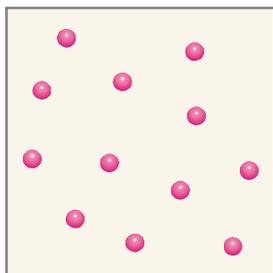
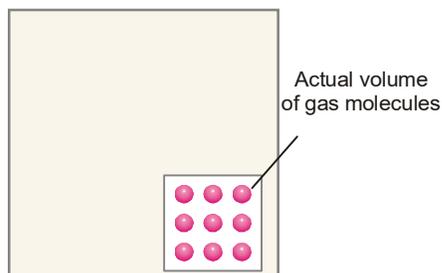


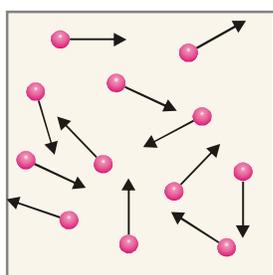
the container. The actual volume of the molecules is negligible compared to the total volume of the gas. The molecules of a given gas are identical and have the same mass (m).



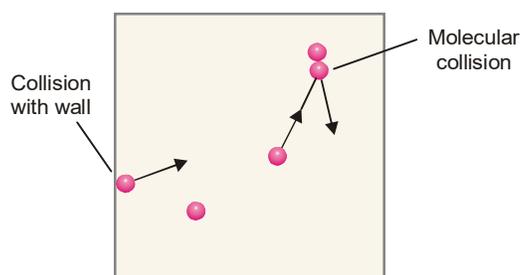
■ **Figure 10.13**
A gas is made of molecules dispersed in space in the container.



■ **Figure 10.14**
Actual volume of the gas molecules is negligible.



■ **Figure 10.15**
Gas molecules are in constant motion in all possible directions.



■ **Figure 10.16**
Molecules move in straight line and change direction on collision with another molecule or wall of container.

- (2) Gas molecules are in constant random motion with high velocities. They move in straight lines with uniform velocity and change direction on collision with other molecules or the walls of the container. Pool table analogy is shown in Fig.10.17.



■ **Figure 10.17**
Gas molecules can be compared to billiard balls in random motion, bouncing off each other and off the sides of the pool table.

- (3) The distance between the molecules are very large and it is assumed that van der Waals attractive forces between them do not exist. Thus **the gas molecules can move freely, independent of each other.**
- (4) All collisions are perfectly elastic. Hence, **there is no loss of the kinetic energy of a molecule during a collision.**
- (5) **The pressure of a gas is caused by the hits recorded by molecules on the walls of the container.**
- (6) The average kinetic energy $\left(\frac{1}{2}mv^2\right)$ of the gas molecules is directly proportional to absolute temperature (Kelvin temperature). This implies that **the average kinetic energy of molecules is the same at a given temperature.**

How Does an Ideal Gas Differ from Real Gases ?

A gas that confirms to the assumptions of the kinetic theory of gases is called an ideal gas. It obeys the basic laws strictly under all conditions of temperature and pressure.

The **real gases** as hydrogen, oxygen, nitrogen etc., are opposed to the assumptions (1), (2) and (3) stated above. Thus :

- (a) The actual volume of molecules in an ideal gas is negligible, while in a real gas it is appreciable.
- (b) There are no attractive forces between molecules in an ideal gas while these exist in a real gas.
- (c) Molecular collisions in an ideal gas are perfectly elastic while it is not so in a real gas.

For the reasons listed above, real gases obey the gas laws under moderate conditions of temperature and pressure. At very low temperature and very high pressure, the clauses (1), (2) and (3) of kinetic theory do not hold. Therefore, under these conditions the real gases show considerable deviations from the ideal gas behaviour.

DERIVATION OF KINETIC GAS EQUATION

Starting from the postulates of the kinetic molecular theory of gases we can develop an important equation. This equation expresses PV of a gas in terms of the number of molecules, molecular mass and molecular velocity. This equation which we shall name as the *Kinetic Gas Equation* may be derived by the following clauses.

Let us consider a certain mass of gas enclosed in a cubic box (Fig. 10.18) at a fixed temperature. Suppose that :

the length of each side of the box	= l cm
the total number of gas molecules	= n
the mass of one molecule	= m
the velocity of a molecule	= v

The kinetic gas equation may be derived by the following steps :

(1) Resolution of Velocity v of a Single Molecule Along X , Y and Z Axes

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

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

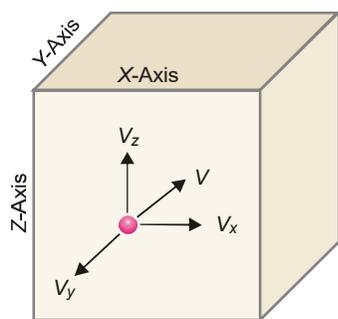
Now we can consider the motion of a single molecule moving with the component velocities independently in each direction.

(2) The Number of Collisions Per Second on Face A Due to One Molecule

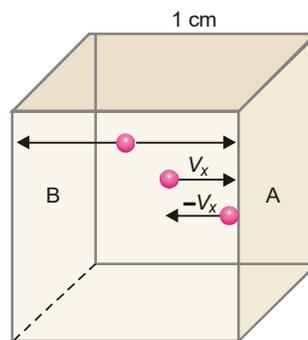
Consider a molecule moving in OX direction between opposite faces A and B . It will strike the face A with velocity v_x and rebound with velocity $-v_x$. To hit the same face again, the molecule must travel l cm to collide with the opposite face B and then again l cm to return to face A . Therefore,

$$\text{the time between two collisions of face } A = \frac{2l}{v_x} \text{ seconds}$$

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



■ **Figure 10.18**
Resolution of velocity v into components V_x , V_y and V_z .



■ **Figure 10.19**
Cubic box showing molecular collisions along X axis.

(3) The Total Change of Momentum on All Faces of the Box Due to One Molecule Only

Each impact of the molecule on the face A causes a change of momentum (mass \times velocity) :

$$\begin{aligned} \text{the momentum before the impact} &= mv_x \\ \text{the momentum after the impact} &= m(-v_x) \\ \therefore \text{the change of momentum} &= mv_x - (-mv_x) \\ &= 2mv_x \end{aligned}$$

$$\text{But the number of collisions per second on face } A \text{ due to one molecule} = \frac{v_x}{2l}$$

Therefore, the total change of momentum per second on face A caused by one molecule

$$= 2m v_x \times \left(\frac{v_x}{2l} \right) = \frac{m v_x^2}{l}$$

The change of momentum on both the opposite faces A and B along X -axis would be double *i.e.*, $2mv_x^2/l$ similarly, the change of momentum along Y -axis and Z -axis will be $2mv_y^2/l$ and $2mv_z^2/l$ respectively. Hence, the overall change of momentum per second on all faces of the box will be

$$\begin{aligned} &= \frac{2mv_x^2}{l} + \frac{2mv_y^2}{l} + \frac{2mv_z^2}{l} \\ &= \frac{2m}{l} (v_x^2 + v_y^2 + v_z^2) \\ &= \frac{2m}{l} v^2 \quad \left(v^2 = v_x^2 + v_y^2 + v_z^2 \right) \end{aligned}$$

(4) Total Change of Momentum Due to Impacts of All the Molecules on All Faces of the Box

Suppose there are N molecules in the box each of which is moving with a different velocity v_1, v_2, v_3 , etc. The total change of momentum due to impacts of all the molecules on all faces of the box

$$= \frac{2m}{l} (v_1^2 + v_2^2 + v_3^2 + \dots)$$

Multiplying and dividing by n , we have

$$\begin{aligned} &= \frac{2mN}{l} \left(\frac{v_1^2 + v_2^2 + v_3^2 + \dots}{n} \right) \\ &= \frac{2mN}{l} u^2 \end{aligned}$$

where u^2 is the **mean square velocity**.

(5) Calculation of Pressure from Change of Momentum; Derivation of Kinetic Gas Equation

Since force may be defined as the change in momentum per second, we can write

$$\text{Force} = \frac{2mN}{l} u^2$$

But

$$\text{Pressure} = \frac{\text{Total Force}}{\text{Total Area}}$$

$$P = \frac{2mNu^2}{l} \times \frac{1}{6l^2} = \frac{1}{3} \frac{mNu^2}{l^3}$$

Since l^3 is the volume of the cube, V , we have

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

or

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

This is the fundamental equation of the kinetic molecular theory of gases. It is called the **Kinetic Gas equation**. This equation although derived for a cubical vessel, is equally valid for a vessel of any shape. The available volume in the vessel could well be considered as made up of a large number of infinitesimally small cubes for each of which the equation holds.

Significance of the term u . As stated in clause (4) u^2 is the mean of the squares of the individual velocities of all the N molecules of the gas. But $u = \sqrt{u^2}$. Therefore u is called the **Root Mean Square (or RMS) Velocity**.

KINETIC GAS EQUATION IN TERMS OF KINETIC ENERGY

If N be the number of molecules in a given mass of gas,

$$\begin{aligned} P V &= \frac{1}{3} mNu^2 && \text{(Kinetic Gas equation)} \\ &= \frac{2}{3} N \times \frac{1}{2} mu^2 \\ &= \frac{2}{3} N \times e \end{aligned}$$

where e is the average kinetic energy of a single molecule.

$$\therefore P V = \frac{2}{3} N e = \frac{2}{3} E$$

$$\text{or} \quad PV = \frac{2}{3}E \quad \dots(1)$$

where E is the total kinetic energy of all the N molecules. The expression (1) may be called the kinetic gas equation in terms of kinetic energy.

We know that the General ideal gas equation is

$$PV = nRT \quad \dots(2)$$

From (1) and (2)

$$\frac{2}{3}E = nRT \quad \dots(3)$$

For one mole of gas, the kinetic energy of N molecules is,

$$E = \frac{3RT}{2} \quad \dots(4)$$

Since the number of gas molecules in one mole of gas is N_0 (Avogadro number),

$$e = \frac{E}{N_0} = \frac{3RT}{2N_0}$$

$$\text{or} \quad e = \frac{3RT}{2N_0} \quad \dots(5)$$

substituting the values of R , T , N_0 , in the equation (5), the average kinetic energy of a gas molecule can be calculated.

SOLVED PROBLEM 1. Calculate the average kinetic energy of a hydrogen molecule at 0°C .

SOLUTION

$$e = \frac{3RT}{2N_0}$$

Here

$$R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

$$T = 273 \text{ K}; \quad N_0 = 6.02 \times 10^{23}$$

$$\therefore e = \frac{3}{2} \times \frac{8.314 \times 10^7 \times 273}{6.02 \times 10^{23}} = 5.66 \times 10^{-14} \text{ erg}$$

Thus the average kinetic energy of H_2 at 0°C is $5.66 \times 10^{-14} \text{ erg}$

SOLVED PROBLEM 2. Calculate the kinetic energy of two moles of N_2 at 27°C . ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

SOLUTION

$$\text{We know} \quad E = \frac{3}{2}nRT$$

$$\text{Here,} \quad T = 27 + 273 = 300 \text{ K}; n = 2; R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

Substituting these values, we have

$$E = \frac{3}{2} \times 2 \times 8.314 \times 300 = 7482.6 \text{ J}$$

Therefore the kinetic energy of two moles of N_2 is **7482.6 J**.

DEDUCTION OF GAS LAWS FROM THE KINETIC GAS EQUATION**(a) Boyle's Law**

According to the Kinetic Theory, there is a direct proportionality between absolute temperature and average kinetic energy of the molecules *i.e.*,

$$\frac{1}{2}mNu^2 \propto T$$

or
$$\frac{1}{2}mNu^2 = kT$$

or
$$\frac{3}{2} \times \frac{1}{3}mNu^2 = kT$$

or
$$\frac{1}{3}mNu^2 = \frac{2}{3}kT$$

Substituting the above value in the kinetic gas equation $PV = \frac{1}{3}mNu^2$, we have

$$PV = \frac{2}{3}kT$$

The product PV , therefore, will have a constant value at a constant temperature. This is Boyle's Law.

(b) Charles' Law

As derived above,

$$PV = \frac{2}{3}kT$$

or
$$V = \frac{2}{3} \times \frac{k}{P}T$$

At constant pressure,

$$V = k' T$$

$$\text{where } \left(k' = \frac{2}{3} \times \frac{k}{P} \right)$$

or
$$V \propto T$$

That is, at constant pressure, volume of a gas is proportional to Kelvin temperature and this is Charles' Law.

(c) Avogadro's Law

If equal volume of two gases be considered at the same pressure,

$$PV = \frac{1}{3}m_1N_1u_1^2 \quad \dots \text{Kinetic equation as applied to one gas}$$

$$PV = \frac{1}{3}m_2N_2u_2^2 \quad \dots \text{Kinetic equation as applied to 2nd gas}$$

$$\therefore \frac{1}{3}m_1N_1u_1^2 = \frac{1}{3}m_2N_2u_2^2 \quad \dots(1)$$

When the temperature (T) of both the gases is the same, their mean kinetic energy per molecule will also be the same.

i.e.,
$$\frac{1}{3}m_1u_1^2 = \frac{1}{3}m_2u_2^2 \quad \dots(2)$$

Dividing (1) by (2), we have

$$N_1 = N_2$$

Or, under the same conditions of temperature and pressure, equal volumes of the two gases contain the same number of molecules. This is Avogadro's Law.

(d) Graham's Law of Diffusion

If m_1 and m_2 are the masses and u_1 and u_2 the velocities of the molecules of gases 1 and 2, then at the same pressure and volume

$$\frac{1}{3}m_1N_1u_1^2 = \frac{1}{3}m_2N_2u_2^2$$

By Avogadro's Law $N_1 = N_2$

$$\therefore m_1u_1^2 = m_2u_2^2$$

or $\left(\frac{u_1}{u_2}\right)^2 = \frac{m_2}{m_1}$

If M_1 and M_2 represent the molecular masses of gases 1 and 2,

$$\left(\frac{u_1}{u_2}\right)^2 = \frac{M_2}{M_1}$$

$$\frac{u_1}{u_2} = \sqrt{\frac{M_2}{M_1}}$$

The rate of diffusion (r) is proportional to the velocity of molecules (u), Therefore,

$$\frac{\text{Rate of diffusion of gas 1}}{\text{Rate of diffusion of gas 2}} = \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

This is Graham's Law of Diffusion.

DISTRIBUTION OF MOLECULAR VELOCITIES

While deriving Kinetic Gas Equation, it was assumed that all molecules in a gas have the same velocity. But it is not so. When any two molecules collide, one molecule transfers kinetic energy ($\frac{1}{2}mv^2$) to the other molecule. The velocity of the molecule which gains energy increases and that of the other decreases. Millions of such molecular collisions are taking place per second. Therefore, the velocities of molecules are changing constantly. Since the number of molecules is very large, a fraction of molecules will have the same particular velocity. In this way there is a broad distribution of velocities over different fractions of molecules. In 1860 James Clark Maxwell calculated the distribution of velocities from the laws of probability. He derived the following equation for the distribution of molecular velocities.

$$\frac{dN_c}{N} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} e^{-\frac{MC^2}{2RT}} C^2 dc$$

where

dN_c = number of molecules having velocities between C and $(C + dc)$

N = total number of molecules

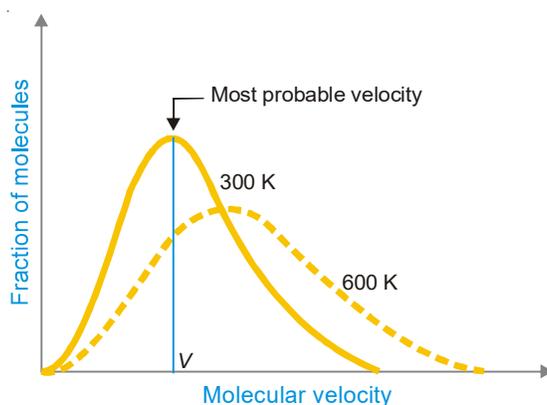
M = molecular mass

T = temperature on absolute scale (K)

The relation stated above is called **Maxwell's law of distribution of velocities**. The ratio $\frac{dN_c}{N}$ gives the fraction of the total number of molecules having velocities between C and $(C + dc)$. Maxwell plotted such fractions against velocity possessed by the molecules. The curves so obtained illustrate the salient features of Maxwell distribution of velocities.

Fig. 10.20. Shows the distribution of velocities in nitrogen gas, N_2 , at 300 K and 600 K. It will be noticed that :

- (1) A very small fraction of molecules has either very low (close to zero) or very high velocities.
- (2) Most intermediate fractions of molecules have velocities close to an average velocity represented by the peak of the curve. This velocity is called the **most probable velocity**. It may be defined as the velocity possessed by the largest fraction of molecules corresponding to the highest point on the Maxwellian curve.
- (3) At higher temperature, the whole curve shifts to the right (dotted curve at 600 K). This shows that **at higher temperature more molecules have higher velocities and fewer molecules have lower velocities**.



■ **Figure 10.20**
Distribution of molecular velocities in nitrogen gas, N_2 , at 300 K and 600 K.

DIFFERENT KINDS OF VELOCITIES

In our study of kinetic theory we come across three different kinds of molecular velocities :

- (1) the Average velocity (V)
- (2) the Root Mean Square velocity (μ)
- (3) the Most Probable velocity (v_{mn})

Average Velocity

Let there be n molecules of a gas having individual velocities $v_1, v_2, v_3, \dots, v_n$. The ordinary average velocity is the arithmetic mean of the various velocities of the molecules.

$$\bar{v} = \frac{v_1 + v_2 + v_3 + \dots + v_n}{n}$$

From Maxwell equation it has been established that the average velocity v_{av} is given by the expression

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

Substituting the values of R , T , π and M in this expression, the average value can be calculated.

Root Mean Square Velocity

If $v_1, v_2, v_3, \dots, v_n$ are the velocities of n molecules in a gas, μ^2 , the mean of the squares of all the velocities is

$$\mu^2 = \frac{v_1^2 + v_2^2 + v_3^2 \dots + v_n^2}{n}$$

Taking the root

$$\mu = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 \dots + v_n^2}{n}}$$

μ is thus the **Root Mean Square velocity or RMS velocity**. It is denoted by u .

The value of the RMS of velocity u , at a given temperature can be calculated from the Kinetic Gas Equation.

$$PV = \frac{1}{3}mNu^2 \quad \dots \text{Kinetic Equation}$$

$$u^2 = \frac{3PV}{mN}$$

For one mole of gas

$$PV = RT$$

Therefore,

$$u^2 = \frac{3RT}{M} \quad \dots M \text{ is molar mass}$$

$$u = \sqrt{\frac{3RT}{M}}$$

By substituting the values of R , T and M , the value of u (RMS velocity) can be determined.

RMS velocity is superior to the average velocity considered earlier. With the help of u , the total Kinetic energy of a gas sample can be calculated.

Most Probable Velocity

As already stated the most probable velocity is possessed by the largest number of molecules in a gas. According to the calculations made by Maxwell, the most probably velocity, v_{mp} , is given by the expression.

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

Substituting the values of R , T and M in this expression, the most probably velocity can be calculated.

Relation between Average Velocity, RMS Velocity and Most Probable Velocity

We know that the average velocity, \bar{v} , is given by the expression

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

and

$$\mu = \sqrt{\frac{3RT}{M}}$$

\therefore

$$\frac{\bar{v}}{\mu} = \frac{\sqrt{\frac{8RT}{\pi M}}}{\sqrt{\frac{3RT}{M}}} = \sqrt{\frac{8}{3\pi}}$$

$$= 0.9213$$

or

$$\bar{v} = \mu \times 0.9213 \quad \dots(1)$$

That is, **Average Velocity = 0.9213 × RMS Velocity**

The expression for the most probably velocity, v_{mp} , is

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

and

$$\mu = \sqrt{\frac{3RT}{M}}$$

\therefore

$$\frac{v_{mp}}{\mu} = \sqrt{\frac{2RT}{M}} \times \sqrt{\frac{M}{3RT}} = \sqrt{\frac{2}{3}} = 0.8165$$

or

$$v_{mp} = \mu \times 0.8165 \quad \dots(2)$$

That is,

$$\text{Most Probable Velocity} = 0.8165 \times \text{RMS Velocity}$$

RMS can be easily calculated by the application of Kinetic Gas equation. Knowing the value of RMS, we can find the average velocity and the most probable velocity from expressions (1) and (2).

CALCULATION OF MOLECULAR VELOCITIES

The velocities of gas molecules are exceptionally high. Thus velocity of hydrogen molecule is 1,838 metres sec^{-1} . While it may appear impossible to measure so high velocities, these can be easily calculated from the Kinetic Gas equation. Several cases may arise according to the available data.

While calculating different types of velocities, we can also make use of the following expressions stated already.

$$\text{RMS velocity,} \quad \mu = \sqrt{\frac{3RT}{M}}$$

$$\text{Average velocity,} \quad \bar{v} = \sqrt{\frac{8RT}{M}}$$

$$\text{Most Probable velocity,} \quad v_{mp} = \sqrt{\frac{2RT}{M}}$$

Case 1. Calculation of Molecular Velocity when temperature alone is given

$$PV = \frac{1}{3}mNu^2 \quad (\text{Kinetic Gas equation})$$

where

$$N = N_0 \quad (\text{Avogadro's number})$$

Thus we have,

$$M = m \times N_0 = \text{molecular mass of the gas}$$

$$\therefore u = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} \quad (\because PV = RT \text{ for 1 mole})$$

But

$$\begin{aligned} R &= 8.314 \times 10^7 \text{ ergs deg}^{-1} \text{ mol}^{-1} \\ &= 0.8314 \times 10^8 \text{ ergs deg}^{-1} \text{ mol}^{-1} \end{aligned}$$

\therefore

$$\begin{aligned} u &= \sqrt{\frac{3 \times 0.8314 \times 10^8 \times T}{M}} \\ &= 1.58 \times 10^4 \times \sqrt{\frac{T}{M}} \text{ cm sec}^{-1} \end{aligned}$$

where T is Kelvin temperature and M the molar mass.

SOLVED PROBLEM. Calculate the root mean square velocity of CO_2 molecule at 1000°C .

SOLUTION

$$T = 273 + 1000 = 1273 \text{ K}; M = 44$$

Applying the equation

$$u = 1.58 \times 10^4 \times \sqrt{\frac{T}{M}}$$

we have

$$u = 1.58 \times 10^4 \times \sqrt{\frac{1273}{44}}$$

$$u = 84985 \text{ cm sec}^{-1} \text{ or } 849.85 \text{ m sec}^{-1}$$

Case 2. Calculation of Molecular Velocity when temperature and pressure both are given.

In such cases we make use of the following relation based on Kinetic Gas equation.

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

We know that 1 mole of a gas at STP occupies a volume of 22400 ml (known as molar volume). But before applying this relation the molar volume is reduced to the given conditions of temperature and pressure.

SOLVED PROBLEM. Calculate the RMS velocity of chlorine molecules at 12°C and 78 cm pressure.

SOLUTION

At STP :

$$V_1 = 22400 \text{ ml}$$

$$T_1 = 273 \text{ K}$$

$$P_1 = 76 \text{ cm}$$

At given conditions :

$$V_2 = ?$$

$$T_2 = 12 + 273 = 285 \text{ K}$$

$$P_2 = 78 \text{ cm}$$

Applying

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

we have

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{76 \times 22400 \times 285}{273 \times 78} = 22785 \text{ ml}$$

we know that

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

$$P = h d g = 78 \times 13.6 \times 981 \text{ dynes cm}^{-2}$$

$$V = 22785 \text{ ml}; M = 71$$

\therefore

$$u = \sqrt{\frac{3 \times 78 \times 13.6 \times 981 \times 22785}{71}}$$

$$u = 31652 \text{ cm sec}^{-1} \text{ or } 316.52 \text{ m sec}^{-1}$$

Case 3. Calculation of Molecular Velocity at STP

Here we use the relation

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

where

$$P = 1 \text{ atm} = 76 \times 13.6 \times 981 \text{ dynes cm}^{-2}$$

$$V = 22,400 \text{ ml}$$

M = Molar mass of the gas

SOLVED PROBLEM. Calculate the average velocity of nitrogen molecule at STP.

SOLUTION

In this example we have,

$$P = 1 \text{ atm} = 76 \times 13.6 \times 981 \text{ dynes cm}^{-2}$$

$$V = 22,400 \text{ ml}$$

$$M = 28$$

Substituting these values in the equation

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

we have

$$= \sqrt{\frac{3 \times 76 \times 13.6 \times 981 \times 22400}{28}}$$

$$= 49,330 \text{ cm sec}^{-1}$$

$$\therefore \text{Average velocity} = 0.9213 \times 49330 \text{ cm sec}^{-1}$$

$$= 45,447 \text{ cm sec}^{-1}$$

Case 4. Calculation of Molecular Velocity when pressure and density are given

In this case we have

$$u = \sqrt{\frac{3PV}{M}} \quad \text{or} \quad u = \sqrt{\frac{3P}{D}} \quad \left[\frac{M}{V} = D \right]$$

where P is expressed in dynes cm^{-2} and D in gm ml^{-1} .

SOLVED PROBLEM. Oxygen at 1 atmosphere pressure and 0°C has a density of 1.4290 grams per litre. Find the RMS velocity of oxygen molecules.

SOLUTION

We have

$$P = 1 \text{ atm} = 76 \times 13.6 \times 981 \text{ dynes cm}^{-2}$$

$$D = 1.4290 \text{ g l}^{-1} = \frac{1.4290}{1000} \text{ g ml}^{-1}$$

$$= 0.001429 \text{ g ml}^{-1}$$

Applying

$$u = \sqrt{\frac{3P}{D}}$$

we get

$$u = \sqrt{\frac{3 \times 76 \times 13.6 \times 981}{0.001429}} = 46138 \text{ cm sec}^{-1}$$

Case 5. Calculation of most probable velocity

In this case we have

$$v_{mp} = 1.29 \times 10^4 \sqrt{\frac{T}{M}}$$

where T expressed in Kelvin and M to mass.

SOLVED PROBLEM. Calculate the most probable velocity of nitrogen molecules, N_2 , at $15^\circ C$.

SOLUTION

$$T = 273 + 15 = 288 \text{ K}$$

We know that

$$\begin{aligned} v_{mp} &= 1.29 \times 10^4 \sqrt{\frac{T}{M}} \\ &= 1.29 \times 10^4 \sqrt{\frac{288}{28}} \\ &= 4.137 \times 10^4 \text{ cm sec}^{-1} \end{aligned}$$

COLLISION PROPERTIES

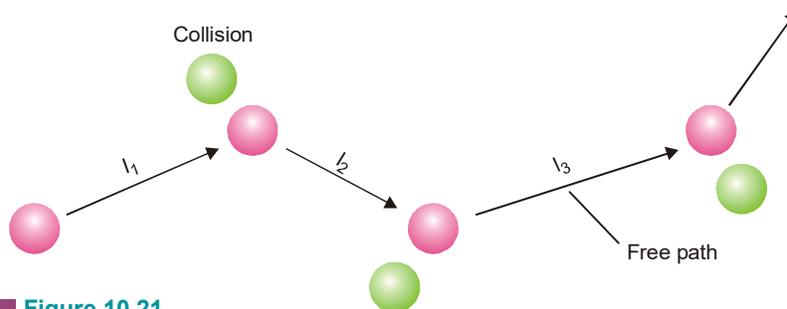
In the derivation of Kinetic gas equation we did not take into account collisions between molecules. The molecules in a gas are constantly colliding with one another. The transport properties of gases such as diffusion, viscosity and mean free path depend on molecular collisions. We will now discuss some properties of gases which determine the frequency of collisions.

The Mean Free Path

At a given temperature, a molecule travels in a straight line before collision with another molecule. The distance travelled by the molecule before collision is termed *free path*. The free path for a molecule varies from time to time. **The mean distance travelled by a molecule between two successive collisions is called the Mean Free Path.** It is denoted by λ . If l_1, l_2, l_3 are the free paths for a molecule of a gas, its free path

$$\lambda = \frac{l_1 + l_2 + l_3 + \dots + l_n}{n}$$

where n is the number of molecules with which the molecule collides. Evidently, the number of molecular collisions will be less at a lower pressure or lower density and longer will be the mean free path. The mean free path is also related with the viscosity of the gas.



■ **Figure 10.21**
The mean free path illustrated.

The mean free path, λ , is given by the expression

$$\lambda = \eta \sqrt{\frac{3}{Pd}}$$

where

P = pressure of the gas

d = density of the gas

η = coefficient of viscosity of the gas

By a determination of the viscosity of the gas, the mean free path can be readily calculated. At STP, the mean free path for hydrogen is 1.78×10^{-5} cm and for oxygen it is 1.0×10^{-5} cm.

Effect of Temperature and Pressure on Mean Free Path

(a) Temperature

The ideal gas equation for n moles of a gas is

$$PV = nRT \quad \dots(i)$$

where n is the number of moles given by

$$n = \frac{\text{Number of molecules}}{\text{Avogadro's Number}} = \frac{N}{N_0}$$

Substituting this in equation (i) we get

$$PV = \frac{N}{N_0}RT$$

or

$$\frac{N}{V} = \frac{PN_0}{RT}$$

At constant pressure

$$N \propto \frac{1}{T} \quad \dots(ii)$$

The mean free path is given by

$$\begin{aligned} \lambda &= \frac{\text{Distance travelled by the molecule per second}}{\text{Number of collisions per c.c.}} \\ &= \frac{\bar{v}}{\sqrt{2} \pi \sigma^2 \bar{v} \bar{N}} \\ &= \frac{1}{\sqrt{2} \pi \sigma^2 \bar{N}} \quad \dots(iii) \end{aligned}$$

combining equations (ii) and (iii), we get

$$\lambda \propto T$$

Thus, *the mean free path is directly proportional to the absolute temperature.*

(b) Pressure

We know that the pressure of a gas at certain temperature is directly proportional to the number of molecules per c.c. *i.e.*

$$P \propto \bar{N}$$

and mean free path is given by

$$\lambda = \frac{1}{\sqrt{2} \pi \sigma^2 \bar{N}}$$

Combining these two equations, we get

$$\lambda \propto \frac{1}{P}$$

Thus, **the mean free path of a gas is directly proportional to the pressure of a gas at constant temperature.**

SOLVED PROBLEM 1. At 0°C and 1 atmospheric pressure the molecular diameter of a gas is 4Å. Calculate the mean free path of its molecule.

SOLUTION. The mean free path is given by

$$\lambda = \frac{1}{\sqrt{2} \pi \sigma^2 \bar{N}}$$

where σ is the molecular diameter

and \bar{N} is the no. of molecules per c.c.

Here $\sigma = 4\text{Å} = 4 \times 10^{-8} \text{ cm}$.

We know 22400 ml of a gas 0°C and 1 atm. pressure contains 6.02×10^{23} molecules.

$$\begin{aligned} \therefore \text{No. of molecules per c.c., } \bar{N} &= \frac{6.02 \times 10^{23}}{22400} \\ &= 2.689 \times 10^{19} \text{ molecules} \end{aligned}$$

Substituting the values, we get

$$\begin{aligned} \sigma &= \frac{1}{1.414 \times 3.14 \times (4 \times 10^{-8})^2 \times 2.689 \times 10^{19}} \\ &= \frac{1}{1.414 \times 3.14 \times 16 \times 2.689 \times 10^3} \\ &= 0.524 \times 10^{-5} \text{ cm} \end{aligned}$$

SOLVED PROBLEM 2. The root mean square velocity of hydrogen at STP is $1.83 \times 10^5 \text{ cm sec}^{-1}$ and its mean free path is $1.78 \times 10^{-5} \text{ cm}$. Calculate the collision number at STP.

SOLUTION. Here root mean square velocity

$$\mu = 1.831 \times 10^5 \text{ cm sec}^{-1}$$

We know average velocity $\bar{v} = 0.9213 \times \text{RMS velocity}$

$$= 0.9213 \times 1.831 \times 10^5 \text{ cm sec}^{-1}$$

$$= 1.6869 \times 10^5 \text{ cm sec}^{-1}$$

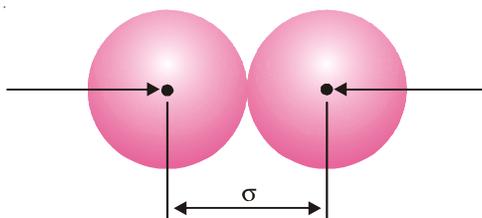
$$\text{The mean free path} = \frac{\text{Average velocity}}{\text{Collision Number}}$$

$$\begin{aligned} \therefore \text{Collision Number} &= \frac{\text{Average velocity}}{\text{Mean free path}} \\ &= \frac{1.6869 \times 10^5 \text{ cm sec}^{-1}}{1.78 \times 10^{-5} \text{ cm}} \\ &= 9.4769 \times 10^9 \text{ sec}^{-1} \end{aligned}$$

The Collision Diameter

When two gas molecules approach one another, they cannot come closer beyond a certain distance. **The closest distance between the centres of the two molecules taking part in a collision is called the Collision Diameter.** It is denoted by σ . Whenever the distance between the centres of two molecules is σ a collision occurs.

The collision diameter is obviously related to the mean free path of molecules. **The smaller the collision or molecular diameter, the larger is the mean free path.**



■ **Figure 10.22**
Collision diameter of molecules.

The collision diameter can be determined from viscosity measurements. The collision diameter of hydrogen is 2.74 Å and that of oxygen is 3.61 Å.

The Collision Frequency

The collision frequency of a gas is defined as :

the number of molecular collisions taking place per second per unit volume (c.c.) of the gas.

Let a gas contain \bar{N} molecules per c.c. From kinetic consideration it has been established that the number of molecules, n , with which a single molecule will collide per second, is given by the relation

$$n = \sqrt{2} \pi \bar{v} \sigma^2 N$$

where \bar{v} = average velocity; σ = collision diameter.

If the total number of collisions taking place per second is denoted by Z , we have

$$\begin{aligned} Z &= \sqrt{2} \pi \bar{v} \sigma^2 N \times N \\ &= \sqrt{2} \pi \bar{v} \sigma^2 N^2 \end{aligned}$$

Since each collision involves two molecules, the number of collision per second per c.c. of the gas will be $Z/2$.

$$\begin{aligned} \text{Hence the collision frequency} &= \frac{\sqrt{2} \pi \bar{v} \sigma^2 N^2}{2} \\ &= \frac{\pi \bar{v} \sigma^2 N^2}{\sqrt{2}} \end{aligned}$$

Evidently, the collision frequency of a gas increases with increase in temperature, molecular size and the number of molecules per c.c.

Effect of Temperature and Pressure on Collision Frequency

(i) Effect of Temperature

We know collision frequency is given by

$$Z = \frac{\pi \bar{v} \sigma^2 \bar{N}^2}{\sqrt{2}} \quad \dots(i)$$

From this equation it is clear that

$$Z \propto \bar{v}$$

But $\mu \propto \sqrt{T}$

or $Z \propto \sqrt{T}$

Hence collision frequency is directly proportional to the square root of absolute temperature.

(ii) Effect of Pressure

From equation (i), we have

$$Z \propto \bar{N}^2 \quad \dots(ii)$$

where \bar{N} is the number of molecules per c.c. But we know that the pressure of the gas at a certain temperature *i.e.*

$$P \propto \bar{N} \quad \dots(iii)$$

combining equation (ii) and (iii) we get

$$Z = P^2$$

Thus the collision frequency is directly proportional to the square of the pressure of the gas.

SPECIFIC HEAT RATIO OF GASES

The Specific heat is defined as the amount of heat required to raise the temperature of one gram of a substance through 1°C. It may be measured at constant volume or at a constant pressure and though the difference in the two values is negligible in case of solids and liquids, it is appreciable in case of gases and a ratio of the two values gives us valuable information about the atomicity of a gas molecule.

Specific Heat at Constant Volume

It is the amount of heat required to raise the temperature of one gas through 1°C while the volume is kept constant and the pressure allowed to increase. It is denoted by the symbol C_v . In Physical Chemistry it is more common, however, to deal with one gram mole of the gas and the heat required in such case is called **Molecular Heat** and is represented at constant volume by C_v .

It is possible to calculate its value by making use of the Kinetic theory.

Consider one mole of a gas at the temperature T . Its kinetic energy is $\frac{1}{2}mnu^2$. From the kinetic gas equation

$$\begin{aligned} PV &= \frac{1}{2}mnu^2 \\ &= \frac{2}{3} \times \frac{1}{2}mnu^2 = RT \end{aligned}$$

$$\text{or} \quad \frac{1}{2}mnu^2 (= \text{KE}) = \frac{3}{2}RT$$

If the temperature is raised by 1°C to $(T+1)K$ kinetic energy becomes $\frac{3}{2}R(T+1)$.

$$\begin{aligned} \therefore \text{Increase in kinetic energy} &= \frac{3}{2}R(T+1) - \frac{3}{2}RT \\ &= \frac{3}{2}R \end{aligned}$$

If, therefore, it be assumed that the heat supplied to a gas at constant volume is used up entirely in increasing the kinetic energy of the moving molecules, and consequently increasing the temperature,

the value of C_v should be equal $\frac{3}{2}R$. It is actually so for monoatomic gases and vapours because such molecules can execute only translatory motion along the three co-ordinate axes. Motion of monoatomic gas molecules is the simplest and can be resolved into three perpendicular components

along the co-ordinate axes. Thus the energy of such a molecule can be considered to be composed of three parts as

$$\frac{1}{2}mv^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

The number of square terms involved in determining the total kinetic energy of a molecule is often referred to as the **Degrees of freedom of motion**. Such molecules have three degrees of freedom of motion. According to the principle of equipartition of energy, total energy of the molecule is equally distributed among all its degrees of freedom. But in the case of diatomic and polyatomic molecules, the heat supplied may not only increase this **kinetic energy of translation** of the molecules as a whole but also cause an increase in the energy in the inside of the molecules which we may call as **intramolecular energy**. This intramolecular energy may be the **vibration energy** *i.e.*, energy of the atoms executing vibrations with respect to each other along their line of centres or **rotational energy** which manifests itself in the rotation of the molecules about axes perpendicular to the line of centres. There will be other degrees of freedom for rotational and vibrational modes of motion also. For such cases the heat needs will be complex and are denoted by 'x' – a factor which depends upon vibrational and rotational degrees of freedom. Vibrational degrees of freedom rapidly increase with the increase in the total number of atoms in a molecule but the degrees of freedom are two for linear diatomic and three for non-linear diatomic molecules in case of rotational motion.

Consequently in such cases the molecular heat will be greater than $\frac{3}{2}R$ by the factor x.

or
$$C_v = \frac{3}{2}R + x$$

The value of x varies from gas to gas and is zero for monoatomic molecules.

Specific Heat at Constant Pressure

It may be defined as the amount of heat required to raise the temperature of one gram of gas through 1°C, the pressure remaining constant while the volume is allowed to increase. It is written as c_p and the Molecular heat in this gas is represented as C_p .

Now, whenever a gas expands it has to do work against external pressure. It means that when a gas is heated under constant pressure, the heat supplied is utilised in two ways :

- (1) **in increasing the kinetic energy of the moving molecules** and this has already been shown to be equal to $\frac{3}{2}R + x$ cal.
- (2) **in performing external work done by the expanding gas**. The work done by the gas is equivalent to the product of the pressure and the change in volume. Let this change in volume be ΔV when the constant pressure is P and the initial volume is V .

For 1 g mole of the gas at temperature T ,

$$PV = RT \quad \dots(i)$$

At temperature $(T+1) K$

$$P(V+\Delta V) = R(T+1) \quad \dots(ii)$$

Subtracting (i) from (ii)

$$P \times \Delta V = R$$

Hence R cal must be added to the value of $\frac{3}{2}R$ cal in order to get the thermal equivalent of the energy supplied to one gram mole of the gas in the form of heat when its temperature is raised by 1°C.

$$\therefore C_p = \frac{3}{2}R + R = \frac{5}{2}R \quad (\text{for monoatomic molecules})$$

For di- and polyatomic molecules, it will be $\frac{3}{2}R + x$.

Specific Heat Ratio

The ratio of the molecular heats will be the same as the ratio of the specific heats. It is represented by the symbol γ .

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R + x}{\frac{3}{2}R + x}$$

For monoatomic molecules, $x = 0$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = \mathbf{1.667}$$

For diatomic molecules in most cases, $S = R$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5} = \mathbf{1.40}$$

For polyatomic molecules, very often $x = \frac{3}{2}R$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R + \frac{3}{2}R}{\frac{3}{2}R + \frac{3}{2}R} = \frac{8}{6} = \mathbf{1.33}$$

These results are found to be in accord with experimental observations at 15°C given in the Table that follows and thus **specific heat ratio helps us to determine the atomicity of gas molecules**. The theoretical difference between C_p and C_v as calculated above is R and its observed value also shown in the table below comes out to about 2 calories.

Gas	C_p	C_v	$C_p - C_v = R$	$g = C_p/C_v$	Atomicity
Helium	5.00	3.01	1.99	1.661	1
Argon	4.97	2.98	1.90	1.667	1
Mercury vapour	6.93	4.94	1.99	1.40	2
Nitrogen	6.95	4.96	1.99	1.40	2
Oxygen	6.82	4.83	1.49	1.41	2
Carbon dioxide	8.75	6.71	2.04	1.30	3
Hydrogen sulphide	8.62	6.53	2.09	1.32	3

DEVIATIONS FROM IDEAL BEHAVIOUR

An ideal gas is one which obeys the gas laws or the gas equation $PV = RT$ at all pressures and temperatures. However no gas is ideal. Almost all gases show significant deviations from the ideal behaviour. Thus the gases H_2 , N_2 and CO_2 which fail to obey the ideal-gas equation are termed **nonideal or real gases**.

Compressibility Factor

The extent to which a real gas departs from the ideal behaviour may be depicted in terms of a new function called the **Compressibility factor**, denoted by Z . It is defined as

$$Z = \frac{PV}{RT}$$

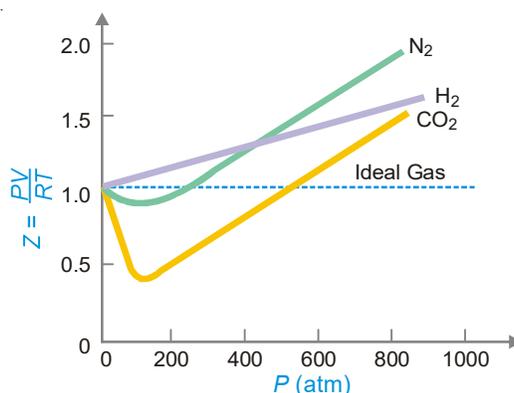
The deviations from ideality may be shown by a plot of the compressibility factor, Z , against P .

For an ideal gas, $Z = 1$ and it is independent of temperature and pressure. The deviations from ideal behaviour of a real gas will be determined by the value of Z being greater or less than 1. **The difference between unity and the value of the compressibility factor of a gas is a measure of the degree of nonideality of the gas.**

For a real gas, the deviations from ideal behaviour depend on (i) pressure; and temperature. This will be illustrated by examining the compressibility curves of some gases discussed below with the variation of pressure and temperature.

Effect of Pressure Variation on Deviations

Fig. 10.23 shows the compressibility factor, Z , plotted against pressure for H_2 , N_2 and CO_2 at a constant temperature.



■ **Figure 10.23**
Z versus P plots for H_2 , N_2 and CO_2 at 300 K.

At very low pressure, for all these gases Z is approximately equal to one. This indicates that at low pressures (upto 10 atm), real gases exhibit nearly ideal behaviour. As the pressure is increased, H_2 shows a continuous increase in Z (from $Z = 1$). Thus the H_2 curve lies above the ideal gas curve at all pressures.

For N_2 and CO_2 , Z first decreases ($Z < 1$). It passes through a minimum and then increases continuously with pressure ($Z > 1$). For a gas like CO_2 the dip in the curve is greatest as it is most easily liquefied.

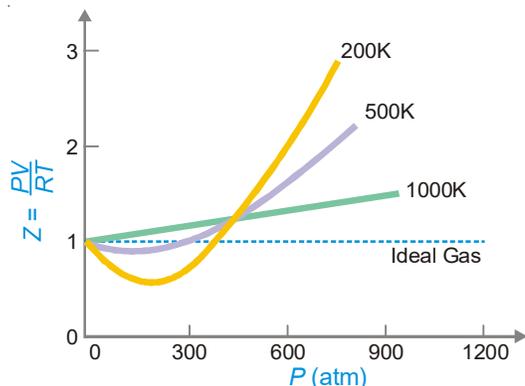
Effect of Temperature on Deviations

Fig 10.24 shows plots of Z or PV/RT against P for N_2 at different temperatures. It is clear from the shape of the curves that **the deviations from the ideal gas behaviour become less and less with increase of temperature**. At lower temperature, the dip in the curve is large and the slope of the curve is negative. That is, $Z < 1$. As the temperature is raised, the dip in the curve decreases. At a certain temperature, the minimum in the curve vanishes and the curve remains horizontal for an appreciable range of pressures. At this temperature, PV/RT is almost unity and the Boyle's law is obeyed. Hence this temperature for the gas is called **Boyle's temperature**. The Boyle temperature of each gas is characteristic *e.g.*, for N_2 it is 332 K.

Conclusions

From the above discussions we conclude that :

- (1) **At low pressures and fairly high temperatures, real gases show nearly ideal behaviour and the ideal-gas equation is obeyed.**
- (2) **At low temperatures and sufficiently high pressures, a real gas deviates significantly from ideality and the ideal-gas equation is no longer valid.**



■ **Figure 10.24**
Z versus P plots for N_2 at different temperatures.

- (3) The closer the gas is to the liquefaction point, the larger will be the deviation from the ideal behaviour.

EXPLANATION OF DEVIATIONS – VAN DER WAALS EQUATION

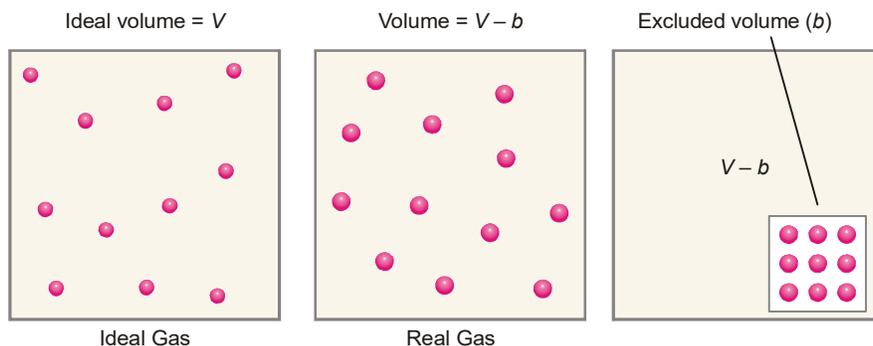
van der Waals (1873) attributed the deviations of real gases from ideal behaviour to two erroneous postulates of the kinetic theory. These are :

- (1) **the molecules in a gas are point masses and possesses no volume.**
- (2) **there are no intermolecular attractions in a gas.**

Therefore, the ideal gas equation $PV = nRT$ derived from kinetic theory could not hold for real gases. van der Waals pointed out that both the pressure (P) and volume (V) factors in the ideal gas equation needed correction in order to make it applicable to real gases.

Volume Correction

The volume of a gas is the free space in the container in which molecules move about. **Volume V of an ideal gas is the same as the volume of the container.** The dot molecules of ideal gas have zero-volume and the entire space in the container is available for their movement. However, van der Waals assumed that molecules of a real gas are rigid spherical particles which possess a definite volume.



■ **Figure 10.25**
Volume of a Real gas.

The volume of a real gas is, therefore, ideal volume minus the volume occupied by gas molecules (Fig. 10.25). If b is the effective volume of molecules per mole of the gas, the volume in the ideal gas

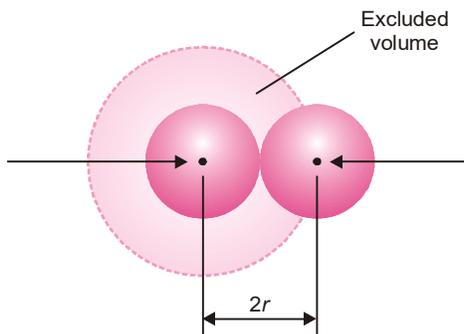
equation is corrected as :

$$(V - b)$$

For n moles of the gas, the corrected volume is :

$$(V - nb)$$

where b is termed the **excluded volume** which is constant and characteristic for each gas.



■ **Figure 10.26**

Excluded volume for a pair of gas molecules.

Excluded volume is four times the actual volume of molecules. The excluded volume is not equal to the actual volume of the gas molecules. In fact, it is four times the actual volume of molecules and can be calculated as follows.

Let us consider two molecules of radius r colliding with each other (Fig. 10.26). Obviously, they cannot approach each other closer than a distance ($2r$) apart. 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 spherical space is excluded volume per pair of molecules. Thus,

$$\begin{aligned} \text{excluded volume for two molecules} &= \frac{4}{3}\pi(2r)^3 \\ &= 8\left(\frac{4}{3}\pi r^3\right) \\ \text{excluded volume per molecule } (V_e) &= \frac{1}{2} \times 8\left(\frac{4}{3}\pi r^3\right) \\ &= 4V_m \end{aligned}$$

where V_m is the actual volume of a single molecule.

Therefore, in general, excluded volume of the gas molecules is four times the actual volume of molecules.

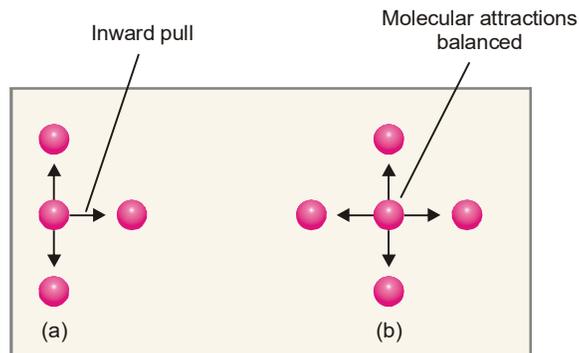
Pressure Correction

A molecule in the interior of a gas is attracted by other molecules on all sides. These attractive forces cancel out. But a molecule about to strike the wall of the vessel is attracted by molecules on one side only. Hence it experiences an inward pull (Fig. 10.27). Therefore, it strikes the wall with reduced velocity and the actual pressure of the gas, P , will be less than the ideal pressure. If the actual pressure P , is less than P_{ideal} by a quantity p , we have

$$P = P_{\text{ideal}} - p$$

or

$$P_{\text{ideal}} = P + p$$



■ **Figure 10.27**

(a) A molecule about to strike the wall has a net inward pull;

(b) A molecule in the interior of gas has balanced attractions.

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

$$p \propto C_A \times C_B$$

or

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

or

$$p = \frac{an^2}{V^2}$$

where n is total number of gas molecules in volume V and a is proportionality constant characteristic of the gas. Thus the pressure P in the ideal gas equation is corrected as :

$$\left(P + \frac{an^2}{V^2} \right)$$

for n moles of gas.

VAN DER WAALS EQUATION

Substituting the values of corrected pressure and volume in the ideal gas equation, $PV = nRT$, we have

$$\left(p + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

This is known as **van der Waals equation** for n moles of a gas. For 1 mole of a gas ($n = 1$), van der Waals equation becomes

$$\left(p + \frac{a}{V^2} \right) (V - b) = RT$$

Constant a and b in van der Waals equation are called **van der Waals constants**. These constants are characteristic of each gas.

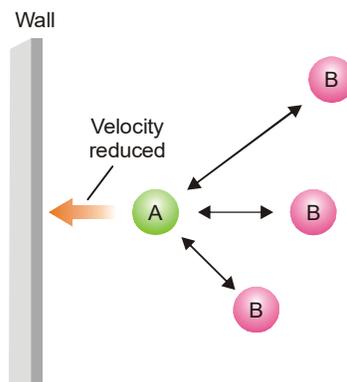
Determination of a and b

From the expression (1), the value of a is given by the relation

$$a = \frac{pV^2}{n^2}$$

If the pressure is expressed in atmospheres and volume in litres,

$$a = \frac{(\text{pressure}) (\text{volume})^2}{\text{mol}^2} = \frac{\text{atm litre}^2}{\text{mol}^2}$$



■ **Figure 10.28**

The striking molecule A is pulled inward by molecules B which reduces the velocity of A and causes the decrease of pressure.

Thus a is expressed in **atm litre² mol⁻²** units.

Since nb is excluded volume for n moles of gas,

$$b = \frac{\text{volume}}{n} = \frac{\text{litre}}{\text{mole}}$$

If volume is expressed in litres, **b is expressed in litre mol⁻¹** units.

SI units of a and b . If pressure and volume are taken in SI units, we have

$$a = \frac{(\text{pressure}) (\text{volume})}{(\text{mol})^2} = \frac{(\text{Nm}^{-2}) (\text{m}^3)^2}{(\text{mol})^2}$$

$$= \text{Nm}^4 \text{mol}^{-2}$$

and

$$b = \text{Volume mol}^{-1}$$

$$= \text{m}^3 \text{mol}^{-1}$$

The values of (a) and (b) can be determined by knowing the P , V and T of a gaseous system under two different conditions. Table 10.2 gives values of a and b for some common gases.

TABLE 10.2. VAN DER WAALS CONSTANTS FOR SOME COMMON GASES

Gas	a		b	
	atm litre ² mol ⁻²	N m ⁴ mol ⁻²	litre mol ⁻¹	10 ³ m ³ mol ⁻¹
Hydrogen	0.245	0.0247	0.0266	0.0266
Oxygen	1.360	0.1378	0.0318	0.0318
Nitrogen	1.390	0.1408	0.0391	0.0391
Chlorine	6.493	0.6577	0.0562	0.0562
Carbon dioxide	3.590	0.3637	0.0428	0.0428
Ammonia	4.170	0.4210	0.0371	0.0371
Sulphur dioxide	6.710	0.6780	0.0564	0.0564

SOLVED PROBLEM. Calculate the pressure exerted by 1.00 mole of methane (CH_4) in a 250 mL container at 300 K using van der Waals equation. What pressure will be predicted by ideal gas equation ?

$$a = 2.253 \text{ L}^2 \text{ atm mol}^{-2}, b = 0.0428 \text{ L mol}^{-1}; R = 0.0821 \text{ L atm mol}^{-1} \text{ K}.$$

SOLUTION

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT \quad \dots \text{van der Waals equation}$$

Dividing by $(V - nb)$ and solving for P

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Substituting $n = 1$, $R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$, $V = 0.250 \text{ L}$, $T = 300 \text{ K}$ and the values of a and b , we have

$$P = \frac{1 \times 0.0821 \times 300}{0.250 - (1 \times 0.0428)} - \frac{1^2 \times 2.253}{(0.250)^2}$$

$$= 82.8 \text{ atm}$$

The ideal gas equation predicts that

$$P = \frac{nRT}{V} = \frac{1 \times 0.0821 \times 300}{0.250}$$

$$= 98.5 \text{ atm}$$

Limitations of van der Waals Equation

van der Waals equation explains satisfactorily the general behaviour of real gases. It is valid over a wide range of pressures and temperatures. However, **it fails to give exact agreement with experimental data at very high pressures and low temperatures.** Dieterici (1899) proposed a modified van der Waals equation. This is known as **Dieterici equation.** For one mole of gas, it may be stated as

$$P(V - b) = RTe^{-a/VRT}$$

Here the terms (a) and (b) have the same significance as in van der Waals equation.

Interpretation of Deviations from van der Waals equation

For one mole of gas, van der Waals equation is

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT \quad \dots(1)$$

or
$$PV = RT + Pb - \frac{a}{V} + \frac{ab}{V^2} \quad \dots(2)$$

Now we proceed to interpret the deviations of real gases from ideal behaviour as depicted in Figs. 10.21 and 10.22.

(a) At low pressure. When P is small, V will be large. Thus both the terms Pb and ab/V^2 in equation (2) are negligible compared to a/V . Ignoring these,

$$PV = RT - \frac{a}{V}$$

or
$$\frac{PV}{RT} = 1 - \frac{a}{VRT}$$

$$\text{or } Z = 1 - \frac{a}{VRT}$$

Thus **at low pressure, the compressibility factor is less than 1**. This explains the initial portions of Z/P curves of N_2 and CO_2 which lie below the ideal curve. As the pressure is increased, V decreases and the value of Z increases. Hence the curves show upward trend.

(b) At high pressures. When P is large, V will be small. Therefore the terms a/V and ab/V^2 are negligible in comparison with Pb . Hence equation (2) is reduced to

$$PV = RT + Pb$$

$$\text{or } \frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

$$\text{or } Z = 1 + \frac{Pb}{RT}$$

Thus at high pressures, Z is greater than 1 and Z/P lies above the ideal gas curve. With the increase of pressure, the value of Z will be still higher. This accounts for the rising parts of the curves in Fig. 10.18.

(c) At extremely low pressures. At extremely low pressures, V becomes very large. Hence all the terms Pb , a/V and ab/V^2 in equation (2) are negligibly small. These could be ignored compared to RT . Thus equation (2) reduces to

$$PV = RT$$

Hence, **at low pressures real gases behave ideally.**

(d) At high temperatures. At high temperatures, volume will be large ($V \propto T$). Hence P will be small. Then in the equation (2) the term RT predominates the other terms and the equation is reduced to

$$PV = RT$$

Thus **at extremely high temperatures real gases tend to show ideal behaviour.**

However, at low temperatures, both P and V will be small and the net result of Pb , $-a/V$, and ab/V^2 will be appreciable. Therefore the deviations would be quite prominent.

(e) Exceptional behaviour of hydrogen. Because of the small mass of H_2 molecule, the attractions between the molecules are negligible. Hence the term ' a ' is extremely small and the terms a/V and ab/V^2 in equation (2) can be ignored. The equation now becomes

$$PV = RT + Pb$$

$$\text{or } \frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

$$\text{or } Z = 1 + \frac{Pb}{RT}$$

Since Z is always greater than 1, **the Z/P curve throughout lies above the ideal curve.**

SOLVED PROBLEM 1. One mole of water vapour is confined to a 20 litre flask at 27°C . Calculate its pressure using

(a) van der Waal's equation

(b) Ideal gas equation

Given that

$$a = 5.464 \text{ litre}^2 \text{ atm mol}^{-1}$$

$$b = 0.0305 \text{ litre mol}^{-1}$$

$$R = 0.0821 \text{ litre atm. deg}^{-1} \text{ mol}^{-1}$$

SOLUTION. (a) using van der Waal's equation

$$\left(P + a \frac{n^2}{V^2}\right)(V - nb) = nRT$$

Here $n = 1$ mole ; $T = 27 + 273 = 300$ K

$R = 0.0821$ litre atm. deg⁻¹ mol⁻¹; $a = 5.464$ litre² atm. mol⁻¹ and $b = 0.0305$ litre mol⁻¹; $P = ?$
 $V = 20$ litre. Substituting the values, we get

$$\left[P + \frac{5.464 \times 1^2}{(20)^2}\right][20 - 1 \times 0.0305] = 1 \times 0.0821 \times 300$$

$$[P + 0.01366][19.9695] = 24.6$$

or
$$P = \frac{24.6}{19.9695} - 0.01366$$

$$= 1.23187 - 0.01366 = \mathbf{1.21821 \text{ atm}}$$

(b) using van der Waal's equation

$$PV = nRT$$

or
$$P = \frac{n}{V} RT$$

Substituting the values, we get

$$P = \frac{1}{20} \times 0.0821 \times 300 = \mathbf{1.2315 \text{ atm}}$$

SOLVED PROBLEM 2. Two moles of NH₃ are enclosed in a five litre flask at 27°C. Calculate the pressure exerted by the gas assuming that

- (i) the gas behaves like an ideal gas.
- (ii) the gas behaves like a real gas

SOLUTION. Here

$$n = 2 ; T = 300 \text{ K} ; V = 5 \text{ litres}$$

$$R = 0.082 \text{ atm. litre K}^{-1} \text{ mol}^{-1}$$

(i) when the gas behaves like an ideal gas

$$PV = nRT \text{ or } P = \frac{n}{V} RT$$

Substituting the values

$$P = \frac{2 \times 0.082 \times 300}{5} = \mathbf{9.84 \text{ atm}}$$

(ii) when the gas behaves like a real gas

$$\left(P + a \frac{n^2}{V^2}\right)(V - nb) = nRT$$

or
$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

Substituting the values we get

$$P = \frac{2 \times 0.082 \times 300}{5 - 2 \times 0.037} - \frac{4.14 \times 2^2}{5^2}$$

$$= 9.9879 - 0.667 = \mathbf{9.3028 \text{ atm}}$$

LIQUEFACTION OF GASES – CRITICAL PHENOMENON

A gas can be liquefied by lowering the temperature and increasing the pressure. At lower temperature, the gas molecules lose kinetic energy. The slow moving molecules then aggregate due to attractions between them and are converted into liquid. The same effect is produced by the increase of pressure. The gas molecules come closer by compression and coalesce to form the liquid.

Andres (1869) studied the $P-T$ conditions of liquefaction of several gases. He established that for every gas there is a temperature below which the gas can be liquefied but above it the gas defies liquefaction. This temperature is called the critical temperature of the gas.

The **critical temperature**, T_c , of a gas may be defined as that temperature above which it cannot be liquefied no matter how great the pressure applied.

The **critical pressure**, P_c , is the minimum pressure required to liquefy the gas at its critical temperature.

The **critical volume**, V_c , is the volume occupied by a mole of the gas at the critical temperature and critical pressure.

T_c , P_c and V_c are collectively called the **critical constants** of the gas. All real gases have characteristic critical constants.

TABLE 10.4. THE CRITICAL CONSTANTS OF SOME COMMON GASES

Gas	Critical temperature (K)	Critical pressure (atm)	Critical volume ($ml/mole$)
Helium	5.3	2.26	57.8
Hydrogen	33.2	12.8	65.0
Nitrogen	126.0	33.5	90.1
Oxygen	154.3	50.1	74.4
Carbon dioxide	304.0	72.9	94.0
Ammonia	405.5	111.5	72.1
Chlorine	407.1	76.1	123.8
Sulphur dioxide	430.3	77.7	122.3

At critical temperature and critical pressure, the gas becomes identical with its liquid and is said to be in **critical state**. The smooth merging of the gas with its liquid is referred to as the **critical phenomenon**. Andrews demonstrated the critical phenomenon in gases by taking example of carbon dioxide.

Andrews Isotherms of Carbon Dioxide

The $P-V$ curves of a gas at constant temperature are called **isotherms** or **isothermals**. For an ideal gas $PV = nRT$ and the product PV is constant if T is fixed. Hence the isotherms would be rectangular parabolas.

For an ideal gas $PV = nRT$ and the product PV is constant if T is fixed. Hence the isotherms would be rectangular parabolas.

Andrews plotted the isotherms of carbon dioxide for a series of temperatures. From Fig. 10.30 can be seen that there are three types of isotherms *viz.*, those above 31°C , those below 31°C ; and the one at 31°C .

(a) **Isotherms above 31°C .** The isotherm at 25°C is a rectangular hyperbola and approximates to the isotherm of ideal gas. So are all other isotherms above 31°C . Thus in the region

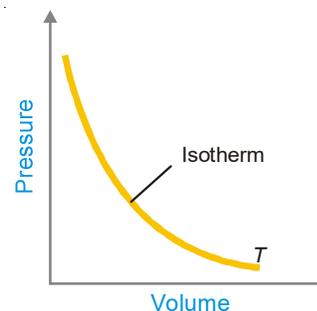


Figure 10.29
Isotherm of an ideal gas at temperature T .