Unit III

Gases

1. THE KINETIC MOLECULAR THEORY OF GASES

In your lower classes you have very well studied about the behaviour of gases. Some basic laws like Boyel's law, charle's law . . . & very commonly use the ideal gas equation.

At the time of their enunciation, the various gas laws were only empirical generalisations based on experimental observations. There was no theoretical background to justify them. In the nineteenth century, however, Kronig, Clausius, Maxwell and Boltzmann developed a theory, known as kinetic molecular theory of gases, which provide sound theoretical basis for the various gas laws. Essential aspects of the theory have been discussed below.

1.1 Postulates of kinetic molecular theory

1. A gas consists of a large no. of minute particles, called molecules. The molecules are so small that their actual volm is a negligable fraction of the total volm (space) occupied by the gas.

2. The molecules are in a state of continuous rapid ~~balls~~ motion in all possible dirns, colliding in a random manner with one another and with the walls of the vessel.

3. The molecules of a gas are hard rigid balls (point mass) so that their molecular colln's are perfectly elastic & there is no net loss of energy may be transferred from one molecule to another but it is not converted into any other form of energy such as heat.

4. There are no attractive forces amongest molecules & the walls of the vessel in which the gas is present. The molecules move ~~ide~~ independently of one another. In fact, there are no intermolecular forces of attraction or repulsion amongst the molecules of a perfect (ideal gas).

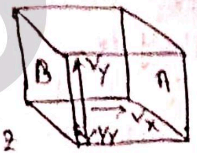
5. The pressure of a gas is due to the bombardment of the molecules on the walls of the vessel containing the gas.

1.2 JUSTIFICATION FOR THE POSTULATES

The above postulates appear to be justified by experience as discussed below.

1. The first assumption that the volm of molecules themselves in a gas is a negligible fraction of the total volm occupied by the gas is borne out by the fact that in a gas like oxygen, hydrogen or nitrogen, at NTP. The volm occupied by the molecules themselves is only 0.014 % of the total volm. The remaining 99.986 % of the volm is merely an empty space :

Derivation $PV = \frac{1}{3} mNc^2$



Let us consider a single molecule of the gas having velocity (v). The velocity v can be rese into three mutually ⊥r components x, y, z. Let these components be v_x, v_y & v_z respectively. The compo. are related by the eq –

$$v^2 = v_x^2 + v_y^2 + v_z^2 \quad \text{———} \; (I)$$

Let us consider the motion of the molecule along this x-axis. The change in momentum $mv_x - (-mv_x) = 2mv_x$ ——— (II)

No of collision s^{-1} $= \frac{\text{velocity}}{\text{dist. travelled}} = \frac{v_x}{2l}$ ——— (III) (where 2l is the dist. trav)

momentum transferred s^{-1} to the face A is equal to

$$2mv_x \times v_x/2l = \frac{mv_x^2}{l} \quad \text{———} \; (IV)$$

consequently total momentum transfused $= \frac{mv_x^2}{l} + \frac{mv_x^2}{l} = 2m\frac{v_x^2}{l}$

||ly, The mom. transfused s^{-1} by a single molecule on all 6 faces of the cube will

$$2mv_x^2/l + 2mv_y^2/l + 2mv_z^2/l$$

$$= 2m/l \left[v_x^2 + v_y^2 + v_z^2\right] = 2mv^2/l \quad \text{———} \; (5)$$

Let the individual velocities are $v_1, v_2, v_3 --- v_N$.

Total mom transfused to the walls by N molecules s^{-1}

$$= 2m/l \left[v_1^2 + v_2^2 + v_3^2 + \cdots + v_N^2\right] \quad \text{———} \; (6)$$

multiplying the numarators & denomenators by N, we have,

$$2mN/l \left[\frac{v_1^2 + v_2^2 + v_3^2 + \cdots + v_N^2}{l}\right] \quad \text{———} \; (7)$$

is equal to $2mNc^2/l$ {where c is the rms velocity}

But the total mom. transfused s^{-1} is equal to F

$$F = \frac{2mNc^2}{l}$$

but we have, pressure $= F/A = \frac{2mNc^2}{l \cdot 6l^2}$ [∵ $6l^2$ is the area of the cube]

$$P = \frac{2mNc^2}{6l^3}$$

$$\boxed{PV = \frac{1}{3} mNc^2 \quad (l^3 = V)}$$

Proved

2 KINETIC ENERGY AND TEMPERATUR:

Suppose one mole of a gas is under consideration. The no. of molecules involved will then be NA (The avogadro's no.) The kinetic gas eq. may be written as

$$PV = \frac{1}{3} mNAc^2 = \frac{2}{3} \times \frac{1}{2} mNAc^2 = \frac{2}{3} \times KE \quad —①$$

where KE is the translational KE of 1 mole of the gas and is the (average) KE of all the molecules. This energy is avg because it has been obtained from the eq. $KE = \frac{1}{2} mNc^2$ where c represent an average (rms) velocity of all the molecules are considered as rigid perfectly elastic balls, they do not have any other motion else than translational (in the three dirn). Therefore this KE ie $\frac{1}{2} mN_Ac^2$ is the avg translational energy of one mole of the gas which is simply written as E ie

Average translational energy ie, $KE = \frac{1}{2} mN_Ac^2 = E$ (say)

∴ Eq 1 becomes $PV = \frac{2}{3} E$

But $PV = RT$ (for an ideal gas)

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

$$E = KE = 2/3\, RT \quad —②$$

Since R is a constant

$$E \propto T \quad —③$$

ie, Average translational KE of an ideal gas its proportional to its absolute tempr. It may further be seen that this energy is independent of the nature, volm (or pressure) of the gas. It is just a function of absolute tempr. This is a very important generation arrived at by the application of KT of gas.

3 DERIVATION OF GAS LAWS

Boyle's law: volm of a given amount of a gas at constant tempr is inversely proportional to its presure ie, $V \propto \frac{1}{P}$

We know, $PV = \frac{1}{3} mNc^2$

$$PV = \frac{2}{3} \times \frac{1}{2} mNc^2$$

$$PV = \frac{2}{3} KE \quad [\because KE = \frac{1}{2} mNc^2]$$

$PV = \frac{2}{3} k'T$ [$\because$ KE $\propto$ T. KE $= k'T$]

PV = constant

Thus Boyle's Law is varified

Charl's law: volm of a given amount of a gas at constant P is directly proportional to its absolute tempr T. i.e, $V \propto T$

we know, $PV = \frac{1}{3} mNc^2$

$$PV = \frac{2}{3} \cdot \frac{1}{2} mNc^2$$

$$PV = \frac{2}{3} KE \quad [\because KE = \frac{1}{2} mNc^2]$$

$$PV = \frac{2}{3} k'T \quad \left[\begin{matrix} KE \propto T \\ KE = k'T \end{matrix}\right]$$

$$V = \frac{2}{3} \frac{k'T}{P}$$

$$V = \text{constant} \times T$$

$$\Rightarrow \frac{V}{T} = \text{constant}$$

Avagadro's law:- Avagadro law is equal volm of all gases under the condition of tempr and pressure contains equal no. of molecules

we know, $PV = \frac{1}{3} mNc^2$ for any two gases the kinetic eq may be, $P_1V_1 = \frac{1}{3} m_1N_1c_1^2 = \frac{2}{3} \times \frac{1}{2} m_1N_1c_1^2$

and $P_2V_2 = \frac{1}{3} m_2N_2c_2^2 = \frac{2}{3} \times \frac{1}{2} m_2N_2c_2^2$

when P and V of two gases are the same i.e, when $P_1 = P_2$ and $V_1 = V_2$ it follows that ~~$\frac{1}{2} m_1N_1c_1^2$~~

$$\frac{1}{2} m_1N_1c_1^2 = \frac{1}{2} m_2N_2c_2^2 \text{ ——— ①}$$

If the two gases at the same tempr, then their KE are also same $\frac{1}{2} m_1c_1^2 = \frac{1}{2} m_2c_2^2$ ——— ②

~~Dividing KE are also same $\frac{1}{2} m_1c_1^2 = \frac{1}{2} m_2c_2^2$~~

Dividing eq ① and ⑪ we get, $N_1 = N_2$

Graham's law of diffusion:- It states that the rate of diffusion by two gases under identical condition of tempr and pressure are inversely proportional to the square root of densities.

$$PV = \frac{1}{3} mNc^2$$

$$c^2 = \frac{3PV}{mN} \quad [\because mN = M]$$

$$c = \sqrt{\frac{3PV}{M}}$$

$$c = \sqrt{3P/_{M/V}} \quad [\because \rho = \frac{M}{V}]$$

$$c = \sqrt{3P/_{\rho}}$$

Now, rate of diffusion 'r' of a gas depends upon the velocity i.e, $r \propto c$

So, we can write

$$r = \sqrt{3P/_{\rho}}$$

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

5 Dalton's law of partial pressure:- The total pressure exert by a molecule is equal to $P = P_1 + P_2$.

Dalton's law of partial pressure is, "when in a vessel two or more non-reactive gases are present the total pressure of the gases is equal to sum of ~~thei~~ the partial pressure which each gases exert present alone.

We know, $PV = \frac{1}{3} mNc^2$

Let us suppose 'N_1' molecules each of mass 'm_1' of gas 1 are contain in a vessels of volm 'v'. Then the pressure P_1 is given by

$$P_1 = \frac{m_1 N_1 c_1^2}{3V}$$

lly, $P_2 = \frac{m_2 N_2 c_2^2}{3V}$, where c_1 & c_2 are rms velocity of the molecules 1 & 2 respectively.

If both the gases are present in the same vessel in same time the total pressure P' will be given by $P_T = \frac{m_1 N_1 c_1^2 + m_2 N_2 c_2^2}{3V}$

$$P_T = \frac{m_1 N_1 c_1^2}{3V} + \frac{m_2 N_2 c_2^2}{3V}$$

$$P_T = P_1 + P_2$$

IDEAL AND REAL GASES

Any gas, hypothetical or real, which obeys the ideal gas eq $PV = nRT$ under all conditions of tempr and pressure is called an ideal gas. The real gases like H_2, N_2, O_2, CO_2, SO_2, NH_3 and even the so called noble gases like He & Ar.

A real gas is one which obeys the gas eq approximately and too under conditions of low pressure and high tempr.

All gases are real gases. The higher the pressure and the lower the tempr, the greater are the deviations from the ideal behaviour. In general, the most easily liquefiable and highly soluble gases show ~~higher~~ larger deviations. Thus, gases like CO_2, sulphur dioxide & NH_3 show much larger deviations than hydrogen, oxygen, N_2 etc.

Q:- Difference betn ideal & real gases.

Ans:

Ideal gas	Real gas
1) It obeys ideal gas eq $PV = nRT$ at all tempr & pressure.	1) It obey the eq $PV = nRT$ only approximately & that too under conditions of low pressure & high tempr.
2) The concept of ideal gas is hypothetical	2) All the gases which exist are ~~easily liquefiable~~ show real gases.
3) Gases like H_2, N_2, O_2 etc which do not liquefy easily show nearly ideal behaviour.	3) Gases like CO_2, SO_2, NH_3 etc which are easily liquefiable show large deviations from ideal behaviour.
4) There is intermolecular force betn the molecules	4) There is intermolecular force of attraction or repulsion depending on whether intermolecular separation is larger or smaller
5) The volm of gas molecules is considered to be negligible as compared to the total volm of the gas.	9) The volm of gas molecules cannot be neglected as compared to the total volm of the gas especially at low tempr and high pressure.

Deviation of Real gases from ideal behaviour and compressibility factor :-

Real gases show small to appreciable deviations from ideal gas eq $PV = nRT$. The higher the pressure and the lower the tempr, the greater are the deviations from the ideal behaviour. In general the easily liquefiable and highly soluble gases show ~~higher~~ larger deviations. Thus, gases like CO_2 SO_2 & NH_3 show much larger deviations than hydrogen, O_2, N_2.

The deviations from ideal behaviour ~~than H_2, O_2, N~~ are best represented in terms of the compressibility factor Z which is defined as:

$$Z = \frac{PV}{(PV)_{ideal}} \quad \text{——} \; ①$$

when V is the volm actually occupied by n moles of the gas at pressure P & tempr T.

The equality $\frac{PV}{nRT}$ may be written as: $= \frac{P}{RT}\frac{V}{n} = \frac{PV_m}{RT}$ —— ②

where V_m $(= V/n)$ is the molar volm, ie, the volm actually occupied by one mole of the gas.

For a gas behaving ideally, the product of its pressure P and molar volm V_m is equal to the PV as predicted by the ideal gas eq $PV_m = (PV)_{ideal}$ so that $Z = 1$ under all conditions of tempr and pressure. The deviation of Z from unity is, thus, a measure of the imperfection of the gas under consideration.

The van der waals equation of state –

In 1873, van der waals proposed his famous eqn of state for a non-ideal (real gas) ie, an imperfect gas. He modified the ideal gas eq by suggesting that:

(i) The gas molecules are not point masses but behave like rigid spheres having a certain finite diameter.

(ii) There exist intermolecular forces of attraction betn the gas molecules.

The two correction terms introduced by vander waals are describ below:

Correction due to volm of gas molecules

The ideal gas eq $PV = nRT$ is derived on the ~~eq~~ assumption that the gas molecules are point masses ie, they do not have finite volm. van der waals abandoned this assumption and suggested that the gas molecules do have some volm and correspondin a correction term nb should be subtracted from the total volm V in order to get the ideal volm, i.e., volm which is freely available to the gas molecules to move about and which is compressible. In order to understand the meaning of the correction term nb -

let us consider two gas molecules as impenetrable and incompressible spheres, each of which has a diameter d, as shown in fig. It is evident that the centres of the two spheres cannot approach each other more closely than the distance d. For this pair of molecules, therefore, a sphere of radius d & hence of volm $4/3\pi d^3$, constituting what is known as the excluded volm.

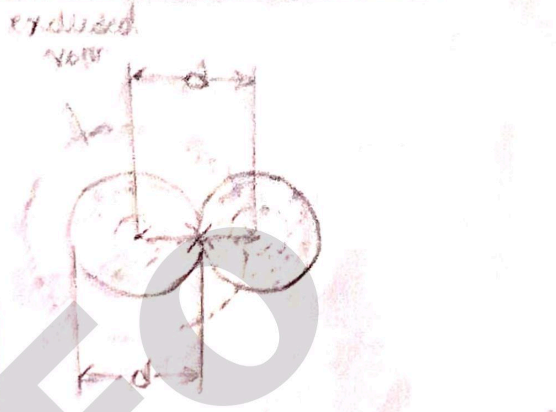


Fig-Illustraction of excluded vol

The excluded volm per mole of the gas would be $N_A \times 4 \times \frac{4}{3}\pi r^3 = b$ where, N_A is the Avogadro's no. The compressible volm per mole of the gas would thus be v-b. If volm v of the gas contain n moles, then the excluded volm would be nb. Hence, the ideal volm which is compressible would be v - nb. The excluded volm b, per mole of a gas is also known as its <u>co-volm</u>. Thus, corrected volm per mole of a gas is given as -

$$= V_m - b \quad \text{———} \ ①$$

where V_m is the volm occupied by one mole of a gas.

Correction due to intermolecular forces of attraction

In the deviation of the ideal gas eq it was assumed that there are no intermolecular forces of attraction. Actually, it is not so. In order to take into account the effect of intermolecular forces of attraction, let us consider a molecule lying somewhere in the middle of the vessel, as shown in fig. As can be seen, it is being attracted uniformly on all the sides by its neighbouring molecules.

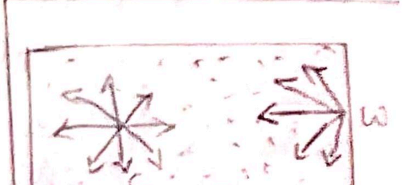


Fig Molecular attract

These force neutralised one another and there is no net resultant attractive force acting on the molecule. However as the molecule approaches the wall of the vessel, as shown at ~~W~~ W, it experiences attractive forces from the bulk of the molecules which are only behind it. Hence, it will strike the wall with a lower velocity and will thus exert a lower presure than it would have done if there was no force of attraction. It is, therefore, ~~nes~~ necessary to

add a ~~larger pressure than it would have done if there was no force of attraction. It is, therefore, necessary~~
add a certain correction factor, p, to the pressure of the gas in order to get the ideal pressure. The correct pressure, there force, should be P + p where p is the correction for pressure P.

Thus the total inward attractive pull on the molecules, which accounts for the correction pressure p, is proportional to the square of the density (ρ) of the gas i.e,

$$p \propto \rho^2 \quad \text{———} ②$$

But, density is inversely proportional to volm and if Vm is the volm occupied by one mole of a gas the value of p for one mole of a gas will be inversely proportional to the square of the volm. Hence,

$$p \propto \frac{1}{V_m^2} = \frac{a}{V_m^2} \quad \text{———} ③$$

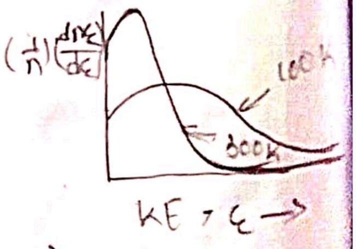
where a is a constant depending upon the nature of the ~~liq~~ gas.

Types of Molecular velocities

Three types of molecular velocities are reckoned with, in the study of gases. These are.

(i) The most probable velocity (α or C_p)
(ii) The average velocity (v or $\bar{c}$ or $\langle c \rangle$)
(iii) The root mean square velocity (c or $\langle c^2 \rangle^{1/2}$).

The most probable velocity (α or C_p) is defined as the velocity possessed by maximum number of molecules of a gas at a given tempr and corresponds to the peak of the distribution curve. in fig.



The average velocity (v or $\vec{c}$ or $\langle c \rangle$) is given by the arithmetic mean of different elocities possessed by the molecules and n is heir total number, then, average velocity is given by -

$$v \text{ or } \vec{c} = \frac{c_1 + c_2 + c_3 + \cdots c_n}{n}$$

If, however $c_1, c_2, c_3 \cdots$ are the velocities possessed by groups $n_1, n_2, n_3 \cdots$ molecules of the gas, respectively, then, average ity is given by -

$$v \text{ or } \vec{c} = \frac{n_1c_1 + n_2c_2 + n_3c_3 + \cdots}{n_1 + n_2 + n_3 + \cdots}$$

The root mean square velocity (c) is defined as the square root of the mean of the squares of different velocities possessed by the molecules of a gas at a given tempr. Evidently the root mean square velocity would be given by.

$$\langle c^2 \rangle^{1/2} \equiv c = \left[\frac{c_1^2 + c_2^2 + c_3^2 + \cdots + c_n^2}{n} \right]^{1/2}$$

where $c_1, c_2, c_3 \cdots c_n$ are the individual velocities of n molecules of the gas, Altermatively:

$$c = \left[\frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + \cdots}{n_1 + n_2 + n_3 + \cdots} \right]^{1/2}$$

where $c_1, c_2, c_3 \cdots$ are velocities possessed by groups of $n_1, n_2, n_3 \cdots$ molecules, respectively.

With the help of the maxwell (eqn 2 sec. 5.1) it is possible to derive mathematical expressions for the three types of velocities, viz viz, the most probable velocity, α; the average velocity, v and the root mean square velocity c. These expressions are as follows:

$$\alpha \text{ or } c_p = (2RT/M)^{1/2}$$

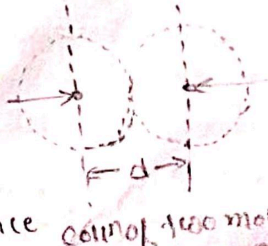
$$v \text{ or } \bar{c} = (8RT/\pi M)^{1/2}$$

$$c = (3RT/M)^{1/2}$$

Collision Parameters

- Collision Diameter

The kinetic theory of gases treats molecules as point-masses. when two such molecules approach each other, a point is reached at which the mutual repulsion betn the molecules (resulting from electronic and nuclear repulsions) become so strong that it causes reversal of the direction of their motion.



colln of two molecules conception colln diameter

The distance betn the centres of the two molecules at the point of their closest approach is known as colln diameter.

It is denoted by d as shown in fig.

It can be easily visualized that if the distance betn the centres of two molecules is less than d, there would be a colln betn them.

collision number :—

The number of molecules with which a given molecules in a given sample of gas are collides in one second is called collision number.