Ph-23
RS-1417 Chapter no: 23 01

Kinetic Theory And The Ideal Gas

Ch(23) P(1)

Q. State and explain gas laws.

Macroscopic Properties

The macroscopic properties of a gas are, the type and amount of gas, the pressure, volume and temperature of the gas. There are different relations or laws called gas laws relating these measurable properties of the gas.

i, **Avogadro's law** This law may be stated as,

At a particular pressure and temperature the volume of a gas, V, is directly proportional to the number of the molecules, N. The volume is independent of the type of gas and the size and mass of the molecule.

or

$$V \propto N$$

or

$$V = C N \quad (P, T, \text{constant}) \quad \text{---} I$$

Here 'c' is the constant of proportionality and it is equal to the slope of line, as shown in the Fig I

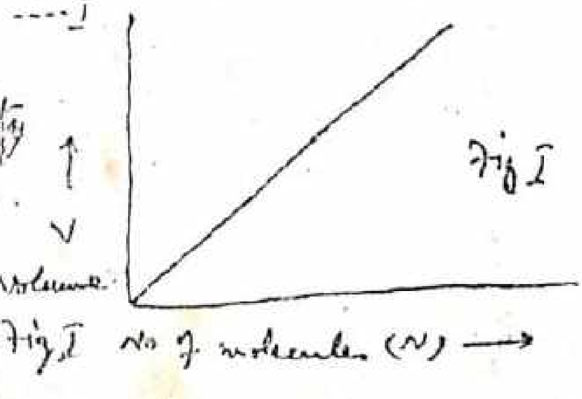


Fig I

This law holds good for all real gases especially at low density (low pressure) and high temperature, because under these conditions a real gas acts like an ideal gas.

ii. Boyle's law. This law may be stated as,

Keeping the number of molecules, N, and the absolute temperature T of the gas constant, the volume V of the gas is inversely proportional to the pressure, P.

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

or

$$V =$$

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

or $$P = \frac{C'}{V} \quad \text{---- ii}$$

or $$PV = C' \quad (N, T, \text{constant})$$

Here C' is the constant, whose value is different for different values of N and T.

$$P_1V_1 = P_2V_2 = C'$$

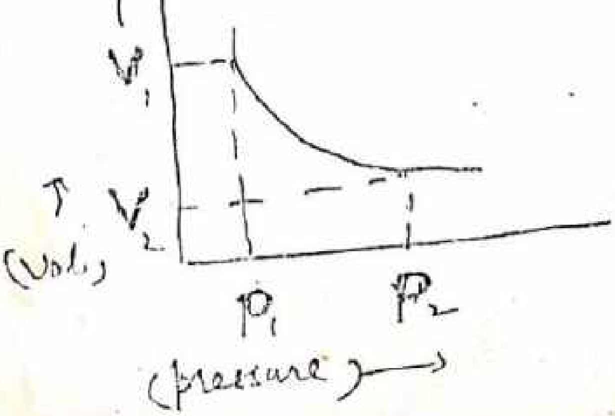


Fig II

The graph between 'P' and 'V' is a curve, as shown in Fig II. but the graph between P and V^{-1} is a straight line as shown in Fig III

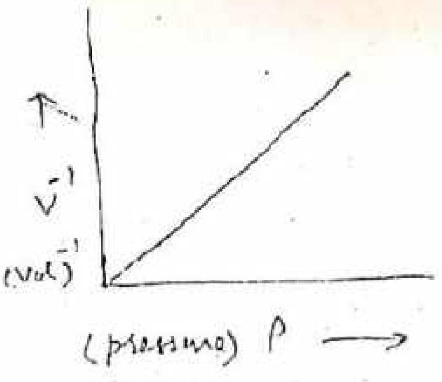


Fig III

(3) Charle's law or Gay-Lussac's law

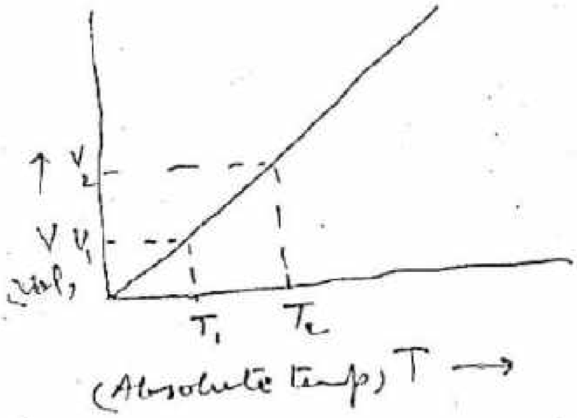
This law may be stated as.

Keeping the number of molecules, N, and the pressure P constant, the volume V of the gas is directly proportional to the absolute temperature T.

or $V \propto T$

or $V = C' T$ ---- III

Here C' is a constant. The graph between 'T' and 'V' is a straight line.



It means that the volume V of the gas varies linearly with the temperature T.

Absolute Zero Absolute zero is that temperature at which the volume of an ideal gas were equal to zero.

quation of state of gas

From Avogadro's law we have

$$V \propto N$$

From Boyle's law, we have

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

From Charles' law, we have

$$V \propto T$$

By combining the above three laws, we get.

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

or

$$V = \frac{NT}{P}\,k$$

or

$$\frac{PV}{NT} = k \quad - - - - - \underline{\text{iv}}$$

Here 'K' is the constant, known as Boltzmann constant. It is a universal constant and its experimental value is

$$k_B = 1.38066 \times 10^{-23}\ \text{J}\,\text{K}^{-1}$$

The number of molecules in one mole of the gas is Avogadro constant, N_A. If 'n' is the number of moles of the gas, then

The n is number of moles,

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

or

$$N = n N_A$$

Putting the value of N in Eq $\underline{IV}$, we get

$$\frac{PV}{n N_A T} = k$$

or

$$PV = n N_A k T$$

$$PV = nRT \quad \text{----} \underline{V}$$

$$\left\{ \begin{array}{l} R = n N_A k \\ R = 8.3145 \; J/mol\,K \end{array} \right.$$

This is known as Equation of State of ideal gas.

Here. 'R' is universal gas constant or molar gas Constant, which is the same for all the gases.

Eq $\underline{V}$ is also known as Ideal gas Equation.

Start

Q. What are the assumptions of kinetic theory of gases (microscopic point of view)

Kinetic Theory of gases. The kinetic theory of gases is the microscopic point of view, according to which the model of an ideal gas includes the following assumption.

Assumptions

1. A gas consists of particles called molecules. If the gas is element or compound then its all the molecules are identical. A molecule may consist one atom or more than one atoms.
2. The A molecules are in random motion and obey Newton's laws of motion
3. The total number of molecules is very large and they follow zigzag paths because of collisions.
4. The volume of the molecules is a negligible fraction of the volume occupied by the gas. It means that the molecules are far apart as compared to their dimensions.
5. The molecules exert no forces on one another except when they collide.
6. The molecules make elastic collisions against one another of negiligible duration.

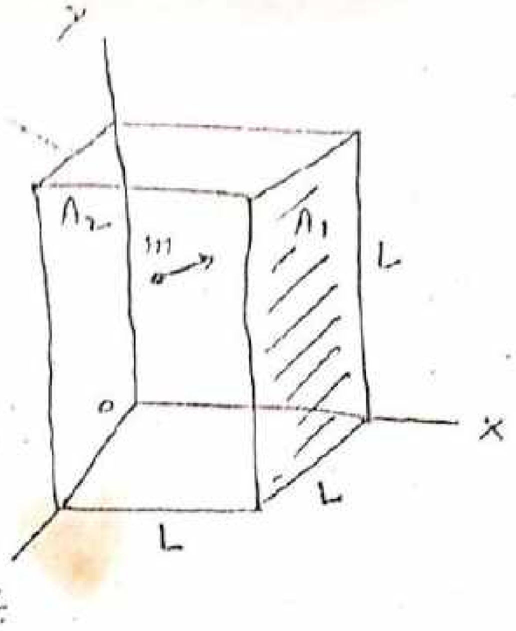
PRESSURE OF GAS ON THE BASIS OF KINETIC THEORY OF GASES

Consider a gas enclosed in a cubical container of edge length L whose walls are perfectly elastic.

The volume of the container is

$V = L^3$

Now consider the faces A_1 and A_2 which are normal to x-axis, the area of each face is L^2.



Let a molecule of mass m is moving with velocity v_1. Its velocity can be resolved into three components v_{x1}, v_{y1} and v_{z1}. When this molecule strikes with face A_1, then its initial momentum is mv_{x1}, after the elastic collision against the wall, its final momentum is $-mv_{x1}$.

Therefore the change in momentum of the molecule is

final momentum - Initial momentum

$= -mv_{x1} - (mv_{x1})$

$= -2mv_{x1}$

Assuming no collisions with other molecules, the molecule moves from A_1 to face A_2 and back from A_2 to A_1, then the interval of time taken is $t = \frac{2L}{v_{x1}}$ and its velocity remains the same.

$s = vt$

$t = \frac{s}{v}$

Then the rate of change of momentum of the 1 molecule is

$$= \frac{-2mv_{x1}}{t} = -\frac{\cancel{2}mv_{x1}}{\frac{\cancel{2}L}{v_{x1}}}$$

$$= -\frac{mv_{x1}^2}{L}$$

This rate of change of momentum of the molecule is equal to the force applied by the wall on the molecules which is the reaction force. According to third law of motion, the force applied by the molecule on the wall is

$$= \frac{mv_{x1}^2}{L}$$

The total force applied by all the 'N' molecules on the face A_1 is

$$F_x = \frac{m}{L}\left(v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \text{------} + v_{xN}^2\right)$$

multiplying and dividing by N.

$$= \frac{mN}{L}\left(\frac{v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \text{------} + v_{xN}^2}{N}\right)$$

The average value of the square of x-component of velocity is

$$\overline{v_x^2} = \frac{v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \text{---} + v_{xN}^2}{N}$$

Therefore

$$F_x = \frac{M}{L}\overline{v_x^2} \qquad \therefore \{ M = mN$$

'M' is the total mass of the gas

Pressure is equal to the force per unit area. Therefore pressure is

$\because A = L^2$ given by

Putting value of F_x

$$P = \frac{F_x}{L^2} = \frac{M}{L^3}\,\overline{v_x^2}$$

$\langle v_x^2 \rangle$

If 'ρ' is the density of gas, then

$$\rho = \frac{M}{L^3} = \frac{M}{V}$$

Therefore the pressure is

$$P = \rho\,\overline{v_x^2}$$

ρ

$P_x = \frac{F_x}{L^2}$

$P_x = \frac{M}{L^3}\overline{v_x^2}$

$P_x = \rho\overline{v_x^2}$

or

$P = \rho\overline{v_x^2}$

Because all sides velocity is equal & P is equal.

As the molecules have random motion, making elastic collisions with one another, but the average components of velocity are equal, therefore the <u>mean square velocity</u> is

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$$

But $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$

Hence $\overline{v^2} = 3\,\overline{v_x^2}$

mass of gas.

$M = Nm$

or $\overline{v_x^2} = \frac{1}{3}\,\overline{v^2}$

Putting this value in equation of pressure, we have

$$P = \frac{1}{3}\rho\,\overline{v^2} = \frac{1}{3}\frac{M}{V}\overline{v^2} = \frac{2}{3}\frac{Nm}{V}\left(\frac{1}{2}m\overline{v^2}\right)$$

where $\overline{v^2}$ is the mean square velocity.

$$\overline{v^2} = \frac{v_1^2 + v_2^2 + v_3^2 + \cdots\cdots v_N^2}{N}$$

The square root of $\overline{v^2}$ is called root mean square velocity, which is given by

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3P}{\rho}}$$

Here 'P' is the pressure and ρ is the density of the gas.

Pascal's law This law may be stated as "The pressure of gas is the same on all sides and everywhere in the interior of the container if the density of the gas is uniform."

KINETIC INTERPRETATION OF THE TEMPERATURE

The equation for the pressure of gas on the basis of kinetic theory is

$$P = \frac{1}{3}\rho\overline{v^2}$$

where 'ρ' is the density and $\rho = \frac{M}{V} = \frac{\text{mass}}{\text{volume}}$

Therefore

$$P = \frac{1}{3}\frac{M}{V}\overline{v^2}$$

or

$$PV = \frac{2}{3}\left(\frac{1}{2}M\overline{v^2}\right) \quad \text{---- I}$$

The equation of state of an ideal gas is

$$PV = nRT \quad \text{--- II}$$

Comparing Eq I and Eq II, we get

$$nRT = \frac{2}{3}\left(\frac{1}{2}M\overline{v^2}\right)$$

$$T = \frac{2}{3nR}\left(\frac{1}{2}M\overline{v^2}\right)$$

or

$$T \propto \left(\frac{1}{2}M\overline{v^2}\right)$$ As $\frac{2}{3nR}$ = constant

Therefore the absolute temperature of the gas is directly proportional to the total average translational kinetic energy of the gas.

Again we have

$$T = \frac{2}{3nR}\left(\frac{1}{2}M\overline{v^2}\right)$$

But mass of gas is $M = Nm$, where m is the mass of one molecule, therefore

$$T = \frac{2}{3nR}\left(\frac{Nm\overline{v^2}}{2}\right)$$

$$= \frac{2N}{3nR}\left(\frac{1}{2}m\overline{v^2}\right) \quad \text{--- iii}$$

Here $(\frac{1}{2}m\overline{v^2})$ is the average translational energy of one molecule. Here 'N' is the total number of molecules and 'n' is the number of moles of the gas.

or $N = nN_A$ $\qquad$ N_A = Avogadro's no.

or $\frac{N}{n} = N_A$.

Therefore the equation for the absolute temperature of gas is

$$T = \frac{2}{3}\frac{N_A}{R}\left(\frac{1}{2}m\overline{v^2}\right)$$

But

$$R = N_A K$$

$$\frac{1}{K} = \frac{N_A}{R}$$

Where 'K' is Boltzmann constant, therefore.

$$T = \frac{2}{3K}\left(\frac{1}{2}m\overline{v^2}\right)$$

$$T \propto \left(\frac{1}{2}m\overline{v^2}\right)$$

The absolute temperature of the gas is directly proportional to the average translation kinetic energy of the molecule. End ✓

Prove that the ratio of the root-mean-square speeds of the molecules of two different gases is equal to the square root of the inverse ratio of their masses at a certain temperature.

The temperature of one gas is

$$T_1 = \frac{2}{3K}\left(\frac{1}{2}m_1\overline{v_1^2}\right) \quad \text{---- } I$$

The temperature of the other gas is

$$T_2 = \frac{2}{3K}\left(\frac{1}{2}m_2\overline{v_2^2}\right) \quad \text{--- } II$$

At the same temperature

$$T_1 = T_2$$

Comparing Eq I and Eq II we get.

$$\frac{2}{3K}\left(\frac{1}{2}m_1\overline{v_1^2}\right) = \frac{2}{3K}\left(\frac{1}{2}m_2\overline{v_2^2}\right)$$

or

$$m_1\overline{v_1^2} = m_2\overline{v_2^2}$$

or

$$\frac{\overline{v_1^2}}{\overline{v_2^2}} = \frac{m_2}{m_1}$$

or

$$\frac{v_{1rms}}{v_{2rms}} = \sqrt{\frac{\overline{v_1^2}}{\overline{v_2^2}}} = \sqrt{\frac{m_2}{m_1}} =$$

Therefore the ratio of the root mean square speeds of two molecules of two different gases is equal to the inverse ratio of their masses at the same temperature. The separation factor 'α' is given by

$$\frac{v_{1rms}}{v_{2rms}} = \sqrt{\frac{N_A m_2}{N_A m_1}} = \sqrt{\frac{M_2}{M_1}}$$

$$\alpha = \sqrt{\frac{m_2}{m_1}} = \sqrt{\frac{M_2}{M_1}}$$

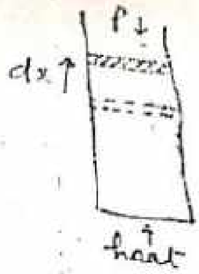
Here M_2 and M_1 are molar masses of two different gases. The different isotopes of an element are separated by diffusion process through porous walls.

(wrong) see from Resnick.

Q. Discuss the work done on the system and does not prove that the work done is ~~independent~~ depends on the path followed.

Consider a gas enclosed in a cylinder fitted with a piston. If the temperature of the gas is increased, then the gas expands and its volume increases.

Let 'p' is the pressure and 'A' is the area of the piston. Then the force applied by the gas on the piston during expansion is 'pA'. According to third law of motion, the force applied by the piston on the gas is



$$F = -pA.$$

If the piston moves through 'dx' [illegible] (upward) Then the work done on the gas is

$$dW = F\,dx$$

$$= -pA\,dx$$

$$= -p\,dV$$

By the gas
$F\uparrow dx$ expansion
on the gas
$F\downarrow dx$ compression
$F\downarrow$ (expansion)

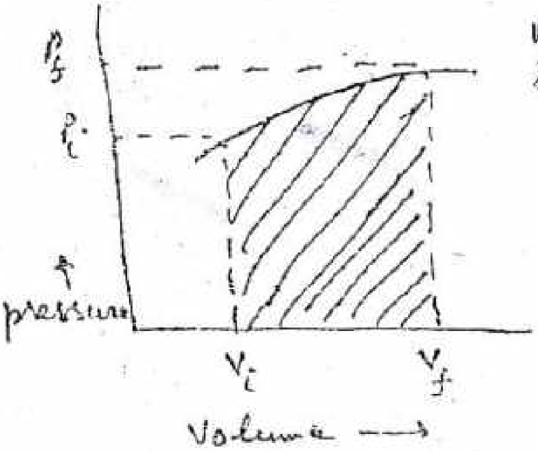
$[dV = A\,dx$
small change in volume

Therefore the total work done on the gas during expansion is

$$W = \int_{V_i}^{V_f} dW$$

$$= -\int_{V_i}^{V_f} p\,dV$$

Variable force



A graph between volume and pressure is shown in the fig. which is called PV diagram. The area under the curve is equal to the work done on the gas.

i, During expansion when $V_f > V_i$, the work done on the gas is negative.

ii, During compression, when $V_f < V_i$, The work done on the gas is positive.

Work is path dependent

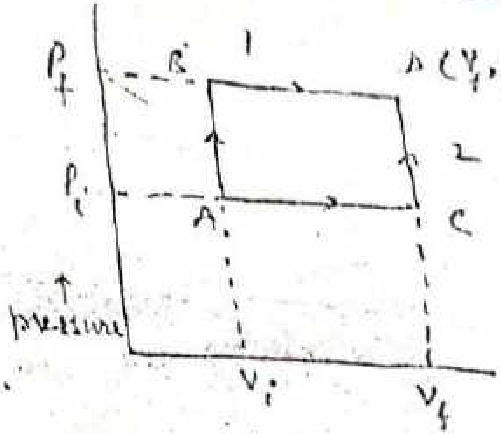
Prove that Pressure force is a non-conservative (2.1) P (1.1)

Q. Prove that the work done on the system depends on the path followed.

conservative - independent
non conservative - depends

Work

Consider a gas enclosed in a cylinder fitted with a piston. The initial pressure and volume are P_i and V_i respectively.



Let the gas is heated at constant volume so that its whole pressure increases from P_i to P_f and then the gas is allowed to expand so that its volume increases from V_i to V_f. This process is represented by the curve ABD (path 1). The work done on the gas during path 1 is

$$\underset{\text{path 1}}{W_{AD}} = W_{AB} + W_{BD}$$

$$= 0 - \int_{V_i}^{V_f} P_f \, dV = - P_f (V_f - V_i) \quad \text{---} \underline{I}$$

Now follow path 2, in which the gas is allowed to expand from vol V_i to V_f at constant pressure P_i and then it is heated so that its pressure increases from P_i to P_f; the path followed is represented by the curve ACD; therefore the work done is

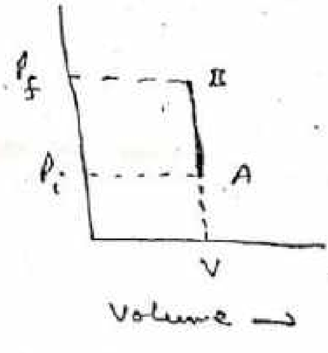
$$\underset{\text{path 2}}{W_{AD}} = W_{AC} + W_{CD}$$

$$= - \int_{V_i}^{V_f} P_i \, dV + 0 = - P_i (V_f - V_i) \quad \text{---} \underline{II}$$

Therefore the work done on the gas is different along different path; although the initial (V_i, P_i) and final conditions (V_f, P_f) are the same. Therefore the work done depends on the path followed. It is also clear from the Fig. that the area under the curve ABD is different from that under the curve ACD.

Q. Discuss the work done i, at constant volume ii, at constant pressure iii, at constant temperature iv, in thermal isolation.

i, WORK DONE AT CONSTANT VOLUME (Isochoric Process)



During isochoric process, the volume of the gas remains constant. If the gas is heated then its temperature and pressure increase at constant volume V. This process is represented by the curve AB in PV diagram. The work done during this process is zero.

$$W = -\int P\,dV = 0 \quad \text{because } dV = 0$$

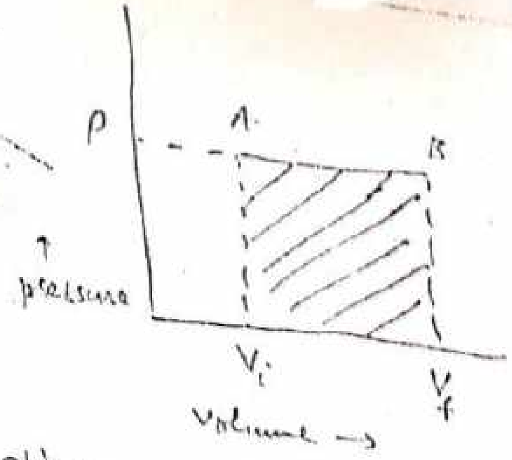
Also the area under the curve AB is zero. Therefore the work done at constant volume is zero.

ii, WORK DONE AT CONSTANT PRESSURE

(Isobaric Process)

CR (23) P (17)

During isobaric process the pressure of the gas is kept constant. Let the gas is heated so that its volume increases from V_i to V_f at constant pressure P. This process is represented by curve AB in PV diagram. During this process the work done

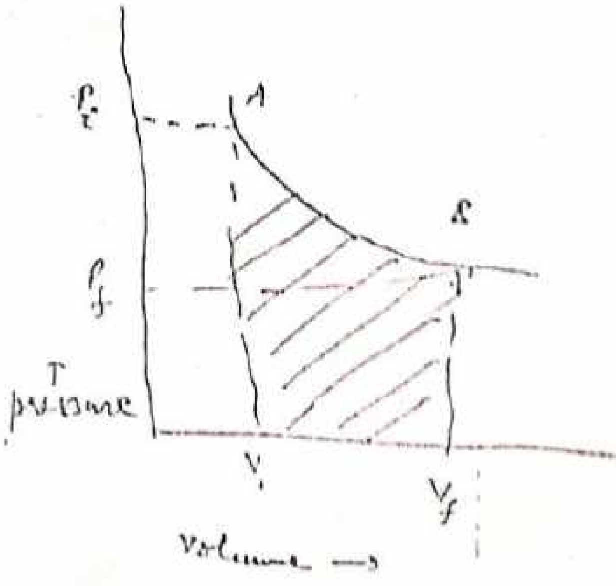


$$W = -\int_{V_i}^{V_f} P\,dV = -P\left|V\right|_{V_i}^{V_f} = -P(V_f - V_i)$$

This is the work done on the gas at constant pressure, which is also equal to the area under the curve AB, as shown in the fig.

ii, WORK DONE AT CONSTANT TEMPERATURE

During isothermal process (Isothermal Process) the temperature of the gas remains constant. If the the gas is heated and the pressure is decreased slowly so that the gas is allowed to expand at constant temp T.



Let the volume of the gas increases from V_i to V_f while the pressure decreases from P_i to P_f at constant temperature T. This process is represented by the curve AB in PV diagram. The work done on the gas at constant temperature is

$$W = -\int_{V_i}^{V_f} P\,dV$$

The equation of state of an ideal gas is

$$PV = nRT$$

or

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

Putting the value of 'P' in the above eq.

$$W = -\int_{V_i}^{V_f} \frac{nRT}{V}\,dV = -nRT\int_{V_i}^{V_f} \frac{dV}{V}$$

$$= -nRT\,\Big|\ln V\Big|_{V_i}^{V_f}$$

$$= -nRT(\ln V_f - \ln V_i)$$

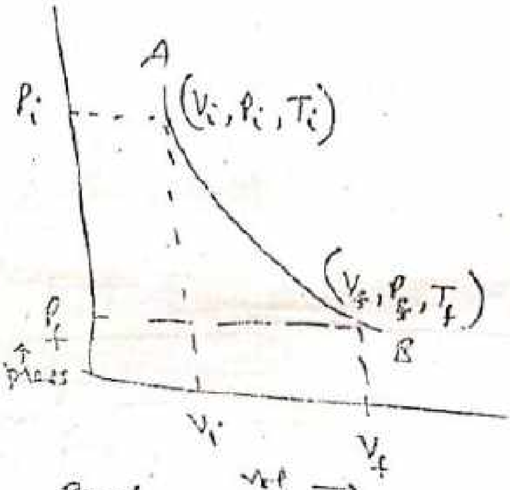
$$= -nRT\ln\left(\frac{V_f}{V_i}\right)$$

This is the work done on the gas at constant temperature which is also equal to the area under the isotherm AB, as shown in the Fig. During isothermal process Boyle's law is applied PV = const.

iv) WORK DONE IN THERMAL ISOLATION (Adiabatic Process)

During adiabatic process no heat enters or leaves the system. which is thermal isolation. In this process the following law is applicable.

$$PV^{\gamma} = K \quad (K \text{ is constant}) \quad \left[\gamma = \frac{C_p}{C_v}\right.$$



During this process temperature, the volume and pressure change. Let the gas is allowed to expand adiabatically so that its volume increases from V_i to V_f while pressure decreases from P_i to P_f and temperature also decreases from T_i to T_f. This process is also represented by adiabatic A-B in PV diagram. The work done during this process is

$$W = -\int_{V_i}^{V_f} P\,dV$$

Putting $P = \frac{K}{V^{\gamma}}$, we get.

$$W = -\int_{V_i}^{V_f} K\frac{dV}{V^{\gamma}} = -K\left|\frac{V^{-\gamma+1}}{-\gamma+1}\right|_{V_i}^{V_f}$$