

# Chapter 13

## Kinetic Theory

### Introduction

What is Kinetic Theory?

- Kinetic theory explains the behaviour of gases based on the idea that the gas consists of rapidly moving atoms or molecules.
- In solids the molecules are very tightly packed as inter molecular space is not present In liquids inter molecular spaces are more as compared to solids and in gases the molecules are very loosely packed as intermolecular spaces are very large.
- The random movement of molecules in a gas is explained by kinetic theory of gases.
- We will also see that why kinetic theory is accepted as a success theory.
- Kinetic theory explains the following:-
  - a) Molecular interpretation of pressure and temperature can be explained.
  - b) It is consistent with gas laws and Avogadro's hypothesis.
  - c) Correctly explains specific heat capacities of many gases.

### 13.2 Molecular nature of matter

- Atomic hypothesis was given by many scientists. According to which everything in this universe is made up of atoms.
- Atoms are little particles that move around in a perpetual order attracting each other when they are little distance apart. But if they are forced very close to each other then they repel.
- **Dalton's atomic theory** is also referred as the molecular theory of matter. This theory proves that matter is made up of molecules which in turn are made up of atoms.
- According to **Gay Lussac's law** when gases combine chemically to yield another gas, their volumes are in ratios of small integers.
- **Avogadro's law** states that the equal volumes of all gases at equal temperature and pressure have the same number of molecules.
- Conclusion: - All these laws proved the molecular nature of gases.
- Dalton's molecular theory forms the basis of Kinetic theory.

### Why was Dalton's theory a success?

- Matter is made up of molecules, which in turn are made up of atoms.
- Atomic structure can be viewed by an electron microscope.

### Solids, Liquids, Gases in terms of molecular structure

Basis of difference	Solids	Liquids	Gases
Inter Atomic Distance(distance between molecules).	Molecules are very tightly packed. Inter atomic distance is minimum.	Molecules are not so tightly packed. Inter atomic distance is more as compared to solids.	Molecules are loosely packed .Free to move. Inter atomic distance is maximum.
Mean Free Path is the average distance a molecule can travel without colliding.	No mean free path.	Less mean free path.	There is mean free path followed by the molecules.

### 13.3 Behaviour of Gases

- Gases at low pressures and high temperatures much above that at which they liquify (or solidify) approximately satisfy a relation between their pressure, temperature and volume:

$$PV=KT \dots \dots \dots \text{(i)}$$

This is the universal relation which is satisfied by all gases.

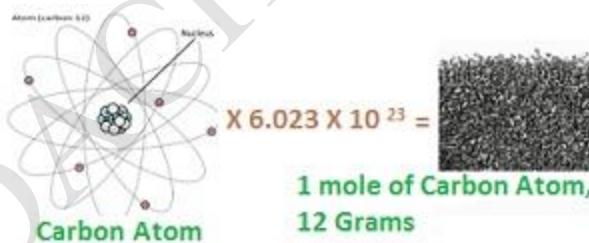
where P, V, T are pressure, volume and temperature respectively, and K is the constant for a given volume of gas. It varies with volume of gas.

$K=Nk_B$  where, N=number of molecules and  $k_B$  = Boltzmann Constant and its value never change.

- From equation (i)  $PV= Nk_B$   
Therefore  $PV/NT = \text{constant}=(k_B)$  (Same for all gases).
- Consider there are 2 gases :-  $(P_1, V_1, T_1)$  and  $(P_2, V_2, T_2)$  where P, V and T are pressure, volume and temperature resp.
- Therefore  $P_1V_1/(N_1T_1) = P_2V_2/(N_2T_2)$
- Conclusion: - This relation is satisfied by all gases at low pressure and high temperature.

#### Justification of the Avogadro's hypothesis from equation of gas

- Avogadro's hypothesis states that equal volumes of all gases at equal temperature and pressure have the same number of molecules.
- Consider the equation  $PV/NT = \text{constant}$  and if P, V and T are same for 2 gases then N(number of molecules) is also same.
- According to Avogadro's hypothesis number of molecules per unit volume is same for all gases at a fixed P and T.  
Avogadro number is denoted by  $N_A$ . Where,  $N_A = 6.02 \times 10^{23}$ . It is universal value.
- Experimentally it has been found that the mass of 24.4 litres of any gas is equal to molecular weight in grams at standard temperature and pressure.



#### Perfect Gas Equation

- Perfect gas equation is given by  $PV = \mu RT$ ,  
Where P, V are pressure, volume, T = absolute temperature,  $\mu$  = number of moles and R = universal gas constant,  $R = k_B N_A$  where,  $k_B$  = Boltzmann constant and  $N_A$  = Avogadro's Number
- This equation tells about the behaviour of gas at a particular situation.
- If a gas satisfies this equation then the gas is known as Perfect gas or an ideal gas.

#### Different Forms of Perfect Gas Equation

- $PV = \mu RT \dots \dots \dots \text{(i)}$

Where  $\mu$  (no. of moles) =  $N/N_A$  where N=no of molecules and  $N_A$  = Avogadro number (no of molecules in 1 mole of gas). Or  $\mu = M/M_0$  where M=mass of sample of gas and  $M_0$  = molar mass.

$$PV = (N/N_A)RT \quad (\text{putting } \mu=N/N_A \text{ in equation(i)})$$

By simplifying  $PV = Nk_B T$

$$PV=Nk_B T \Rightarrow P = (N/V) k_B T \Rightarrow P=nk_B T$$

Where, n(number density) =  $N/V$ . where, N=number of molecules and V=volume.

$$\therefore PV=nk_B T$$

2. Substitute  $\mu = M/M_0$  in equation(i)

$$PV=(M/M_0) RT \Rightarrow P=(M/V)1/M_0 RT \text{ where } M/V = \rho \text{ (mass density of the gas)}$$

$$\therefore P=\rho RT/M_0$$

### Ideal Gas

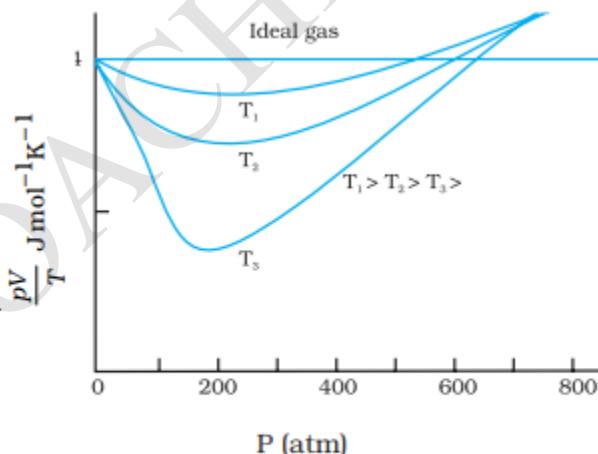
- A gas that satisfies the perfect gas equation exactly at all pressures and temperatures.
- Ideal gas is a theoretical concept.
- No real gas is truly ideal. A gas which is ideal is known as real gas.
- Real gases approach the ideal gas behaviour for low pressures and high temperatures.

### Real gases deviation from ideal gas

- Real gases approach the ideal gas behaviour for low pressures and high temperatures.
- Ideal gas equation  $PV=\mu RT$ , for 1 mole,  $\mu=1$ ,  $PV=RT$   
 $\Rightarrow PV/RT=\text{constant}$

Graph should be a straight line(parallel to x-axis) for ideal gas. This means it has constant value at all temperature and all pressure.

- But in case of real gases graph approach ideal gas behaviour at high temperature and low pressure.
- At high temperature and low pressure molecules are far apart. When temperature is increased the molecules will move randomly far from each other.
- As a result molecular interaction decreases the gas behaves as an ideal gas.
- The ideal behaviour comes into picture when the molecular present inside the gas don't interact with each other.



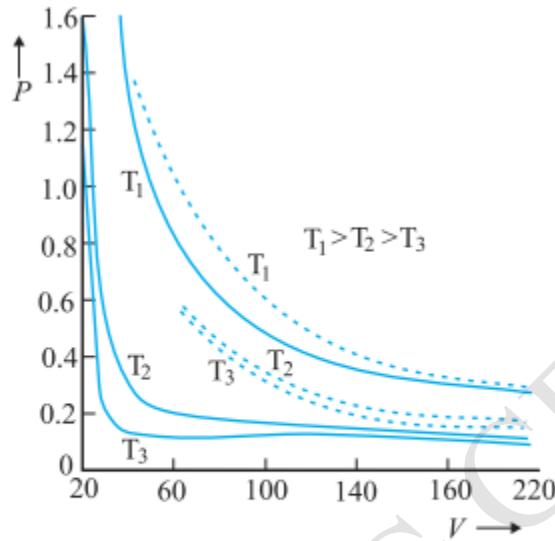
*Real gases approach ideal gas behaviour at low pressures and high temperatures.*

### Deduction of Boyle's law and Charles law from perfect gas equation

1. Boyle's law: -Deriving Boyle's law from perfect gas equation,  $PV=\mu RT$ 
  - Consider  $T$  (temperature) and  $\mu$  (no. of moles) constant.
  - Therefore  **$PV=constant$** .
  - According to Boyle's law, at a constant temperature, pressure of a given mass of gas varies inversely with volume.

2. Charles's law:-Consider If  $P$ (Pressure) is constant, then

- From Perfect gas equation  $PV = \mu RT$ ,  $\Rightarrow V/T = \mu R/P = \text{constant}$
- Therefore  $V/T = \text{constant}$ .
- According to Charles's law for a fixed pressure, volume of a gas is  $\propto$  to its absolute temperature.
- Conclusion: - Ideal gas satisfies the Boyle's law and Charles's law.



Experimental P-V curves (solid lines) for steam at three temperatures compared with Boyle's law (dotted lines).  $P$  is in units of 22 atm and  $V$  in units of 0.09 litres.

### Deducing Dalton's Law of partial pressures

- Dalton's law of partial pressure states that the total pressure of a mixture of ideal gases is the sum of partial pressures.
- Consider if there are several ideal gases mixed together in a vessel, then the total pressure of that vessel is equal to sum of partial pressure.
- Partial pressure is the pressure exerted by a particular gas if only that gas is present in the vessel.
- For example: -

Consider if in a vessel there is a mixture of 3 gases, A, B and C. So the partial pressure of A is equal to pressure exerted only by A and considering B and C are not present.

Similarly partial pressure of B is equal to the pressure exerted only by B and considering A and C are not there.

Similarly for C.

According to Dalton's law the total pressure of mixture is sum of partial pressure of A, partial pressure of B and partial pressure of C.

### To show how perfect gas equation concludes Dalton's law of partial pressure:-

- Suppose there is a mixture of ideal gases which means these gases do not interact with each other.

By perfect gas equation,  $PV = \mu RT$

Where  $V$ =volume of vessel,  $P$ =Pressure and  $T$ =temperature and  $\mu$  (no. of moles).

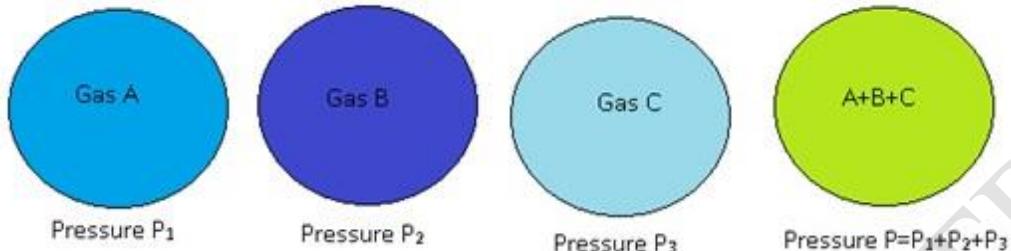
As there are mixture of gases therefore  $\mu = \mu_1 + \mu_2 + \dots$  so on.

$$PV = (\mu_1 + \mu_2 + \dots)RT$$

$$\begin{aligned}
 P &= (\mu_1 + \mu_2 + \dots)RT/V \\
 \Rightarrow P &= \mu_1 RT/V + \mu_2 RT/V + \dots \\
 \therefore P &= P_1 + P_2 + \dots
 \end{aligned}$$

Where  $P_1$ =partial pressure of gas 1 and  $P_2$ =partial pressure of gas 2.

$\therefore P = P_1 + P_2 + \dots$ —total pressure due to the mixture of gases is equal to the sum of the partial pressure of the gas.



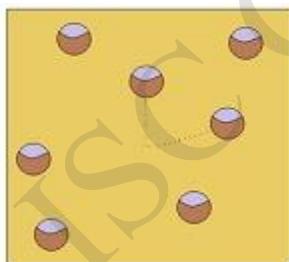
### 13.4 Kinetic Theory of an Ideal Gas

#### Basis of Kinetic Theory: -

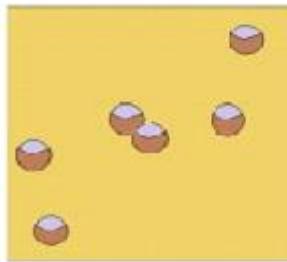
1. Molecules of gas are in incessant random motion, colliding against one another and with the walls of the container.
2. All collisions are elastic.
3. Total Kinetic energy is conserved.
4. Total momentum is conserved.
5. In case of an elastic collision total Kinetic energy and momentum before collision is equal to the total Kinetic energy and momentum after collision.

#### What does Kinetic Theory tells?

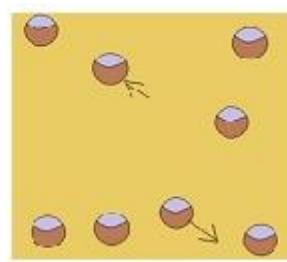
1. At ordinary temperature and pressure the molecular size is very small as compared to inter molecular distance between them.
2. In case of gas, molecules are very far from each other and the size of molecules is small as compared to the distance between them.
3. As a result, interaction between them is negligible. As there is no interaction between the molecules, there will be no force between the molecules.
4. As a result molecules are moving freely as per newton's first law of motion.
5. The molecules should move along straight line but when they come closer they experience the intermolecular forces and as a result their velocities change.
6. This phenomenon is known as collision. These collisions are elastic.



Molecules moving randomly



Molecules colliding with each other



Molecules change their direction after colliding

### 13.4.1 Pressure of an ideal gas based on Kinetic theory

#### Assumptions:-

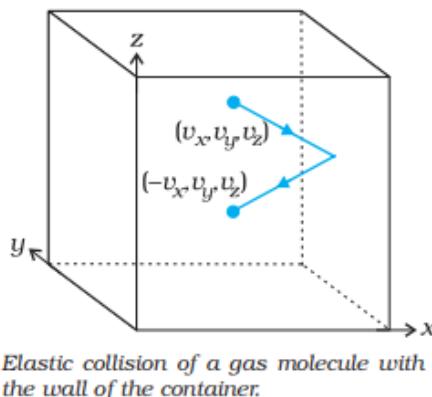
- Consider a cube shape container filled with an ideal gas. We will consider only one molecule; the molecule hits the walls of the container and bounces back.
- Let the velocity of the molecule when it is moving be  $(v_x, v_y, v_z)$ .
- When the molecule bounces back, the velocity will be  $(-v_x, v_y, v_z)$ .
- Change in momentum =  $P_f - P_i$  where  $P_f$  = final momentum and  $P_i$  = initial momentum
- $P_f - P_i = -mv_x - mv_x = -2mv_x$
- This change in momentum is imparted to the wall due to the collision.
- Momentum imparted to the wall in collision by one molecule =  $2mv_x$ 
  - But there are as many molecules, we have to calculate total momentum imparted to the wall by all of them.
  - To calculate the number of molecules that hit the wall:  
Area of wall=  $A$   
 $\therefore$  in time  $\Delta t$ , all molecules within a distance of  $Av_x\Delta t$  can hit the wall.  
but on an average half of molecules move towards the wall and half away from the wall.  
 $\therefore \left(\frac{1}{2}\right) Av_x\Delta t$  will hit the wall.
- $\therefore$  total momentum imparted to the wall =  $2mv_x \times \frac{1}{2}n Av_x\Delta t = Anv_x^2\Delta t m$
- Force exerted on the wall= rate of change of momentum =  $Anv_x^2 m$
- Pressure on the wall  $P = \frac{F}{A} = nmv_x^2$
- $\therefore P = nmv_x^2$  is true for group of molecules moving with velocity  $v_x$

Note:

- i. All the molecules inside the gas will not have the same value of velocity. All will have different velocities
- ii. The above equation therefore, is valid for pressure due to the group of molecules with speed  $v_x$  in the x-direction and n stands for the number density of that group of molecules.
  - Therefore total pressure due to all such groups will be obtained by summing over the contribution due to the molecule  $P = nm\overline{v_x^2}$
  - Where,  $\overline{v_x^2}$  is the average of  $v_x^2$ .
- Since the gas is isotropic the molecules move randomly which means the velocity of all the molecules can be in any direction. Therefore

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}(\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}) = \frac{1}{3}v^2$$

- Therefore, Pressure,  $P = \frac{1}{3}nmv^2$ , where  $v^2$ = average squared speed.



### **Justifying the assumptions:-**

- We have assumed the container containing the gas is a cube. The shape of the container is immaterial.
- For a vessel of any arbitrary shape, we can choose a small infinitesimal (planar) area and can prove the above derivation.
- We will see A and  $\Delta t$  are not there in the final result.
- By Pascal's law pressure in one portion of gas in equilibrium is the same as anywhere else.
- All collisions are neglected.
  - a) The number of molecules hitting the wall in time  $\Delta t$  was found to be  $\left(\frac{1}{2}\right) A v_x \Delta t$ , with random collisions and a steady state of gas.
  - b) Thus, if a molecule with velocity  $(v_x, v_y, v_z)$  acquires a different velocity due to collision with some molecules, there will always be some other molecule with a different initial velocity which after a collision acquires the velocity  $(v_x, v_y, v_z)$ .
  - c) Molecular collision, when they are not too frequent and the time spent in collision is very small compared to the time between collisions, will not have any affect in the above calculation.

### **13.4.2 Kinetic Interpretation of Temperature**

- The average kinetic energy of a molecule is directly proportional to the absolute temperature of the gas.
- It is independent of pressure, volume or nature of the ideal gas.
- Multiplying with V on both sides,

$$PV = \frac{1}{3} n V m \bar{v}^2$$

After simplifying,

$$PV = \frac{2}{3} N \times \frac{1}{2} m \bar{v}^2, \text{ where, } n = N/V$$

N- Number of molecules in a sample.

- Therefore  $PV = \frac{2}{3} E \dots \dots \dots (i)$   
 $E$ - Kinetic energy  $= N \times \frac{1}{2} m \bar{v}^2$   
This is the basis of Kinetic interpretation of temperature.
- Combining eq(i) with the ideal gas equation, we get

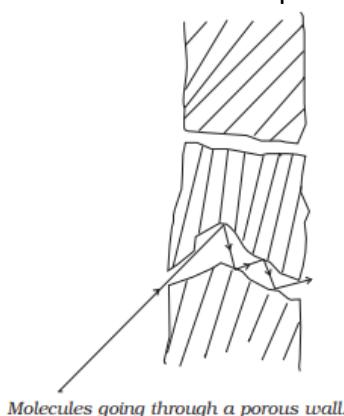
$$E = \frac{3}{2} k_B N T \dots \dots \dots (ii)$$

$$\text{or, } \frac{E}{N} = \frac{1}{2} m \bar{v}^2 = \frac{3}{2} k_B T \dots \dots \dots (iii)$$

This is the average kinetic energy

$$\therefore KE \propto T$$

Hence, temperature can be interpreted as a molecular quantity.



## **Kinetic theory: Consistent with ideal gas equation and gas laws**

### 1. Consistent with ideal gas equation:

$$\text{From kinetic interpretation } \frac{E}{N} = \frac{3}{2} k_B T \Rightarrow E = \frac{3}{2} N k_B T$$

The internal energy of an ideal gas is directly proportional to T

This shows that internal energy of an ideal gas depends only on temperature, not on pressure or volume.

### 2. Consistent with Dalton's law of partial pressures:

$$P = \frac{1}{3} n m v^2, \text{ from kinetic theory}$$

∴ if a vessel contains a mixture of gases,

$$P = \frac{1}{3} [n_1 m_1 \bar{v}_1^2 + n_2 m_2 \bar{v}_2^2 + \dots]$$

in equilibrium average Kinetic energy of molecules of different gasses will be equal

$$\frac{1}{2} m_1 \bar{v}_1^2 = \frac{1}{2} m_2 \bar{v}_2^2 = \dots = \frac{3}{2} k_B T$$

$$\text{Total pressure, } P = \frac{1}{3} \left[ \frac{3}{2} n_1 k_B T + \frac{3}{2} n_2 k_B T + \dots \right]$$

$$P = k_B T [n_1 + n_2 + \dots]$$

$$P = \frac{R}{N_A} [n_1 + n_2 + \dots]$$

$$P = [\mu_1 + \mu_2 + \dots] RT$$

$$P = P_1 + P_2 + \dots$$

This is Dalton's law of partial pressure.

## **Law of Equipartition of energy: Degrees of Freedom**

- Degrees of Freedom can be defined as independent displacements or rotations that specify the orientation of a body or system.
- A molecule free to move in space needs three coordinates to specify its location.
- If it is constrained to move in a plane it needs 2.
- If constrained to move along a line, it needs just one coordinate to locate it.
- For example:- Consider a room and if we tie a thick rope from one wall to another.
- Take a ball which is moving straight on the rope.
- The ball has only 1 degree of freedom. It can move only in one particular dimension.
- Consider if the ball is on the floor which is two-dimensional, then the ball can move along 2 directions.
- The ball has 2 degrees of freedom.
- Consider if we throw the ball in space which is 3 dimensional. Then the ball can move in 3 dimensions.
- Therefore degree of freedom tells us in how many ways a body can move or rotate or vibrate.

## **Categories of Degrees of Freedom**

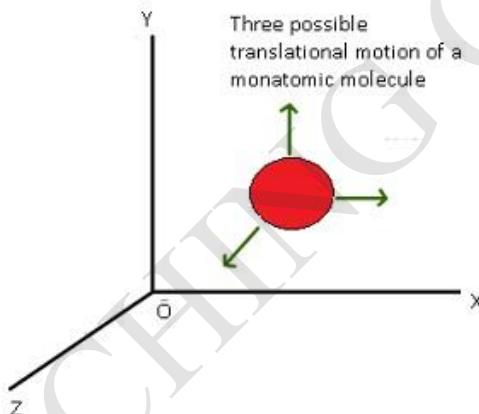
1. Translational degree of freedom.
2. Rotational degree of freedom.
3. Vibrational degree of freedom.

### **Translational degree of freedom:-**

- Translation means motion of the body as a whole from one point to another.
- For example:
- Consider the oxygen molecule; it has 2 oxygen atoms which are bonded together.

- The 2 oxygen atoms along with the bond are considered as whole body.
- When the body as a whole is moving from one point to another is known as translational.
- Consider a molecule which is free to move in space and so it will need 3 coordinates(x, y, z) to specify its location.
- Therefore it has 3 degrees of freedom.
- Similarly a molecule which is free to move in a plane which is 2 dimensional and so it needs 2 coordinates to specify its location.
- Therefore it has 2 degrees of freedom.
- Similarly a molecule which is free to move in line it needs 1 coordinate to specify its location.
- Therefore it has 1 degree of freedom.
- Molecules of monoatomic gas have only translational degrees of freedom. This means gases which have only one atom.
- For example:- Helium atom it consists of only one He atom. It will have translational degrees of freedom.
- Each translational degree of freedom contributes a term that contains square of some variable of motion.
- The variable of motion means the velocity ( $v_x, v_y, v_z$ ).
- The term  $(1/2) mv_x^2$  will contribute to energy. This is Kinetic energy which is involved with the motion of the molecule from one point to another.

In thermal equilibrium, the average of each such term is  $(1/2) k_B T$ .



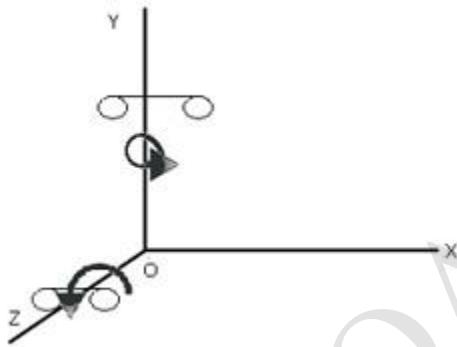
### Rotational Degree of freedom

- Independent rotations that specify the orientation of a body or system.
- There is rotation of one part of the body with respect to the other part.
- Rotational degree of freedom happens only in diatomic gas.
- Diatomic molecules have rotational degrees of freedom in addition to translational degrees of freedom.
- It is possible in diatomic molecules as 2 atoms are connected together by a bond. So the rotation of one atom w.r.t to other atom.
- In diatomic there is translational in addition to that they have rotational degree of freedom also.
- For example: - Two oxygen atoms joined together by a bond. There are two perpendicular axes.
- There are 2 rotations possible along the two axes.
- They have 3 translational degrees of freedom and also 2 rotational degree of rotation.
- Therefore Rotational degree of freedom contributes a term to the energy that contains square of a rotational variable of motion.
- Rotational variable of motion comes from angular momentum  $\omega$ .
- Linear velocity is  $v_x, v_y, v_z$ . Whereas angular velocity is  $w_x, w_y, w_z$ .

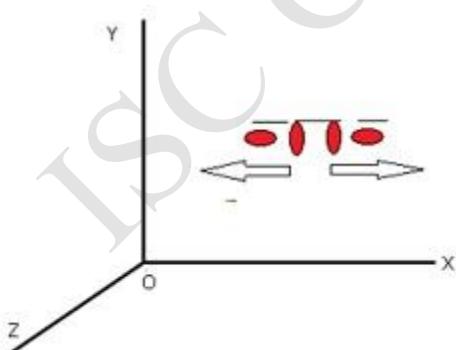
- $E_R(\text{rotational}) = (1/2)(I_1\omega_1) + (1/2)I_2\omega_2$ . These are 3 rotational degrees of freedom along the 2 perpendicular axes.
- The total energy contribution due to the degrees of freedom for oxygen molecule.
- There will be 3 translational degrees of freedom  $(1/2)m_xv_x^2, (1/2)m_yv_y^2, (1/2)m_zv_z^2$
- 2 rotational degrees of freedom  $(1/2)I_1^2\omega_1^2, (1/2)I_2^2\omega_2^2$

### Vibrational degree of freedom

- Some molecules have a mode of vibration, i.e. its atoms oscillate along the inter-atomic axis like a one-dimensional oscillator.
- This vibration is observed in some molecules.
- For example:- CO atoms oscillate along the interatomic axis like a one-dimensional oscillator.
- Consider two atoms they vibrate along the inter-atomic axis.
- The vibrational energy terms contain square of vibrational variables of motion.
- Total vibrational energy term  $E_v = (1/2) m (dy/dt)^2 + (1/2) ky^2$  where  $(1/2) m(dy/dt)^2$  = Kinetic energy and  $(1/2)ky^2$  = Potential energy and  $k$  = force constant one-dimensional oscillator.
- The vibrational degree of freedom contributes 2 terms.



(1)



(2)

(1) Rotational motion along two axis perpendicular to line joining two particles (here y and z directions)

(2) Vibrational motion along line joining the two atoms

### Comparison between 3 energy modes

Translational	Rotational	Vibrational
$E_t = (1/2)mv_x^2$	$E_r = (1/2)I\omega^2$	$E_v = (1/2)m(dy/dt)^2 + (1/2)ky^2$
1 squared term is being contributed	1 squared term is being contributed	2 squared term is being contributed

### Law of Equipartition of energy

According to this law, in equilibrium, the total energy is equally distributed in all possible energy modes, with each mode having an average energy equal to  $(1/2)k_B T$ .

1. Each translational degree of freedom contributes  $(1/2) k_B$
2. Each rotational degree of freedom contributes  $(1/2) k_B$
3. Each vibrational degree of freedom contributes  $2x (1/2)k_B$

### **Specific Heat Capacity for monoatomic gases**

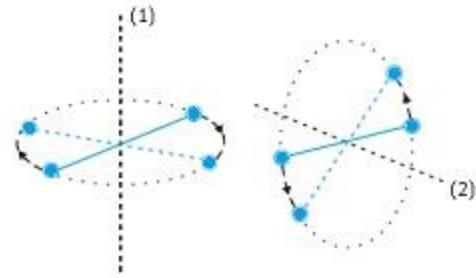
- Monoatomic gases will only have translational degree of freedom.
- Maximum they can have is three translational degrees of freedom.
- Each degree of freedom will contribute  $(1/2) k_B$
- Therefore 3 degrees of freedom will contribute  $(3/2) k_B$
- By using law of equipartition of energy, the total internal energy of 1 mole of gas  $U = (3/2) k_B T x N_A = (3/2) RT$
- Specific heat capacity at constant volume  $C_V = dU/dT = (3/2) R$
- For an ideal gas  $C_P - C_V = R$ , By using equation (i)  $C_P = (5/2)R$
- Ratio of specific heats  $\gamma = C_P/C_V = (5/3)$

### **Specific Heat of Diatomic gases (rigid)**

- A rigid diatomic gas means they will have translational as well as rotational degree of freedom but not vibrational.
- They are rigid oscillator.
- A rigid diatomic molecule will have 3 translational degrees of freedom and 2 rotational degrees of freedom. Total 5 degrees of freedom.
- By law of equipartition of energy, each degree of freedom will contribute  $(1/2) k_B$
- Therefore 5 degree of freedom will contribute  $(5/2) k_B$
- Therefore the total internal energy of 1 mole of gas,  $U = (5/2) k_B T x N_A = (5/2)RT$
- Specific heat capacity at constant volume ( $C_V$ ) =  $dU/dT = (5/2)R$
- Specific heat capacity at constant pressure of a rigid diatomic is given as  $C_P = (7/2)R$
- Ratio of specific heats  $\gamma = C_P/C_V = (7/5)$

### Specific Heat of Diatomic gases (non-rigid)

- A no-rigid diatomic gas has translational, rotational as well as vibrational degrees of freedom.
- There will be 3 translational degrees of freedom and 2 rotational degrees of freedom and 1 vibrational degree of freedom.
- Total contribution by translational=  $(1/2) k_B T$ , rotational=  $2 \times (1/2) k_B T$  and vibrational =  $k_B$
- Total Internal energy for 1 mole =  $(5/2) k_B T + k_B T = (7/2) k_B T = (7/2) RT$ .
- $C_V = dU/dT = (7/2) R$ .
- $C_P = C_V + R = (9/2) R$ .
- $\gamma = C_P/C_V = (9/7)$



There are two independent axes of rotation (1) and (2) normal to the axis joining the two oxygen molecule. It has 3 translational and 2 rotational degrees of freedom

### Specific Heat Capacity for polyatomic gases

- Polyatomic gases will have 3 translational degree of freedom, 3 rotational degrees of freedom and 'f' number of vibrational modes.
- Total internal energy of 1 mole of gas =  $(3 \times (1/2) k_B T + 3 \times (1/2) k_B T + f k_B T) \times N_A$   
 $((3/2) + (3/2) + f) RT = (3+f) RT$ .
- $C_V = dU/dT = (3+f) R$
- $C_P = C_V + R = (4+f) R$
- $\gamma = C_P/C_V = (4+f)/(3+f)$

### Specific Heat Capacity for solids

- Consider there are N atoms in a solid. Each atom can oscillate about its mean position.
- Therefore vibrational degree of freedom =  $k_B T$
- In one-dimensional average energy =  $k_B T$ , in three-dimensional average energy =  $3k_B T$
- Therefore total internal energy (U) of 1 mole of solid =  $3k_B T \times N_A = 3RT$
- At constant pressure,  $\Delta Q = \Delta U + P\Delta V$  change in volume is very less in solids. Therefore  $\Delta V = 0$ .
- $\Rightarrow \Delta Q = \Delta U$
- $C_V = (dU/dT)_V$
- $C_P = (dQ/dT)_P$  as  $\Delta Q = \Delta U$ , Therefore  $C_V = dU/dT = 3R$
- Therefore  $C_P = C_V = 3R$

### Specific Heat Capacity of water

- o Consider water as solid, so it will have 'N' number of atoms.
- o Therefore for each atom average energy  $= 3k_B T$
- o No of molecules in  $H_2O = 3$  atoms.
- o Total internal energy  $U = 3k_B T \times 3 \times N_A = 9RT$ .
- o  $C_V = C_P = 9R$ .

### **Conclusion on Specific heat**

- o According to classical mechanics, the specific heat which is calculated based on degree of freedom should be independent of temperature.
- o However  $T \rightarrow 0$ , degree of freedom becomes inefficient.
- o This shows classical mechanics is not enough; as a result quantum mechanics came into play.
- o According to quantum mechanics minimum non-zero energy is required for degree of freedom to come into play.
- o Specific heats of all substances approach zero as  $T \rightarrow 0$ .

### **Mean free path**

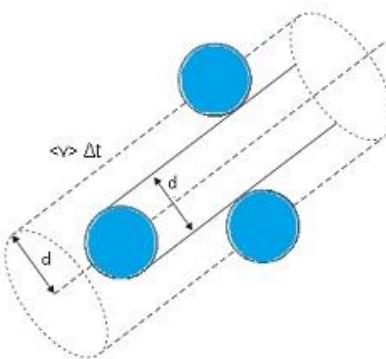
- o Mean free path is the average distance between the two successive collisions.
- o Inside the gas there are several molecules which are randomly moving and colliding with each other.
- o The distance which a particular gas molecule travels without colliding is known as mean free path.

### **Expression for mean free path**

- o Consider each molecule of gas is a sphere of diameter (d). The average speed of each molecule is  $\langle v \rangle$ .
- o Suppose the molecule suffers collision with any other molecule within the distance (d). Any molecule which comes within the distance range of its diameter this molecule will have collision with that molecule.
- o The volume within which a molecule suffer collision  $= \langle v \rangle \Delta t \pi d^2$ .
- o Let number of molecules per unit volume  $= n$
- o Therefore the total number of collisions in time  $\Delta t = \langle v \rangle \Delta t \pi d^2 n$
- o Rate of collision  $= \langle v \rangle \Delta t \pi d^2 n / \Delta t = \langle v \rangle \pi d^2 n$
- o Suppose time between collision  $\tau = 1 / \langle v \rangle \pi d^2 n$
- o Average distance between collision  $= \tau \langle v \rangle = 1 / \pi d^2$
- o  $1 / \pi d^2 n$  this value was modified and a factor was introduced.
- o Mean free path ( $l$ )  $= 1 / \sqrt{2} \pi d^2 n$

**Conclusion:** - Mean free path depends inversely on:

- a) Number density (number of molecules per unit volume)
- b) Size of the molecule.



The volume swept by a molecule in time  $\Delta t$  in which any molecule will collide with it.