantity of heat Q = 200J is absorbed by the system and a work W = 80J is done by it. Along the path adb, Q = 144J
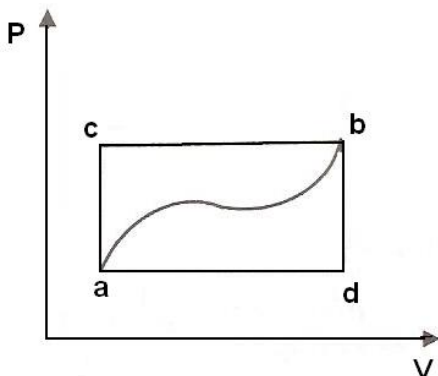
(i)What is the work done along the path adb

(ii)IF the work done on the system along the curvered path ba is 52J, does the system absorb or linerate heat and how much

(iii)If U_a = 40J, what is U_b

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(iv)If U_d = 88J, what is Q for the path db and ad?

Solution
From the first law of thermodynamics, we have
Q = ΔU + ΔW
Q = (U_b − U_a) + W
Where U_b is the internal energy in the state b and U is the internal energy in the stste $_a$
For the path acb, it is given that
Q = 200J (absorption) and
Q = 80J (work done by the system)
∴ U_b − U_a = = Q −W = 200-80 = 120J

Which is the increase in the internal energy of the system for path acb. Whatever be the path between a and b the change in the internal energy will be 120 J only

(i)   To determine the work done along the path adb
        Given Q = 144J
ΔU = U_b − U_a = 120J
Q = (U_b − U_a) + W
 144 = 120 + W
W = 24J
Since W is positive, work is done by the system

(ii)   For the curved return path ba, it is given that
         Given W=-52J (work done on the system)
ΔU = -120 J (negative sign since ΔU = U_a − U_b)
Q = (U_a − U_b) + W
Q = (-120 − 52) J = -172 J
Negative sign indicates heat is extracted out of the system

(iii)   Since U_b − U_a = 120 J and U_a = 40 j
          U_b = U_a +120 = 40 +120 = 160J

(iv)   For path db, the process is isochoric since it is at constant volume
          Work done is zero
          Q = ΔU + W
          Q = ΔU
          Q = U_b − U_d = 160 - 88 = 72 J
          For the path ad,
          Q = Q_{adb} − Q_{db} = 144J - 72 J = 72J

Q) A mass of 8 g of oxygen at the pressure of one atmosphere and at temperature 27°C is enclosed in a cylinder fitted with a frictionless piston. The following operations are performed in the order given

(a) The gas is heated at constant pressure to 127°C

(b) then it is compressed isothermally to its initial volume and

(c) finally it is cooled to its initial temperature at constant volume

(i) What is the heat absorbed by the gas during process (A)?

(ii) How much work is done by the gas in process A

(iii)What is the work done on the gas in process B

(iv)How much heat is extracted from the gas in process (c)

[Specific heat capacity of oxygen C_V = 670 J/KgK;]

Solution:

Volume of gas at temperature 27+273 = 300K = T_2

Molecular weight of Oxygen = 32 thus 8g = 0.2 mole

At STP volume of 1 mole is 22.4 litre Thus volume of 0.25 mole is V_1 = 22.4/4

Thus for formula volume at 27°C is

$$\frac{V_2}{T_2} = \frac{V_1}{T_1}$$

$$V_2 = \frac{T_2}{T_1}V_1$$

$$V_2 = \frac{300}{273} \times \frac{22.4}{4} = \frac{560}{91} \times 10^{-3}\, m^3$$

Similarly

Volume at 127°C is

$$V_3 = V_2 \times \frac{400}{300} = \frac{4}{3}V_2$$

$$\frac{V_3}{V_2} = \frac{4}{3}$$

(i)

For Isothermal compression

dQ = dU + dW = $mC_v\Delta T + P(V_3 - V_2)$

$$dQ = \frac{8}{1000} \times 670 \times 100 + 1.013 \times 10^5 \times \left[\frac{560 \times 10^{-3}}{3 \times 91}\right]$$

dQ = 536 + 207.8 = 743.8 J

(ii)   dW = P($V_3 - V_2$) = 207.8 J

(iii)   Work done in compressing the gas isothermally =

$$W = 2.303\mu RT \log_{10}\left(\frac{V_3}{V_2}\right)$$

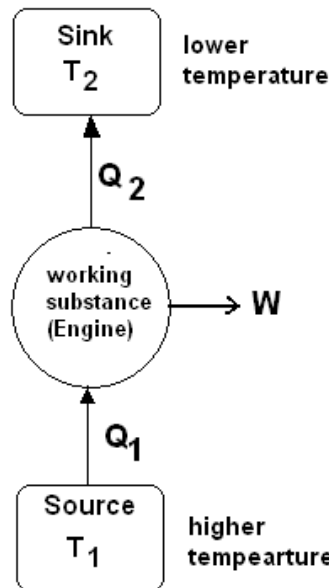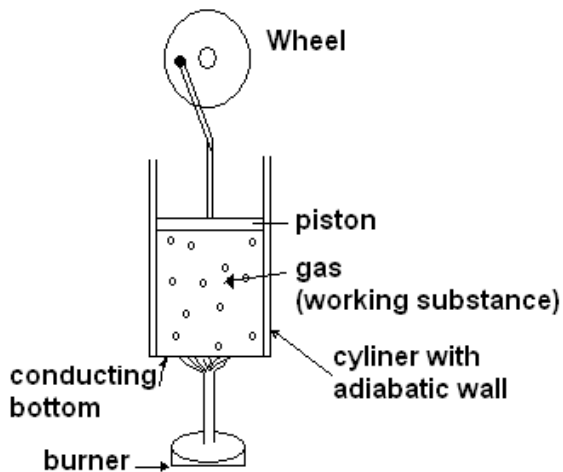$$W = 2.303 \times \frac{m}{M} RT \log_{10}\left(\frac{V_3}{V_2}\right)$$

$$W = 2.303 \times \frac{8}{32} \times 8.31 \times 400 \times \log_{10}\left(\frac{4}{3}\right)$$

$$W = 831 \times 0.2877 = 239.1 \, J$$

(d) Heat given out by the gas in stage (C) = $mC_V \Delta T$

$$\frac{8}{1000} \times 670 \times 100 = 536 \, J$$

Heat Engine

A device converting heat energy into   mechanical work is called heat engines.

A simple heat engine is shown in figure. The gas enclosed in a cylinder with a piston receives heat from the flame of a burner. On absorbing heat energy the gas expands and pushes the piston upwards. So the wheel starts rotating. To continue the rotations of the wheel an arrangement is done in the heat engine so that the piston can move up and down periodically. For this, when piston moves more in upward direction, then hot gas is released from the hole provided on upper side

Here gas is called working substance. The flame of the burner is called heat source and the arrangement in which gas is released is called heat sink.

Following figure shows working of the heat engines by line diagram

In the heat engine, the working substance undergoes a cyclic process. For this the working substance absorbs heat Q_1, from the heat source at higher temperature T, out of which a

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part of energy is converted to mechanical energy (work W) and remaining heat Q_2 is released into the heat sink.

Hence , the net amount of heat absorbed by the working substance is

$Q = Q_1 - Q_2$

But for a cyclic process, the net heat absorbed by the system is equal to the net work done

$\therefore Q = W$

$Q_1 - Q_2 = W$

In the cyclic process, the ratio of the network (W) obtained during one cycle is called the efficiency (η) of the heat engine. That is

$$\eta = \frac{Net\ work\ obtaine\ per\ cycle}{Heat\ absorbed\ per\ cycle}$$

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

$$\eta = 1 - \frac{Q_2}{Q_1}\ \ - - - eq(1)$$

From equation(1) it can be said that if Q_2 = 0, then the efficiency of the heat engine is η = 1. This means that the efficiency of heat engine becomes 100% and total heat supplied to the working substance gets completely converted into work.

In practice, for any engine $Q_2 \neq 0$ means that some heat Q_2 is always wasted hence η<1

Cyclic process and efficiency calculation
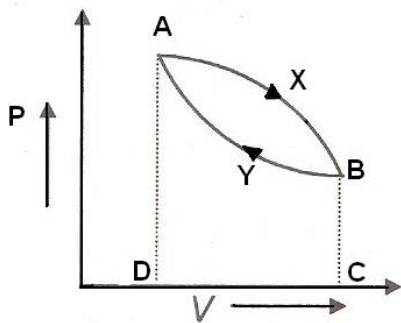
When a system after passing through various intermediate steps returns to its original state, then it is called a cyclic process.

Suppose a gas enclosed in cylinder is expanded from initial stage A to final stage B along path AXB as shown in figure If W_1 be the work done by the system during expansion, then

W_1 = + Area AXBCDA

Now late the gas be compressed from state B to state along the path BYA, so as to return the system to the initial state. If W_2 be the work done on the system during compression, then W_2 = -Area BYADCB

According to sign convention, work done on the system during compression is negative and the net work done in the cyclic process AXBYA is

W = Area AXBCDA – Area BRADCB = Area AXBYA

Which is a positive quantity and hence net work will be done by the system

So the net amount of work done during a cyclic process is equal to the area enclosed by the cyclic path. It is evident from the figure that if the cyclic path is being traced in anticlockwise direction, the expansion curve will be below the compression curve and net

work done during the process will be negative. This implies that the net work will now be done on the system. Applying first law of thermodynamics to cyclic process, we get

ΔQ = ΔU + ΔW

But ΔU = for cyclic process

So ΔQ = ΔW

Solved Numerical

Q) An ideal monoatomic gas is taken round the cycle ABCD where co-ordinates of ABCDP_V diagram are A(p, V), B(2p, V), C(2p, 2V) and D(p, 2V). Calculate work done during the cycle

Solution Area enclosed = pV

Carnot Cycle and Carnot Engine

Carnot engine consists of a cylinder whose sides are perfect insulators of heat except the bottom and a piston sliding without friction. The working substance in the engine is μ mole of a gas at low enough pressure (behaving as an ideal gas). During each cycle of the engine, the working substance absorbs energy as heat from a heat source at constant temperature T_1 and releases energy as heat to a heat sink at a constant lower temperature $T_2 < T_1$.

The cyclic process, shown by P-V graph in figure a, is completed in four stages.
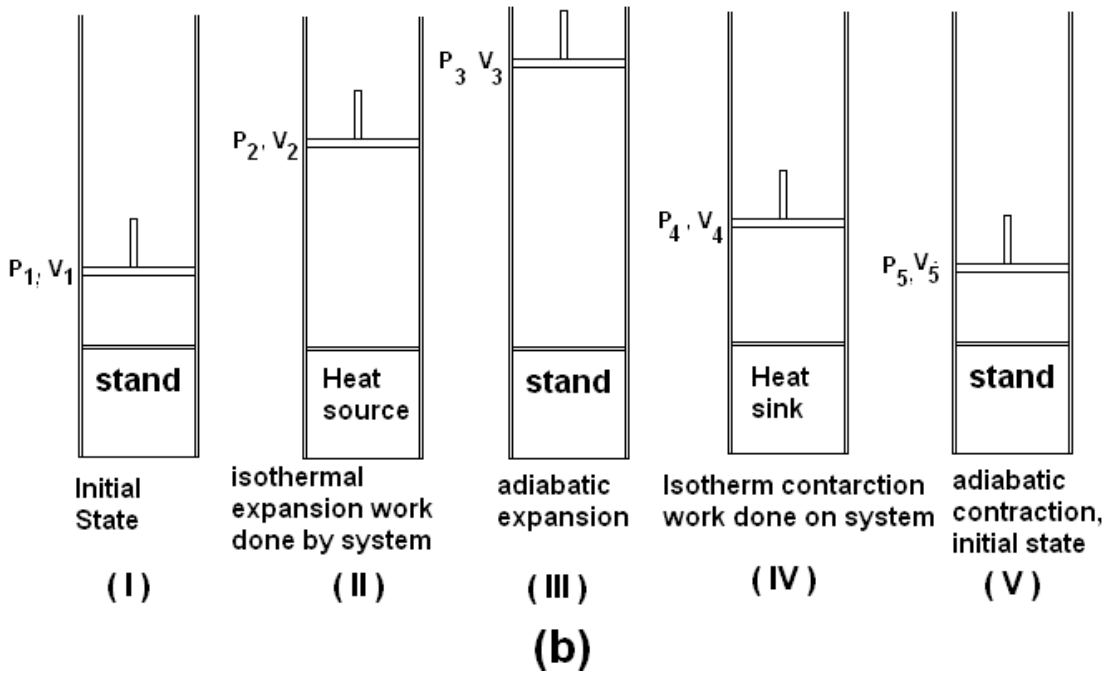

(a)
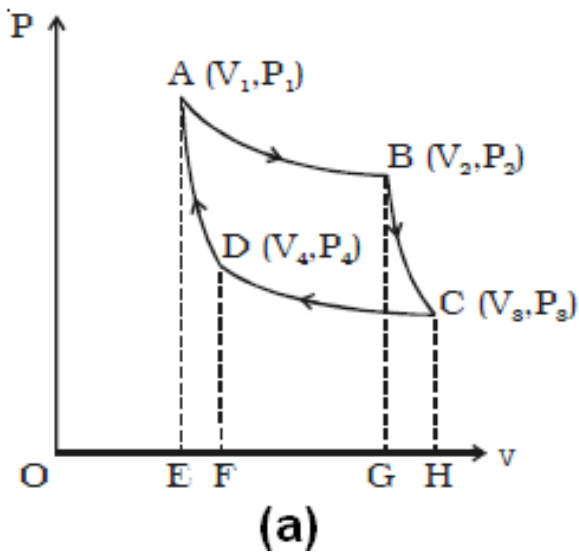
The Carnot engine and its different stages are shown in figure b

(I)   First stage Isothermal expansion of gas from (a → b)

Initial equilibrium state (P_1, V_1, T_1)final equilibrium state (P_2, V_2, T_1) Suppose gas absorbs heat Q_1 during the process. Hence work done is

$$W_1 = Q_1 = \mu RT_1 \ln\left(\frac{V_2}{V_1}\right) \quad - - - \text{eq(1)}$$

Further $P_1V_1 = P_2V_2$ ---- eq(2)

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(b)

(II)   Second stage Adiabatic expansion of gas (b → c)

Now , the cylinder is placed on a thermally insulated stand and the gas is adiabatically expanded to attain the state c (P_3, V_3, T_2).

During this (adiabatic process the gas does not absorb any heat but does work while expanding, so its temperature decreases. For this process

$$P_2 V_2^\gamma = P_3 V_3^\gamma \quad --- eq(3)$$

(III)   Third Stage: Isothermal compression of gas (c→d)

Now, the cylinder is brought in contact with heat sink at temperature T_2 and isothermally compressed slowly to attain an equilibrium state d (P_4, V_4, T_2). Work done on the gas during this process of isothermal compression is negative as work is done on the gas from state c → d is

$$W_2 = Q_2 = -\mu RT_2 \ln\left(\frac{V_4}{V_1}\right)$$

$$W_2 = Q_2 = \mu RT_2 \ln\left(\frac{V_3}{V_4}\right) \quad --- eq(4)$$

Here Q_2 is released by the gas into heat sink

Further for isothermal process

$$P_3 V_3 = P_4 V_4 \quad ---- eq(5)$$

(IV)   Fourth Stage: Adiabatic compression of gas (d →a)

Now, the cylinder is placed on a thermally insulated stand and compressed adiabatically to its original state a ($P_1 V_1 T_1$). This process is adiabatic, therefore, there're is exchange of heat with surrounding, but the work is done on the gas and hence temperature increases from T_2 to T_1

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For this adiabatic process

$$P_4 V_4^{\gamma} = P_1 V_1^{\gamma} \quad --- eq(6)$$

Note that over the whole cycle, the heat absorbed by the gas is Q_1 and the heat given out by the gas is Q_2. Hence the efficiency η of the Carnot engine is

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

From equation (1) and (4)

$$\eta = 1 - \frac{T_2 \ln\left(\frac{V_3}{V_4}\right)}{T_1 \ln\left(\frac{V_1}{V_4}\right)} \quad --- eq(7)$$

Multiplying equation (2), (3), (5) and 6 we get

$$P_1 V_1 P_2 V_2^{\gamma} P_3 V_3 P_4 V_4^{\gamma} = P_2 V_2 P_3 V_3^{\gamma} P_4 V_4 P_1 V_1^{\gamma}$$

$$\therefore (V_2 V_4)^{\gamma-1} = (V_3 V_1)^{\gamma-1}$$

$$\therefore V_2 V_4 = V_3 V_1$$

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$\therefore \ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{V_3}{V_4}\right)$$

Using this result in equation (7) We get efficiency of Carnot engine as

$$\eta = 1 - \frac{T_2}{T_1} \quad --- eq(8)$$

Or

$$\eta = 1 - \frac{low\ temp\ of\ sink}{high\ temperature\ of\ source}$$

Equation (8) shows that the efficiency of the Carnot engine depends only on the temperature of the source and the sink. Its efficiency does not depends on the working substance (if it is ideal gas).
If the temperature of the source (T_1) is infinite or the temperature of the sink (T_2) is absolute zero 9 which is not possible) then only, the efficiency of Carnot engine will be 100%, which is impossible.

Refrigerator / Heat pump and Coefficient of Performance

If the cyclic process performed on the working substance in heat engine is reversed, then the system woks as a refrigerator or heat pump. Figure below shows the block diagram of refrigerator/ heat pump
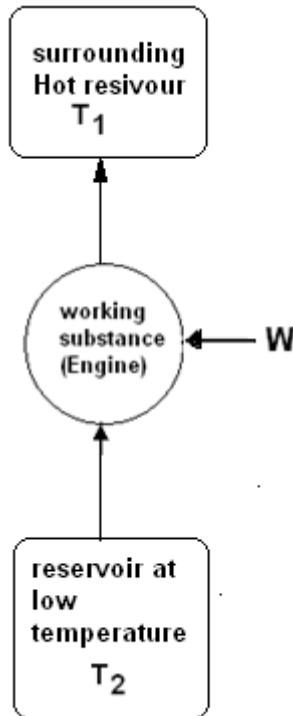
In the refrigerator, the working substance absorbs heat Q_2 from the cold reservoir at lower temperature T_2, external work W, is performed on the working substance and the working substance releases heat Q_1 into the hot reservoir at higher temperature T_1
The ratio of the heat Q_1 absorbed by the working substance to the work W performed on it, is called the coefficient of performance (α) of the refrigerator. That is
$$\alpha = \frac{Q_2}{W}$$
Here heat is released in surrounding
$Q_1 = W + Q_2$
$Q_1 = W + Q_2$
$W = Q_1 - Q_2$

$$\alpha = \frac{Q_2}{Q_1 - Q_2}$$
Here the value of α can be more than 1 ($\because Q_2 > Q_1 - Q_2$), but it can not be infinite