Unit III: GASES

[Gases: Kinetic Theory of Gases: Postulates of Kinetic Theory of Gases and derivation of the kinetic gas equation. Deviation of real gases from ideal behaviour, compressibility factor, causes of deviation. Vander Waals equation of state for real gases. Most probable, average and root mean square velocities (no derivation). Collision number and mean free path of molecules.]

INTRODUCTION

Amongst the three common states of matter, the gaseous state is simplest. The laws of gaseous behaviour are more uniform and are better understood. The well known laws of gaseous behaviour are Boyle's law, Charle's law Graham's law, Dalton's law and Avogadro's law.

In contrast with solids and liquids gases occupy the same volume as that of the closed vessel, they are characterised by low density and high compressibility.

The characteristic properties of gases are given below.

1. **No definite shape and volume**: Gases occupy all available space i.e. the shape and volume of the container in which they are filled.
2. **Expansibility**: Gases have limitless expansibility. They expand to fill the entire vessel they are placed in.
3. **Compressibility**: Gases are easily compressed by application of pressure.
4. **Diffusibility**: Gases can diffuse rapidly through each other to form a homogeneous mixture.
5. **Pressure**: Gases exert pressure on the walls of the container in all direction.
6. **Effect of heat**: When a gas confined in a vessel is heated, its pressure increases. Upon heating in a vessel fitted with a piston, volume of the gas increases.

POSTULATES OF KINETIC THEORY OF GASES

1. Every gas consists of large number of tiny particles called **point masses** i.e. the actual volume of molecules is negligible when compared to the total volume of the gas. For the same gas, all molecules are of same size and mass.
2. The gas molecules are always in a state of rapid **zig-zag motion** in all directions. These molecules collide with each other and with the walls of the containing vessel.
3. A molecule moves in a straight line with **uniform velocity** between two collisions.
4. The molecular collisions are **perfectly elastic** so that there is no net loss of energy when the gas molecules collide with one another or against the walls of the vessel.
5. There are **no attractive forces** operating between molecules or between molecules and the walls of the vessel in which the gas has been contained. The molecule move independently of one another.
6. The pressure of the gas is the **hits recorded** by the molecules on the walls of the container in which the gas is contained.
7. The average kinetic energy of gas molecules is directly proportional to **absolute temperature**. This means that the average kinetic energy of molecules is the same at a given temperature.

DERIVATION OF KINETIC GAS EQUATION

Suppose a volume of gas enclosed in a cubical vessel (fig below) at a fixed temperature.

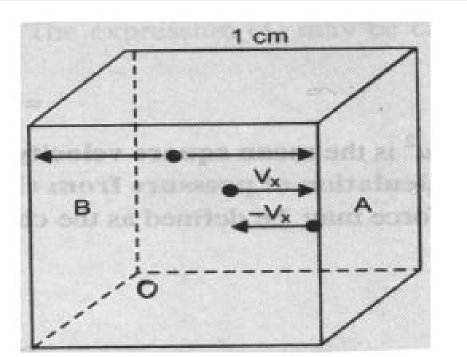
Let's consider

The length of each side of cube = ℓ cm

The number of gas molecules = n

The mass of one molecule = m

The velocity of a molecule = v



Let us consider one single molecule of a gas can be evaluated by calculating the momentum during collisions.

According to kinetic model the molecules of the gas are moving in straight lines in all possible directions. They collide with one another frequently as also with the walls of the container. Since their mutual collisions are perfectly elastic and do not involve the loss of energy, these may be neglected. Here we will, therefore, assume that gas molecules move in all directions but rebound whenever they strike the wall of the container. Now you proceed to derive kinetic gas equation in the following steps:

According to the kinetic theory, a molecule of a gas can move with velocity in any direction velocity is a vector quantity can be resolved into components v_x , v_y, v_z along the X, Y and Z axes. These components are related to velocity v by the following expression.

$$v^2 = v_x^2 + v_y^2 + v_z^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (1)$$

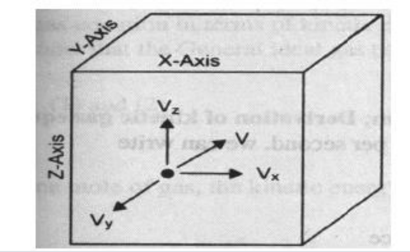
Let us consider a molecule moving in OX direction between opposite faces A and B. It will strike the face A with velocity X and rebound with velocity -X. To hit the same face again the molecule must travel l cm to collide with opposite face B and then again l cm to return to face A. Therefore time taken between two collisions can be calculated as follows:

Total distance covered by one molecule = $l + l = 2l$

Time taken for this collision by one molecule = $\frac{2l}{v_x}$ …………… (2)

In $\frac{2l}{v_x}$ sec, a molecule suffers 1 collision

In 1 sec, no of collisions = $\frac{v_x}{2l}$ ………………………………… (3)



Each impact of the molecule on the face A causes a change of momentum= mass × velocity.

Momentum of the molecule before impact = mv_x

Momentum of the molecule after impact = $-mv_x$

Hence change of momentum = $mv_x - (-mv_x) = 2mv_x$

But the number of collision per second on face A= $\frac{v_x}{2l}$

Therefore total change of momentum per second on face A caused by one molecule$= 2mv_x \times \frac{v_x}{2l}$

$$= \frac{mv_x^2}{l} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (4)$$

As there are two faces along x- direction, total change of momentum per second considering both the faces along x-direction will be $= \frac{2mv_x^2}{l} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (5)$

Similarly, the change of momentum caused by one molecule along y- direction per second will be$= \frac{2mv_y^2}{l}$

and change of momentum caused by one molecule along z- direction per second will be $= \frac{2mv_z^2}{l}$

Total change of momentum caused by one molecule considering along three direction

will be $= \frac{2mv_x^2}{l} + \frac{2mv_y^2}{l} + \frac{2mv_z^2}{l}$

$$= \frac{2m}{l}(v_x^2 + v_y^2 + v_z^2)$$

$$= \frac{2mv^2}{l} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Since there are n molecules in the vessel then total change of momentum due to ‘n’ molecules will be

$$= \frac{2nmv^2}{l} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

$$v^2 - mean\ square\ velocity$$

Since change of momentum per second is force

Hence force $= \frac{2nmv^2}{l}$

Since pressure $= \frac{\text{total force}}{\text{total area}}$

Since there are six faces in a cube, area of each cube is l^2. Hence total area is $6l^2$.

Then pressure, P $= \frac{2nmv^2}{l} \times \frac{1}{6l^2}$

$$= \frac{nmv^2}{3l^3}$$

$\boxed{P = \frac{1}{3}\frac{nmv^2}{V}}$ or $\boxed{P = \frac{1}{3}\frac{Mv^2}{V}}$ …………………. (8) (**Kinetic gas equation**)

(Where $l^3 = V$, volume of the cube, $\mathrm{M = mNa}$; Na – Avogadro′snumber, M – Molar mass of the gas)

Eq. (8) is known as **Kinetic gas equation**. This equation has been derived for a cubical vessel. It is equally valid for vessel of any shape. The available volume in the vessel may be considered as made up of large number of infinitesimally small cubes, for each of them the equation is valid.

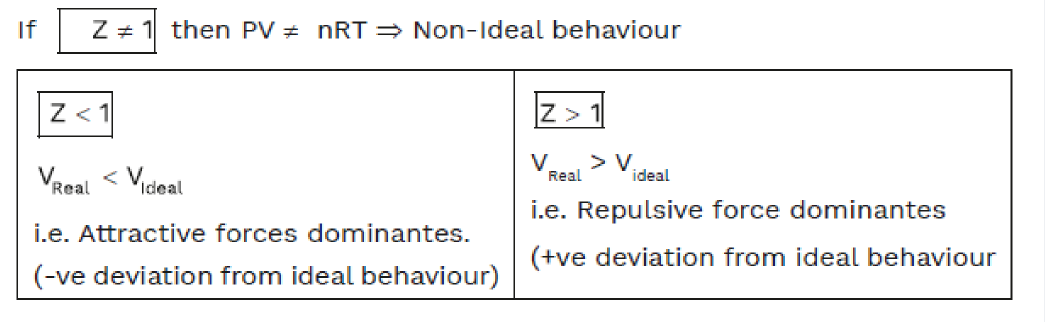
DEVIATION OF REAL GASES FROM IDEAL BEHAVIOUR

An ideal gas is one which obeys the gas laws for the equation PV = RT (for 1 mole of gas) at all pressures and temperatures. However no gas is ideal. They approach perfection as the temperature gets farther from their boiling points. Thus the gases H_2, N_2 and CO_2 which fail to obey the ideal-gas equation are termed as non ideal or real gases.

The extent to which a real gas departs from ideal behaviour may be depicted in terms of a function called compressibility factor, denoted by Z.

It is defined as $\boxed{Z = \frac{PV}{RT}}$

- The **deviation from ideality may be shown by a plot of compressibility factor, Z against P**.
- For **an ideal gas Z =1**. For real gases, the deviation from ideal behaviour will be determined by the value of **Z being greater or less than unity**.
- Temperature and pressure have no effect on an ideal gas, which has a Z value of 1 at all temperatures and pressures.
- For **non-ideal or real gases, Z>1 or Z< 1**. Thus, the value of Z determines the difference between ideal and real gas behaviour.
- The degree of gas non-ideality is represented by the difference between unity and Z.
- Pressure and temperature cause deviations from optimal behaviour in a real gas.
- When **Z < 1, it is a negative deviation**. It shows that the gas is more compressible than expected from ideal behaviour. **When Z > 1, it is a positive deviation**. It shows that the gas is less compressible than expected from ideal behaviour.

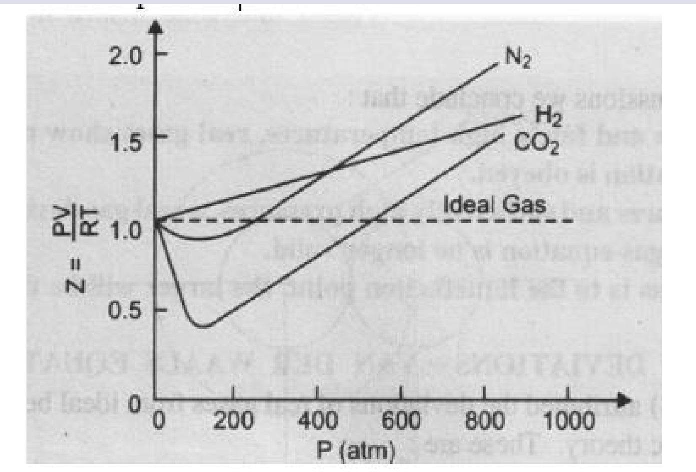


If $\boxed{Z \neq 1}$ then PV ≠ nRT ⇒ Non-Ideal behaviour

$\boxed{Z < 1}$	$\boxed{Z > 1}$
$V_{Real} < V_{Ideal}$ i.e. Attractive forces dominantes. (-ve deviation from ideal behaviour)	$V_{Real} > V_{ideal}$ i.e. Repulsive force dominantes (+ve deviation from ideal behaviour

1. Effect of pressure

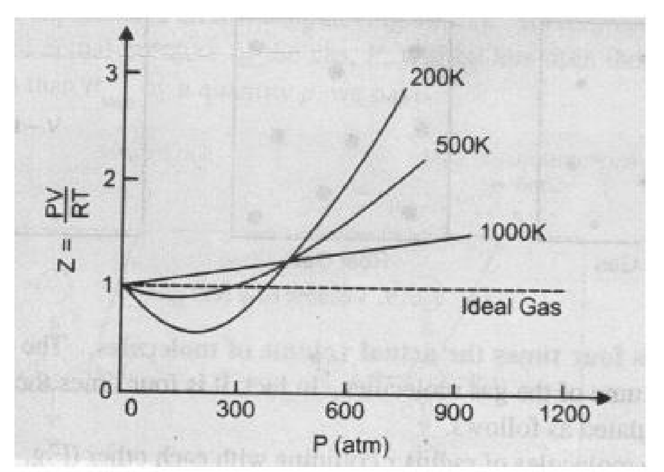
Fig below shows the compressibility factor Z, plotted against pressure for H_2, N_2 and CO_2 at constant temperature.



- At very low pressure for all these gases Z is approximately one. This indicates that all real gases exhibit ideal behaviour (upto 10 atm).
- For H_2 curve lies above ideal gas curve at all pressure.
- For N_2 and CO_2, Z first decreases. It passes to a minimum then increases continuously with increase of pressure.
- For gas like CO_2, the dip in the curve is greatest as it is most easily liquefied.

2. Effect of temperature

Fig below shows plot of Z against P at different temperature for N_2. It is clear from the plot that at low temperature deviation are more and at high temperature the gas tends to become ideal.



- As the temperature rises, the deviations from ideal gas behaviour become smaller and smaller.
- At lower temperatures, the curve dips significantly, and the slope of the curve is negative. In this situation, Z<1
- As the temperature rises, the dip in the curve decreases. The curve's minimum vanishes at a certain temperature and remains horizontal for a wide range of pressures. At this temperature, PV/RT is nearly equal, thus Boyle's law is satisfied. As a result, Boyle's temperature refers to the temperature of the gas.

Important facts to remember

- Real gases perform approximately ideal at low pressures and relatively high temperatures, and the ideal-gas equation is obeyed.
- A real gas deviates greatly from ideality at low temperatures and sufficiently high pressures, and the ideal-gas equation is no longer valid.
- As the gas approaches the liquefaction point, the departure from ideal behaviour grows.

CAUSES OF DEVIATION

The causes of deviations from ideal behaviour may be due to the following two assumptions of kinetic theory of gases-

- **The volume occupied by gas molecules is negligibly small as compared to the volume occupied by the gas**.
- **The forces of attraction between gas molecules are negligible**.

1. **Volume of gas molecules**
   The first assumption is valid only at low pressures and high temperature, when the volume occupied by the gas molecules is negligible as compared to the total volume of the gas. But at low temperature or at high pressure, the molecules being in compressible the volumes of molecules are no more negligible as compared to the total volume of the gas. This means that the actual volume occupied by the gas is slightly less than the volume of the container.
2. **Intermolecular forces**
   The second assumption is not valid when the pressure is high and temperature is low. But at high pressure or low temperature when the total volume of gas is small, the forces of attraction become appreciable and cannot be ignored. Thus, in real gases, there are attractive and repulsive forces between gas molecules, which affect the behavior of the gas. The attractive forces between gas molecules cause the gas molecules to be attracted to each other, which reduces the pressure of the gas. The repulsive forces between gas molecules cause the gas molecules to repel each other, which increases the pressure of the gas.

VAN DER WAALS EQUATION OF STATE FOR REAL GASES

Van der Waal's 1873 studied the postulates of kinetic theory in detail and found that there are two faulty postulates.

(i) The molecules in a gas are point masses and possess no volume.
(ii) There are no intermolecular attractions in a gas.

Van der Waal's was the first to introduce systematically the correction terms due to the above two invalid assumptions in the ideal gas equation PV = nRT.

His corrections are given below.

(a) Volume correction

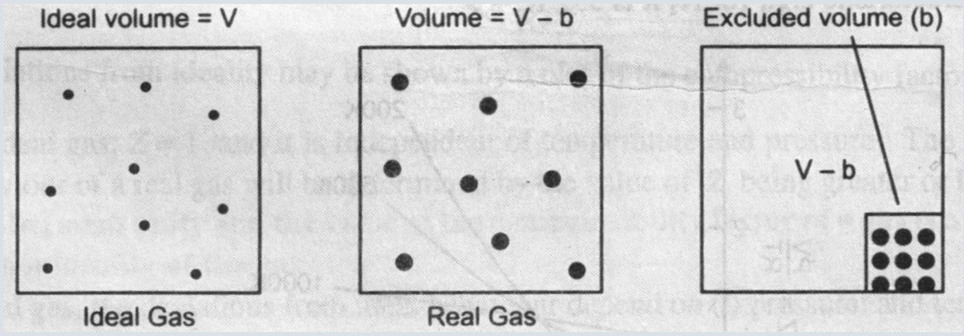
Volume of the gas in the available space for the movement of gas molecules must be considered. Volume V of an ideal gas is the same as the volume of the container. The dot molecule of ideal gas has zero-volume and the entire space in the container is available for their movement. But Van der Waals assume that molecules of real gas are rigid spherical particles which posses a definite volume.
Therefore, volume of real gas = ideal volume – effective volume of gas molecules

If 'b' is the effective volume (or excluded volume) of molecules per mole of the gas then

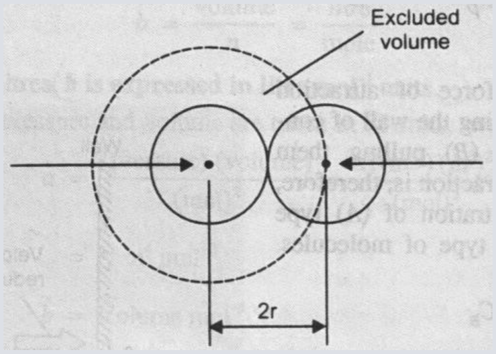
Corrected volume should be

$$V - b = V_{ideal}$$

For 'n' moles $V_{ideal} = V - nb \dots\dots\dots(9)$



Now let us consider two molecules of radius ‘r’ colliding with each other (Fig below) Obviously they cannot approach each other closer than ‘r’.



Therefore, the space indicated by the dotted sphere having radius 2r will not be available to all other molecules of the gas. In other words the dotted space is excluded volume per pair of molecules. Thus,

Excluded volume for two molecules $= \frac{4}{3}\pi(2r)^3$

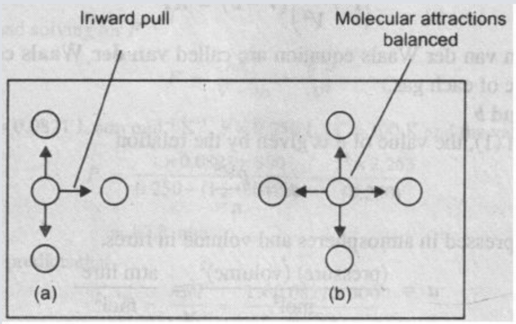
$$= 8 \times \frac{4}{3}\pi r^3$$

Excluded volume per molecule$= \frac{1}{2} \times 8 \times \frac{4}{3}\pi r^3$

$$= 4 \times \frac{4}{3}\pi r^3 \quad = b$$

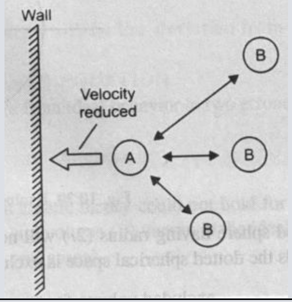
For n moles $\quad = n \times 4 \times \frac{4}{3}\pi r^3 \; = nb$

(b)Pressure correction



A molecule in the interior of gas is attracted by molecules on all sides. The molecules that exert the force on the container will get attracted by molecules of the immediate layer which are assumed not to be exerting pressure. These appealing characteristics cancel each other out. A molecule poised to impact the vessel’s wall, on the other hand, is drawn only by molecules on one side. It feels forced to go inside as a result Therefore, it strikes the wall with reduced velocity and the actual pressure of the gas P, will be less than ideal pressure if the pressure P, is less than P_{ideal} by a quantity p, we have

$$P = P_{ideal} - p$$
$$P_{ideal} = P + p \dots\dots\dots\dots\dots (10)$$



The value of p is determined by the force of attraction between molecules (A) striking the wall of the container and molecules (B) pulling them inward as shown in figure. The net force of attraction is, therefore, is proportional to the concentration of (A) type molecules and also of (B) type of molecules.

Therefore,

$$p\ \alpha C_A \times C_B$$

$$p\ \alpha \frac{n}{V} \times \frac{n}{V}$$

$$p\ \alpha \frac{n^2}{V^2}$$

$p = a\frac{n^2}{V^2}$ (Where, a is the constant of proportionality which depends on the nature of gas. A higher value of ' a ' reflects the increased attraction between gas molecules. , n = Number of moles of real gas, V = Volume of the gas)

Hence ideal pressure from eq. (10)

$$P_{ideal} = P + \frac{an^2}{V^2} \ldots\ldots\ldots\ldots\ldots (10)$$

Substituting the values of ideal volume (Eq. 8) and ideal pressure (Eq. 9) in ideal gas equation i.e. PV=nRT, the modified equation (Van der waals equation) is obtained as

$$\boxed{\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT} \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Van der waals equation or Real gas equation

The units of $a = L^2 atm\, mol^{-1}$; $b = L\, mol^{-1}$

The numerical values of a and b are in the order of $10^{-1} - 10^{-2}$ & $10^{-2} - 10^{-4}$ respectively.

DIFFERENT KIND OF VELOCITIES

(a) Root mean square velocity

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

(b) Average velocity

$$v_{avg} = \sqrt{\frac{2RT}{M}}$$

Where, R-Universal gas constant
R= 8.314 $JK^{-1}mol^{-1}$
T-Temperature in Kelvin
M-Molar mass of the gas

(c) Most probable velocity

$$v_{mp} = \sqrt{\frac{8RT}{\pi M}}$$

COLLISION NUMBER

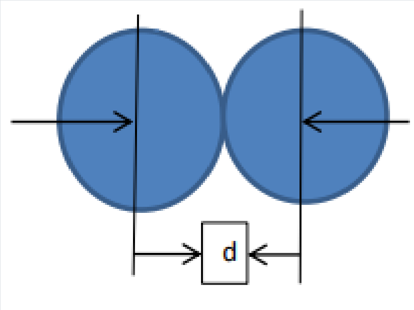
The number of collisions suffered by a single molecule per unit time per unit volume of the gas is known as the collision number.

The closest distance between the centres of the two molecules taking part in collision is called the collision diameter. It is denoted by d

Let a gas contain N molecules per cc.

The total number of collisions taking place per second is denoted by z is given by

$\boxed{z = \sqrt{2}\pi d^2 N^2 v_{avg}}$ where v_{avg} is the average velocity



MEAN FREE PATH OF MOLECULES

According to kinetic theory of gases, at a given temperature, a molecule travels in straight line before collision with another molecule. The distance travelled by the molecule before collision is termed free path.

The mean (or average) distance travelled by a gas molecule between two successive collisions is called the mean free path.

It is denoted by λ. If $\ell_1, \ell_2, \ell_3 \ldots\ldots \ell_n$ are the free paths for a molecule of a gas, its free path

$$\lambda = \frac{\ell_1 + \ell_2 + \ell_3 + \ldots\ldots\ldots\ldots \ell_n}{n}$$

Where n is number of molecules with which that one molecule collides.

Mean free path is also related with viscosity of the gas

$$\lambda = \frac{\mu}{p}\sqrt{\frac{\pi k T}{2m}}$$

λ = mean free path
μ = viscosity
p = pressure
T = temperature
m = molecular mass

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