

Chapter-23

# KINETIC THEORY AND THE IDEAL GAS

## 1. Review of Fundamental Concepts:

### (i) Thermodynamics:

"The branch of physics which deals with the conversion of Heat energy into Mechanical energy and vice versa is called Thermodynamics."

### (ii) Temperature:

"It is the degree of hotness or coldness of a body."

It may be defined as:

"A physical property of the body which determines the direction of flow of heat from one body to the other when they are brought in thermal contact with each other."

### (iii) State Variables (Thermodynamic Coordinates)

The physical quantities which describe the state of a system are called state variables or Thermodynamic co-ordinates, e.g. pressure, volume, temperature, internal energy, Entropy etc. Any relation among these variables is called a gas law.

### (iv) Ideal Gas:

The gas which obeys gas laws under all temperatures

and pressure is called an ideal gas. It is a hypothetical gas. Also called perfect gas. The molecules of ideal gas have no potential energy but only K.E.

### 1) Derivation of State (Ideal Gas law)

From Boyle's law; Volume of a given mass of gas is inversely proportional to its pressure if its temperature is kept constant

$$\text{i.e. } V \propto \frac{1}{P} \quad (1) \quad \text{if } T, N \text{ is const.}$$

From Charles law; The volume of a given mass of gas is directly proportional to its absolute temperature if its pressure is kept const.

$$\text{i.e. } V \propto T \quad (2) \quad \text{if } P, N \text{ is const.}$$

From Gay-Lussac's law; Volume of a gas is directly proportional to number of molecules if P and T are constant.

$$\text{i.e. } V \propto N \quad (3) \quad \text{if } P, T \text{ is const.}$$

Combining (1), (2) and (3) we get

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

$$\frac{PV}{T} \propto N$$

$$\frac{PV}{T} = \text{const} \times N$$

$$\frac{PV}{NT} = \text{const}$$

$$\boxed{\frac{PV}{NT} = K} \quad (4)$$

where K is constant called Boltzmann const.

It is a universal constant. Its value is

$$K = 1.38066 \times 10^{-23} \text{ J/K}$$

If n is the number of moles then  $N = n N_A$ .

So equation (4) becomes

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

$$\text{Putting } N_A K = R$$

$$\frac{PV}{nT} = N_A K$$

$$\frac{PV}{nT} = R$$

$$\boxed{PV = nRT} \quad (A)$$

where R is universal

gas const. Its value is  $R = 8.314 \text{ J/mole} \cdot \text{K}$

Equation (1) is called Equation of state or ideal gas law. This equation gives a mathematical relationship among thermodynamic quantities.

### Sample Problem: 1

An insulated cylinder fitted with a piston (Fig. 2.1) contains oxygen at 20°C temperature and 15 atm. of pressure in volume of 22 litres. The piston is lowered decreasing the volume of gas to 16 litres and raising the temperature to 25°C. Assuming oxygen to behave like an ideal gas under these conditions, what is the final pressure of gas?

Solution:  $P_1 = 15 \text{ atm}$ ,  $P_2 = ?$ ,  $T_1 = 20 + 273 = 293 \text{ K}$   
 $T_2 = 25 + 273 = 298 \text{ K}$ ,  $V_1 = 22 \text{ lit}$ ,  $V_2 = 16 \text{ lit}$   
 Since mass is const

∴ From ideal gas law

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$P_2 = \frac{P_1 V_1 T_2}{T_1 V_2}$$

$$P_2 = \frac{15 \times 22 \times 298}{293 \times 16} = 2.1 \text{ atm}$$

$$P_2 = 2.1 \text{ atm} \quad \text{Ans.}$$

## 2 Kinetic Theory of Ideal Gas:

### Kinetic Theory

The theory which explains the behaviour of gas on the basis of interaction of molecules and the energy they possess is called kinetic theory.

Fundamental Assumptions of K. theory. The kinetic theory is based on the following assumptions.

- (i) A gas consists of particles, called molecules. These molecules are elastic spheres (Hard point masses).
- (ii) The molecules are in random motion and obey Newton's laws of motion. The molecules move in all directions with various velocities.
- (iii) A small volume of the gas contains a large number of molecules. i.e. total number of molecules is large. The velocity of any molecule may change on collision with other molecule or with the wall of container.

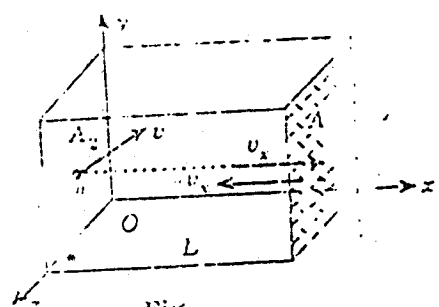
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- (iv) The volume of the molecules is small fraction of the volume occupied by the gas (i.e. volume of the container)
- (v) The molecules exert no force on each other except when they collide. The molecules move freely between the collisions, i.e. molecule move with uniform velocity b/w collisions. So the molecules follow a straight path b/w successive collisions called free path.
- (vi) Collisions are elastic and of negligible duration i.e. collision of molecules with other molecule or with the wall of container conserves momentum and kinetic energy and the time spent during collision is very small compared with the time of independent motion.

### Kinetic Calculations of Pressure

Let us now derive an expression for pressure of an ideal gas on the basis of kinetic theory.

Consider an ideal gas in a cubical container of length  $L$ . All walls perfectly elastic. Let the faces of cubes  $\perp$  to  $x$ -axis be denoted by  $A_1$  and  $A_2$  each of area  $L^2$ . Let  $N$  be the total number of molecules in the container. Consider a molecule of mass ' $m$ ' moving with velocity ' $v$ '. Let  $v_x$ ,  $v_y$  and  $v_z$  be the rectangular components of velocity  $v$ .



The molecules move to face  $A_1$  with velocity  $v_x$ . After collision with  $A_1$ , its velocity becomes  $-v_x$  and rebounds to face  $A_2$  and there is change in  $v_y$  and  $v_z$ .

∴ Momentum of mol before collision =  $m v_x$   
 " " " after " "  $A_1$  =  $-m v_x$   
 Change in momentum = Final momentum - Initial momentum  
 =  $-m v_x - m v_x = -2m v_x$

∴ The momentum is conserved therefore the momentum transferred to face  $A_1$  is  $= 2m v_x$ .

Suppose the molecule reaches face  $A_2$  without any collision with molecule on the way. After collision with  $A_2$ , the molecule goes back to face  $A_1$ . Time taken by the molecule in moving from  $A_1$  to  $A_2$  and back to  $A_1$  is given by,

$$t = \frac{2L}{v_x}$$

The average impulsive force exerted by the molecules on face A, is given by

$$F_x = \frac{\text{Momentum transferred to A}}{\text{Time between successive collisions with A}}$$

$$F_x = \frac{2mv_x}{t} = \frac{2mv_x}{\frac{L}{v_x}}$$

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

**Total Impulsive:** This is the impulsive force exerted by one molecule on A.

Total impulsive force exerted on A, by all the molecules is given by

$$F_x = \frac{mv_{1x}^2}{L} + \frac{mv_{2x}^2}{L} + \dots + \frac{mv_{Nx}^2}{L}$$

$$= \frac{mv_{1x}^2 + mv_{2x}^2 + \dots + mv_{Nx}^2}{L}$$

$$F_x = \frac{m}{V} \cdot (v_{1x}^2 + v_{2x}^2 + \dots + v_{Nx}^2) \quad (1)$$

where  $v_{1x}$  = x-comp. of velocity of molecule 1.

$v_{2x}$  = " " " " " " " 2

$v_{3x}$  = " " " " " " " 3 and so on.

As pressure is defined as the force per unit area

So pressure is obtained by dividing equation (1) by area of face A i.e.  $L^2$

$$\therefore P = \frac{F_x}{L^2} = \frac{1}{L^2} \times F_x$$

$$P = \frac{1}{L^2} \times \frac{m}{L} (v_{1x}^2 + v_{2x}^2 + \dots + v_{Nx}^2)$$

$$P = \frac{m}{L^3} (v_{1x}^2 + v_{2x}^2 + \dots + v_{Nx}^2)$$

Now as N is the total number of molecules each of mass 'm'. So total mass of the gas = Nm.

$\therefore$  Density  $\rho$  of the gas is total mass per unit volume

$$\text{So } \rho = \frac{Nm}{L^3}$$

$$\therefore \frac{\rho}{N} = \frac{m}{L^3}$$

$\therefore$  expression (2) becomes

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$$P = \frac{f}{N} (V_{1x}^2 + V_{2x}^2 + \dots + V_{Nx}^2)$$

$$= \rho \left( \frac{V_{1x}^2 + V_{2x}^2 + \dots + V_{Nx}^2}{N} \right)$$

The quantity within brackets is mean square velocity of gas molecule along x-axis and is denoted by  $\bar{V}_x^2$ .

∴ The above expression for pressure becomes

$$P = \rho \bar{V}_x^2$$

For any molecule  $V^2 = V_x^2 + V_y^2 + V_z^2$

$$\bar{V}^2 = \bar{V}_x^2 + \bar{V}_y^2 + \bar{V}_z^2 \quad (a)$$

As the molecules in random motion

$$\therefore \bar{V}_x^2 = \bar{V}_y^2 = \bar{V}_z^2$$

∴ Expression (a) becomes

$$\bar{V}^2 = \bar{V}_x^2 + \bar{V}_y^2 + \bar{V}_z^2$$

$$= 3\bar{V}_x^2$$

$$\bar{V}_x^2 = \frac{1}{3} \bar{V}^2$$

∴ Expression (1) of pressure becomes

$$P = \rho \left( \frac{1}{3} \bar{V}^2 \right)$$

$$P = \frac{1}{3} \rho \bar{V}^2 \quad (4)$$

The equation (4) holds even if the container contains a mixture of molecules of different masses. Moreover the equation is independent of shape of container. A cubical shape is taken just for simplification of calculations.

### Root Mean Square Speed:

From equation (4)  $\bar{V}^2 = \frac{3P}{\rho}$

Taking square root on both sides we get

$$\sqrt{\bar{V}^2} = \sqrt{\frac{3P}{\rho}}$$

$$\bar{V} = \sqrt{\frac{3P}{\rho}}$$

where  $\bar{V}$  is called root-mean square speed and is denoted by  $V_{rms}$

$$\therefore V_{rms} = \sqrt{\frac{3P}{\rho}}$$

(6-A)

## Sample Problem-3

Assuming that the speed of sound in a gas is the same as the root mean square speed of the molecules, show how the speed of sound for an ideal gas would depend on the temperature?

density of gas is

$$\rho = \frac{M \cdot n}{V}$$

If  $M$  is the mass of one mole and  $n$  is the number of moles of the gas, then

$$\rho = \frac{nM}{V}$$

$$V = \frac{nM}{\rho} \quad \text{--- (i)}$$

From ideal gas law

$$pV = nRT$$

$$V = \frac{nRT}{p} \quad \text{--- (ii)}$$

From (i) & (ii)

$$\frac{nM}{\rho} = \frac{nRT}{p}$$

$$\frac{M}{\rho} = \frac{RT}{p}$$

$$\therefore \frac{p}{\rho} = \frac{RT}{M} \quad \text{--- (iii)}$$

$$\therefore \text{AS } v_{rms} = \sqrt{\frac{3RT}{M}}$$

If  $v_1$  &  $v_2$  are the speeds of sound in a gas at temps  $T_1$  &  $T_2$ , then

$$v_1 = \sqrt{\frac{3RT_1}{M}}, \quad v_2 = \sqrt{\frac{3RT_2}{M}}$$

$$\therefore \frac{v_1}{v_2} = \sqrt{\frac{T_1}{T_2}}$$

eg if  $v_1 = 331 \text{ m/s}$  at  $0^\circ\text{C}$  or  $273\text{K}$  then the speed of sound at any other temp (say)  $27^\circ\text{C}$  or  $300\text{K}$  is given by

$$\frac{331}{v_2} = \sqrt{\frac{273}{300}} \quad \text{OR} \quad \boxed{v_2 = 347 \text{ m/s}} \quad \text{Ans.}$$

### Sample Problem - 2

Calculate the rms mean square speed of hydrogen molecules at 0°C and 1 atm. pressure, assuming hydrogen to be an ideal gas. Under these condition hydrogen has a density of  $8.99 \times 10^{-2} \text{ Kg/m}^3$ .

Sol.  $P = 1 \text{ atm} = 1.01 \times 10^5 \text{ N/m}^2$ ,  $T = 0^\circ\text{C} = 273 \text{ K}$   
 $\rho = 8.99 \times 10^{-2} \text{ Kg/m}^3$ ,  $V_{\text{rms}} = ?$

As  $V_{\text{rms}} = \sqrt{\frac{3P}{\rho}}$

Putting the values we get

$$V_{\text{rms}} = \sqrt{\frac{3 \times 1.01 \times 10^5}{8.99 \times 10^{-2}}} = \sqrt{0.337 \times 10^7}$$

$$= \sqrt{3.37 \times 10^6} = 1.84 \times 10^3$$

$V_{\text{rms}} = 1840 \text{ m/s}$  ms.

at any other temp. say 27°C or 300K is given by

$$\frac{V_2}{V_1} = \sqrt{\frac{273}{300}}$$

$$\frac{V_2}{331} = \sqrt{\frac{300}{273}}$$

$$V_2 = 331 \times \sqrt{\frac{300}{273}}$$

$V_2 = 347 \text{ m/s}$

### 3. Kinetic Interpretation of Temperature:

The pressure of ideal gas on the basis of K. theory is given by

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

Multiplying both sides by V we get

$$PV = \frac{1}{3} (\rho V) \bar{v}^2$$

But  $\rho V = \text{Total}^3 \text{ mass of the gas.}$

If  $n$  is the number of moles and  $M$  is the mass of one mole of gas.

Then total mass of the gas =  $nM = \rho V$

$$\therefore PV = \frac{1}{3} nM \bar{v}^2 \quad (1)$$

$$\text{or } PV = \frac{2}{3} \left( \frac{1}{2} nM \bar{v}^2 \right)$$

From ideal gas law  $PV = nRT$ .



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$$3RT = \frac{2}{3} \left( \frac{1}{2} M \bar{V}^2 \right)$$

$$RT = \frac{2}{3} \left( \frac{1}{2} M \bar{V}^2 \right)$$

$$\text{or } \frac{1}{2} M \bar{V}^2 = \frac{3}{2} RT \quad (2)$$

$$\text{i.e. } \frac{1}{2} M \bar{V}^2 \propto T \quad \text{as } \frac{3}{2} R = \text{const}$$

As  $M$  is the mass of one mole. So we find that average translational K.E per mole of an ideal gas is directly proportional to the absolute temp. of the ideal gas.

Dividing eq. (2) by avogadro's number  $N_A$

$$\left( \frac{1}{2} \frac{M \bar{V}^2}{N_A} \right) = \frac{3}{2} \frac{R \cdot T}{N_A}$$

$$\therefore M = m N_A, \quad \frac{M}{N_A} = m$$

$$\therefore \frac{1}{2} m \bar{V}^2 = \frac{3}{2} \frac{R}{N_A} T$$

where  $m$  is the mass of one molecule.

$\therefore \frac{1}{2} m \bar{V}^2$  is the average translational K.E per molecule.

Now  $\frac{R}{N_A}$  = molar gas const. per molecule and is called Boltzmann const. denoted by  $k$ .

$\therefore$  The above expression becomes

$$\frac{1}{2} m \bar{V}^2 = \frac{3}{2} kT \quad (3)$$

$$T = \frac{2}{3k} \left( \frac{1}{2} m \bar{V}^2 \right)$$

From equation (2) and (3) it is clear that average kinetic energy per mole and average K.E per molecule depend on absolute temp. of gas.

For two different gases at the same temp.  $T$  and pressure  $P$  eq. (4) can be written as

$$\frac{2}{3k} \left( \frac{1}{2} m_1 \bar{V}_1^2 \right) = \frac{2}{3k} \left( \frac{1}{2} m_2 \bar{V}_2^2 \right)$$

$$\text{or } m_1 \bar{V}_1^2 = m_2 \bar{V}_2^2$$

$$\frac{\bar{V}_1^2}{\bar{V}_2^2} = \frac{m_2}{m_1}$$

$$\frac{\sqrt{\bar{V}_1^2}}{\sqrt{\bar{V}_2^2}} = \frac{\sqrt{m_2}}{\sqrt{m_1}}$$

$$\text{but } \sqrt{\bar{V}^2} = V_{rms}$$

$$\therefore \frac{V_{rms1}}{V_{rms2}} = \sqrt{\frac{m_2}{m_1}} \quad \text{or}$$

According to equation (4) the ratio of root mean square speeds of molecules of two different gases is equal to the inverse ratio of their masses.

Equation (4) represents Graham's law of diffusion.

According to this law; Under the same conditions of temperature and pressure, the rates of diffusion of two gases are inversely proportional to the square root of their masses i.e. the molecules of lighter gas escape faster than the heavier one.

The ratio of number of molecules of two gases that pass through the porous partition in a short time interval is called separation factor  $\alpha$ . So  $\alpha$  is equal to ratio of their root mean square (rms) speeds.

$$\alpha = \frac{V_1 \text{ rms}}{V_2 \text{ rms}}$$

$\therefore$  from equation (4)

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

### Sample Problem-4

Natural uranium consists primarily of two isotopes  $U^{235}$  (0.7%) and  $U^{238}$  (99.3%). Only  $U^{235}$  is easily fissionable. In a sample of the gas  $UF_6$  (Uranium hexafluoride), it is desired to increase the abundance of  $U^{235}$  from 0.7% to 3% by forcing the gas  $n$  times through a porous barrier. Find  $n$ .

Sol. Molar mass of  $U^{235}F_6 = M_1 = 0.349 \text{ kg/mol}$

" " " "  $U^{238}F_6 = M_2 = 0.352 \text{ kg/mol}$

After passing <sup>once</sup> through porous partition,  $U^{235}$  will increase by  $\alpha$

$$\therefore \alpha = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{0.352}{0.349}} = 1.0043$$

$\therefore$  After passing  $n$  times,  $U^{235}$  will increase by  $\alpha^n$

$$\therefore \alpha^n \left( \frac{0.007}{0.993} \right) = \left( \frac{0.03}{0.97} \right)$$

Putting value of  $\alpha$  we get

$$(1.0043)^n \left( \frac{0.007}{0.993} \right) = \left( \frac{0.03}{0.97} \right)$$

$$(1.0043)^n = \left( \frac{0.03}{0.97} \right) \times \left( \frac{0.993}{0.007} \right)$$

$$(1.0043)^n = \frac{0.02979}{6.79 \times 10^{-3}} = \frac{29.79}{6.79}$$

$$(1.0043)^n = 4.387$$

$$\log (1.0043)^n = \log 4.387$$

$$n \log (1.0043) = 0.642$$

$$n = \frac{0.642}{0.0018103}$$

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$$n = \frac{0.642 \times 10^3}{1.86} = \frac{642}{1.86}$$

$$n = 345 \quad \text{Ans}$$

#### 4. Work Done on gas during Expansion:

Consider a gas contained in a cylinder having movable piston.

If we raise the temperature of gas, the gas expands and moves the piston up. The upward force exerted by the gas due to its pressure  $P$  is  $PA$  where  $A$  is the area of the piston.

By Newton's third law, the piston exerts an equal and opposite force

$$F = -PA \text{ on the gas}$$

So work done on the gas is

$$W = \int F dx$$

$$W = \int -PA dx \quad (1)$$

where  $dx$  is the displacement of the piston. The -ve sign shows the force exerted by the piston on the gas is opposite to the displacement of the piston.

On the other hand if we decrease the temp. of the gas, it contracts and the work done on the gas is +ve because force exerted by the piston and displacement are in the same direction.

If the piston moves through a distance  $dx$ , then volume of the gas changes by  $dV = A dx$ .

So equation (1) becomes

$$W = - \int P dV \quad (2)$$

If the volume changes from  $V_i$  to  $V_f$  then,

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

If the gas expands  $dV$  is +ve and work done on the gas is -ve. i.e.

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

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

$$W = -P(V_f - V_i) \quad V_f > V_i \quad (3)$$

i.e. work done on the gas during expansion is -ve. Conversely if the gas contracts,  $dV$  is -ve and work done on the gas is +ve. i.e.

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

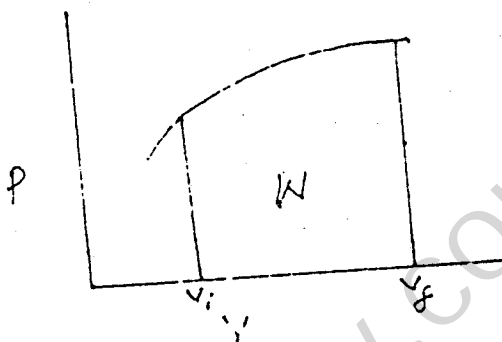
$$W = P(V_i - V_f), \quad V_f < V_i \quad (4)$$

i.e. work done on the gas during compression is +ve. So we arrive at the result that:

(i) Work done on a gas is negative if volume increases and

(ii) Work done on a gas is positive if volume decreases.

The magnitude of work done on the gas is represented by the area under the pressure-volume curve called P-V diagram



Q. Prove that pressure force is non-conservative:

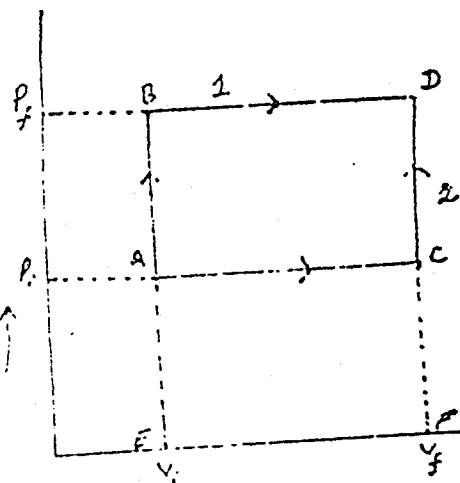
### Pressure Force is non-conservative:

We want to prove that work done on the gas is not independent of the path i.e. work done on the gas along two different paths is different.

For this purpose, let us take an ideal gas from the initial conditions  $P_i$  and  $V_i$  (point A) to final conditions  $P_f, V_f$  (Point D). We take two different paths b/w A and D, i.e. Path 1 (ABD) and path 2 (ACD) as shown in the fig.

Along path ABD first pressure increases from  $P_i$  to  $P_f$  at constt volume  $V_i$  along AB and then volume increases from  $V_i$  to  $V_f$  at constt pressure  $P_f$  along BD.

∴ total work done is equal to the area of rectangle BDEF (the area below the line BD)



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∴ Work done on the gas along path 1 (ABD) is given by

$$W_{ABD} = W_{AB} + W_{BD}$$

Now  $W_{AB} = 0$  because  $dv = 0$  i.e. volume is constt  
 and  $W_{BD} = - \int_{V_i}^{V_f} P dv = - P_f \int_{V_i}^{V_f} dv = - P_f (V_f - V_i)$

∴  $W_{BD} = - P_f (V_f - V_i)$  because  $P = P_f$  along path B.

∴  $W_{ABD} = 0 - P_f (V_f - V_i)$

$$\boxed{W_{ABD} = - P_f (V_f - V_i)} \quad (1)$$

Now along path ACD first volume increases from  $V_i$  to  $V_f$  at constt pressure  $P_i$  along AC and then pressure increases from  $P_i$  to  $P_f$  at constt volume along CD.

The total work done is equal to the area of rectangle ABFC (The area below the line AC)

∴ Work done on the gas along path 2 (ACD) is given by

$$W_{ACD} = W_{AC} + W_{CD}$$

Now  $W_{AC} = - \int_{V_i}^{V_f} P dv = - P_i (V_f - V_i)$  because  $P = P_i$  along path AC

and  $W_{CD} = 0$  because  $dv = 0$  i.e. volume is constt.

$$\boxed{W_{ACD} = - P_i (V_f - V_i)} \quad (2)$$

From equations (1) and (2) we see that

$$W_{ABD} \neq W_{ACD}$$

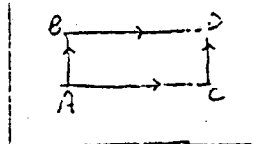
So work done on the ideal gas along two different paths is different.  
 Hence pressure force is non-conservative.

### 5. Work done at constant volume:

The work is zero in that process in which volume remains constt, i.e.  $dv = 0$  and hence  $W = 0$  as shown along path AB & CD. The

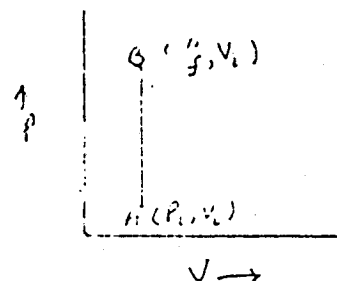
volume remains constt. So work along AC and CD is zero.

It should be noted that it is not sufficient that the process should start and end at the same volume but volume must be constt throughout the process for the work to be zero. For the process ACDB in fig. the volume  $V \rightarrow$



starts and ends at  $V_i$  but the work is definitely not zero. The work is

Zero only for vertical paths AB and CD. The paths AB and CD represent process at const. volume. The process in which volume remains const. is called isochoric process. In the PV diagram it is represented by a vertical line as shown.



### 6. Work done at constant Pressure:

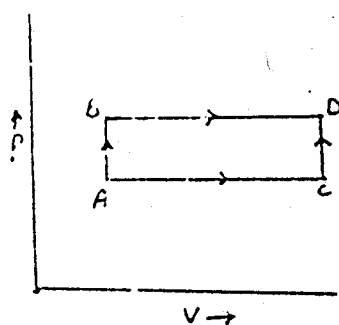
The eq.  $W = \int_{V_i}^{V_f} P dV$  gives the work at const. pressure

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

$$W = -P(V_f - V_i) \quad (\text{const } P)$$

As shown the paths AC and BD are the examples of work done at const. pressure.

It should be noted, work done on the gas is -ve for both of these paths AC & BD because volume increases in both the processes.



### 7. Work done at constant Temp.

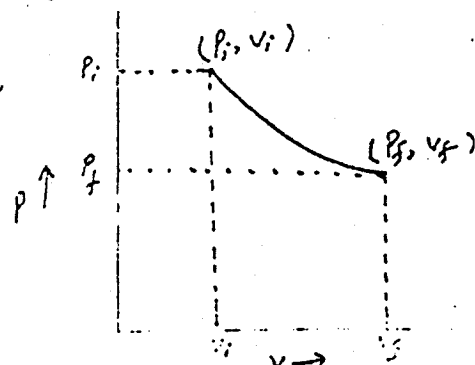
If the gas expands or contracts at const. Temp, the process is called isothermal process. i.e. the process in which Temp. remains constant is called isothermal process. In this process Boyle's law  $PV = \text{const}$  can be applied.

This process is represented in the PV diagram, by hyperbola as shown. This hyperbolic curve called an isotherm.

The work done in isothermal process is calculated by the equation

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

By ideal gas equation  $PV = nRT$   
 $P = \frac{nRT}{V}$



$$\begin{aligned}
 W &= - \int_{V_i}^{V_f} \frac{nRT}{V} dV \\
 &= -nRT \int_{V_i}^{V_f} \frac{dV}{V} \\
 &= -nRT \left[ \ln V \right]_{V_i}^{V_f} = -nRT (\ln V_f - \ln V_i) \\
 &= -nRT \ln \frac{V_f}{V_i} \quad (\text{const } T)
 \end{aligned}$$

The work is -ve when  $V_f > V_i$  and +ve when  $V_f < V_i$ .

## 8. Work done at Thermal Isolation: (Adiabatic Condition)

The process in which cylinder is completely insulated from its surroundings such that heat can't enter or leave the gas is called an adiabatic process. So in this process heat has no way to enter or leave the gas. So during adiabatic, the temp of the gas changes when work is done.

This process is represented by the equation

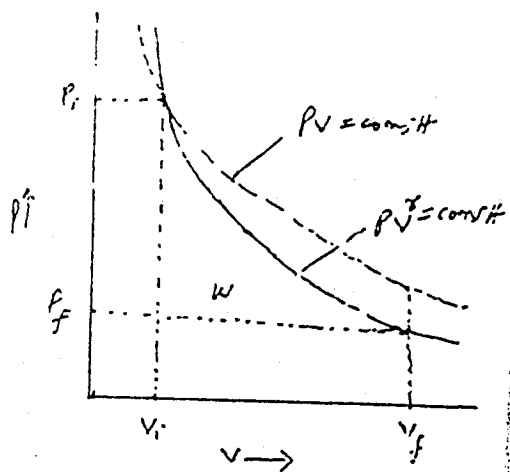
$$P V^\gamma = \text{const} \quad (1)$$

where  $\gamma$  is the ratio of specific heats.

$$\text{i.e. } \gamma = \frac{C_p}{C_v}$$

On a PV diagram, this process is represented by a hyperbolic curve steeper than an isotherm. The hyperbolic curve so obtained is called an adiabat.

The value of  $\gamma$  ranges from 1.1 to 1.8. Because it is greater than 1 so adiabat is steeper than isotherm. So work done in adiabatic process is less than work done in isothermal process.



If we denote eq. (1) constant by  $K$ , then

$$\begin{aligned}
 P V^\gamma &= K \\
 P &= \frac{K}{V^\gamma}
 \end{aligned}$$

$$\begin{aligned}
 W &= - \int_{V_i}^{V_f} P dV = - \int_{V_i}^{V_f} \frac{K}{V^\gamma} dV \\
 &= -K \int_{V_i}^{V_f} V^{-\gamma} dV = -K \left[ \frac{V^{-\gamma+1}}{-\gamma+1} \right]_{V_i}^{V_f}
 \end{aligned}$$

$$= \frac{K}{\gamma-1} \left[ V_f^{-\gamma+1} - V_i^{-\gamma+1} \right]$$

$$= \frac{1}{\gamma-1} \left[ K V_f^{-\gamma+1} - K V_i^{-\gamma+1} \right]$$

Putting  $K = P_i V_i^\gamma = P_f V_f^\gamma$  we get

$$W = \frac{1}{\gamma-1} \left[ P_f V_f - P_i V_i \right] \quad (2)$$

During expansion  $V_f > V_i$  and  $P_f < P_i$ . So work done on the gas is -ve

Using ideal gas law  $PV = nRT$  the equation (2) can be expressed in terms of temperature as

$$P_i V_i = nRT_i$$

$$P_f V_f = nRT_f$$

$$\therefore P_f V_f - P_i V_i = nRT_f - nRT_i$$

$$P_f V_f - P_i V_i = nR(T_f - T_i)$$

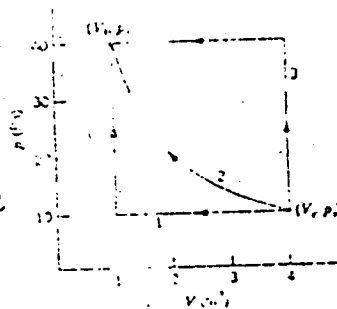
$\therefore$  Equation (2) becomes

$$W = \frac{nR}{\gamma-1} [T_f - T_i]$$

During expansion  $T_f < T_i$ . So work done on the gas is -ve.

### Sample Problem-5

Sample Problem 5: A sample of gas consisting of 0.1 mol is expanded from a volume of 4.0 m<sup>3</sup> to 1.0 m<sup>3</sup> while its pressure falls from 10 to 30 Pa. Compare the work done along the three different paths shown in Fig. 10.



Solution (i) Work done along path 1

Path 1 consists of two processes, one at constt pressure and the other at constt volume

$$P_i = 10 \text{ Pa}; V_f = 1 \text{ m}^3; V_i = 4 \text{ m}^3$$

Work done at constt pressure  $W_1 = -P(V_f - V_i)$

$$= -10(1-4) = -10(-3) = 30 \text{ J}$$

Work done at constt volume is zero

$$\therefore \text{Total work done along path 1} = 30 \text{ J} + 0 = 30 \text{ J}$$

$$\therefore \boxed{W_1 = 30 \text{ J}} \quad \text{Ans.}$$

(ii) Work done along path II ( $P_i = 10 \text{ Pa}, V_i = 4 \text{ m}^3, V_f = 1 \text{ m}^3$ )

Path II shows an isothermal process ( $T = \text{constt}$ )



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$$W_2 = -nRT \ln \frac{V_f}{V_i}$$

Since  $P_i V_i = P_f V_f = nRT$

$$\begin{aligned} \therefore W_2 &= -P_i V_i \ln \frac{V_f}{V_i} \\ &= -10 \times 4 \ln \frac{1}{4} = -40 \ln \frac{1}{4} \\ &= -40 \times (-1.386) \end{aligned}$$

$$\boxed{W_2 = 55 \text{ J}} \quad \text{Ans.}$$

(iii) Work done along path III.

Path III consists of two processes, one at const volume and the other at const pressure.

$$P_f = 40 \text{ Pa}; \quad V_f = 1 \text{ m}^3, \quad V_i = 4 \text{ m}^3$$

$$\text{Work done at const volume} = 0$$

$$\begin{aligned} \text{Work done at const pressure} &= -P(V_f - V_i) \\ &= -P_f(V_f - V_i) \\ &= -40(1 - 4) = -40 \times -3 \\ &= 120 \text{ Joule} \end{aligned}$$

$\therefore$  Total work done along path - III is

$$W_3 = 0 + 120$$

$$\boxed{W_3 = 120 \text{ J}} \quad \text{Ans}$$

### Sample Problem - 6

Problem. 2.5: (a) Find the Bulk modulus  $K$  for an adiabatic process involving an ideal gas. (b) Use the adiabatic bulk modulus to find the speed of sound in the gas as a function of temperature. Evaluate in air at  $20^\circ\text{C}$  ( $\gamma = 1.4$ )

Sol: (i) Bulk modulus for adiabatic process =  $\beta = ?$

$$\gamma = 1.4 \text{ for air. } T = 20^\circ\text{C} = 20 + 273 = 293 \text{ K}$$

(ii) Speed of sound wave as a function of temp =  $v = ?$

(a) By definition

$$\beta = \frac{-dP}{\frac{dV}{V}} = -V \frac{dP}{dV} \quad (1)$$

For an adiabatic process

$$PV^\gamma = \text{const}$$

$$V^\gamma dP + P\gamma V^{\gamma-1} dV = 0$$

$$V^\gamma dP = -\gamma P V^{\gamma-1} dV$$

$$V^\gamma dP = -\gamma P V^{\gamma-1} dV$$

$$dP = -\frac{\gamma P}{V} dV$$

$$-\frac{dP}{dV} = \frac{\gamma P}{V}$$

$$-V \frac{dP}{dV} = \gamma P$$

$$-V \frac{dP}{dV} = \gamma P \quad (ii)$$

Comparing (i) and (ii) we get

$$\beta = \gamma P \quad \text{Ans.}$$

(b)

As  $V = \sqrt{\frac{\beta}{\rho}}$

$$= \sqrt{\frac{\gamma P}{\rho}}$$

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

$$V = \sqrt{\frac{\gamma nRT}{V \rho}}$$

$$\frac{m}{V} = \rho$$

$$m = \rho V$$

$$V = \sqrt{\frac{\gamma nRT}{m}}$$

$$\therefore V = \sqrt{\frac{N n R T}{n M}} = \sqrt{\frac{\gamma R T}{M}}$$

For air  $M = 0.029 \text{ Kg/mol}$

$$V = \sqrt{\frac{1.4 \times 8.31 \times 293}{0.029}}$$

$$V = 342.846$$

$$V = 343 \text{ m/s} \quad \text{Ans.}$$

## Q. The Internal Energy of an Ideal Gas:

The molecules of ideal gas have no force of attraction b/w them.

So the molecules of ideal gas have only K.E and no P.E. The temp. of ideal gas depends only on translational K.E.

The ideal gas has no internal energy due to vibrational and rotational motions.

The ideal gas has internal energy only due to translational K.E

For  $n$  moles of an ideal gas at temp 'T' the internal energy of ideal gas is written as

$$E_{\text{int}} = n \left( \frac{1}{2} M \bar{v}^2 \right) = \frac{3}{2} n R T \quad (1)$$

So we find that internal energy of the ideal gas depends only on its temperature. It does not depend on pressure and volume of gas.

We can change internal energy of the ideal gas by doing work on the gas or by allowing the gas to do work on the surroundings.

Suppose the ideal gas in cylinder is insulated from the surroundings and a work 'w' is done on the gas. This work done on the gas changes the internal energy of the gas.

∴ By law of conservation of energy

$$\Delta E_{\text{int}} = W$$

If the work done on the gas is +ve then change in internal energy is also +ve. So expression (1) becomes

$$\Delta E_{\text{int}} = \frac{3}{2} n R \Delta T \quad (2)$$

So the temperature change is also +ve. If -ve work is done on the gas by moving the piston upward then change in internal energy and change in temp are -ve

For diatomic gases (gases with two atoms in each molecule) e.g.  $O_2$ ,  $N_2$ , so the molecules have K.E. due to rotation about their centre of mass.

So internal energy of diatomic gas is due to translational K.E. + due to rotational K.E.

Consider a diatomic molecule consisting of two atoms as shown. The axis of diatomic molecule is along Z-axis

There is no rotational K.E. of diatomic molecule about Z-axis because  $I_z = 0$

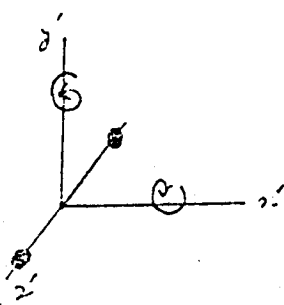
So there are two rotational K.E.'s of the diatomic molecule about x' and y' axis.

∴ The rotational K.E. of diatomic molecule is

$$(K.E.)_{\text{rot}} = \frac{1}{2} I_{x'} \omega_{x'}^2 + \frac{1}{2} I_{y'} \omega_{y'}^2$$

So the total K.E. of diatomic molecule is equal to the sum of translational and rotational parts.

$$\therefore (K.E.)_{\text{Total}} = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 + \frac{1}{2} I_{x'} \omega_{x'}^2 + \frac{1}{2} I_{y'} \omega_{y'}^2 \quad (3)$$



According to theorem of equipartition of energy the average energy of gas molecule per degree of freedom is same and is equal to  $\frac{1}{2} kT$  where  $k$  is Boltzmann's constant and  $T$  is the absolute temp of the gas.

So the total internal energy of  $N$  molecules by using law of equipartition of energy is given by;

$$E_{int} = N \left( \frac{1}{2} kT \right)$$

For a monoatomic gas which has 3 degrees of freedom per volume molecule, the internal energy is given by

$$E_{int} = 3 \left( \frac{1}{2} kT \right)$$

∴ Total internal energy of  $N$  molecules is

$$E_{int} = N \left( \frac{3}{2} kT \right) = \frac{3}{2} NkT$$

$$E_{int} = \frac{3}{2} RT$$

$$\frac{R}{N} = k$$

$$R = Nk$$

This is the internal energy of one mole of monoatomic gas whose molecule has 3 degrees of freedom.

For  $n$  moles; the above expression becomes

$$E_{int} = \frac{3}{2} nRT$$

For a diatomic gas which has five degrees of freedom per molecule; the internal energy is given by

$$E_{int} = \frac{5}{2} nRT$$

For a polyatomic gas (more than two atoms per molecule) which has 6 degrees of freedom per molecule, the internal energy is given by

$$E_{int} = \frac{6}{2} nRT$$

$$E_{int} = 3nRT$$

For a diatomic gas molecule free to vibrate has 7 degrees of freedom i.e.  $7 = (3+2+2)$  the internal energy is given by

$$E_{int} = \frac{7}{2} nRT$$

The vibrational terms in the internal energy are effective at high temp. At low temp. the vibrational and rotational motions can be frozen, so that at low temp. only three translational degrees of freedom

2.0

are present. The experiments with gas molecule collisions shows that the internal energy of an atom is quantised.

### Sample Problem-7

Example Problem 7. A cylinder contains one mole of gas at the initial point with volume  $V_i = 4 \text{ cm}^3$  and pressure  $P_i = 10 \text{ atm}$ . If the cylinder be removed from the thermal reservoir, and let us compress the gas adiabatically, until its volume is  $V_f = 1 \text{ cm}^3$ , find the change in internal energy of the gas, assuming it to be helium (a monoatomic gas with  $\gamma = 1.66$ ).

Sol:  $V_i = 4 \text{ cm}^3$ ;  $P_i = 10 \text{ atm}$      $V_f = 1 \text{ cm}^3$ ,  $\gamma = 1.66$   
 $\Delta E_{int} = ?$ ,  $R = 8.315 \text{ J/mol.K}$ ,  $n = 0.11 \text{ mol}$

As  $E_{int} = \frac{3}{2} nRT$     (1)

To find  $\Delta T$  we calculate  $T_i$  and  $T_f$ . For  $T_f$  we calculate  $P_f$  as

$$\frac{P_f V_f^\gamma}{\gamma} = \frac{P_i V_i^\gamma}{\gamma}$$

$$P_f = \frac{P_i V_i^\gamma}{V_f^\gamma}$$

$$P_f = \frac{10 \times (4)^{1.66}}{(1)^{1.66}} = 10 \times 9.98 = 99.8$$

$$P_f = 100 \text{ atm}$$

Now  $P_i V_i = nRT_i$

$$T_i = \frac{P_i V_i}{nR}$$

$$= \frac{10 \times 4}{0.11 \times 8.31} = \frac{40}{0.914}$$

$$T_i = 44 \text{ K}$$

Now  $T_f = \frac{P_f V_f}{nR}$

$$= \frac{100}{0.11 \times 8.31} = \frac{100}{0.914}$$

$$T_f = 109 \text{ K}$$

$$\therefore \Delta T = T_f - T_i$$

$$= 109 - 44$$

$$\Delta T = 65 \text{ K}$$

Putting the values of  $n$ ,  $R$  and  $\Delta T$  in eq(1) we get

$$\Delta E_{int} = \frac{3}{2} nR \Delta T$$

$$= \frac{3}{2} \times 0.11 \times 8.31 \times 65 = 1.5 \times 0.11 \times 8.31 \times 65$$

$$\Delta E_{int} = 89 \text{ Joules}$$

Ans

## 10. Intermolecular Forces:

Forces b/w molecules are of electromagnetic origin. All molecules contain electric charges. However the molecules are electrically neutral because the charge of electron is equal and opposite to the +ve charge of the nucleus.

When two molecules approach each other, the +ve and -ve charges are slightly displaced from their equilibrium positions and the average distance b/w opposite charges in the two molecules becomes less than the distance b/w like charges. As a result the intermolecular forces are short range forces.

If the two molecules come so close together that their outer charges overlap, the intermolecular forces become repulsive in nature. It is due to this repulsion that molecules rebound after collision in gases.

In a solid the molecules vibrate about their mean position but do not have enough energy to escape from each other.

In a liquid the molecules have greater vibrational K.E. In a gas the molecules have greatest K.E. In a gas the average distance b/w molecules is much greater than effective range of intermolecular forces. The intermolecular forces are  $10^{29}$  times greater than gravitational forces. These intermolecular forces can produce acceleration of  $10^5 \text{ m/s}^2$  in a molecule but this acceleration lasts for a very short time.

## 11. The Vander Waals Equations of State:

Kinetic theory of gases gives microscopic description of behaviour of ideal gas. But some of the assumptions of ideal gas model are not true for real gases. e.g. due to intermolecular forces the molecules have a small but non-zero diameter which is against the assumption of ideal gas model according to which size of molecule is negligible.

Moreover the range of intermolecular forces may be greater than the size of the molecule which is against our assumption that intermolecular forces are short range forces.

So the ideal gas equation needs modifications to account for the effect of finite size molecule and presence of intermolecular forces.

### (i) Effect of Finite Size of Molecules:

To consider the effect of finite size of molecule we consider the molecule in the form of a hard sphere of diameter 'd'. The distance b/w the centres of two molecules can't be less than 'd'. The free volume occupied by a molecule is occupied by molecule is decreased by the volume of a hemisphere of radius 'd' centered on the other molecule.

If  $b$  is the decrease in volume due to molecules in one mole then decrease in volume due to molecules in  $n$  moles =  $n \cdot b$ .

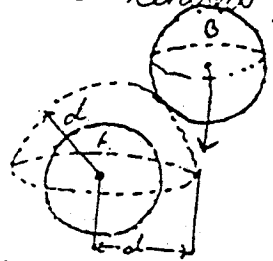
If  $V$  is the volume of container then the volume available to the gas is not  $V$  but  $V - n \cdot b$ .

So the ideal gas equation takes the form,

$$P(V - nb) = nRT$$

$$P = \frac{nRT}{V - nb} \quad (1)$$

This shows that  $V - nb$  pressure of real gas is increased. Due to smaller volume the molecules have more collisions and thus pressure is increased.



### (ii) Effect of Intermolecular Forces:

To consider the effect of intermolecular forces, we take the range of intermolecular forces equal to diameter 'd' of molecule.

Let us consider a single molecule which is about to collide the wall of container. This molecule also experiences attractive forces from other molecules lying within a distance 'd'.

The sum of all the intermolecular forces gives a resultant force on the molecule under consideration, directed away from the wall.

So the molecule collides with the wall with a smaller force and hence smaller pressure.

So due to intermolecular forces the pressure is reduced.  
 The decrease in pressure is proportional to the number of molecules per unit volume  $\frac{N}{V}$ .

Total decrease in pressure due to intermolecular forces is proportional to  $(\frac{N}{V})^2$

If we replace  $N$  by  $n$ , where  $N$  is the number of molecules and  $n$  is the number of moles. Then expression (1) for pressure becomes

$$P = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$$

$$P_0 + a\left(\frac{n}{V}\right)^2 = \frac{nRT}{V-nb}$$

$$\left[P_0 + a\left(\frac{n}{V}\right)^2\right](V-nb) = nRT$$

This is called Vander Waals equation of state. The constants 'a' and 'b' can be determined experimentally and are called Vander Waals constants.