KINETIC THEORY OF GASES

Boyle's Law: *At constant temperature volume of given mass of gas is inversely proportional to its pressure.*

$$V \alpha \frac{1}{P} \text{ or } PV = \text{constant}$$

Charle's Law: *At constant pressure volume of a given mass of gas is directly proportional to its absolute temperature.*

$$V \alpha T \text{ or } \frac{V}{T} = \text{constant}$$

*For 1° rise in temp.

$$V_t = Vo(1 + \frac{t}{273.15})$$

Gay Lussac's Law: At constant volume, pressure of a given mass of gas is directly proportional to its absolute temp.

$$\frac{P}{T} = \text{constant.}$$

For 1^0C rise in temperature $P_t = P_o (1 + \frac{t}{273.15})$

Ideal Gas Equation: for n mole of gas

PV=nRT,

for 1 mole , PV=RT

Universal gas constant: R = 8.31 J $mol^{-1}K^{-1}$

Boltzmann constant: $k_B = \frac{R}{N_A}$**where k_B = Boltzmann constant, N_A = Avogadro's no.**

Ideal gas: A gas which obeys gas law strictly is an ideal or perfect gas. The molecules of such a gas are of point size and there is no force of attraction between them.

Assumptions of Kinetic Theory of Gases

1. All gases consist of molecules which are rigid, elastic spheres identical in all respect for a given gas.

2. The size of a molecule is negligible as compared with the average distance between two molecules.

3. During the random motion, the molecules collide with one another and with the wall of the vessel.The collisions are almost instantaneous.

4. The molecular density remains uniform throughout the gas.

5. The collisions are perfectly elastic in nature and there are no forces of attraction or repulsion between them.

Pressure exerted by gas:

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

Where: n=no. of molecules per unit volume.

m=mass of each molecule.

$\overline{v^2}$ =mean of square speed.

V = Volume

M = mass of gas

Average Kinetic energy of a gas: If M is molecular mass and V is molecular volume and m is mass of each molecule. Then

1. Mean K.E per mole of a gas,

$$E = \frac{1}{2}M\overline{v^2} = \frac{3}{2}PV = \frac{3}{2}RT = \frac{3}{2}K_B N_A T$$

2. Mean K.E per molecule of a gas,

$$\vec{E} = \frac{1}{2}m\overline{v^2} = \frac{1}{2}k_B T$$

3. K.E of 1gram of gas,

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}\frac{RT}{M_0}$$ M_0 gram molecular weight

Avogadro Law: Equal volume of all gases under similar condition of temp. and pressure contain equal number of molecules.

Avogadro Number:

$$N_A = 6.0225 \times 10^{23} \text{ mol}^{-1}$$

Graham's Law of diffusion:

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

r = rate of diffusion

ρ = density

Delton's law of partial pressure: Total pressure exerted by a mixture of non-reacting gases occupying a given volume is equal to the sum of partial pressures which gas would exert if it alone occupied the same volume at given temp.

$$P = P_1 + P_2 + P_3 + \ldots \ldots \ldots$$

Average Speed :- $\overline{V} = \frac{v_1 + v_2 + v_3 + \ldots + v_n}{n}$

$$\bar{v} = \sqrt{\frac{8k_bT}{\pi m}} = \sqrt{\frac{8RT}{\pi M_0}}$$

Root mean square:

$$V_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + \cdots + v_n^2}{n}}$$

$$V_{rms} = \sqrt{\frac{3K_BT}{m}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}}$$

Most probable speed:

$$V_{mp} = \sqrt{\frac{2K_BT}{m}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2PV}{M}}$$

Relation between : $\bar{v}$, $\overline{v_{rms}}$ & v_{mp}

$$\bar{v} = 0.92v_{rms}, v_{mp} = 0.816v_{rms}$$

$$v_{rms} : \bar{v} : v_{mp} = 1.73 : 1.6 : 1.41$$

Therefore: $v_{rms} > \bar{v} > v_{mp}$

Degree of freedom:

f = 3N-k

where , f = no. of degree of freedom.

N = no. of of atoms in a molecule. k = no. of independent relation between the atoms.

1. Monoatomic gas – 2 degree of freedom.
2. Diatomic gas – 5 degree of freedom.

Law of equipartion of energy: For any thermodynamical system in thermal equilibrium, the energy of the system is equally divided amongst its various degree of freedom and energy associated with each degree of freedom corresponding to each molecule is $\frac{1}{2} K_B T$, where K_B is the Boltzmann's constant and T is absolute temperature.

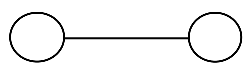
- The law of equipartition of energy holds good for all degrees of freedom whether translational , rotational or vibrational.
- A monoatomic gas molecule has only translational kinetic energy

$$E_t = 1/2mV_x^2 + 1/2mV_y^2 + 1/2mV_z^2 = 3/2K_BT$$

So a monoatomic gas molecule has only three (translational) degrees of freedom.

- In addition to translational kinetic energy, a diatomic molecule has two rotational
  Kinetic energies

$$E_t + E_r = 1/2mV_x^2 + 1/2mV_y^2 + 1/2mV_z^2 + 1/2I_YW_y^2 + 1/2I_zW_z^2$$



Here the line joining the two atoms has been taken as x-axis about which there is no rotation. So, the degree of freedom of a diatomic molecule is 5, it does not vibrate.

At very high temperature, vibration is also activated due to which two extra degree of freedom emerge from vibrational energy. Hence at very high temperature degree of freedom of diatomic molecule is seven.

***(**Each translational and rotational degree of freedom corresponds to one mole of absorption of energy and has energy $1/2k_BT$).

Internal Energies & specific heats of monoatomic, diatomic& polyatomic gases:

1. If 'f' is degree of freedom then for a gas of polyatomic molecules energy associated with 1 mole of gas,

$$U = \frac{f}{2}RT \quad , \quad C_v = \frac{f}{2}R$$

$$C_p = \left(1 + \frac{f}{2}\right) R, \;\; \gamma = \frac{C_p}{C_v} = 1 + \frac{2}{f}$$

2. For a monoatomic gas f=3,

$$U = \frac{3}{2}RT \quad , \quad C_v = \frac{3}{2}R$$

$$C_p = \frac{5}{2} R, \qquad \gamma = 1.66$$

3. For a diatomic gas with no vibrational mode f=5, so

$$U = \frac{5}{2}RT \quad , \quad C_v = \frac{5}{2}R$$

$$C_p = \frac{7}{2} R, \qquad \gamma = 1.4$$

4. For a diatomic gas with vibrational mode f=7, so

$$U = \frac{7}{2}RT \quad , \quad C_v = \frac{7}{2}R$$

$$Cp = \frac{9}{2} R \;\; , \gamma = 1.28$$

Meanfree path: It is the average distance covered by a molecule between two successive collisions. It is given by,

$$\overline{\lambda} = \frac{1}{\sqrt{2}(n\pi d^2)}$$

Where,n is no. density and ‘d’ is diameter of the molecule.

Brownian Equation :-The zig-zag motion of gas molecules is Brownian motion which occurs due to random collision of molecules.

Memory Map

Kinetic Theory of gases

1. $V_{rms} = \sqrt{\frac{3p}{\rho}}$

3. $V_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}}$

2. $E = \frac{3}{2}\ RT$

4. $V \ \alpha \sqrt{T}$

Law of Equipartion of Energy

$\frac{1}{2}\, m v_x{}^{2} = \frac{1}{2}\, m v_y{}^{2}$

$= \frac{1}{2}\, m v_{2=}{}^{2} = \frac{1}{2}\, k_B T$

$P = \frac{1}{3}\ P\overrightarrow{C^2}$

Mean free Path

$\bar{\lambda} = \frac{1}{\sqrt{2}\, n\pi d^2}$

Specific Heats

$r = 1 + \frac{2}{f}$ where $r = \frac{C_p}{C_v}$

and f=degree of freedom

(1 Marks Question)

1. What type of motion is associated with the molecules of a gas?

Ans:- Brownian motion.

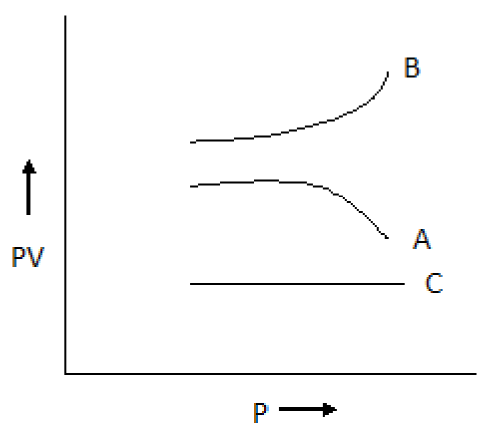
2. On which factors does the average kinetic energy of gas molecules depend?

Ans:- The average K.E. of a gas molecule depends only on the absolute temperature of the gas and is directly proportional to it.

3. Why do the gases at low temperature and high pressure, show large deviations from ideal behaviour?

Ans:- At low temperature and high pressure , the intermolecular attractions become appreciable. So, the volume occupied by the gas molecules cannot be neglected in comparison to the volume of the gas. Hence the real gases show large from ideal gas behaviour.

4. Following fig. shows the variation of the product PV with respect to the pressure (P) of given masses of three gases, A,B,C. The temperature is kept constant. State with proper arguments which of these gases is ideal.



Ans:- Gas ‘C’ is ideal because PV is constant for it. That is gas ‘C’ obeys Boyle’s law at all pressures.

5. When a gas is heated, its temperature increases. Explain it on the basis of kinetic theory of gases.

Ans:- When a gas is heated, the root mean square velocity of its molecules increases. As $V_{rms} \alpha \sqrt{T}$ so temperature of the gas increases.

6. The ratio of vapour densities of two gases at the same temperature is 8:9. Compare the rms. velocity of their molecules?

Ans :- $\frac{(Vrms)1}{(Vrms)2} = \sqrt{\frac{M2}{M1}} = \sqrt{\frac{\rho 2}{\rho 1}} = \sqrt{\frac{9}{8}} = 3 : 2\sqrt{2}$

7. Cooking gas containers are kept in a lorry moving with uniform speed. What will be the effect on temperature of the gas molecules?

Ans:- As the lorry is moving with a uniform speed, there will be no change in the translational motion or K.E. of the gas molecules. Hence the temperature of the gas will remain same.

8. What is the mean translational kinetic energy of a perfect gas molecule at temperature T?

Ans:- A perfect gas molecule has only translational K.E.

$$E = 3/2\ k_B T$$

9. Name two factors on which the degrees of freedom of a gas depend?

Ans:- (i) Atomicity of the gas molecule.

(ii) Shape of the molecule.

(iii) Temperature of gas.

10. Define absolute zero, according to kinetic interpretation of temperature?

Ans:- Absolute zero is the temperature at which all molecular motion ceases.

(2 Marks question)

1. Write the relation between the pressure and kinetic energy per unit volume of a gas. Water solidifies into ice at 273 K. What happens to the K.E. of water molecules?

Ans:- P = 2/3 E. The K.E. of water molecules gas partly converted into the binding energy of the ice.

2. The absolute temperature of a gas is increased 4 times its original value. What will be the change in r.m.s. velocity of its molecules?

Ans:- $V_{rms} \alpha \sqrt{T}$

$V'_{rms} \alpha \sqrt{4T}$

$V'_{rms} / V_{rms} = 2$

$V'_{rms} = 2V_{rms}$

Change in rms velocity of molecules = $V'_{rms} - V_{rms}$

$= V_{rms}$

3.What will be the ratio of the root mean square speeds of the molecules of an ideal gas at 270K and 30K?

Ans :- $V_{rms} / V'_{rms} = \sqrt{\frac{T}{T'}} = \sqrt{\frac{270}{30}} = 3 : 1$

4.A mixture of Helium and Hydrogen gas is filled in a vessel at 30 degree Celsius. Compare the root mean square velocities of the molecules of these gases at this temperature.

(atomic weight of Hydrogen is 4)

Ans :- $(V_{rms})He/(V_{rms})H_2 = \{(M_{H2})/(M_{He})\}^{1/2} = \sqrt{\frac{2}{4}} = 1 : 2\sqrt{2}$

5.The velocities of three molecules are 3V,4V and 5V.Determine the root mean square velocity.

Ans:- $V_{rms} = \sqrt{\frac{50}{3}}V = 4.08V$

6. Write the equation of state for 16g of O_2**.**

Ans :- No. of moles in 32g of O_2 = 1

No. of moles in 16g of O_2 = 1/9 x 16 = ½

As pv = nRT and n=1/2

So, PV= $\frac{1}{2}$ RT

7. Should the specific heat of monoatomic gas be less than, equal to or greater than that of a diatomic gas at room temperature? Justify your answer.

Ans :- Specific heat of a gas at constant volume is equal to f/2R.

For monoatomic gases f = 3 so C_v = 3/2 R.

For diatomic gases f = 5 so C_v = 5/2 R.

Hence the specific heat for monoatomic gas is less than that for a diatomic gas.

8. A gas in a closed vessel is at the pressure P_o. If the masses of all the molecules be made half and their speeds be made double, then find the resultant pressure?

Ans:- $P_o = \frac{1}{3} \frac{mN}{V} \overline{V^2}$ $= \frac{1}{3} \frac{mN}{2V} (2V)^2 = 2P_0$

9. A box contains equal number of molecules of hydrogen and oxygen. If there is a fine hole in the box, which gas will leak rapidly? Why?

Ans :- $V_{rms} \propto \frac{1}{\sqrt{M_0}}$

Hence hydrogen gas will leak more rapidly because of its smaller molecular mass.

10. When a gas filled in a closed vessel is heated through 1^0C, its pressure increases by 0.4 %. What is the initial temperature of the gas?

Ans:- P` = P = 0.4/100. P, T` = T + 1

By Gay Lussac's law P/T = (P + 0.4/100.P)/T + 1,

$$\frac{P}{T} = \left(P + \frac{.4}{100}\,P\right) \div\ (T+1)$$

$$\frac{(\mathrm{P+.004P})}{\mathrm{T+1}} = \frac{\mathrm{P(1.004)}}{\mathrm{T+1}}$$

T+1= (1.004)T

1=.004T

T=250K

(3 Marks Questions)

1. Show that rms velocity of O_2 is $\sqrt{2}$ times that of SO_2. Atomic wt. of Sulphur is 32 and that of oxygen is 16.

Ans. $V \propto \frac{1}{\sqrt{M}}$. $\frac{V_{O_2}}{V_{SO_2}} = \sqrt{\frac{64}{32}} = \sqrt{2}$

Or $v_{O_2} = \sqrt{2}\ SO_2$.

2. Calculate the temperature at which rms velocity of SO_2 is the same as that of Oxygen at $27°C$.

Ans. For O_2, $V_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3R \times 300}{32}}$

For SO_2, $V_{rms} = \sqrt{\frac{3R\acute{T}}{M_0}} = \sqrt{\frac{3R \times \acute{T}}{64}}$

As $V_0 = V$ $\therefore \sqrt{\frac{3R\acute{T}}{64}} = \sqrt{\frac{3R \times 300}{32}}$

$\acute{T}$ = 600t = 600 – 273 = 327°C.

3. Calculate the total no. of degrees of freedom possessed by the molecules in $1 cm^3$ of H_2 gas at NTP

Ans. No. of H_2 Molecules in 22.4 liters or 22400 cm^3 at NTP $= 6.02\ \times 10^{23}$.

$\therefore$ No. of H_2 Molecules in 1 cm^3 at NTP $= \frac{6.02 \times 10^{23}}{22400}$ = 2.6875 $\times 10^{19}$.

No. of degrees of freedom associated with each H_2 (a diatomic) molecule = 5

$\therefore$ Total no. of degree of freedom associated with $1cm^3$ gas

$$= 2.6875 \times 10^{19} \times 5 = 1.3475 \times 10^{20}.$$

4. Derive Boyle's law on the basis of Kinetic Theory of Gases.

5. Derive Charles's law on the basis of Kinetic Theory of Gases.

6. State Dalton's law of partial pressures. Deduce it from Kinetic Theory of Gases.

7. Using the expression for pressure exerted by a gas, deduce Avogadro's law and Graham's law of diffusion.

8. State the number of degree of freedom possessed by a monoatomic molecule in space. Also give the expression for total energy possessed by it at a given temperature. Hence give the total energy of the atom at 300 K.

9. At what temperature is the root mean square speed of an atom in an argon gas cylinder equal to the rms speed of helium gas atom at $-20℃$? Atomic mass of argon = 39.9 u and that of helium = 4.0 u.

Ans. Root mean square speed for argon at temperature T

$$V = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3RT}{39.9}}$$

Root mean square speed for helium at temp. $20℃$ is

$$\acute{V} = \sqrt{\frac{3R \times 253}{4}}$$

As V = $\acute{V}$ so we have $\sqrt{\frac{3RT}{39.9}} = \sqrt{\frac{3R \times 253}{4}}$

$$= \frac{T}{39.9} = \frac{253}{4} \quad \text{or } T = \frac{253 \times 39.9}{4}$$

T = 2523.7 K

10. From a certain apparatus the diffusion rate of Hydrogen has an average value of 28.7 $cm^3 s^{-1}$; the diffusion of another gas under the same conditions is measured to have an average rate of $7.2 cm^3 s^{-1}$. Identify the gas.

Ans. From Graham's law of diffusion,

$$\frac{r_1}{r_2} = \sqrt{\frac{M_1}{M_2}}$$

$$M_2 = \left(\frac{r_1}{r_2}\right)^2 M_1 = \left(\frac{28.7}{7.2}\right)^2 \times 2$$

$$= 31.78 \approx 32$$

Thus the unknown gas is Oxygen.

(Long Questions)

11. Prove that the pressure exerted by a gas is $P = \frac{1}{3}\rho\overline{c^2}$ where ρ is the density and c is the root mean square velocity.

12.What are the basic assumptions of Kinetic Theory of Gases? On their basis derive an expression for the pressure exerted by an ideal gas.