Chapter

13

Kinetic Theory of Gases

Gas

In gases the intermolecular forces are very weak and its molecule may fly apart in all directions. So the gas is characterized by the following properties.

(i) It has no shape and size and can be obtained in a vessel of any shape or size.

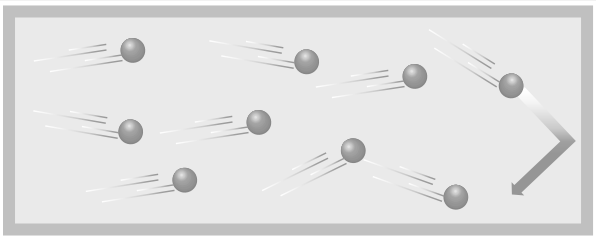
(ii) It expands indefinitely and uniformly to fill the available space.

(iii) It exerts pressure on its surroundings.

(iv) Intermolecular forces in a gas are minimum.

(v) They can easily compressed and expand.

Assumption of Ideal Gases (or Kinetic Theory of Gases)



Kinetic theory of gases relates the macroscopic properties of gases (such as pressure, temperature *etc*.) to the microscopic properties of the gas molecules (such as speed, momentum, kinetic energy of molecule *etc*.)

Actually it attempts to develop a model of the molecular behaviour which should result in the observed behaviour of an ideal gas. It is based on following assumptions :

(1) Every gas consists of extremely small particles known as molecules. The molecules of a given gas are all identical but are different than those of another gas.

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

(3) Their size is negligible in comparison to intermolecular distance (10^{-9} *m*)

(4) The volume of molecules is negligible in comparison to the volume of gas. (The volume of molecules is only 0.014% of the volume of the gas).

(5) Molecules of a gas keep on moving randomly in all possible direction with all possible velocities.

(6) The speed of gas molecules lie between zero and infinity

(7) The gas molecules keep on colliding among themselves as well as with the walls of containing vessel. These collisions are perfectly elastic.

(8) The time spent in a collision between two

molecules is negligible in comparison to time between two successive collisions.

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

(10) No attractive or repulsive force acts between gas molecules.

(11) Gravitational attraction among the molecules is ineffective due to extremely small masses and very high speed of molecules.

(12) Molecules constantly collide with the walls of container due to which their momentum changes. The change in momentum is transferred to the walls of the container. Consequently pressure is exerted by gas molecules on the walls of container.

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

Gas Laws

(1) **Boyle's law :** For a given mass of an ideal gas at constant temperature, the volume of a gas is inversely proportional to its pressure.

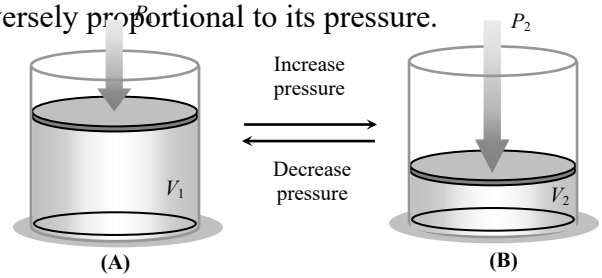


Fig. 13.1

i.e. $V \propto \frac{1}{P}$ or $PV = \text{constant} \Rightarrow P_1V_1 = P_2V_2$

(i) $PV = P\left(\frac{m}{\rho}\right) = \text{constant} \Rightarrow \frac{P}{\rho} = \text{constant}$ or $\frac{P_1}{\rho_1} = \frac{P_2}{\rho_2}$

(As volume $= \frac{m}{\rho(\text{Density of the gas})}$ and m = constant)

(ii) $PV = P\left(\frac{N}{n}\right) = \text{constant} \Rightarrow \frac{P}{n} = \text{constant}$ or $\frac{P_1}{n_1} = \frac{P_2}{n_2}$

(iii) As number of molecules per unit volume $n = \frac{N}{V}$

$\Rightarrow V = \frac{N}{n}$ also N = constant

(iv) Graphical representation : If m and T are constant

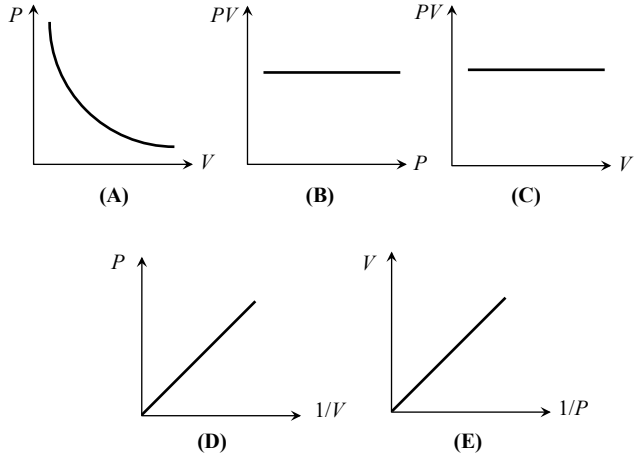


Fig. 13.2

(2) **Charle's law :** If the pressure remaining constant, the volume of the given mass of a gas is directly proportional to its absolute temperature.

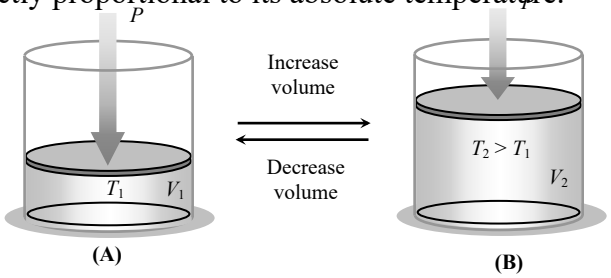


Fig. 13.3

i.e., $V \propto T \Rightarrow \frac{V}{T} = \text{constant} \Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$

(i) $\frac{V}{T} = \frac{m}{\rho T} = \text{constant}$ (As volume $V = \frac{m}{\rho}$)

or $\rho T = \text{constant} \Rightarrow \rho_1 T_1 = \rho_2 T_2$

(ii) If the pressure remains constant, the volume of the given mass of a gas increases or decreases by $\frac{1}{273.15}$ of its volume at $0°C$ for each $1°C$ rise or fall in temperature.

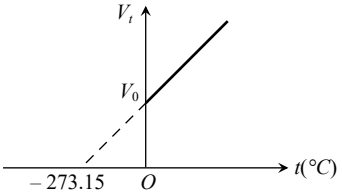


Fig. 13.4

$V_t = V_0\left(1 + \frac{1}{273.15}t\right)$.

This is Charle's law for centigrade scale.

(v) Graphical representation: If m and P are constant

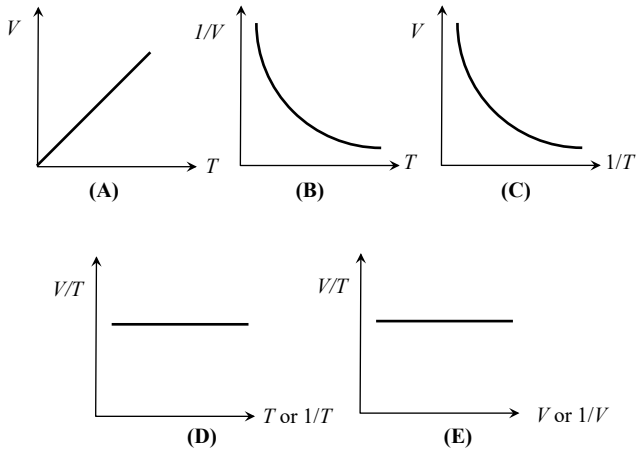


Fig. 13.5

(3) **Gay-Lussac's law or pressure law :** The volume remaining constant, the pressure of a given mass of a gas is directly proportional to its absolute temperature.

$P \propto T$ or $\frac{P}{T} = \text{constant} \Rightarrow \frac{P_1}{T_1} = \frac{P_2}{T_2}$

(i) The volume remaining constant, the pressure of a given mass of a gas increases or decreases by $\frac{1}{273.15}$ of its pressure at $0°C$ for each $1°C$ rise or fall in temperature.

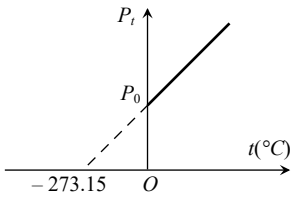


Fig. 13.5

$$P_t = P_0\left[1 + \frac{1}{273.15}t\right]$$

This is pressure law for centigrade scale.

(ii) **Graphical representation :** If m and V are constants

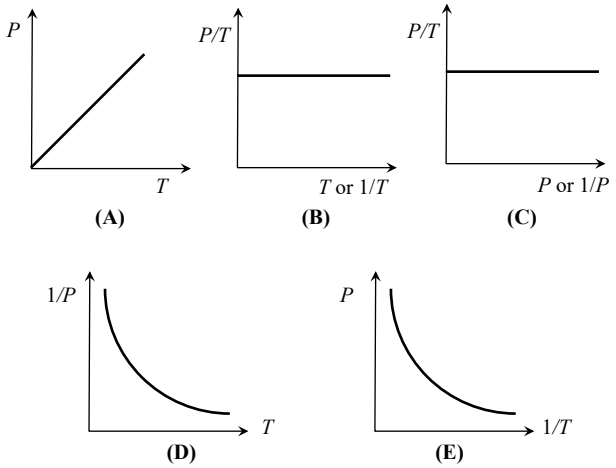


Fig. 13.6

(4) **Avogadro's law :** Equal volume of all the gases under similar conditions of temperature and pressure contain equal number of molecules *i.e.* $N_1 = N_2$.

(5) **Grahm's law of diffusion :** When two gases at the same pressure and temperature are allowed to diffuse into each other, the rate of diffusion of each gas is inversely proportional to the square root of the density of the gas *i.e.* $r \propto \frac{1}{\sqrt{\rho}} \propto \frac{1}{\sqrt{M}}$ (M is the molecular weight of the gas) $\Rightarrow \frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}} = \sqrt{\frac{M_2}{M_1}}$

If V is the volume of gas diffused in t *sec* then

$$r = \frac{V}{t} \Rightarrow \frac{r_1}{r_2} = \frac{V_1}{V_2} \times \frac{t_2}{t_1}$$

(6) **Dalton's law of partial pressure :** The total pressure exerted by a mixture of non-reacting gases occupying a vessel is equal to the sum of the individual pressures which each gases 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.

Equation of State or Ideal Gas Equation

The equation which relates the pressure (P) volume (V) and temperature (T) of the given state of an ideal gas is known as ideal gas equation or equation of state.

For 1 mole of gas $\frac{PV}{T} = R$ (constant) $\Rightarrow PV = RT$

where R = universal gas constant.

Table 13.1 : Different forms of gas equation

Quantity of gas	Equation	Constant
1 mole gas	$PV = RT$	R = universal gas constant
μ mole gas	$PV = \mu RT$	

1 molecule of gas	$PV=\left(\frac{R}{N_A}\right)T=kT$	k = Boltzmann's constant
N molecules of gas	$PV = NkT$	
1 gm of gas	$PV=\left(\frac{R}{M}\right)T=rT$	r = Specific gas constant
m gm of gas	$PV = mrT$	

(1) **Universal gas constant (R) :** Universal gas constant signifies the work done by (or on) a gas per mole per kelvin.

$$R=\frac{PV}{\mu T}=\frac{\text{Pressure}\times\text{Volume}}{\mu\times\text{Temperature}}=\frac{\text{Work done}}{\mu\times\text{Temperature}}$$

(i) At S.T.P. the value of universal gas constant is same for all gases $R = 8.31\frac{J}{mole\times kelvin}=1.98\frac{cal}{mole\times kelvin}\simeq 2\frac{cal}{mol\times kelvin}$

$$=0.8221\frac{litre\times atm}{mole\times kelvin}.$$

(ii) Dimension : $[ML^2T^{-2}\theta^{-1}]$

(2) **Boltzman's constant (k) :** It is represented by per mole gas constant *i.e.*, $k=\frac{R}{N}=\frac{8.31}{6.023\times10^{23}}$ $=1.38\times10^{-23}\ J/K$

It's dimension : $[ML^2T^{-2}\theta^{-1}]$

(3) **Specific gas constant (r) :** It is represented by per gram gas constant *i.e.*, $r=\frac{R}{M}$. It's unit is $\frac{Joule}{gm\times kelvin}$ and dimension $[L^2T^{-2}\theta^{-1}]$

Since the value of M is different for different gases. Hence the value of r is different for different gases. *e.g.* It is maximum for hydrogen $r_{H_2}=\frac{R}{2}$

Real Gases

(1) The gases actually found in nature are called real gases.

(2) They do not obeys gas Laws.

(3) For exactly one mole of an ideal gas $\frac{PV}{RT}=1$. Plotting the experimentally determined value of $\frac{PV}{RT}$ for exactly one mole of various real gases as a function of pressure P, shows a deviation from identity.

(4) The quantity $\frac{PV}{RT}$ is called the compressibility factor and should be unit for an ideal gas.

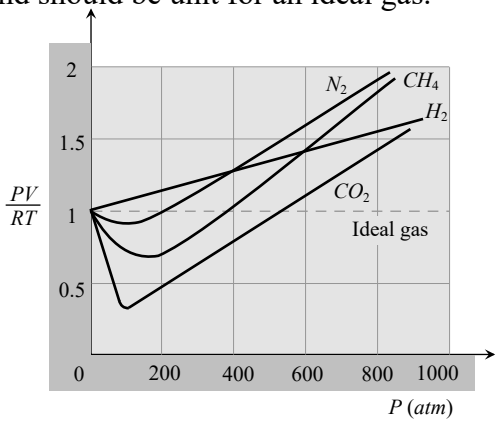


Fig. 13.7

(5) Deviation from ideal behaviour as a function of temperat

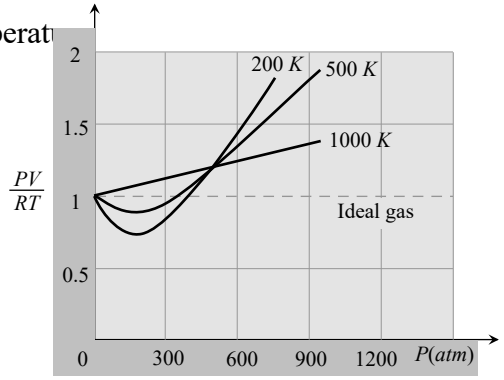


Fig. 13.8

(6) A real gas behaves as ideal gas most closely at low pressure and high temperature. Also can actual gas can be liquefied most easily which deviates most from ideal gas behaviour at low temperature and high pressure.

(7) **Equation of state for real gases :** It is given by Vander Waal's with two correction in ideal gas equation. The it know as Vander Waal's gas equation.

(i) **Volume correction :** Due to finite size of molecule, a certain portion of volume of a gas is covered by the molecules themselves. Therefore the space available for the free motion of molecules of

gas will be slightly less than the volume V of a gas. Hence the effective volume becomes $(V - b)$.

(ii) **Pressure correction :** Due to intermolecular force in real gases, molecule do not exert that force on the wall which they would have exerted in the absence of intermolecular force. Therefore the observed pressure P of the gas will be less than that present in the absence of intermolecular force. Hence the effective pressure becomes $\left(P + \frac{a}{V^2}\right)$.

(iii) **Vander Waal's gas equations**

For 1 *mole* of gas $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

For μ *moles* of gas $\left(P + \frac{a\mu^2}{V^2}\right)(V - \mu b) = \mu RT$

Here a and b are constant called Vander Waal's constant.

Dimension : $[a] = [ML^5 T^{-2}]$ and $[b] = [L^3]$

Units : $a = N \times m^4$ and $b = m^3$.

(8) **Andrews curves** : The pressure (P) versus volume (V) curves for actual gases are called Andrews curves.

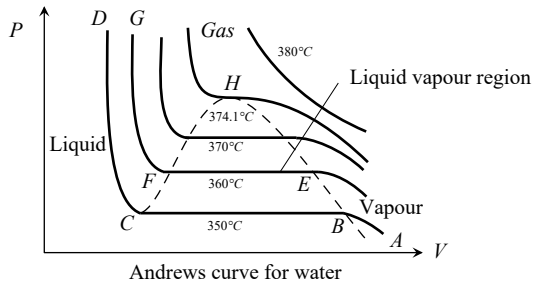


Fig. 13.9

(i) At 350°C, part AB represents vapour phase of water, in this part Boyle's law is obeyed $\left(P \propto \frac{1}{V}\right)$. Part BC represents the co-existence of vapour and liquid phases. At point C, vapours completely change to liquid phase. Part CD is parallel to pressure axis which shows that compressibility of the water is negligible.

(ii) At 360°C portion representing the co-existence of liquid vapour phase is shorter.

(iii) At 370°C this portion is further decreased.

(iv) At 374.1°C, it reduces to point (H) called critical point and the temperature 374.1°C is called critical temperature (T_c) of water.

(v) The phase of water (at 380°C) above the critical temperature is called gaseous phase.

(9) **Critical temperature, pressure and volume :** The point on the P-V curve at which the matter gets converted from gaseous state to liquid state is known as critical point. At this point the difference between the liquid and vapour vanishes *i.e.* the densities of liquid and vapour become equal.

(i) **Critical temperature (T_c) :** The maximum temperature below which a gas can be liquefied by pressure alone is called critical temperature and is characteristic of the gas. A gas cannot be liquefied if its temperature is more than critical temperature.

CO_2 (31.1°C), O_2 (–118°C), N_2 (–147.1°C) and H_2O (374.1°C)

(ii) **Critical pressure (P_c) :** The minimum pressure necessary to liquify a gas at critical temperature is defined as critical pressure CO_2 (73.87 *bar*) and O_2 (49.7*atm*)

(iii) **Critical volume (V_c) :** The volume of 1 mole of gas at critical pressure and critical temperature is defined as critical volume CO_2 ($95 \times 10^{-6}\ m^3$)

(iv) **Relation between Vander Waal's constants and T_c, P_c, V_c**

$$T_c = \frac{8a}{27Rb},\quad P_c = \frac{a}{27b^2},\quad V_c = 3b,$$

$$a = \frac{27R^2}{64}\frac{T_c^2}{P_c},\quad b = \frac{R}{8}\left(\frac{T_c}{P_c}\right) \text{ and } \frac{P_c V_c}{T_c} = \frac{3}{8}R$$

Pressure of an Ideal Gas

Consider an ideal gas (consisting of N molecules each of mass m) enclosed in a cubical box of side L.

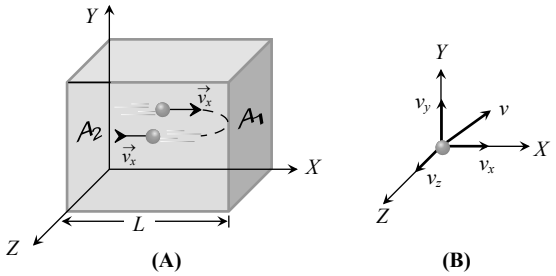


Fig. 13.10

(1) **Instantaneous velocity :** Any molecule of gas moves with velocity $\vec{v}$ in any direction

where $\vec{v} = v_x\hat{i} + v_y\hat{j} + v_z\hat{k} \Rightarrow v = \sqrt{v_x^2 + v_y^2 + v_z^2}$. Due to random motion of molecule $v_x = v_y = v_z \Rightarrow v^2 = 3v_x^2 = 3v_y^2 = 3v_z^2$

(2) **Time during collision :** Time between two successive collision with the wall A_1.

$$\Delta t = \frac{\text{Distance travelled by molecule between two successive collision}}{\text{Velocity of molecule}}$$

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

(3) **Collision frequency (n) :** It means the number of collision per second. Hence $n = \frac{1}{\Delta t} = \frac{v_x}{2L}$

(4) **Change in momentum :** This molecule collides with the shaded wall (A_1) with velocity v_x and rebounds with velocity $-v_x$.

The change in momentum of the molecule

$$\Delta p = (-mv_x) - (mv_x) = -2mv_x$$

As the momentum remains conserved in a collision, the change in momentum of the wall A_1 is $\Delta p = 2mv_x$

After rebound this molecule travel toward opposite wall A_2 with velocity $-v_x$, collide to it and again rebound with velocity v_x towards wall A_1.

(5) **Force on wall :** Force exerted by a single molecule on shaded wall is equal to rate at which the momentum is transferred to the wall by this molecule.

i.e. $F_{\text{Single molecule}} = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{(2L/v_x)} = \frac{mv_x^2}{L}$

The total force on the wall A_1 due to all the molecules $F_x = \frac{m}{L}\sum v_x^2 = \frac{m}{M}(v_{x_1}^2 + v_{x_2}^2 + v_{x_3}^2 + ...) = \frac{mN}{L}\overline{v_x^2}$

$\overline{v_x^2}$ = mean square of x component of the velocity.

(6) **Pressure :** Now pressure is defined as force per unit area, hence pressure on shaded wall $P_x = \frac{F_x}{A} = \frac{mN}{AL}\overline{v_x^2} = \frac{mN}{V}\overline{v_x^2}$

For any molecule, the mean square velocity $\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$; by symmetry $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} \Rightarrow \overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{\overline{v^2}}{3}$

Total pressure inside the container

$P = \frac{1}{3}\frac{mN}{V}\overline{v^2} = \frac{1}{3}\frac{mN}{V}v_{rms}^2$ (where $v_{rms} = \sqrt{\overline{v^2}}$)

(7) **Relation between pressure and kinetic energy :** As we know $P = \frac{1}{3}\frac{mN}{V}v_{rms}^2 = \frac{1}{3}\frac{M}{V}v_{rms}^2 \Rightarrow P = \frac{1}{3}\rho v_{rms}^2$ ... (i)

[As $M = mN$ = Total mass of the gas and $\rho = \frac{M}{V}$]

$\therefore$ K.E. per unit volume $E = \frac{1}{2}\left(\frac{M}{V}\right)v_{rms}^2 = \frac{1}{2}\rho v_{rms}^2$ ...(ii)

From (i) and (ii), we get $P = \frac{2}{3}E$

i.e. the pressure exerted by an ideal gas is numerically equal to the two third of the mean kinetic energy of translation per unit volume of the gas.

(8) **Effect of mass, volume and temperature on pressure :** $P = \frac{1}{3}\frac{mN}{V}v_{rms}^2$ or $P \propto \frac{(mN)T}{V}$ [As $v_{rms}^2 \propto T$]

(i) If volume and temperature of a gas are constant $P \propto mN$ *i.e.* Pressure $\propto$ (Mass of gas).

i.e. if mass of gas is increased, number of molecules and hence number of collision per second increases *i.e.* pressure will increase.

(ii) If mass and temperature of a gas are constant. $P \propto (1/V)$, *i.e.*, if volume decreases, number of collisions per second will increase due to lesser effective distance between the walls resulting in greater pressure.

(iii) If mass and volume of gas are constant, $P \propto (v_{rms})^2 \propto T$

i.e., if temperature increases, the mean square speed of gas molecules will increase and as gas molecules are moving faster, they will collide with the walls more often with greater momentum resulting in greater pressure.

Various Speeds of Gas Molecules

The motion of molecules in a gas is characterised by any of the following three speeds.

(1) **Root mean square speed :** It is defined as the square root of mean of squares of the speed of different molecules

$$i.e.\ v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + v_4^2 + ...}{N}} = \sqrt{\overline{v^2}}$$

(i) From the expression of pressure $P = \frac{1}{3}\rho v_{rms}^2$

$$\Rightarrow v_{rms} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3PV}{\text{Massof gas}}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3kT}{m}}$$

where $\rho = \frac{\text{Massof gas}}{V} = \text{Densityof the gas}$, $M = \mu \times$ (mass of gas), $pV = \mu RT$, $R = kN_A$, $k =$ Boltzmann's constant,

$m = \frac{M}{N_A} =$ mass of each molecule.

(ii) With rise in temperature *rms* speed of gas molecules increases as $v_{rms} \propto \sqrt{T}$.

(iii) With increase in molecular weight *rms* speed of gas molecule decreases as $v_{rms} \propto \frac{1}{\sqrt{M}}$. *e.g.*, *rms* speed of hydrogen molecules is four times that of oxygen molecules at the same temperature.

(iv) *rms* speed of gas molecules is of the order of *km/s* *e.g.*, at NTP for hydrogen gas

$$(v_{rms}) = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \times 273}{2 \times 10^3}} = 1840\, m/s.$$

(v) *rms* speed of gas molecules is $\sqrt{\frac{3}{\gamma}}$ times that of speed of sound in gas, as $v_{rms} = \sqrt{\frac{3RT}{M}}$ and $v_s = \sqrt{\frac{\gamma RT}{M}} \Rightarrow v_{rms} = \sqrt{\frac{3}{\gamma}} v_s$

(vi) *rms* speed of gas molecules does not depends on the pressure of gas (if temperature remains constant) because $P \propto \rho$ (Boyle's law) if pressure is increased *n* times then density will also increases by *n* times but v_{rms} remains constant.

(vii) Moon has no atmosphere because v_{rms} of gas molecules is more than escape velocity (v_e).

A planet or satellite will have atmosphere only if $v_{rms} < v_e$

(viii) At $T = 0$; $v_{rms} = 0$ *i.e.* the *rms* speed of molecules of a gas is zero at 0 *K*. This temperature is called absolute zero.

(2) **Most probable speed :** The particles of a gas have a range of speeds. This is defined as the speed which is possessed by maximum fraction of total number of molecules of the gas. *e.g.*, if speeds of 10 molecules of a gas are 1, 2, 2, 3, 3, 3, 4, 5, 6, 6 *km/s*, then the most probable speed is 3 *km/s*, as maximum fraction of total molecules possess this speed.

Most probable speed $v_{mp} = \sqrt{\frac{2P}{\rho}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2kT}{m}}$

(3) **Average speed :** It is the arithmetic mean of the speeds of molecules in a gas at given temperature.

$$v_{av} = \frac{v_1 + v_2 + v_3 + v_4 + ...}{N}$$

and according to kinetic theory of gases

Average speed $v_{av} = \sqrt{\frac{8P}{\pi\rho}} = \sqrt{\frac{8}{\pi}\frac{RT}{M}} = \sqrt{\frac{8}{\pi}\frac{kT}{m}}$

Maxwell's Law (or the Distribution of Molecular Speeds

(1) The v_{rms} gives us a general idea of molecular speeds in a gas at a given temperature. This doesn't mean that the speed of each molecule is v_{rms}. Many of the molecules have speed less than v_{rms} and many have speeds greater than v_{rms}.

(2) Maxwell derived as equation given the distribution of molecules in different speed as follow

$$dN = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}} dv$$

where dN = Number of molecules with speeds between v and $v + dv$.

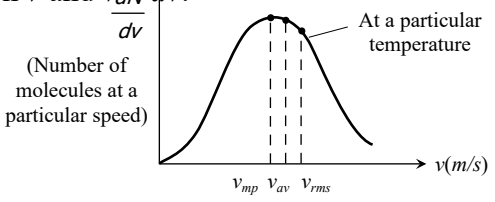


Fig. 13.11

(3) Graph between $\frac{dN}{dv}$ (number of molecules at a particular speed) and v (speed of these molecules). From the graph it is seen that $\frac{dN}{dv}$ is maximum at most probable speed.

This graph also represent that $v_{rms} > v_{av} > v_{mp}$

(Order remember trick RAM)

$\Rightarrow \quad \sqrt{\frac{3RT}{M}} > \sqrt{\frac{8RT}{\pi M}} > \sqrt{\frac{2RT}{M}} \Rightarrow$

$1.77\sqrt{\frac{RT}{M}} > 1.6\sqrt{\frac{RT}{M}} > 1.41\sqrt{\frac{RT}{M}}$

Area bonded by this curve with speed axis represents the number of molecules corresponds to that velocity range. This curve is asymmetric curve.

Effect of temperature on velocity distribution : With temperature rise the $\frac{dN}{dv}$ vs v. Curve shift towards right and becomes broader.

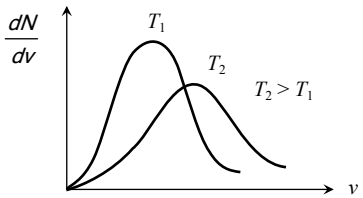


Fig. 13.12

(Because with temperature rise average molecular speed increases).

Mean Free Path

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

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

During two successive collisions, a molecule of a gas moves in a straight line with constant velocity and

Let $\lambda_1, \lambda_2, \lambda_3 .....$ be the distance travelled by a gas molecule during n collisions respectively, then the mean free path of a gas molecule is given by

$$\lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + ... + \lambda_n}{n}$$

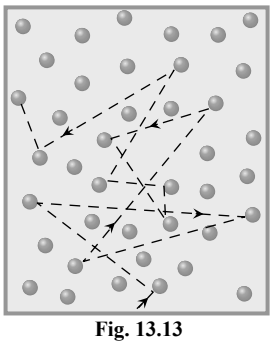


Fig. 13.13

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

where d = Diameter of the molecule,

n = Number of molecules per unit volume

(3) As $PV = \mu RT = \mu NkT \Rightarrow \frac{N}{V} = \frac{P}{kT} = n =$ Number of molecule per unit volume so $\lambda = \frac{1}{\sqrt{2}} \frac{kT}{\pi d^2 P}$.

(4) From $\lambda = \frac{1}{\sqrt{2}\pi n d^2} = \frac{m}{\sqrt{2}\pi (mn) d^2} = \frac{m}{\sqrt{2}\pi d^2 \rho}$

[As m = Mass each molecule, mn = Mass per unit volume = Density = ρ]

(5) If average speed of molecule is v then $\lambda = v \times \frac{t}{N} = v \times T$

[As N = Number of collision in time t, T = time interval between two collisions].

(i) As $\lambda \propto \frac{1}{\rho}$ and $\lambda \propto m$ *i.e.* the mean free path is inversely proportional to the density of a gas and directly proportional to the mass of each molecule.

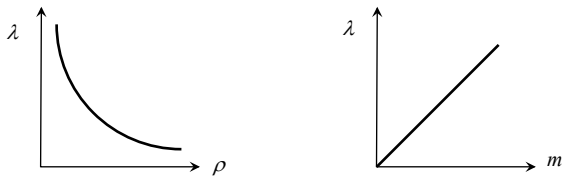


Fig. 13.14

(ii) As $\lambda = \frac{1}{\sqrt{2}} \frac{kT}{\pi d^2 P}$. For constant volume and hence constant number density n of gas molecules, $\frac{P}{T}$ is constant so that λ will not depend on P and T. But if volume of given mass of a gas is allowed to change with P or T then $\lambda \propto T$ at constant pressure and $\lambda \propto \frac{1}{P}$ at constant temperature.

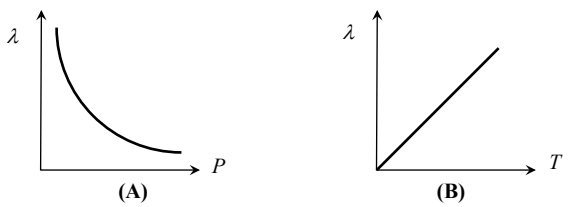


Fig. 13.15

Degree of Freedom

The term degree of freedom of a system refers to the possible independent motions, systems can have. or

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

The independent motions can be translational, rotational or vibrational or any combination of these.

So the degree of freedom are of three types :

(i) Translational degree of freedom

(ii) Rotational degree of freedom

(iii) Vibrational degree of freedom

General expression for degree of freedom

$f = 3A - B$; where A = Number of independent particles,

B = Number of independent restriction

(1) **Monoatomic gas :** Molecule of monoatomic gas can move in any direction in space so it can have three independent motions and hence 3 degrees of freedom (all translational)

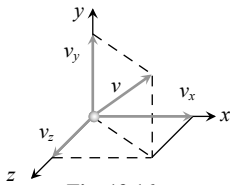


Fig. 13.16

(2) **Diatomic gas :** Molecules of diatomic gas are made up of two atoms joined rigidly to one another through a bond. This cannot only move bodily, but also rotate about one of the three co-ordinate axes. However its moment of inertia about the axis joining the two atoms is negligible compared to that about the other two axes.

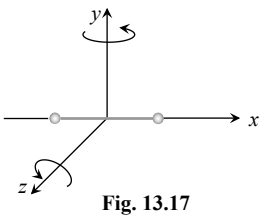


Fig. 13.17

Hence it can have only two rotational motion. Thus a diatomic molecule has 5 degree of freedom : 3 translational and 2 rotational.

(3) **Triatomic gas (Non-linear) :** 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.

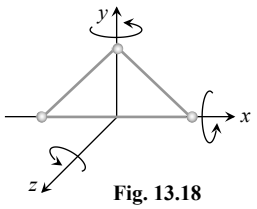


Fig. 13.18

Table 13.2 ; Degree of freedom for different gases

Atomicity of gas	Example	A	B	$f = 3A - B$	Figure A
Monoatomic	*He*, *Ne*, *Ar*	1	0	$f = 3$	
Diatomic	H_2, O_2, N_2, Cl_2 *etc.*	2	1	$f = 5$	A–B–A
Triatomic non linear	H_2O	3	3	$f = 6$	
Triatomic linear	CO_2, $BeCl_2$	3	2	$f = 7$	

The above degrees of freedom are shown at room temperature. Further at high temperature, in case of diatomic or polyatomic molecules, the atoms with in the molecule may also vibrate with respect to each other. In such cases, the molecule will have an additional degrees of freedom, due to vibrational motion.

An object which vibrates in one dimension has two additional degree of freedom. One for the potential energy and one for the kinetic energy of vibration.

A diatomic molecule that is free to vibrate (in addition to translation and rotation) will have $7 (2 + 3 + 2)$ degrees of freedom.

Kinetic Energy of Ideal Gas

In ideal gases, the molecules are considered as point particles. For point particles, there is no internal excitation, no vibration and no rotation. The point particles can have only translational motion and thus only translational energy. For an ideal gas the internal energy can only be tranlational kinetic energy.

Hence kinetic energy (or internal energy) of 1 mole ideal gas

$$E = \frac{1}{2} M v_{rms}^2 = \frac{1}{2} M \times \frac{3RT}{M} = \frac{3}{2} RT$$

Table 13.3 : Various Translational kinetic energies

Quantity of gas	Kinetic energy
1 mole gas	$\frac{3}{2}RT$; R = Universal gas constant
μ mole gas	$\frac{3}{2}\mu RT$
1 molecule	$\frac{3}{2}kT$; k = Boltzmann's constant
N molecule	$\frac{3}{2}NkT$
1 *gm* gas	$\frac{3}{2}rT$; r = Specific gas constant
m *gm* gas	$\frac{3}{2}mrT$

(1) Kinetic energy per molecule of gas does not depends upon the mass of the molecule but only depends upon the temperature of the gas. As $E=\frac{3}{2}kT$ or $E \propto$ T *i.e.* molecules of different gases say *He*, H_2 and O_2 *etc*. at same temperature will have same translational kinetic energy though their *r.m.s.* speed are different.

(2) For two gases at the same temperature $m_1(v_{rms})_1^2 = m_2(v_{rms})_2^2$

(3) Kinetic energy per mole of gas depends only upon the temperature of gas.

(4) Kinetic energy per *gram* of gas depend upon the temperature as well as molecular weight (or mass of one molecule) of the gas. $E_{gram}=\frac{3}{2}\frac{k}{m}T \Rightarrow E_{gram} \propto \frac{T}{m}$

(5) From the above expressions it is clear that higher the temperature of the gas, more will be the average kinetic energy possessed by the gas molecules at $T = 0$, $E = 0$ *i.e.* at absolute zero the molecular motion stops.

Law of Equipartition of Energy

According to this law, for any system in thermal equilibrium, the total energy is equally distributed among its various degree of freedom. And each degree of freedom is associated with energy $\frac{1}{2}kT$ (where $k=1.38\times10^{-23}\ J/K$, T = absolute temperature of the system).

(1) At a given temperature T, all ideal gas molecules no matter what their mass have the same average translational kinetic energy; namely, $\frac{3}{2}kT$. When measure the temperature of a gas, we are also measuring the average translational kinetic energy of it' s molecules.

(2) At same temperature gases with different degrees of freedom (*e.g.*, *He* and H_2) will have different average energy or internal energy namely $\frac{f}{2}kT$. (f is different for different gases)

(3) Different energies of a system of degree of freedom f are as follows

(i) Total energy associated with each molecule = $\frac{f}{2}kT$

(ii) Total energy associated with N molecules = $\frac{f}{2}NkT$

(iii) Total energy associated with μ mole = $\frac{f}{2}RT$

(iv) Total energy associated with μ molen = $\frac{f}{2}\mu RT$

(v) Total energy associated with each gram = $\frac{f}{2}rT$

(iv) Total energy associated with m gram = $\frac{f}{2}mrT$

Specific Heat (C_P and C_V) of a Gas

The specific heat of gas can have many values, but out of them following two values are very important

(1) **Specific heat at constant volume (C_V) :** The specific heat of a gas at constant volume is defined as the quantity of heat required to raise the temperature of unit mass of gas through $1°C$ or $1\ K$ when its volume is kept constant, *i.e.*, $c_V=\frac{(\Delta Q)_V}{m\Delta T}$

If instead of unit mass, 1 mole of gas is considered, the specific heat is called molar specific heat at constant volume and is represented by capital C_v.

$$C_V = Mc_V = \frac{M(\Delta Q)_V}{m\Delta T} = \frac{1}{\mu}\frac{(\Delta Q)_V}{\Delta T} \qquad \left[\text{As } \mu = \frac{m}{M}\right]$$

(2) **Specific heat at constant from (C_P) :** The specific heat of a gas at constant pressure is defined as the quantity of heat required to raise the temperature of unit mass of gas through 1 K when its pressure is kept constant, *i.e.*, $c_P = \frac{(\Delta Q)_p}{m\Delta T}$

If instead of unit mass, 1 mole of gas is considered, the specific heat is called molar specific heat at constant pressure and is represented by C_p.

$$C_p = MC_p = \frac{M(\Delta Q)_p}{m\Delta T} = \frac{1}{\mu}\frac{(\Delta Q)_p}{\Delta T} \qquad \left[\text{As } \mu = \frac{m}{M}\right]$$

Mayer's Formula

(1) Out of two principle specific heats of a gas, C_P is more than C_V because in case of C_V, volume of gas is kept constant and heat is required only for raising the temperature of one gram mole of the gas through 1°C or 1 K. Hence no heat, what so ever, is spent in expansion of the gas.

It means that heat supplied to the gas increases its internal energy only *i.e.* $(\Delta Q)_V = \Delta U = \mu C_V \Delta T$

.....(i)

(2) While in case of C_P the heat is used in two ways

(i) In increasing the temperature of the gas by ΔT

(ii) In doing work, due to expansion at constant pressure (ΔW)

So $(\Delta Q)_P = \Delta U + \Delta W = \mu C_P \Delta T$ .....(ii)

From equation (i) and (ii) $\mu C_P \Delta T - \mu C_V \Delta T = \Delta W$

$\Rightarrow \quad \mu \Delta T(C_P - C_V) = P\Delta V \Rightarrow \quad C_P - C_V = \frac{P\Delta V}{\mu \Delta T} = R$

[For constant pressure, $\Delta W = P\Delta V$ also from $PV = \mu RT$,

$P\Delta V = \mu R\Delta T$]

This relation is called Mayer's formula and shows that $C_P > C_V$ *i.e.* molar specific heat at constant pressure is greater than that at constant volume.

Specific Heat in Terms of Degree of Freedom

(1) C_V **:** For a gas at temperature T, the internal energy $U = \frac{f}{2}\mu RT \Rightarrow$ Change in energy $\Delta U = \frac{f}{2}\mu R\Delta T$

... (i)

Also, as we know for any gas heat supplied at constant volume $(\Delta Q)_V = \mu C_V \Delta T = \Delta U$

... (ii)

From equation (i) and (ii) $C_V = \frac{1}{2} fR$

(2) C_P **:** From the Mayer's formula $C_p - C_v = R$

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

(3) **Ratio of C_p and C_v (γ) :**

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

(i) Value of γ is different for monoatomic, diatomic and triatomic gases.

$$\gamma_{mono} = \frac{5}{3} = 1.6, \gamma_{di} = \frac{7}{5} = 1.4, \gamma_{tri} = \frac{4}{3} = 1.33$$

(ii) Value of γ is always more than 1. So we can say that always $C_P > C_V$.

Gaseous Mixture

If two non-reactive gases are enclosed in a vessel of volume V. In the mixture μ_1 moles of one gas are mixed with μ_2 moles of another gas. If N_A is Avogadro's number then

Number of molecules of first gas $N_1 = \mu_1 N_A$

and number of molecules of second gas $N_2 = \mu_2 N_A$

(1) Total mole fraction $\mu = (\mu_1 + \mu_2)$.

(2) If M_1 is the molecular weight of first gas and M_2 that of second gas.

Then molecular weight of mixture

$$M = \frac{\mu_1 M_1 + \mu_2 M_2}{\mu_1 + \mu_2}$$

(3) Specific heat of the mixture at constant volume will be

$$C_{V_{mix}} = \frac{\mu_1 C_{V_1} + \mu_2 C_{V_2}}{\mu_1 + \mu_2} = \frac{\frac{m_1}{M_1} C_{V_1} + \frac{m_2}{M_2} C_{V_2}}{\frac{m_1}{M_1} + \frac{m_2}{M_2}}$$

(4) Specific heat of the mixture at constant pressure will be

$$C_{P_{mix}} = \frac{\mu_1 C_{P_1} + \mu_2 C_{P_2}}{\mu_1 + \mu_2} = \frac{\mu_1\left(\frac{\gamma_1}{\gamma_1 - 1}\right)R + \mu_2\left(\frac{\gamma_2}{\gamma_2 - 1}\right)R}{\mu_1 + \mu_2}$$

$$= \frac{R}{\mu_1 + \mu_2}\left[\mu_1\left(\frac{\gamma_1}{\gamma_1 - 1}\right) + \mu_2\left(\frac{\gamma_2}{\gamma_2 - 1}\right)\right]$$

$$= \frac{R}{\frac{m_1}{M_1} + \frac{m_2}{M_2}}\left[\frac{m_1}{M_1}\left(\frac{\gamma_1}{\gamma_1 - 1}\right) + \frac{m_2}{M_2}\left(\frac{\gamma_2}{\gamma_2 - 1}\right)\right]$$

(5) $$\gamma_{\text{mixture}} = \frac{C_{P_{mix}}}{C_{V_{mix}}} = \frac{\frac{(\mu_1 C_{P_1} + \mu_2 C_{P_2})}{\mu_1 + \mu_2}}{\frac{(\mu_1 C_{V_1} + \mu_2 C_{V_2})}{\mu_1 + \mu_2}}$$

$$= \frac{\mu_1 C_{P_1} + \mu_2 C_{P_2}}{\mu_1 C_{V_1} + \mu_2 C_{V_2}} = \frac{\left\{\mu_1\left(\frac{\gamma_1}{\gamma_1 - 1}\right)R + \mu_2\left(\frac{\gamma_2}{\gamma_2 - 1}\right)R\right\}}{\left\{\mu_1\left(\frac{R}{\gamma_1 - 1}\right) + \mu_2\left(\frac{R}{\gamma_2 - 1}\right)\right\}}$$

$$\therefore \gamma_{\text{mixture}} = \frac{\frac{\mu_1\gamma_1}{\gamma_1 - 1} + \frac{\mu_2\gamma_2}{\gamma_2 - 1}}{\frac{\mu_1}{\gamma_1 - 1} + \frac{\mu_2}{\gamma_2 - 1}} = \frac{\mu_1\gamma_1(\gamma_2 - 1) + \mu_2\gamma_2(\gamma_1 - 1)}{\mu_1(\gamma_2 - 1) + \mu_2(\gamma_1 - 1)}$$

Tips & Tricks

✍ The cooking gas cylinder contains L.P.G. (Liquid Petroleum gas) which is saturated [illegible] as pressure of saturated vapours is independent of vo (at constant temperature). the pressure of coming out of the cylinder remains constant till the cylinder becomes empty.

✍ If the number of molecules in a gas increases, then the temperature, kinetic energy and pressure of the gas increases because $P \propto n$, $T \propto n$ and kinetic energy $\propto T \propto n$.

✍ At constant volume if T increases then $\bar{v}$, v_{rms}, P and collision frequency increases.

✍ If two gases are filled in vessel then nothing can be predicted about the pressure of gases. However their mean molecular energies will be same but their *rms* velocities will be different.

✍ The average distance between two gas molecules at NTP is 10^{-9} *m*.

✍ The space available for a single gas molecule at NTP is 37.2×10^{-2} m^2.

✍ The molecules of gases will escape out from a planet if the temperature of planet $T \le \frac{Mv_e^2}{3R}$; where v_e = escape velocity from the planet, R = universal, gas constant and M = Molecular mass of the gas.

✍ As f (degree of freedom) increases then $C_P\uparrow$, $C_V\uparrow$ and $\gamma\uparrow$.

✍ The number of molecules present in 1 *gm mole* of a gas is defined as Avogadro number (N_A).

$N_A = 6.023\times10^{23}$ per *gm mole* $= 6.023\times10^{26}$ per *kg mole*.

At S.T.P. or N.T.P. (T = 273 *K* and P = 1 *atm*) 22.4 *litre* of each gas has 6.023×10^{23} molecule

✍ One mole of any gas at S.T.P. occupy 22.4 *litre* of volume

e.g. 32 *gm* oxygen, 28 *gm* nitrogen and 2*gm* hydrogen occupy the same volume at S.T.P.

✍ For any gas 1 *mole* = M *gram* = 22.4 *litre* = 6.023×10^{23} molecule.

✍ $v_{rms} : v_{av} : v_{mp} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2} = \sqrt{3} : \sqrt{2.5} : \sqrt{2}$

✍ For oxygen gas molecules v_{rms} = 461 *m/s*, v_{av} = 424.7 *m/s* and v_{rms} = 376.4 *m/s*

✍ An atom in a solid though has no degree of freedom for translational and rotational motion, due to vibration along 3 axes has $3 \times 2 = 6$ degrees of freedom (and not like an ideal gas molecule). When a diatomic or polyatomic gas dissociates into atoms it behaves as monoatomic gas whose degree of freedom are changed accordingly

✍ In General a polyatmic molecule has 3 translational, 3 rotational degree of freedom and a

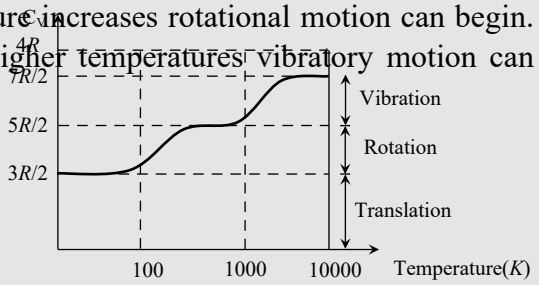
certain number of vibration mode f_{vib}. Hence $\gamma_{poly} = \frac{4 + f_{vib}}{3 + f_{vib}}$.

✍ Only average translational kinetic energy of a gas contributes to its temperature. Two gases with the same average translational kinetic energy have the same temperature even if one has grater rotational energy and thus greater internal energy.

✍ Unsaturated vapours obey gas laws while saturated vapours don't.

✍ For real gases effective volume is considered as $(V - \mu b)$ where $b = 4N_A\left(\frac{4}{3}\pi r^3\right)$; r = radius of each molecule and N_A = avogrado number.

✍ Variation of degree of freedom of a diatomic gas (H_2) with temperature. At very low temperature only translation is possible. as the temperature increases rotational motion can begin. At still higher temperatures vibratory motion can begin.



Ordinary Thinking

Objective Questions

Gas Laws

1. The temperature of a gas at pressure P and volume V is 27°C. Keeping its volume constant if its temperature is raised to 927°C, then its pressure will be **[MP PMT 1985]**
   (a) 2 P (b) 3 P
   (c) 4 P (d) 6 P

2. 4 moles of an ideal gas is at 0°C. At constant pressure it is heated to double its volume, then its final temperature will be **[MP PET 1990]**
   (a) 0°C (b) 273°C
   (c) 546°C (d) 136.5°C

3. Every gas (real gas) behaves as an ideal gas **[CPMT 1997; RPMT 2000; MP PET 2001]**
   (a) At high temperature and low pressure
   (b) At low temperature and high pressure
   (c) At normal temperature and pressure
   (d) None of the above

4. Boyle's law holds for an ideal gas during **[AFMC 1994; KCET 1999]**
   (a) Isobaric changes (b) Isothermal changes
   (c) Isochoric changes (d) Isotonic changes

5. S.I. unit of universal gas constant is **[MNR 1988; MP PMT 1994; UPSEAT 1999]**
   (a) $cal/°C$ (b) J/mol
   (c) $Jmol^{-1}K^{-1}$ (d) J/kg

6. Molecules of a gas behave like **[J & K CET 2000]**
   (a) Inelastic rigid sphere
   (b) Perfectly elastic non-rigid sphere
   (c) Perfectly elastic rigid sphere
   (d) Inelastic non-rigid sphere