Kinetic Theory of Gases

Important Points:

1. Assumptions:

a) Every gas consists of extremely small particles called molecules.

b) The molecules of a gas are identical, spherical, rigid and perfectly elastic point masses.

c) Their size is negligible in comparison to intermolecular distance ($10^{-9}\ m$)

d) The volume of molecules is negligible in comparison to the volume of gas.

e) Molecules of a gas are in random motion in all directions with all possible velocities.

f) The speed of gas molecules lies between zero and infinity

g) The gas molecules collide among themselves as well as with the walls of vessel. These collisions are perfectly elastic.

h) The time spent in a collision between two molecules is negligible in comparison to time between two successive collisions.

i) The number of collisions per unit volume in a gas remains constant.

j) No attractive or repulsive force acts between gas molecules.

k) Gravitational attraction among the molecules is negligible due to their small masses and very high speed.

l) The change in momentum is transferred to the walls of the container causes pressure.

m) The density of gas is constant at all points of the container.

2. Mean Free Path:

a) The distance travelled by a gas molecule between two successive collisions is known as free path.

b) If $\lambda_1, \lambda_2, \lambda_3$ .....Are the distances travelled by a gas molecule during n collisions respectively, then mean free path of a gas molecule $\lambda = \dfrac{\lambda_1 + \lambda_2 + \lambda_3 + ... + \lambda_n}{n}$

3. Dalton's Law of Partial Pressure:

The total pressure exerted by a mixture of non-reacting gases in a vessel is equal to the sum of the individual pressures which each gas exert if it alone occupied the same volume at a given temperature.

For n gases $P = P_1 + P_2 + P_3 + ...P_n$

Where p = pressure exerted by mixture and $P_1, P_2, P_3, ...P_n$ = partial pressure of component gases.

4. The perfect gas equation

$$PV = \mu RT$$

$$\mu = \frac{M}{M_0} = \frac{mass\ of\ the\ gas}{molar\ mass}.$$

5. Kinetic theory of an ideal gas gives the relation $P = \dfrac{1}{3} n m v^2$

Where n is number density of molecules, m the mass of the molecule and is the mean of squared speed.

6. Kinetic interpretation of temperature.

$$\frac{1}{2} m v^2 = \frac{3}{2} K_B T$$

$$v_{rms} = \sqrt{\frac{3K_B T}{m}}$$

7. The translational kinetic energy

$$E = \frac{3}{2} K_B NT.$$

8. Degrees of Freedom:

The total number of independent ways in which a system can possess energy is called the degree of freedom (*f*).

a) Monatomic Gas: Molecule of monatomic gas can have three independent motions and hence 3 degrees of freedom (all translational).

b) Diatomic Gas: Molecule of diatomic gas has 5 degree of freedom.3 translational and 2 rotational.

c) Triatomic Gas: A non-linear molecule can rotate about any of three co-ordinate axes. Hence it has 6 degrees of freedom: 3 translational and 3 rotational.

Very Short Answer Questions

1. Define Mean Free Path.

A. The distance travelled by a gas molecule between two successive collisions is known as free path.

$$\lambda = \frac{\text{total distance travelled by a gas molecule between successive collisons}}{\text{total number of collisons}}$$

Let $\lambda_1, \lambda_2, \lambda_3 ....$ be the distance travelled by a gas molecule during n collisions respectively, mean free path $\lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + ... + \lambda_n}{n}$

2. Name two prominent phenomena which provide conclusive evidence of molecular motion.

A. Dalton's law, Avogadro's Law.

3. How does kinetic theory justify Avogadro hypothesis and show that Avogadro Number in different gases is same?

A. Avogadro's Law:

Avogadro law states that at the same temperature and pressure equal volumes of all gases contain the same number of molecules.

Consider 1 c.c of each gas at the same temperature and pressure. Let n_1 and n_2 be the number of molecules per c.c. m_1 and m_2 their masses and C_1 and C_2 their root mean square velocities in the two gases respectively. According to kinetic theory of gases we have

$$P = \frac{1}{3} m_1 n_1 C_1^2 = \frac{1}{3} m_2 n_2 C_2^2 \quad \text{....... (i)}$$

$$\text{or} \quad m_1 n_1 C_1^2 = m_2 n_2 C_2^2$$

Since the temperatures are the same, there will be no change in temperature when the two gases are mixed. This is possible only if the mean kinetic energy per molecule in the two gases is the same. Hence,

$$\frac{1}{2} m_1 C_1^2 = \frac{1}{2} m_2 C_2^2 \quad \text{or} \quad m_1 C_1^2 = m_2 C_2^2 \quad \text{....... (ii)}$$

From (i) and (ii), we find $n_1 = n_2$

i.e., the numbers of molecules per c.c. in the two gases are equal.

4. When does a real gas behaves like an Ideal Gas?

A. A real gas behaves as an ideal gas at low pressure and high temperature.

5. State Boyle's law and Charles' law.

A. Boyle's Law:

At constant temperature, the volume of a given mass of gas in inversely proportional to its pressure.

If P and V be the pressure and volume of a given mass of gas at constant temperature T, then

PV = a constant.

Charles' Law at Constant Pressure:

At constant Pressure, the volume of given mass of gas is directly proportional to its absolute temperature.

If V is the volume and T is the absolute temperature of a gas at constant pressure, then

V / T = constant.

Charles' Law at Constant Volume:

At constant volume, the pressure of a given mass of a gas is directly proportional to its absolute temperature.

If P is pressure and T is the absolute temperature of a given mass of a gas, then

$$\frac{P}{T} = \text{Constant}$$

6. State Dalton's Law of Partial Pressure

A. Dalton's law of Partial Pressure:

The total pressure exerted by a mixture of non-reacting gases in a vessel is equal to the sum of the individual pressures which each gas exerts if it alone occupied the same volume at a given temperature.

For *n* gases $P = P_1 + P_2 + P_3 + ...P_n$

Where p = pressure exerted by mixture and $P_1, P_2, P_3, ...P_n$ = partial pressure of component gases.

7. Pressure of an ideal gas in a container is independent of shape of the container. Explain.

A. The pressure of an ideal gas in a container is given by $P = \frac{1}{3} nm\overline{v}^2$ which is independent of shape of the container.

8. Explain the concept of degrees of freedom for molecules of a gas.

A. **Degrees of Freedom:**

The total number of independent ways in which a system can possess energy is called the degree of freedom (*f*).

1) Mono-Atomic Gas: molecule of mono-atomic gas can have three independent translational motions and hence it has 3 degrees of freedom.

2) Di-Atomic Gas: molecule of diatomic gas has 5 degree of freedom i.e. 3 translational and 2 rotational.

3) Tri-atomic Gas: a non-linear molecule can rotate about any of three co-ordinate axes. Hence it has 6 degrees of freedom i.e. 3 translational and 3 rotational. At high temperature the molecule will have additional degrees of freedom due to vibrational motion. Hence the molecule will have 7 degrees of freedom.

9. What is the expression between pressure and kinetic energy of a gas molecule?

A. If P is the pressure and E is the kinetic energy

$$P = \frac{1}{3}\rho C^2 = \frac{2}{3}\times\frac{1}{2}\rho C^2 = \frac{2}{3}E$$

Where $E = \frac{1}{2}\rho C^2$ is the mean kinetic energy per unit volume of the gas.

Hence the pressure of a gas is numerically equal to two-thirds of the mean kinetic energy per unit volume of the molecules.

10. The absolute temperature of a gas is increased by 3 times. What will be the increase in rms velocity of the gas molecule?

A. $v_{rms} = \sqrt{\frac{3KT}{m}}$

$T_1 = T$; $T_2 = 3T$

$$\frac{v_1}{v_2} = \sqrt{\frac{T_1}{T_2}} \Rightarrow \frac{v_1}{v_2} = \sqrt{\frac{T}{3T}}$$

$$\therefore v_2 = \sqrt{3}\, v_{rms}$$

Short Answer Questions

1. Explain the kinetic interpretation of Temperature?

A. Kinetic Interpretation of Temperature:

The internal energy of an ideal gas, which is purely the kinetic energy of the gas particles $E = \frac{3}{2} K_B NT$ where K_B is Boltzmann constant, n is the total number of molecules, t is the absolute temperature of the gas.

Then $\frac{E}{N} = \frac{3}{2} K_B T$ is the average kinetic energy of a gas molecule

Also, $\frac{3}{2} K_B T = \frac{1}{2} m\bar{v}^2$

Hence the mean kinetic energy per molecule in a given mass of gas is proportional to the absolute temperature of the gas.

2. How specific heat capacity of mono atomic, diatomic and poly atomic gases can be explained on the basis of law of Equipartition of Energy?

A. Law of Equipartition of Energy:

for any system in thermal equilibrium, the total energy is equally distributed among all of its degree of freedom and each degree of freedom is associated with energy $\frac{1}{2} kT$

(where k = 1.38´10^{-23} j/k and t = absolute temperature of the system).

Specific Heat Capacity - Monatomic Gas:

The monatomic gas molecules can have only the translational motion. According to the theory of equipartition of energy, this energy will be equally divided among the three translational degrees of freedom.

The total energy u of 1 gram molecule of the gas at the absolute temperature t is given by u =3/2 rat

Where r is the gas constant per gram molecule.

If CV is the molar specific heat at constant volume, then $c_V = \frac{dU}{dT}$ = 3/2r

If c_p is the molar specific heat at constant pressure, then

$c_p - c_V = r$ or $c_p = c_V + r = \frac{5}{2}r$

Diatomic Gas:

For diatomic gases, remembering that they have in all five degrees of freedom, three translational and two rotational, the total energy is given by

$$u = \frac{5}{2} rt$$

Hence $c_V = \frac{5}{2}r$ and $c_V = \frac{7}{2}r$

Poly atomic Gas:

Polyatomic gases have 3 translational and 3 rotational degrees of freedom and additional degrees of freedom due to vibration motion. Hence one mole of such a gas has

$$C_v = 3 + f_{vib} \text{ and } C_p = 4 + f_{vib}$$

3. Explain the concept of absolute zero of temperature on the basis of kinetic theory

A: According to kinetic theory of gases, we have the equation for the pressure $P = \frac{1}{3}mn\bar{v}^2$,

From the perfect gas equation, $P = \frac{\rho RT}{M_0}$

$$\therefore P = \frac{1}{3}mn\bar{v}^2 = \frac{\rho RT}{M_0}$$

If T = 0 then the mean of squared speed becomes zero. Hence pressure becomes zero. Then the gas converts into liquids. Thus this temperature is called absolute zero.

4. Prove that the average kinetic energy of a molecule of an ideal gas is directly proportional to the absolute temperature of the gas.

A. The pressure exerted by a gas of n molecules and occupying a volume V is given by

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

Or $$PV = \frac{1}{3} mnC^2$$

If V is the volume occupied by a gram-molecule of the gas and M the molecular weight, then $M = mN$

Where N is Avogadro's Number $\therefore PV = \frac{1}{3} MC^2$

Using the perfect gas equation PV = RT,

$$\frac{1}{3}MC^2 = RT \quad \text{Or} \quad \frac{1}{2}MC^2 = \frac{3}{2}RT$$

Dividing both sides by Avogadro's, number N , we have $\frac{1}{2}\frac{M}{N}C^2 = \frac{3}{2}\frac{R}{N}T$

But $\frac{M}{N}$ = m and $\frac{R}{N}$ = k, a constant, known as the Boltzmann's gas constant.

$$\therefore mC^2 = \frac{3}{2} kT$$

Hence the mean kinetic energy per molecule in a given mass of gas is proportional to the absolute temperature of the gas

5. Two thermally insulated vessels 1 and 2 of volumes V_1 and V_2 are joined with a valve and filled with air at temperatures (T_1, T_2) and pressure (P_1, P_2) respectively. If the valve joining the two vessels is opened, what will be the temperature inside the vessels at equilibrium?

A: $n_1T_1 + n_2T_2 = (n_1 + n_2)T$

$$P_1V_1 + P_2V_2 = \left(\frac{P_1V_1}{T_1} + \frac{P_2V_2}{T_2}\right)T$$

(R is canceled on both sides)

$$\Rightarrow T = \frac{(P_1V_1 + P_2V_2)T_1T_2}{(P_1V_1T_2 + P_2V_2T_1)}$$

T is the temperature inside the vessels at equilibrium.

6. What is the ratio of r.m.s. speed of oxygen and hydrogen molecules at the same temperature?

A. $v \, \alpha \frac{1}{\sqrt{m}} \Rightarrow \frac{v_1}{v_2} = \sqrt{\frac{m_1}{m_2}} = \frac{\sqrt{M_O}}{M_H} = \sqrt{\frac{2}{32}} = \frac{1}{4}$

7`. Four molecules of a gas have speeds 1, 2, 3 and 4km/s. find the rms speed of the gas molecule.

A. $v_{\text{rms}} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + v_4^2}{4}} = \sqrt{\frac{1^2 + 2^2 + 3^2 + 4^2}{4}} = 2.7386$

8. If a gas has f Degree of Freedom, find the ratio of C_p and C_v

A. $C_V = \frac{f}{2}R, C_P = C_V + R = \frac{f}{2}R + R = \left(1 + \frac{f}{2}\right)R$

$$\frac{C_P}{C_V} = \frac{\left(1+\frac{f}{2}\right)}{\frac{f}{2}R} = \frac{f}{2}R = 1 + \frac{2}{f}$$

9. Calculate the molecular kinetic energy of 1 gram of helium (molecular weight 4) at $127^0 C$. Given $R = 8.31 J mol^{-1} K^{-1}$

A. Kinetic energy = $\frac{3}{2}K_B T = \frac{3}{2} \times 1.38 \times 10^{-23} \times 400 = 8.28 \times 10^{-21} J$

10. When pressure increases by 2%, what is the percentage decrease in the volume of a gas, assuming Boyle's law is obeyed?

A: $\frac{P_1}{P_2} = \frac{V_2}{V_1} \Rightarrow \frac{P}{\frac{102P}{100}} = \frac{V_2}{V_1}$

$$\frac{100}{102} = \frac{V_2}{V_1} \Rightarrow \frac{V_2 - V_1}{V} = \frac{100 - 102}{100}$$

$$\frac{\Delta V}{V} = \frac{-2}{100} \frac{\Delta V}{V} \times 100 = 2\%$$

Long Answer Questions

1. Derive an expression for the pressure of an ideal gas in a container from kinetic theory and hence give kinetic interpretation of temperature.

A. Consider an ideal gas enclosed in a cubical container of side *l*.

1) Consider a molecule of mass 'm' moving with velocity $\vec{v}$. The velocity $\vec{v}$ is resolved in to components $\vec{v_x}, \vec{v_y}$ and $\vec{v_z}$ along x, y and z axes respectively so that

$$v^2 = v_x^2 + v_y^2 + v_z^2.$$

Since the gas is isotropic $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \left(\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}\right) = \frac{1}{3}\overline{v^2}$

Where $\overline{v^2}$ is the mean of squared speed?

2) In a small time interval Δt, a molecule within a distance $v_x \Delta t$ from the wall will hit the wall. Hence molecules within the volume $Av_x\Delta t$ only can hit the wall in time Δt. But, on the average, half of these are moving towards the wall and the other half away from the wall. Hence the number of molecules hitting the wall in time Δt is $\frac{1}{2}Av_x\Delta tn$. Where n is the number of molecules per unit volume.

3) Since the collision of the molecule with the wall of the container is elastic, the molecule rebounds with the same velocity. Then change in momentum of the

Molecules are $(-mv_x - mv_x) = -2mv_x$. By the principle of conservation of momentum, the momentum imparted to the wall in the collision $= 2mv_x$.

The total momentum transferred to the wall in time Δt is $Q = (2mv_x)\left(\frac{1}{2}nAv_x\Delta t\right)$

4) Since the force on the wall is the rate of change of momentum and pressure is force per unit area $P = \frac{Q}{A\Delta t} = nmv_x^2$

$$\therefore P = \frac{1}{3}nm\overline{v}^2 \quad (\therefore \overline{v}_x^2 = \frac{1}{3}\overline{v}^2)$$

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