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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:-
- Molecular interpretation of pressure and temperature can be explained.
- It is consistent with gas laws and Avogadro's hypothesis.
- Correctly explains specific heat capacities of many gases.



Molecular nature of matter



John Dalton

- 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 rebel.
 - For example: - Consider a block of gold. It consists of molecules which are constantly moving.
- 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.

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:
 - $PV=KT$ (i)
 - This is the universal relation which is satisfied by all gases.
 - where P, V, T are pressure, volume and temperature resp. 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) $PV= Nk_B T$
 - 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 $P_1 V_1 / (N_1 T_1) = P_2 V_2 / (N_2 T_2)$
 - Conclusion: - This relation is satisfied by all gases at low pressure and high temperature.



Problem:- An oxygen cylinder of volume 30 litres has an initial gauge pressure of 15 atm and a temperature of 27 °C. After some oxygen is withdrawn from the cylinder, the gauge pressure drops to 11 atm and its temperature drops to 17 °C. Estimate the mass of oxygen taken out of the cylinder ($R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$, molecular mass of $\text{O}_2 = 32 \text{ u}$).

Answer:- Volume of oxygen, $V_1 = 30 \text{ litres} = 30 \times 10^{-3} \text{ m}^3$

Gauge pressure, $P_1 = 15 \text{ atm} = 15 \times 1.013 \times 10^5 \text{ Pa}$

Temperature, $T_1 = 27^\circ\text{C} = 300 \text{ K}$

Universal gas constant, $R = 8.314 \text{ J mole}^{-1} \text{ K}^{-1}$

Let the initial number of moles of oxygen gas in the cylinder be n_1 .

The gas equation is given as:

$$P_1 V_1 = n_1 R T_1$$

$$n_1 = P_1 V_1 / R T_1 = (15.195 \times 10^5 \times 30 \times 10^{-3}) / (8.314) \times 300 = 18.276$$

But, $n_1 = m_1 / M$ Where, m_1 = Initial mass of oxygen

M = Molecular mass of oxygen = 32 g

$$m_1 = n_1 M = 18.276 \times 32 = 584.84 \text{ g}$$

After some oxygen is withdrawn from the cylinder, the pressure and temperature reduces.

Volume, $V_2 = 30 \text{ litres} = 30 \times 10^{-3} \text{ m}^3$

Gauge pressure, $P_2 = 11 \text{ atm} = 11 \times 1.013 \times 10^5 \text{ Pa}$

Temperature, $T_2 = 17^\circ\text{C} = 290 \text{ K}$

Let n_2 be the number of moles of oxygen left in the cylinder.

The gas equation is given as:

$$P_2 V_2 = n_2 R T_2$$

$$n_2 = P_2 V_2 / R T_2$$

$$= (11.143 \times 10^5 \times 30 \times 10^{-3}) / (8.314 \times 290)$$

$$= 13.86$$

But, $n_2 = m_2 / M$ Where, m_2 is the mass of oxygen

remaining in the cylinder $m_2 = n_2 M = 13.86 \times 32$

$$= 453.1 \text{ g}$$

The mass of oxygen taken out of the cylinder is given by the relation:

Initial mass of oxygen in the cylinder – Final mass of oxygen in the cylinder

$$= m_1 - m_2$$

$$= 584.84 \text{ g} - 453.1 \text{ g}$$

$$= 131.74 \text{ g}$$

$$= 0.131 \text{ kg}$$

Therefore, 0.131 kg of oxygen is taken out of the cylinder.

Problem:- An air bubble of volume 1.0 cm^3 rises from the bottom of a lake 40 m deep at a temperature of 12 °C. To what volume does it grow when it reaches the surface, which is at a temperature of 35 °C?

Answer:- Volume of the air bubble, $V_1 = 1.0 \text{ cm}^3 = 1.0 \times 10^{-6} \text{ m}^3$

Bubble rises to height, $d = 40 \text{ m}$

Temperature at a depth of 40 m, $T_1 = 12^\circ\text{C} = 285 \text{ K}$

Temperature at the surface of the lake, $T_2 = 35^\circ\text{C} = 308 \text{ K}$

The pressure on the surface of the lake:

$$P_2 = 1 \text{ atm} = 1 \times 1.013 \times 10^5 \text{ Pa}$$

The pressure at the depth of 40 m:

$P_1 = 1 \text{ atm} + \rho g h$ Where, ρ is the density of water = 10^3 kg/m^3 g is the acceleration due to gravity = 9.8 m/s^2

$$\text{Therefore, } P_1 = 1.013 \times 10^5 + 40 \times 10^3 \times 9.8 = 493300 \text{ Pa}$$

We have: $P_1 V_1/T_1 = P_2 V_2/T_2$

Where, V_2 is the volume of the air bubble when it reaches the surface

$$V_2 = P_1 V_1 T_2 / T_1 P_2$$

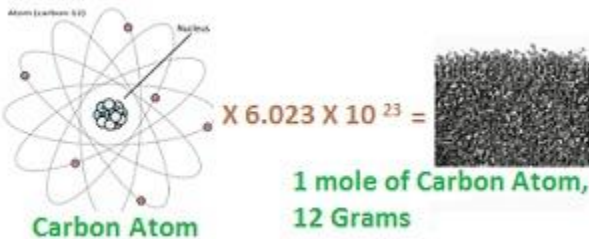
$$= (493300) (1.0 \times 10^{-6}) 308 / (285 \times 1.013 \times 10^5)$$

$$= 5.263 \times 10^{-6} \text{ m}^3 \text{ or } 5.263 \text{ cm}^3$$

Therefore, when the air bubble reaches the surface, its volume becomes 5.263 cm^3 .

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 denotes Avogadro number.
- $N_A = 6.02 \times 10^{23}$. 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.



Problem:- Molar volume is the volume occupied by 1 mole of any (ideal) gas at standard temperature and pressure (STP: 1 atmospheric pressure, 0°C). Show that it is 22.4 litres.

Answer:- The ideal gas equation relating pressure (P), volume (V), and absolute temperature (T) is given as: $PV = nRT$

Where, R is the universal gas constant = $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

n = Number of moles = 1

T = Standard temperature = 273 K

P = Standard pressure = $1 \text{ atm} = 1.013 \times 10^5 \text{ Nm}^{-2}$

$$= 0.0224 \text{ m}^3$$

$$= 22.4 \text{ litres}$$

Hence, the molar volume of a gas at STP is 22.4 litres.

Perfect Gas Equation

- Perfect gas equation is given by $PV = \mu RT$,
 - Where P, V are pressure, volume, T = absolute temperature, μ = 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

1. $PV = \mu RT$ (i)
 - Where μ (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 $\mu = M/M_o$ where M =mass of sample of gas and M_o = molar mass.
 - $PV = (N/N_A)RT$ (putting $\mu = N/N_A$ 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 we get **$PV = nk_B T$**
2. Substitute $\mu = M/M_o$ in equation(i)
 - $PV = (M/M_o) RT \Rightarrow P = (M/V) 1/M_o RT$ where
 - ρ (mass density of the gas) = M/V
 - Therefore **$P = \rho RT/M_o$**

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.

Problem:-

Estimate the total number of air molecules (inclusive of oxygen, nitrogen, water vapour and other constituents) in a room of capacity 25.0 m^3 at a temperature of 27°C and 1 atm pressure.

Answer:-

Volume of the room, $V = 25.0 \text{ m}^3$

Temperature of the room, $T = 27^\circ \text{C} = 300 \text{ K}$

Pressure in the room, $P = 1 \text{ atm} = 1 \times 1.013 \times 10^5 \text{ Pa}$

The ideal gas equation relating pressure (P), Volume (V), and absolute temperature (T) can be written as:

$$PV = k_B N T$$

Where,

k_B is Boltzmann constant = $1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$

N is the number of air molecules in the room

$$N = PV / k_B T$$

$$= 1.013 \times 10^5 \times 25 / 1.38 \times 10^{-23} \times 300$$

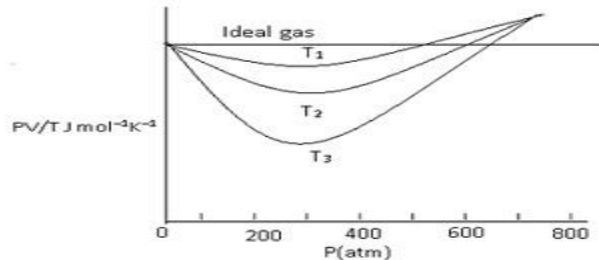
$$= 6.11 \times 10^{26} \text{ molecules}$$

Therefore, the total number of air molecules in the given room is 6.11×10^{26}

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.

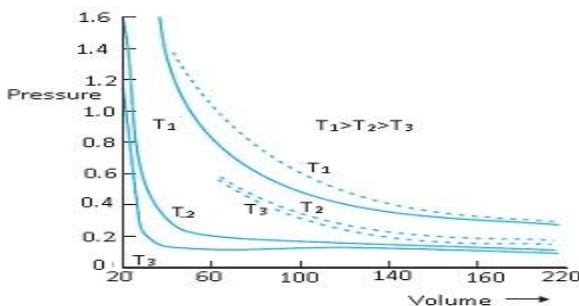
- This means it has constant value at all temperature and all pressure.
- But in case of real gases graph approach ideal gas behaviour at high temperature and low pressure.
- At high temperature and low pressure molecules are far apart. When temperature is increased the molecules will move randomly far 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.



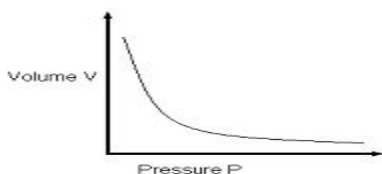
Real gases approach ideal gas behaviour at low pressures and high temperatures.

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

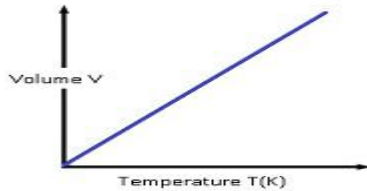
1. Boyle's law: -Deriving Boyle's law from perfect gas equation, $PV = \mu RT$
 - Consider T (temperature) and μ (no. of moles) constant.
 - Therefore **$PV = \text{constant}$** .
 - According to Boyle's law, at a constant temperature, pressure of a given mass of gas varies inversely with volume.
2. 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.



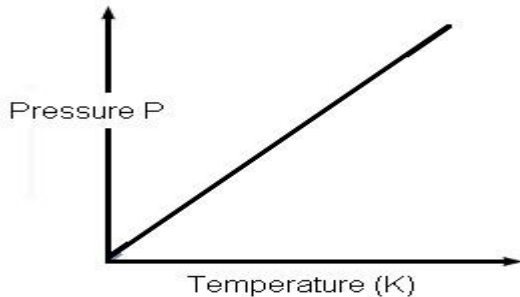
Experimental P-V curves (solid lines) for steam at three temperatures compared with Boyle's law (dotted lines). P is in units of 22 atm and V in units of 0.09 litres.



(Boyle's law)



(Charles's law)



(Gay-Lussac law)

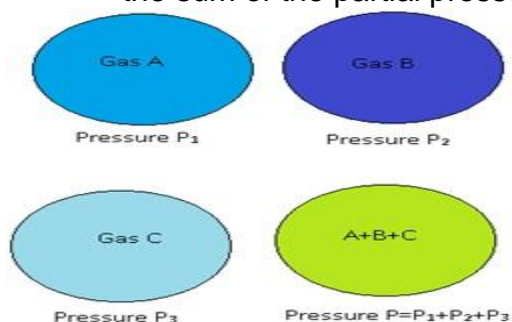
Deducing Dalton's Law of partial pressures

- 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 μ (no. of moles).
 - As there are mixture of gases therefore $\mu = \mu_1 + \mu_2 + \dots$ so on.
 - $PV = (\mu_1 + \mu_2)RT$
 - $P = (\mu_1 + \mu_2)RT/V \Rightarrow \mu_1 RT/V + \mu_2 RT/V + \dots$
 - $P = P_1 + P_2 + \dots$

- 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.



Problem: -Estimate the fraction of molecular volume to the actual volume occupied by oxygen gas at STP. Take the diameter of the oxygen to be 3\AA .

Answer:- At STP, Temperature = 273K and Pressure=1atm, diameter= $3\text{\AA} = 3 \times 10^{-8}$ cm. Actual volume by 1mole O_2 gas at STP =22.4l = 22400cm³.

Molecular volume of $O_2 = \frac{4}{3} \pi r^3 \times N_A$
 $= \frac{4}{3} 3.14 \times (1.5 \times 10^{-8})^3 \times 6.02 \times 10^{23} = 8.51 \text{cm}^3$

Therefore, Ratio =8.51/22400 = 3.8×10^{-4}

Problem:- The density of water is 1000kg m^{-3} . The density of water vapour at 100°C and 1 atm pressure is 0.6kg m^{-3} . The volume of a molecule multiplied by the total number gives, what is called, molecular volume. Estimate the ratio (or fraction) of the molecular volume to the total volume occupied by the water vapour under the above conditions of temperature and pressure.

Answer:- For a given mass of water molecules, the density is less if volume is large. So the volume of the vapour is $1000/0.6 = 1666.67$ (or 1.67×10^3) times larger. If densities of bulk water and water molecules are same, then the fraction of molecular volume to the total volume in liquid state is 1. As volume in vapour state has increased, the fractional volume is less by the same amount, i.e. 6×10^{-4} .

Problem: - Estimate the volume of a water molecule if the density of water is 1000kg m^{-3} . The density of water vapour at 100°C and 1 atm pressure is 0.6kg m^{-3} ?

Answer: - In the liquid (or solid) phase, the molecules of water are quite closely packed. The density of water molecule may therefore, be regarded as roughly equal to the density of bulk water = 1000kg m^{-3} . To estimate the volume of a water molecule, we need to know the mass of a single water molecule. We know that 1 mole of water has a mass approximately equal to $(2 + 16) \text{g} = 18 \text{g} = 0.018 \text{kg}$.

Since 1 mole contains about 6×10^{23} molecules (Avogadro's number), the mass of a molecule of water is $(0.018)/(6 \times 10^{23}) \text{kg} = 3 \times 10^{-26} \text{kg}$. Therefore, a rough estimate of the volume of a water molecule is as follows:

Volume of a water molecule

$$= (3 \times 10^{-26} \text{kg}) / (1000 \text{kg m}^{-3})$$

$$= 3 \times 10^{-29} \text{m}^3$$

$$= \frac{4}{3} \pi (\text{Radius})^3$$

Hence, Radius $\approx 2 \times 10^{-10} \text{m} = 2 \text{\AA}$.

Problem:- What is the average distance between atoms (interatomic distance) in water?

Answer: A given mass of water in vapour state has 1.67×10^3 times the volume of the same mass of water in liquid state. This is also the increase in the amount of volume

available for each molecule of water. When volume increases by 10^3 times the radius increases by $V^{1/3}$ or 10 times, i.e., $10 \times 2 \text{ \AA} = 20 \text{ \AA}$. So the average distance is $= 2 \times 20 = 40 \text{ \AA}$.

Problem:- A vessel contains two nonreactive gases: neon (monatomic) and oxygen (diatomic). The ratio of their partial pressures is 3:2. Estimate the ratio of (i) number of molecules and (ii) mass density of neon and oxygen in the vessel. Atomic mass of Ne = 20.2 u, molecular mass of $O_2 = 32.0$ u.

Answer:- Partial pressure of a gas in a mixture is the pressure it would have for the same volume and temperature if it alone occupied the vessel. (The total pressure of a mixture of non-reactive gases is the sum of partial pressures due to its constituent gases.) Each gas (assumed ideal) obeys the gas law.

Since V and T are common to the two gases, we have

$$P_1 V = \mu_1 RT \text{ and } P_2 V = \mu_2 RT, \text{ i.e. } (P_1/P_2) = (\mu_1 / \mu_2).$$

Here 1 and 2 refer to neon and oxygen respectively. Since $(P_1/P_2) = (3/2)$ (given), $(\mu_1 / \mu_2) = 3/2$

(i) By definition $\mu_1 = (N_1/N_A)$ and $\mu_2 = (N_2/N_A)$ where N_1 and N_2 are the number of molecules of 1 and 2, and N_A is the Avogadro's number.

Therefore, $(N_1/N_2) = (\mu_1 / \mu_2) = (3/2)$.

(ii) We can also write $\mu_1 = (m_1/M_1)$ and $\mu_2 = (m_2/M_2)$ where m_1 and m_2 are the masses of 1 and 2; and M_1 and M_2 are their molecular masses. (Both m_1 and M_1 ; as well as m_2 and M_2 should be expressed in the same units). If ρ_1 and ρ_2 are the mass densities of 1 and 2 respectively, we have,

$$= (1/2) (m_1/V)/m_2/V = (m_1/m_2) (1/2) (M_1/M_2)$$

$$= (3/2) (20.2/32.0)$$

$$= 0.947$$

Problem:- An air bubble of volume 1.0 cm^3 rises from the bottom of a lake 40m deep at a temperature of 12°C . To what volume does it grow when it reaches the surface, which is at temperatures of 35°C ?

Answer:- Let the depth (d) of the lake = 40m. Temperature (T_1) at the bottom = $12^\circ\text{C} = 285\text{K}$ and (V_1) Volume of air bubble = $1.0 \text{ cm}^3 = 1 \times 10^{-6} \text{ m}^3$. Temperature at the surface (T_2) = $35^\circ\text{C} = 308\text{K}$, Pressure at the surface (P_2) = 1 atm = 1.013×10^5 Pa.

$$\text{Pressure at the bottom } P_1 = P_2 + \rho dg$$

$$= 1 + 10^3 \times 9.8 \times 40$$

$$= 493300 \text{ Pa}$$

$$\text{Also } (P_1 V_1)/T_1 = (P_2 V_2)/T_2$$

$$V_2 = (P_1 V_1 T_2)/P_2 T_1$$

After calculating,

$$V_2 = 5.263 \text{ cm}^3$$

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.
 - 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

Pressure of an ideal gas based on Kinetic theory

Assumptions:-

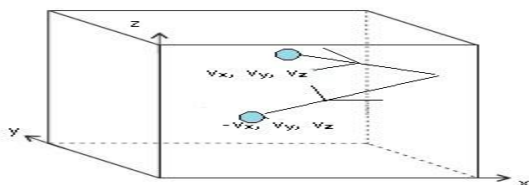
- Consider a cube shape container filled with an ideal gas. We will consider only one molecule; the molecule hits the walls of the container and bounces back.
- Let the velocity of the molecule when it is moving be (v_x, v_y, v_z) .
- When the molecule bounces back, the velocity will be $(-v_x, v_y, v_z)$.
- 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.

- o Momentum imparted to the wall in collision by one molecule = $2mv_x$
 - But as there are 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 Δt , all molecules within a distance of $(Av_x\Delta t)$ can hit the wall.
 - This means all molecules in time Δt lying within the volume $Av_x\Delta t$ can hit the wall.
 - But on an average half of molecules move towards the wall and half away from the wall.
 - Therefore $(1/2) Av_x\Delta t$ will hit the wall.
 - Therefore Number of molecules that hit the wall = (number of
 - Total molecules that hit the wall = $(1/2)n Av_x\Delta t$
- Therefore Total momentum imparted to the wall = $2m v_x \times (1/2)n Av_x\Delta t$
- After simplifying **Total momentum imparted to the wall = $Anv_x^2\Delta tm$**
- Force exerted on the wall = Rate of change of momentum = Anv_x^2m
- Pressure on the wall $P = F/A = nmv_x^2$
- Therefore **$P = nmv_x^2$** . This 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.
- (ii) All will have different velocities.
- (iii) 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.
 - o Therefore total pressure due to all such groups will be obtained by summing over the contribution due to all molecules $P = nm \overline{v_x^2}$
 - o where $\overline{v_x^2}$ is the average of v_x^2

- Since gas is isotropic the molecules move randomly which means the velocity of all the molecules can be in any direction .Therefore
- $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = (1/3) [\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}] = (1/3) \overline{v^2}$
- Therefore Pressure $P = (1/3) nm \overline{v^2}$ where $\overline{v^2}$ = average of squared speed.



Elastic collision of a gas molecule with the wall of the container

Justifying the assumptions:-

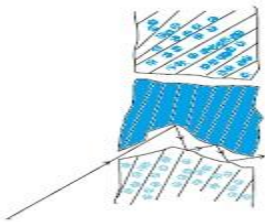
1. We have assumed the container containing the gas is a cube. The shape of the container is immaterial.
2. For a vessel of any arbitrary shape, we can choose a small infinitesimal (planar) area and can prove the above derivation.
3. We will see A and Δt are not there in the final result.
4. By Pascal's law pressure in one portion of gas in equilibrium is the same as anywhere else.
5. All collisions are neglected.
1. The number of molecules hitting the wall in time Δt was found to be $\frac{1}{2} n A v_x \Delta t$, with random collisions and a steady state of gas.
2. 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) .
3. 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 effect in the above calculation.



Kinetic Interpretation of Temperature

- The average kinetic energy of a molecule is directly \propto 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,
 - $PV = \frac{1}{3} n V m \overline{v^2}$
 - After simplifying,
 - $PV = \frac{2}{3} N \times \frac{1}{2} m \overline{v^2}$ where $n = N/V$
 - Where N = no of molecules in a sample.

- Therefore $PV = (2/3) E$ (i). Where $E =$ Kinetic energy. $E = N \times (1/2)m \overline{v^2}$
 - This is the basis of Kinetic interpretation of temperature.
- From Ideal gas Equation: $-PV = \mu RT = N/N_A \times k_B \times T \times N_A \times T$
 - By simplifying, $= Nk_B T$ (ii)
 - From equation (i) and (ii)
 - $(2/3)E = Nk_B T$
 - $E = (3/2)N k_B T$
 - Dividing E by N , equation becomes,
- **$E/N = (3/2)k_B T$**
 - Where $E/N =$ average Kinetic energy, $(3/2)k_B =$ constant and $T =$ absolute temperature.
- Therefore we can say that average **.K.E $\propto T$**
 - ✓ From here we can say that temperature can be interpreted as molecular quantity.



Molecules going through a porous wall

Problem:-

Estimate the average thermal energy of a helium atom at (i) room temperature (27 °C), (ii) The temperature on the surface of the Sun (6000 K), (iii) the temperature of 10 million Kelvin (the typical core temperature in the case of a star).

Answer:-

At room temperature, $T = 27^\circ\text{C} = 300 \text{ K}$

Average thermal energy = $(3/2) kT$

Where k is Boltzmann constant = $1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$

$(3/2) kT = (3/2) \times 1.38 \times 10^{-23} \times 300 = 6.21 \times 10^{-21} \text{ J}$

Hence, the average thermal energy of a helium atom at room temperature (27°C) is $= 6.21 \times 10^{-21} \text{ J}$.

On the surface of the sun, $T = 6000 \text{ K}$

Average thermal energy = $(3/2) kT$

$= (3/2) \times 1.38 \times 10^{-23} \times 6000$

$= 1.241 \times 10^{-19} \text{ J}$

Hence, the average thermal energy of a helium atom on the surface of the sun is

$= 1.241 \times 10^{-19} \text{ J}$.

At temperature, $T = 10^7 \text{ K}$

Average thermal energy = $(3/2) kT$

$= (3/2) \times 1.38 \times 10^{-23} \times 10^7$

$= 2.07 \times 10^{-16} \text{ J}$

Hence, the average thermal energy of a helium atom at the core of a star is 2.07×10^{-16}

Kinetic theory: Consistent with ideal gas equation and gas laws

1. Consistent with ideal gas equation:

a. From Kinetic interpretation $E/N = (3/2) k_B T \Rightarrow E = (3/2) N k_B T$

- ❖ The internal energy of an ideal gas is $\propto T$.
- ❖ 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:

b. $P = (1/3) n m \overline{v^2}$ From Kinetic theory

- ❖ Therefore if a vessel contains a mixture of gases
- ❖ $P = (1/3) [n_1 m_1 \overline{v_1^2} + n_2 m_2 \overline{v_2^2} + \dots]$
- ❖ In Equilibrium average Kinetic energy of molecules of different gases will be equal,
 - $(1/2) m_1 \overline{v_1^2} = (1/2) m_2 \overline{v_2^2} = (3/2) k_B T = (3/2) k_B T$
- ❖ Total pressure $P = (1/3) [(3/2) n_1 k_B T + (3/2) n_2 k_B T + (3/2) n_3 k_B T + \dots]$
- ❖ After simplifying, $P = k_B T [n_1 + n_2 + n_3 + \dots]$
- ❖ $P = R/N_A [n_1 + n_2 + n_3 + \dots]$
- ❖ $P = [\mu_1 + \mu_2 + \dots] RT$
- ❖ $P = P_1 + P_2 + \dots$ This is Dalton's law of partial pressures.

Problem: At what temperature is the root mean square speed of an atom in an argon gas cylinder equal to rms speed of a helium gas atom at -20°C ? (Atomic mass of Ar=39.9u, of He=4.0u).

Answer:-

$$T_{\text{He}} = 20^\circ\text{C} = 253\text{K}$$

$$M_{\text{Ar}} = 39.9\text{u}$$

$$M_{\text{He}} = 4\text{u}$$

$$\text{From Kinetic Theory } = E/N = (3/2) k_B T$$

$$(1/2) m \overline{v^2} = (3/2) k_B T$$

$$\overline{v^2} = 3k_B T/m$$

$$v_{\text{rms}} = \sqrt{3k_B T/m} \text{ where } k_B = R/N \text{ and } m = M/N_A$$

$$(v_{\text{rms}})_{\text{He}} = (v_{\text{rms}})_{\text{Ar}}$$

$$\sqrt{3k_B T_{\text{He}}/M_{\text{He}}} = \sqrt{3k_B T_{\text{Ar}}/M_{\text{Ar}}}$$

$$T_{\text{Ar}} = (T_{\text{He}} \times M_{\text{Ar}}) / M_{\text{He}} = (253 \times 39.9) / 4$$

$$= 2.52 \times 10^3 \text{K}$$

Problem:- A flask contains argon and chlorine in the ratio of 2:1 by mass.

The temperature of the mixture is 27°C . Obtain the ratio of (i) average kinetic energy per molecule, and (ii) root mean square speed v_{rms} of the molecules of the two gases. Atomic mass of argon = 39.9 u; Molecular mass of chlorine = 70.9 u.

Answer:- The important point to remember is that the average kinetic energy (per molecule) of any (ideal) gas (be it monoatomic like argon, diatomic like chlorine or polyatomic) is always equal to $(3/2) k_B T$. It depends only on temperature, and is independent of the nature of the gas.

(i) Since argon and chlorine both have the same temperature in the flask, the ratio of average kinetic energy (per molecule) of the two gases is 1:1.

(ii) Now $\frac{1}{2} m v_{\text{rms}}^2 = \text{average kinetic energy per molecule} = (3/2) k_B T$ where m is the mass of a molecule of the gas. Therefore,

$$v_{\text{rmsAr}}^2 / v_{\text{rmsCl}}^2 = M_{\text{Cl}} / M_{\text{Ar}} = 70.9 / 39.9 = 1.77$$

where M = the molecular mass of the gas. (For argon, a molecule is just an atom of argon.)

Taking square root of both sides, $v_{\text{rmsAr}} = v_{\text{rmsCl}} = 1.33$

Problem:- Uranium has two isotopes of masses 235 and 238 units. If both are present in Uranium hexafluoride gas which would have the larger average speed? If atomic mass of fluorine is 19 units, estimate the percentage difference in speeds at any temperature.

Answer:- At a fixed temperature the average energy $= \frac{1}{2} m \langle v^2 \rangle$ is constant. So smaller the mass of the molecule, faster will be the speed. The ratio of speeds is inversely proportional to the square root of the ratio of the masses. The masses are 349 and 352 units. So $v_{349} / v_{352} = (352 / 349)^{1/2} = 1.0044$.

Hence difference = 0.44 %.

[^{235}U is the isotope needed for nuclear fission. To separate it from the more abundant isotope ^{238}U , the mixture is surrounded by a porous cylinder.]

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 two.
- 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 degree of freedoms.
 - 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.



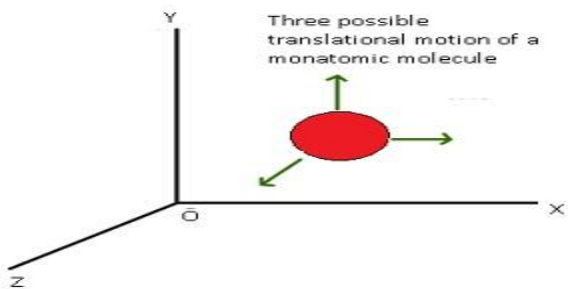
Categories of Degrees of Freedom

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 $(1/2) m v_x^2$ will contribute to energy. This is Kinetic energy which is involved with the motion of the molecule from one point to another.

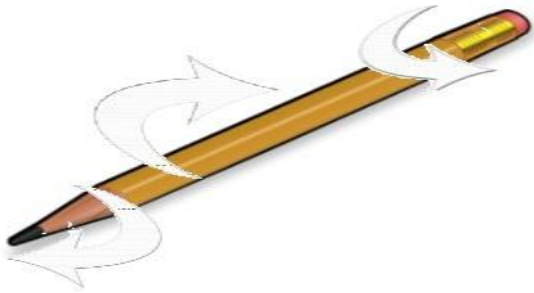
In thermal equilibrium, the average of each such term is $(1/2) k_B T$.



Rotational Degree of freedom

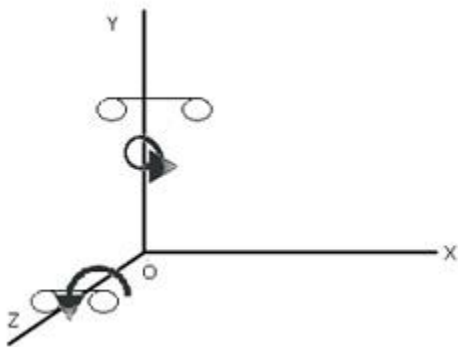
- Independent rotations that specify the orientation of a body or system.
 - There is rotation of one part of the body with respect to the other part.
- Rotational degree of freedom happens only in diatomic gas.
- Diatomic molecules have rotational degrees of freedom in addition to translational degrees 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 ω .
- 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 degree of freedom $(1/2)m_x v_x^2, (1/2)m_y v_y^2, (1/2)m_z v_z^2$
 - 2 rotational degree of freedom $(1/2)I_1\omega_1^2, (1/2)I_2\omega_2^2$

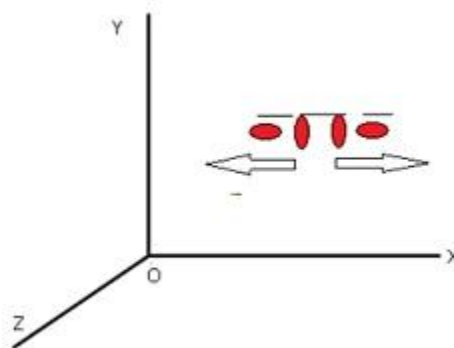


Vibrational degree of freedom

- 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 2 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 $(1/2) m(dy/dt)^2 = \text{Kinetic energy}$ and $(1/2)ky^2 = \text{Potential energy}$ and $k = \text{force constant}$ 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

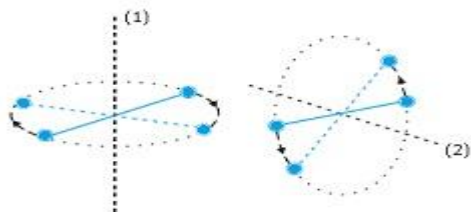
- Monoatomic gases will only have translational degree of freedom.
- Maximum they can have is three translational degrees of freedom.
- Each degree of freedom will contribute $(1/2) k_B$
- Therefore 3 degrees of freedom will contribute $(3/2) k_B$
- By using law of equipartition of energy, the total 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 $C_V = dU/dT = (3/2) R(i)$
- 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 = $k_B T$
- 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 = $3 k_B T$
- Therefore total internal energy (U) of 1 mole of solid = $3 k_B T \times N_A = 3 RT$
- 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

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

Conclusion on Specific heat

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

Mean free path

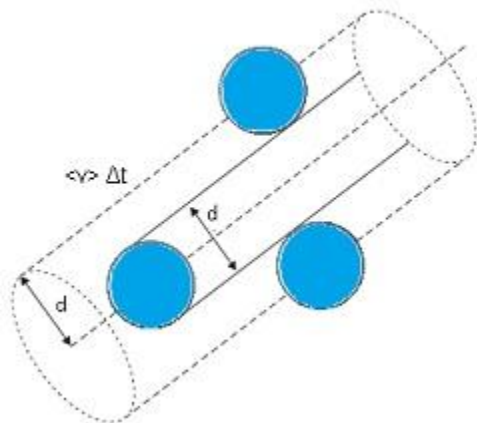
- Mean free path is the average distance between the two successive collisions.
- Inside the gas there are several molecules which are randomly moving and colliding with each other.
- The distance which a particular gas molecule travels without colliding is known as mean free path.

Expression for mean free path

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

Conclusion: - Mean free path depends inversely on:

1. Number density (number of molecules per unit volume)
2. Size of the molecule.



The volume swept by a molecule in time Δt in which any molecule will collide with it.

Problem:- Estimate the mean free path and collision frequency of a nitrogen molecule in a cylinder containing nitrogen at 2.0 atm and temperature 17 °C. Take the radius of a nitrogen molecule to be roughly 1.0 Å. Compare the collision time with the time the molecule moves freely between two successive collisions (Molecular mass of N₂ = 28.0 u).

Answer:- Mean free path = 1.11×10^{-7} m

Collision frequency = 4.58×10^9 s⁻¹

Successive collision time $\approx 500 \times$ (Collision time)

Pressure inside the cylinder containing nitrogen, P = 2.0 atm = 2.026×10^5 Pa

Temperature inside the cylinder, T = 17°C = 290 K

Radius of a nitrogen molecule, r = 1.0 Å = 1×10^{-10} m

Diameter, d = $2 \times 1 \times 10^{-10} = 2 \times 10^{-10}$ m

Molecular mass of nitrogen, M = 28.0 g = 28×10^{-3} kg

The root mean square speed of nitrogen is given by the relation:

$$v_{\text{rms}} = \sqrt{3RT/M}$$

Where,

R is the universal gas constant = $8.314 \text{ J mole}^{-1} \text{ K}^{-1}$

Therefore $v_{\text{rms}} = \sqrt{(3 \times 8.314 \times 290) / (28 \times 10^{-3})}$

= 508.26 m/s

The mean free path (l) is given by the relation:

$$l = \frac{kT}{\sqrt{2} \times d^2 \times P}$$

Where, k is the Boltzmann constant = $1.38 \times 10^{-23} \text{ kgm}^2 \text{ s}^{-2} \text{ K}^{-1}$

Therefore $l = \frac{1.38 \times 10^{-23} \times 290}{\sqrt{2} \times (2 \times 10^{-10})^2 \times 2.026 \times 10^5}$

= 1.11×10^{-7} m

Collision frequency = v_{rms} / l

= $508.26 / 1.11 \times 10^{-7}$

= 4.58×10^9 s⁻¹

Collision time is given as:

$$T = d / v_{\text{rms}}$$

= $2 \times 10^{-10} / 508.26 = 3.93 \times 10^{-13}$ s

Time taken between successive collisions:

$T' = l / v_{\text{rms}} = 1.11 \times 10^{-7} \text{ m} / 508.26 \text{ m/s} = 2.18 \times 10^{-10}$ s

$T' / T = 2.18 \times 10^{-10} \text{ s} / 3.93 \times 10^{-13} = 500$

Hence, the time taken between successive collisions is 500 times the time taken for a collision. Thank You

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