SEMESTER–I (Period–II)

2

TOPIC

Kinetic Theory of Gases

C11CH2

Learning Objectives

Upon completion of this topic, learners will:

- Describe the concept of pressure
- Explain and apply Boyles, Charles', Gay-Lussac's, Avogadro's to observations of gas behavior
- Perform calculations using the Ideal Gas Equation
- Apply the concept of the gas laws to gas phase reactions and perform stoichiometric calculations using gas properties, masses, moles, limiting reagents and percent yield
- Describe the relationship between partial pressure and the total pressure as described in Dalton's Law of partial pressure
- Apply the ideas of Kinetic Molecular Theory to a variety of gas phenomena
- Discuss the Root Mean Square Velocity as it relates to gas particles
- Discuss effusion and diffusion in relation to Graham's Law
- Explain the general principles of the hard sphere model and the van der Waal's Model of gas and
- Discuss the concept of chemistry in the atmosphere.

Out of three states of matter, i.e., solid, liquid and gases, the gaseous state is simplest one. Kinetic energy of molecules in gases is more in comparison to that of solids and liquids. Molecules in gases have more thermal energy hence move almost like free entities. Gases have no fixed volume and shape, have very low density hence are highly compressible. Gases exert pressure, on the walls of container, that is equal in all directions. Gases have quality of diffusion hence mix evenly and uniformly.

Experimental studies show that gases behaviour follow some relative patterns among their measurable properties like **mass**, **volume**, **pressure**, and **temperature**. These relationships between measurable properties of gases are known as **gas laws**.

2.1. PRESSURE

Gases exert outward force on the walls of the container in which they are enclosed. The outward force experienced by the walls is due to bombardment of gas molecules on the walls. This *outward force per unit area of the walls* is termed as **gas pressure.**

Units of Gas Pressure

Pressure is force per unit area

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} \qquad \ldots(i)$$

By definition,

$$\begin{aligned}\text{Force} &= \text{Mass} \times \text{Acceleration}\\ &= \frac{\text{Mass} \times \text{Velocity}}{\text{Time}} = \frac{\text{Mass} \times \text{Distance}}{\text{Time} \times \text{Time}}\\ &= \frac{\text{kg} \times \text{m}}{\text{s} \times \text{s}}\end{aligned}$$

Thus, SI unit of force is $kg\ ms^{-2}$ which is called *newton* (**N**)

$$1\ \text{N} = 1\ \text{kg ms}^{-2}$$

Putting SI units of force (N) and area (m^2) we get SI unit of pressure as N/m^2 or $\mathbf{Nm^{-2}}$. This SI unit of pressure is called *pascal* (**Pa**) in the honour of French mathematician and physicist *Blaise Pascal*

$$1\ \text{Pa} = 1\ \text{N m}^{-2}$$

Now, 1000 Pa = 1 kilo pascal abbriviated as **kPa.**

For gases, this unit of pressure is very small. Hence pressure is generally expressed in terms of bigger unit named as **bar.** One bar represents 100 kilo pascal. Thus

$$1\ \text{bar} = 100\ \text{kPa} = 10^5\ \text{Pa}$$

It may be noted that the older unit of pressure of the gases was *atmosphere* which was abbreviated as **atm.** The relationship between these units is given as follows:

$$1\ \text{atm} = 1.01325\ \text{bar} = 1.01325 \times 10^5\ \text{Pa}$$

or

$$1\ \text{bar} = 0.987\ \text{atm} = 10^5\ \text{Pa}$$

Measurement of Gas Pressure

The pressures other than atmospheric pressure are measured by device is called **manometer.**

There are two types of manometer *open end* and *closed end* manometers

(*a*) **Open end manometer.** It consists of U tube partially filled with mercury. One limb of the tube is shorter than the other. The shorter limb is connected to the vessel containing the gas where as the longer limb is open as shown in Fig. 2.1. The mercury in the longer tube is subjected to the atmospheric pressure while mercury in the shorter tube is subjected to the pressure of the gas.

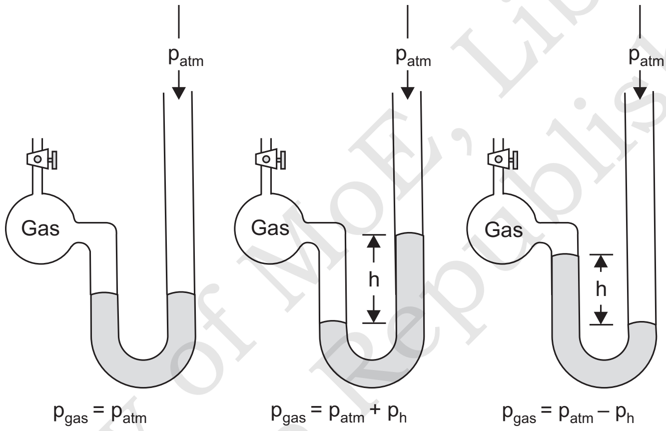


Fig 2.1. Measurement of gas pressure.

There are three possibilities described as follows:

(*i*) If the level of Hg in the two limbs is same, then

Gas pressure (p_{gas}) = *atmospheric pressure* (p_{atm})

(*ii*) If the level of Hg in the longer limb is higher, then

Gas pressure (p_{gas})

$= p_{atm}$ + (*difference between the two levels*)

$= p_{atm} + p_h$

(*iii*) If the level of Hg in the shorter limb is higher, then

Gas pressure (p_{gas})

$= P_{atm}$ – (*difference between the two levels*)

$= P_{atm} - p_h$.

(*b*) **Closed end manometer.** This is generally used to measure low gas pressures. It also consists of U-tube with one limb shorter than the other and partially filled with mercury as shown in Fig. 2.2. The space above mercury on the closed end is completely evacuated. The shorter limb is connected to the vessel containing gas. The gas exerts pressure on the mercury in the shorter limb and forces its level down.

Gas pressure (p_{gas})
= [*Difference in the Hg level in two limbs*]

or $p_{gas} = p_h$

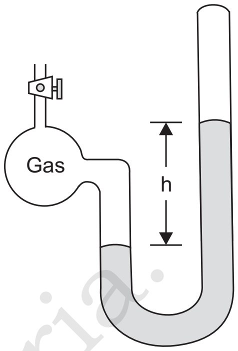


Fig. 2.2. Closed end manometer

It may be noted that **open end manometer** is better suited for measuring pressures **equal to or greater** than atmospheric pressure. On the other hand, **closed end manometer** is suited to measure pressures **below atmospheric pressure.**

2.2. GAS LAWS

Physical properties of gases like volume change with the change in temperature and pressure. The relationships between physical properties of gas as outcome of researches are formulated as gas laws. Some of the gas laws are Boyle's Law, Charles' Law, Gay Lussac's Law, Avogadro's Law and Dalton's Law.

BOYLE'S LAW—Pressure-Volume Relationship

This law describes the ***pressure-volume*** relationship of gases at constant temperature. It was given by Anglo-Irish scientist Robert Boyle (1662) and is known after his name as **Boyle's law**. The law states that:

The volume of a fixed mass of a gas is inversely proportional to its pressure at constant temperature.

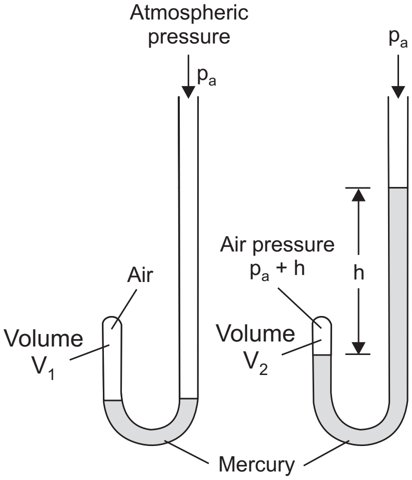


Fig. 2.3

The law can be demonstrated by the simple experiment as described below. Take a J shape tube as shown in Fig. 2.3. Tube is partially filled with mercury. Pressure is now increased by putting more mercury into the open limb. The volume of air enclosed in the space above mercury in shorter limb is noted each time. It is found that as pressure increases, the volume of enclosed air gradually decreases from V_1 to V_2.

Mathematical Interpretation of the Law

Mathematically, the law may be expressed as:

$$V \propto \frac{1}{p} \qquad \text{(\textit{Temperature and mass constant})}$$

or $$V = k_1 \frac{1}{p} \quad \text{where } k_1 \text{ is constant of proportionality}$$

or $$PV = k_1 = \text{constant.}$$

The value of the constant k_1 depends upon *amount of the gas, temperature of the gas* and the *units* in which P and V are expressed.

Thus, another statement of Boyle's law may be given as follows:

For a given amount of the gas, the product of pressure and volume is constant at constant temperature.

Let V_1 be the volume of a given mass of the gas having pressure p_1 at temperature T. Now if the pressure is changed to p_2 at the same temperature, let the volume changes to V_2. The quantitative relationship between the four variables p_1, V_1, p_2 and V_2 is:

$$\boldsymbol{p_1V_1 = p_2V_2} \quad \text{or} \quad \boldsymbol{\frac{p_1}{p_2} = \frac{V_2}{V_1}} \qquad \text{(\textit{T and n constant})}$$

The **experimental verification** of the law can be carried out by measuring the values of volumes of a given mass of a gas at different pressures keeping the temperature constant. In each case the product pV is found to be constant. The values of pressures and volumes of fixed mass (0.09 mol) of N_2 at constant temperature, 300 K are given in Table 2.1.

Table 2.1. Effect of Pressure on Volume of 0.09 mole of CO_2 at 300 K

Pressure $p \times 10^3$ Pa	*Volume* $V \times 10^{-3}$ m^3	$1/V$ (m^{-3})	$pV \times 10^2$ Pa m^3
2.0	112.0	8.90	2.24
2.5	89.2	11.2	2.23
3.5	64.2	15.6	2.247
4.0	56.25	17.7	2.25
6.0	37.40	26.7	2.244
8.0	28.1	35.6	2.248
10.0	22.4	44.6	2.240

Example 2.1. *In a J tube partially filled with mercury the volume of air column is 4.2 mL and the mercury level in the two limbs is same. Some mercury is, now added to the tube so that the volume of air enclosed in shorter limb is now 2.8 mL. What is the difference in the levels of mercury in this situation. Atmospheric pressure is reported to be 1.0 bar.*

Solution.

Initial pressure $p_1 = 1 \text{ bar} = 0.987 \text{ atm}$

$= 0.987 \times 760 = 750.12 \text{ mm Hg}$

Final pressure $p_2 = (p_1 + h)$

$V_1 = 4.2 \text{ mL}; V_2 = 2.8 \text{ mL}$

$$p_2V_2 = p_1V_1 \quad \text{or} \quad p_2 = \frac{p_1V_1}{V_2}$$

$$= \frac{750.12 \times 4.2}{2.8} = 1125.18 \text{ mm Hg}$$

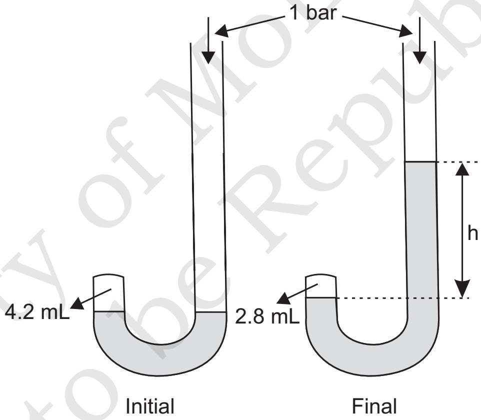


Fig. 2.4

Now, $1125.18 = 750.12 + h$

or $h = 1125.18 - 750.12$

$= 375.06$ mm Hg or **37.50 cm Hg.**

CHARLES' LAW—Volume Temperature Relationship

This law describes the ***volume-temperature*** relationship of gases at constant pressure. It was put forwarded by the French chemist *Jacques Charles* in 1787 and was further developed in 1802 by *Joseph Gay Lussac*. This law can be stated as:

The volume of a fixed mass of a gas increases or decreases by $\frac{1}{273.15}$ of its volume at 0°C for each degree rise or fall of temperature, provided pressure is kept constant.

If V_0 is the volume of given mass of the gas at 0°C

Then, V_1, the volume of the gas at 1°C

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

V_2, the volume of the gas at 2°C

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

V_t, the volume of the gas at t°C

$$= V_0\left(1+\frac{t}{273.15}\right) \qquad \text{...(2.1)}$$

Absolute scale of temperature. By carrying out the similar calculations it can be shown that the volume of the gas below 0°C will be less than V_0. For example, the volume of the gas at – t°C

$$V_{(-t)} = V_0\left(1-\frac{t}{273.15}\right)$$

Thus, decrease of temperature results in the decrease in the volume of the gas and ultimately, the volume should become *zero* at – 273.15°C. It means that any further lowering of temperature is impossible because it would correspond to negative volume which is meaningless. Hence, an important conclusion can be drawn from the above discussion that the *lowest possible temperature* is – 273.15°C. This lowest possible temperature at which all the gases are supposed to occupy zero volume is called **Absolute zero.** A scale of temperature based upon this choice of zero is called **absolute scale of temperature.** Since this scale was suggested by the British scientist *Lord Kelvin,* it is also known after his name as **Kelvin scale of temperature.**

Careful measurements have revealed that absolute zero of temperature is – 273.15°C. Temperatures on the Kelvin scale are indicated by writing the letter K. By convention, the degree sign (°) is not used while expressing temperatures on Kelvin scale. For example,

$$-273.15°C = 0\ K$$

The relationship between Kelvin scale and celsius scale is:

$$\mathbf{T(K) = t(^\circ C) + 273.15}$$

where, '**T**' is the temperature on Kelvin scale while '**t**' is the temperature on Celsius scale.

Alternative Statement of Charles' Law

We have already derived the relationship between the volume of a given mass of the gas at t°C (V_t) and that at 0°C (V_0).

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

$$= V_0\left(\frac{273.15 + t}{273.15}\right) = V_0\,\frac{T_t}{T_0}$$

where T is corresponding temperature on Kelvin scale.

or $$\frac{V_t}{T_t} = \frac{V_0}{T_0}$$

$\therefore$ $$\frac{V}{T} = \text{constant} = k_2 \qquad \text{(at constant } p \text{ and } n\text{)}$$

Thus, $$V = k_2T \quad \text{or} \quad V \propto T \qquad \text{(at constant } p \text{ and } n\text{)}$$

Here, k_2 is a constant whose value depends upon pressure of the gas, amount of the gas and the units of volume (V).

This leads to an alternative statement of Charles' law as:

> ***The volume of the fixed mass of a gas at constant pressure is directly proportional to the temperature on Kelvin scale.***

Let V_1 be the volume of a certain mass of a gas at temperature T_1 and at pressure p. If temperature is changed to T_2 keeping pressure constant, the volume changes to V_2. The relationship between four variables V_1, T_1, V_2 and T_2 is:

$$\frac{\mathbf{V_1}}{\mathbf{T_1}} = \frac{\mathbf{V_2}}{\mathbf{T_2}} \qquad (\textit{p and n constant})$$

The **experimental verification** of the law can be done by measuring the volumes of the given mass of a gas at different temperatures keeping the pressure constant. In each case the ratio V/T comes out to be constant. The *volume-temperature* data for 1 mol of N_2 at 1 bar pressure is given in Table 2.2.

Table 2.2. Volume-Temperature Data for N2 Gas at 1 bar Pressure

Temperature		*Volume*	*(V/T)*
°C (t)	*K(T)*	*(dm^3)*	*(dm^3K^{-1})*
– 50	223.15	18.52	0.083
0	273.15	22.67	0.083
50	323.15	26.82	0.083
100	373.15	30.97	0.083
150	423.15	35.12	0.083

GAY LUSSAC'S LAW—Pressure Temperature Relationship

This law describes the ***pressure-temperature*** relationship of gases at constant volume. It is also called **Amonton's law.**

The law is similar to Charles' law and is given by **Joseph Gay Lussac.** It states that ***pressure of a fixed mass of a gas at constant volume is directly proportional to the temperature on Kelvin scale.***

Mathematically, $$p \propto T \qquad \text{(At constant } n, V\text{)}$$

or $$\frac{p}{T} = k_3 \qquad \text{(constant)}$$

The value of k_3 depends upon volume of gas, amount of the gas and the units of pressure (p).

Let p_1 be the pressure of a certain mass of a gas at temperature T_1 and having a volume V. Now, if temperature is changed to T_2 at the same volume so that the corresponding pressure becomes p_2. Then according to the law:

$$\frac{p_1}{T_1} = \frac{p_2}{T_2} \qquad \text{(At constant } n \text{ and } V\text{)}$$

The law can be illustrated by pressure-temperature graph. The plot of p *vs* T for a fixed mass of a gas at constant volume is a straight line as shown in Fig. 2.5. This plot of p *vs* T at constant T and n is called **isometric**. The slops of various isometrics at different volumes are different but all these lines meet the temperature axis on extrapolation at 0 (K) as shown in Fig. 2.5.

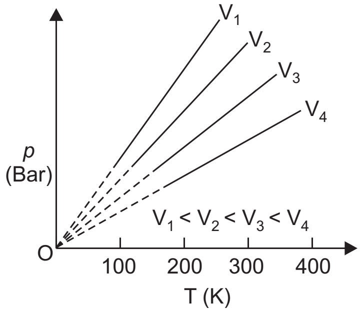


Fig. 2.5. Isometrics of ideal gas.

Example 2.2. *A sample of a gas is found to occupy a volume of 900 cm^3 at 27°celsius. Calculate the temperature at which it will occupy a volume of 300 cm^3, provided the pressure is kept constant.*

Solution. Here, $V_1 = 900 \text{ cm}^3 \qquad V_2 = 300 \text{ cm}^3$

$$T_1 = (27 + 273) \text{ K} = 300 \text{ K}, \ T_2 = ?$$

Applying Charles' law, $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$

$$T_2 = \frac{V_2 \times T_1}{V_1} = \frac{300 \text{ cm}^3 \times 300 \text{ K}}{900 \text{ cm}^3}$$

$$= 100 \text{ K} = 100 - 273 = -\mathbf{173°C.}$$

AVOGADRO'S LAW—Volume Amount Relationship

This law describes the ***volume-amount*** relationship of gases at constant temperature and pressure. It was given by Amedeo Avogadro in 1811. It states that ***equal volumes of all the gases under similar conditions of temperature and pressure contain equal number of molecules.***

For example, 1 mol of all the gases contain 6.023×10^{23} molecules. At the same time 1 mol of all the gases at 273.15 K (0°C) and 1 bar pressure occupy a volume of 22.7 L (22.7×10^{-3} m^3). This means that as long as the temperature and pressure remain constant the volume of the gas is directly proportional to the number of molecules or in other words, the amount of the gas. Mathematically we can write

$$V \propto N \qquad (T \text{ and } p \text{ are constant})$$

The number of molecules N is directly proportional to number of moles (n)

$$\therefore \qquad V \propto n \qquad (T \text{ and } p \text{ are constant})$$

or $\qquad V = k_4 n \qquad k_4$ is constant of proportionality

Now, if m is the mass of the gas having molar mass equal to M, then the number of moles (n) are given as

$$n = \frac{m}{M}$$

$$\therefore \qquad V = k_4 \frac{m}{M}$$

or $\qquad M = k_4 \dfrac{m}{V} \quad$ or $\quad k_4 . d$

where d is density of gas.

The above relationship implies that density of the gas at a given temperature and pressure is directly proportional to its molar mass.

2.3. IDEAL GAS EQUATION

A gas that follows Boyle's law, Charles' law and Avogadro's law strictly at all conditions, is called **Ideal gas.** It is assume that inter-molecular forces are not present between the molecules of ideal gas. Real gases follow these laws only under certain specific conditions when forces of interaction are practically negligible. In all other situations the real gases deviate from ideal behaviour.

The combination of various gas laws namely; *Boyle's law, Charles' law* and *Avogadro's law* leads to the development of the mathematical relation which relates four variables *pressure, volume, absolute temperature* and *number of moles of ideal gas*. The equation so formulated is called **ideal gas equation.**

The ideal gas equation can be derived by combining Boyle's law, Charles' law and Avogadro's law as follows:

According to Boyle's law

$$V \propto \frac{1}{P} \quad (\textit{at constant T and n}) \qquad \ldots(i)$$

According to Charle's law

$$V \propto T \text{ (at constant } P \text{ and } n) \qquad \ldots(ii)$$

According to Avogadro's law

$$V \propto n \; (\textit{at constant T and P}) \qquad \ldots(iii)$$

Combining (*i*), (*ii*) and (*iii*)

$$V \propto \frac{nT}{P}$$

or $$pV \propto nT$$

or $$\mathbf{pV = nRT} \qquad \ldots(2.2)$$

where, **R** is constant of proportionality and is known as **universal gas constant.**

Equation (2.2) is called **ideal gas equation.** This equation is applicable to any gas under those conditions when behaviour of gas approaches ideal behaviour. Since this equation relates four variables which are used to describe the state of any gas, it is also known as **equation of state for ideal gas.** It may be noted that out of the four variables, the two namely; *pressure* (p) and *temperature* (T) are **intensive** variables as they do not depend on the bulk or quantity of the gas. The other two variables, *i.e., volume* (V) and *mole* (n) are **extensive** variables as they depend upon the bulk or quantity of the gas.

2.4. DENSITY AND MOLAR MASS OF GASEOUS SUBSTANCE

We have studied in unit one that the number of moles (n) of the substance is related to the molar mass (M) as

$$n = \frac{w}{M}$$

where, w = mass in gram.

Substituting this value in the ideal gas equation we can get the relationship between density and molar mass,

$$pV = nRT = \frac{w}{M} RT$$

$$p = \frac{wRT}{MV} \quad \text{or} \quad p = \frac{dRT}{M}$$

where d is the density of gas $\left[d = \frac{\text{Mass}}{\text{Volume}} = \frac{w}{V}\right]$

or $$\boldsymbol{p = \frac{dRT}{M}} \qquad \text{...(2.3)}$$

Nature of the Gas Constant (R)

In order to understand the significance of R, let us examine the nature of quantities in the ideal gas equation:

$$pV = nRT \quad \text{or} \quad R = \frac{pV}{nT} = \frac{\text{Pressure} \times \text{Volume}}{\text{Moles} \times \text{Temperature}}$$

$$R = \frac{\frac{\text{Force}}{\text{Area}} \times \text{Volume}}{\text{Moles} \times \text{Temperature}} = \frac{\frac{\text{Force}}{(\text{Length})^2} \times (\text{Length})^3}{\text{Moles} \times \text{Temperature}}$$

$$= \frac{\text{Force} \times \text{Length}}{\text{Moles} \times \text{Temperature}}$$

Since force × length = work energy

$$\therefore \quad R = \frac{\text{Work}}{\text{Moles} \times \text{Temperature}}$$

Thus, **R** *represents* ***work done per degree per mole.***

Since work can be expressed in different systems of units, **R** will have different numerical values in different systems.

2.5. DALTON'S LAW OF PARTIAL PRESSURES

This law describes the relation between the pressure of the mixture of non-reacting gases enclosed in a vessel to their individual pressures. The law was given by John Dalton in 1807. It states:

At constant temperature, the pressure exerted by a mixture of two or more non-reacting gases enclosed in a definite volume, is equal to the sum of the individual pressures which each gas would exert if present alone in the same volume at the same temperature.

The individual pressures of gases are known as **partial pressures.**

If p_{Total} is the pressure of the mixture of non-reacting gases at temperature T and volume V, and $p_1, p_2, p_3,$ ...... represent the partial pressures of the gases, then

$$p_{Total} = p_1 + p_2 + p_3 + \ldots\ldots \ (T, V \text{ are constant})$$

The law can be **illustrated** by considering the following example. Suppose we have three containers of capacity 1 litre each; one containing *x moles* of nitrogen, the other *y moles* of oxygen and the third having a mixture of *x moles* of nitrogen and *y moles* oxygen. All the three containers, are kept at the same temperature.

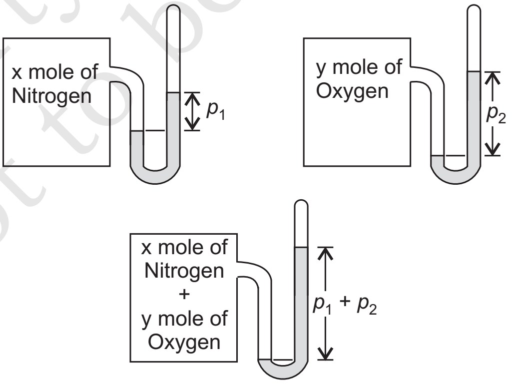


Fig. 2.6. Illustration of Dalton's law of partial pressures.

Now, if the manometer, attached to first container shows a pressure p_1 and that attached to second container shows a pressure p_2. Then the pressure in the third container is $p_1 + p_2$.

Utility of Dalton's law. This law is useful in calculating the pressure of the gas collected by the displacement of water. The gas being collected over water also contains water vapours. The observed pressure of the moist gas is equal to the sum of the pressure of the dry gas and the pressure of the water vapours. The pressure of the water vapours is constant at a given temperature and is known as **aqueous tension** at that temperature. Thus,

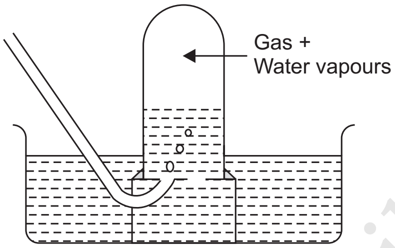


Fig. 2.7. Collection of gas over water.

$$p_{\text{observed}} = p_{\text{gas}} + \textit{aqueous tension}$$

$$\therefore \quad p_{\text{gas}} = p_{\text{observed}} - \textit{aqueous tension}$$

Aqueous tension of water at different temperatures is given in Table 2.3.

Table 2.3. Aqueous Tension (Vapour Pressure) of Water as a Function of Temperature

Temperature (K)	*Pressure (bar)*	*Temperature (K)*	*Pressure (bar)*
273.15	0.0060	295.15	0.0260
283.15	0.0121	297.15	0.0295
288.15	0.0168	299.15	0.0331
291.15	0.0204	301.15	0.0372
293.15	0.0230	303.15	0.0418

Example 2.3. *A certain quantity of a gas occupies a volume of 0.1 L when collected over water at 288 K and 0.92 bar pressure. The same gas occupied a volume of 0.085 L at S.T.P. in dry conditions. Calculate the aqueous tension at 288 K.*

Solution. Let the aqueous tension at 288 K be p bar

Thus, pressure of the dry gas at 288 K

$$= (0.92 - p) \text{ bar.}$$

Now, $p_1 = (0.92 - p)$ bar $\quad p_2 = 1$ bar.

$V_1 = 0.1$ L $\quad V_2 = 0.085$ L

$T_1 = 288$ K $\quad T_2 = 273.15$ K.

According to gas equation,

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \quad \text{or} \quad p_1 = \frac{p_2V_2T_1}{V_1T_2}$$

Substituting the values,

$$0.92 - p = \frac{1 \times 0.085 \times 288}{0.1 \times 273.15} = 0.896$$

$$p = \mathbf{0.024\ bar.}$$

2.6. KINETIC MOLECULAR THEORY OF GASES

The various gas laws which we have studied so far were based on the experimental facts. There was no theoretical background for their justification. In order to explain the behaviour of gases and answer the questions such as, why do they exert pressure or why a volume is inversely proportional to pressure, etc., it became necessary to develop a molecular theory, *i.e., a mental picture* which is able to provide explanation for our experimental observations. Maxwell, Boltzmann, Clausius, etc., suggested a theoretical model which is known as **kinetic molecular theory of gases** or **microscopic model of gases.**

The Microscopic Model of Gases

The various assumptions of kinetic theory are related to atoms and molecules which cannot be seen. Thus, kinetic theory is said to give us a *microscopic model* of gases. The **various postulates** of the theory are:

1. *All gases are made up of very large number of extremely small particles called* **molecules.**
2. *The molecules are separated from one another by large spaces so that the actual volume occupied by the molecules is negligible as compared to the total volume of the gas.*
3. *The molecules are not at rest but possess rapid random motion. During their motion, they collide with one another and also against the walls of the container.*
4. *The pressure of the gas is due to bombardment of the gas molecules against the walls of the container.*
5. *The collisions of the molecules with each other and with the walls of the container are perfectly elastic, i.e., there is no loss or gain of kinetic energy. However, there may be redistribution of energy during such collisions.*

6. *There are no attractive or repulsive forces between the molecules of the gas. They are completely independent of each other.*
7. *At any instant, different molecules possess different velocities and hence, different energies. However, the average kinetic energy of the molecules is directly proportional to the absolute temperature.*

Kinetic Gas Equation

Kinetic gas equation is the mathematical relation that has been derived on the basis of various postulates of kinetic molecular theory. It relates pressure (p), volume (V) of N molecules of the gas at a given temperature to the root mean square speed. If m is mass of gas molecule, c is the r.m.s. N is total number of molecules then *kinetic gas equation* is:

$$\boldsymbol{p}\mathbf{V} = \frac{\mathbf{1}}{\mathbf{3}}\ \mathbf{mNc^2}.$$

Average Kinetic Energy of Gas

The ***average kinetic energy*** of gas molecules can be calculated on the basis of kinetic gas equation.

According to kinetic gas equation

$$p = \frac{1}{3}\ (\mathrm{N/V})\ mc^2$$

For one mol of the gas, $\mathrm{N} = \mathrm{N_A}$

$$\therefore \qquad p\mathrm{V} = \frac{1}{3}\ \mathrm{N_A}\ mc^2$$

Also for 1 mol of ideal gas, $p\mathrm{V} = \mathrm{RT}$

$$\therefore \qquad \frac{1}{3}\ \mathrm{N_A}\ mc^2 = \mathrm{RT}$$

$$\text{or} \qquad \frac{1}{2}\times\frac{2}{3}\ \mathrm{N_A}\ mc^2 = \mathrm{RT} \quad \text{or} \quad \frac{1}{2}\ mc^2 = \frac{3}{2}\ \mathrm{RT}$$

Now $\frac{1}{2}\ mc^2$ represents average kinetic energy ($\overline{\mathrm{E}}_k$) of the molecule.

$$\therefore \qquad \overline{\mathbf{E}}_{\boldsymbol{k}} = \frac{3}{2}\ \mathbf{RT} \quad \text{or} \quad \overline{\mathbf{E}}_{\boldsymbol{k}} = \frac{3}{2}\ \mathbf{kT}$$

(where $k = \mathrm{R/N_A}$ and called Boltzmann constant)

Since R or k are constant, thus, it can be concluded that $\overline{\mathbf{E}}_{\boldsymbol{k}}$ ***of gas*** $\propto$ ***T.***

2.7. MOLECULAR VELOCITY

Molecular velocity is generally expressed in terms of: (*i*) *Most probable velocity*, (*ii*) *average velocity* and (*iii*) *root mean square velocity.*

(*i*) **Most probable velocity (c^* or u_{mp}).** *It is the velocity possessed by maximum number of gas molecules at a given temperature. c* is related to temperature (T) and molar mass (M) as follows*

$$c^* \text{ (or } u_{mp}) = \sqrt{\frac{2RT}{M}}$$

(*ii*) **Average velocity ($\bar{c}$ or u_{av}).** *It is the arithmatic mean of the velocity of different molecules of the gas at a given temperature.* If n_1 molecules have velocity v_1, n_2 molecules have velocity v_2, n_3 molecules have velocity v_3 and so on. Then,

$$\bar{c} \text{ (or } u_{av}) = \frac{n_1v_1 + n_2v_2 + n_3v_3 + \ldots\ldots}{(n_1 + n_2 + n_3 + \ldots\ldots)}$$

Average *velocity* is related to the molar mass (M) of the gas and the temperature (T) as follows.

$$\bar{c} \text{ (or } u_{av}) = \sqrt{\frac{8RT}{\pi M}}$$

(*iii*) **Root mean square velocity (c or $u_{r.m.v.}$).** *It is the square root of the arithmatic mean of the squares of velocities of various molecules of the gas at a given temperature.* If v_1, v_2, v_3, ... are velocities of n_1, n_2, n_3, ... molecules respectively, then

$$c \text{ or } u_{\text{r.m.v.}} = \sqrt{\frac{n_1v_1^2 + n_2v_2^2 + n_3v_3^2 + \ldots\ldots}{(n_1 + n_2 + n_3 + \ldots\ldots)}}$$

Root mean square velocity is related to temperature (T), pressure (p), volume (V) and molar mass (M) of the gas by the following expressions

$$c \text{ or } u_{\text{r.m.v.}} = \sqrt{\frac{3RT}{M}} \quad \text{or} \quad \sqrt{\frac{3pV}{M}}$$

Relationship between different types of velocities.

The different types of velocities are related as :

$$\mathbf{c^* : \bar{c} : c} = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$= 1.414 : 1.596 : 1.732$$

$$= \mathbf{1 : 1.128 : 1.224}$$

For any gas at a given temperature,

$$c > \bar{c} > c^*$$

It may also be noted that

$$\mathbf{\bar{c} = 0.921 \times c} \text{ and}$$
$$\mathbf{c^* = 0.817 \times c}$$

Example 2.4. *Calculate Average kinetic energy of 32 g of methane molecules at 27°C. R = 8.314 JK⁻¹ mol⁻¹.*

Solution. Average kinetic energy is given as

$$E_K = \frac{3nRT}{2}$$

Here, $n = \frac{32}{16} = 2$; $R = 8.314\ JK^{-1}\ mol^{-1}$;

$$T = 300\ K$$

$$\therefore \quad E_K = \frac{3 \times 2 \times 8.314 \times 300}{2} = \mathbf{7482.6\ J}$$

Maxwell's Distribution of Speeds

Gases consist of tiny particles separated from the one another by large empty space and moving rapidly at random in all the directions. In the course of their motion, they collide with one another and also with the walls of the container. Due to frequent collisions, the speeds and direction of motion of molecules keep on changing. Thus, all the molecules in a sample of a gas do not have same speeds. Although it is not possible to find out the speeds of individual molecules, yet from the probability considerations it has become possible to work out the distribution of molecules between different speeds. This distribution is referred to as *Maxwell-Boltzmann* distribution in honour of the scientists who developed it. It may be noted that ***distribution of speeds remains constant at given temperature although individual speeds of molecules may change.*** Maxwell plotted the fraction of molecules having different speeds against the speeds at given temperature.

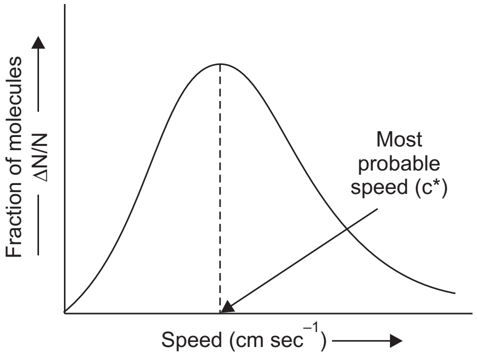


Fig. 2.8. Maxwell's distribution of speeds at a particular temperature.

The curve so obtained is shown in Fig. 2.8 and is called *Maxwell's distribution curve.*

The important **features of Maxwell's distribution curve** can be summed up as follows:

(*i*) *The fraction of molecules with very low or very high speeds is very small.*

(*ii*) *The fraction of molecules possessing higher and higher speeds goes on increasing till it reaches the peak and thereafter it starts decreasing.*

(*iii*) *The area under the curve gives the total number of gas molecules.*

(*iv*) *The maximum fraction of molecules possesses a speed corresponding to the peak in the curve. This speed corresponding to the peak in the curve is referred to as most probable speed.*

The **most probable speed** may be defined as the *speed possessed by the maximum fraction of molecules at a given temperature.*

As most probable speed is **inversely** proportional to molar mass ($c^* = \sqrt{2RT/M}$). This implies that at the same temperature; lighter gases move faster than heavier gases. It is evident from the distribution curves of Cl_2 and N_2 gases at 300 in Fig. 2.9.

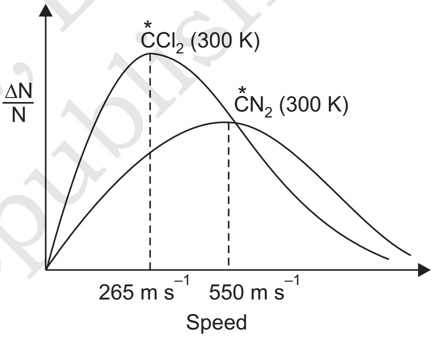


Fig. 2.9. Maxwell Boltzmann distribution curves for Cl_2 and N_2 at 300 K.

Effect of Temperature on Distribution of Speeds

It may be noted carefully that fraction of molecules having most probable speed remains the same so long as temperature remains same. However, on increasing the temperature of the gas, the molecular motion becomes rapid and consequently, the value of *most probable speed* also increases.

From the curves shown in Fig. 2.10. It is evident that as the temperature rises, following changes are observed.

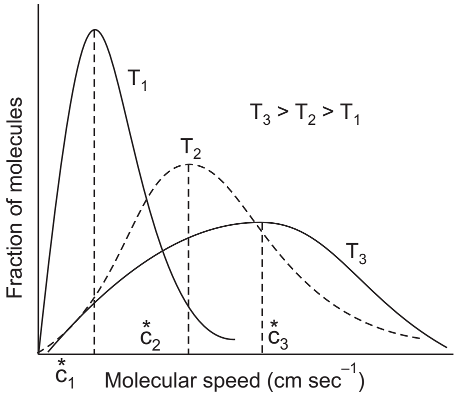


Fig. 2.10. Maxwell's distribution curves at different temperatures.

- The entire curve shifts towards right.
- The most probable speed increases.
- The fraction of molecules having most probable speed decreases.
- The curve becomes broader in the middle range, indicating that more number of molecules have speeds near most probable speed.
- The fraction of molecule having higher speed increases.
- The fraction of molecules having lower speed decreases.

2.8. BEHAVIOUR OF REAL GASES; DEVIATION FROM IDEAL GAS BEHAVIOUR

So far we have been discussing the *p*VT behaviour for an ideal gas, *i.e.*, a *gas which obeys the gas laws and the gas equation $pV = nRT$ strictly at all temperatures and pressures*. The molecules of ideal gas are assumed to be volumeless points with no attractive/repulsive forces between one another. In fact, no real gas strictly obeys the ideal gas law at all temperatures and pressures. Deviations from ideal behaviour are observed particularly at high pressures and low temperatures.

For example, if we plot a graph between the product *p*V versus *p* for different gases at constant temperature we should get a straight line parallel to the pressure axis because according to Boyle's law, *p*V is constant at all pressures. In fact, we do not get a straight line. There is a significant deviation from the ideal behaviour. Plots of *p*V versus *p* for different real gases at 273 K is given in Fig. 2.11. There are two type of curves in Fig. 2.11.

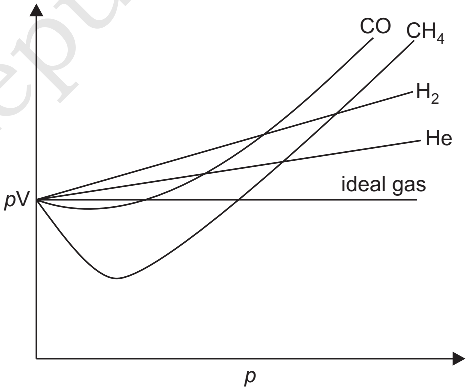


Fig. 2.11. Plots of *p*V *vs p* of some real gases at 273 K.

(*a*) Gases like H_2 and He follow the gas equation at extremely low pressures, but *p*V increases regularly as the pressure increases. Such gases are said to show *positive deviation.*

(*b*) For gases like CO and CH_4, *p*V shows a negative deviation in the beginning, reaches a minimum value (which is different for different gases) and there after it starts increasing with increase of pressure. It crosses the line for ideal gas and then shows a positive deviation continuously.

Cause of Deviation

The study of the curves given in Fig. 2.11 raises the following questions

- *Why do gases deviate from ideal behaviour? and*
- *What are the conditions under which real gases deviate from ideality?*

In order to find answer to these questions let us examine the postulates of Kinetic theory once again. We find that two of the assumptions of the kinetic theory do not hold good at all conditions. These are:

(*a*) *There is no force of attraction and repulsion between the molecules of a gas.*

(*b*) *Volume of the molecules of a gas is negligibly small in comparison to the empty space between them.*

If assumption **‘*a*’** is correct, the gases will never undergo liquefaction. However, on the contrary, we know that gases do liquify at low temperatures and high pressures. This indicates the presence of attractive forces among the gas molecules. This view is also supported by the observation that cooling is caused when the compressed gas is allowed to expand. The decrease of temperature occurs because work has to be done to overcome the attractive forces. Further, the liquid obtained as a result of liquefaction of gas is difficult to compress. This shows the existence of repulsive forces which are powerful enough to prevent further squashing of molecules in tiny volume.

If assumption **‘*b*’** is correct, then the plot of p *vs* V at constant T based on the experimental data and that based on theoretical calculations from Boyle’s law (ideal gas) should coincide. However, deviations are observed in the behaviour at high pressures as shown in Fig. 2.12.

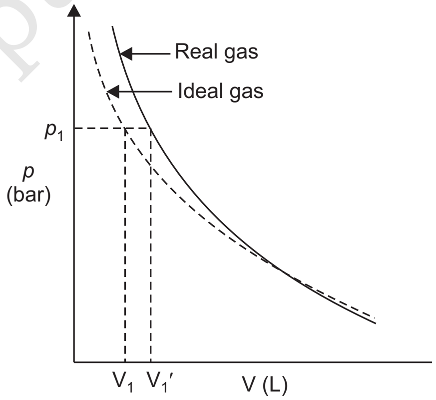


Fig. 2.12. Plot of p vs V for real and ideal gas.

It is apparent that at high pressures (p_1) the measured volume (V_1') is more than the ideal volume (V_1). At low pressures the measured volume and ideal volumes approach each other. The reason for this behaviour is that at high pressures molecules of gases are very close to each other and the volume occupied by the molecules cannot be neglected in comparison to the empty space between them. It is because the total volume of gas decreases considerably but volume of molecules remains same as they are not compressible. For examples, if we assume molecules to be hard spheres ($r = 2 \times 10^{-9}$ m), then volume of the molecules at room temperature (25°C) is about 0.1% of the volume of gas at 1 bar pressure and it is about 1% of the volume of gas at 10 bar pressure. Thus, at high pressures gas molecules get less space for free movement and *molecular interaction* start operating. This affects the actual pressure exerted by the molecules on the walls of the container. Molecules do not strike the walls with full impact because these are dragged back by other molecules due to molecular attractive forces. ***Hence, real gases show ideal behaviour when pressure approaches zero but deviations from ideal behaviour is observed at high pressures.*** Therefore, the two postulates **'*a*'** and **'*b*'** of kinetic-molecular theory need revision.

Van Der Waal's Equation of State for Real Gases

Van Der Waal in 1873 modified the ideal gas equation $p_i V_i = n\text{RT}$ by introducing two correction terms, *one for the volume* and *the other for the pressure*, to make the equation applicable to real gases as well.

(*a*) **Volume correction.** As pointed out earlier, that the volume of the molecules is not negligible as compared to the total volume of the gas. This implies that the molecules are not free to move about in the entire volume (V) which we observe. Thus, the free volume available to the gas molecules is smaller than the observed volume. In other words, *the ideal volume (V_i) is smaller than the observed volume (V).* Hence some correction term has to be subtracted from the observed volume to get the ideal volume.

Let the correction term by v

$\therefore$ ideal volume $V_i = (V - v)$

Now v the volume to be excluded is directly proportional to the number of molecules (N) which in turn depends upon the number of moles (n).

Thus, $v \propto n$ or $v = nb$

where, b is constant of proportionality and is called van der Waal constant. Substituting the value of v, we get

Ideal volume, $(V_i) = (V - nb)$

Here, n = Number of moles of real gas

b = Constant which depends on nature of real gas.

Significance of constant 'b'. The constant '**b**' is called *co-volume* or *excluded volume per mol of a gas*. Its units are **litre mol^{-1}.** It is a measure of effective size of gas molecules. The value of **b** is *four times* the actual volume of the molecules (*Refer solution of VSAQ. 17 of Study Questions).*

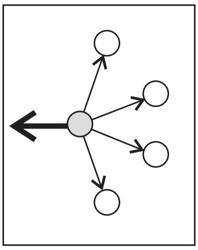


Fig. 2.13. Molecule striking the wall experiences inward pull.

(*b*) **Pressure correction.** The pressure of the gas is due to the force with which molecules of the gas collide with the walls of the container. Since the intermolecular attractions cannot be neglected at low temperatures and high pressures. Therefore the molecules which are going to strike the walls experience some backward drag due to inward pull of adjacent molecules as shown in the diagram. As a result, the molecules strike the walls with a smaller force because of the *inward pull*. Consequently, the pressure that we observe (P) is relatively smaller than the pressure if there were no attractive forces. In other words, *the observed pressure* (p) *is smaller than the ideal pressure* (p_i). Thus, in order to get the ideal pressure (p_i) some correction term has to be added to the observed pressure (p).

Let the correction terms be p'

$\therefore$ Ideal pressure $p_i = (p + p')$

Now, p is directly proportional to the square of the density or square of (n/V)

Thus, $$p' \propto (n/V)^2$$
$$= a\, n^2/V^2$$

where, a is constant of proportionality called another van der Waal constant.

Hence, ideal pressure (p_i) = $\left(p + \dfrac{an^2}{V^2}\right)$

Here, n = Number of moles of real gas
V = Volume of the gas
a = A constant, whose value depends upon the nature of the gas.

Significance of 'a'. The value of constant '**a**' gives the idea of the magnitude of attractive forces between the molecules of the gas. Its units are **atm L^2 mol^{-2} or bar L^2 mol^{-2}.** Larger the value of **a,** larger will be the intermolecular attraction among the gas molecules.

Substituting the values of ideal volume and ideal pressure, the modified equation is obtained as

$$\left(\mathbf{p} + \frac{\mathbf{an^2}}{\mathbf{V^2}}\right)(\mathbf{V} - \mathbf{nb}) = \mathbf{nRT} \qquad \ldots(2.8)$$

The constants a and b are also called **van der Waal constants.**

It may be noted that gases show *positive deviations* ($Z > 1$) when *effect of molecular volume dominates*. Similarly, *negative deviations* ($Z < 1$) are shown when the *effect of molecular attraction predominates*.

van der Waal constants for some gases are given in Table 2.4.

Table 2.4. van der Waal Constants for Some Gases

Gas	*a* *(atm L^2 mol^{-2})*	*b* *(L mol^{-1})*	*Gas*	*a* *atm L^2 mol^{-2})*	*b* *(L mol^{-1})*
He	0.034	0.0236	CO_2	3.6	0.043
H_2	0.0245	0.0267	HCl	3.8	0.041
O_2	1.36	0.0318	NH_3	4.0	0.036
N_2	1.37	0.0391	SO_2	6.7	0.056

Difference between Ideal Gas and Real Gas

The main differences between ideal gas and real gas are given below in tabular form.

Ideal Gas	*Real Gas*
1. Ideal gas obeys all the gas laws at all temperature and pressures.	1. It obeys gas law only at very low pressures and high temperatures.
2. Volume of molecules is negligible as compared to total volume of gas.	2. Volume of molecules is not negligible.
3. Attractive forces among the molecules do not exist.	3. Attractive forces among the molecules do exist particularly high pressures and low temperatures.
4. It obeys the equation of state $pV = nRT$.	4. It obeys van der Waal equation $(p + an^2/V^2)(V - nb) = nRT$.
5. It is hypothetical.	5. All existing gases are real.

Example 2.5. *Calculate the pressure exerted by 8.5 g of ammonia (NH_3) contained in 0.5 L vessel at 300 K. For ammonia a = 4.0 atm L^2 mol^{-2}, b = 0.036 L mol^{-1}. Compare the value with the calculated value if the gas were considered as ideal.*

Solution. Number of moles of ammonia

$$n = \frac{8.5}{17} = 0.5 \text{ mols}$$

According to van der Waal's equation,

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

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

$$= \frac{0.5 \times 0.082 \times 300}{(0.5 \times 0.5 \times 0.036)} = \frac{4(0.5)^2}{(0.5)^2}$$

$$= \mathbf{21.51 \text{ atm.}}$$

If the gas were considered ideal, then the value of pressure (p) can be obtained by using ideal gas equation as

$$p = \frac{nRT}{V} = \frac{0.5 \times 0.82 \times 300}{0.5} = \mathbf{24.6 \text{ atm.}}$$

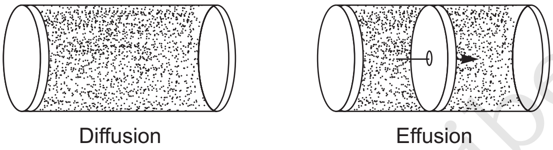
2.9. EFFUSION AND DIFFUSION

Gas molecules move almost freely in the space available to them. When a gas contained in a container is allowed to come out of a hole, the process is called **effusion**. Rate of effusion depends upon the difference in pressure inside and outside of the container and mass of the gas molecules as a result of which lighter gases effuse with more speed and heavier gases effuse with less speed.

Gas molecules travel freely and collide with other molecules and hence travel in many different directions until they occupy the available space uniformly. This process is called **diffusion**. In diffusion molecules move from high concentration to low concentration of molecules. When a bottle of perfume is opened in one corner of a room, perfume molecules move and spread in the room evenly making perfume smell available throughout the room.

Effusion. Effusion is the process in which a gas escapes from a container through a whole of diameter considerably smaller than the mean free path of molecules. The gas effuses out of the balloon overtime.

Molecules move randomly and collide with other molecules consistently. The average distance travelled by a molecule between two collisions is known as **mean free path** of that particle. Nitrogen gas has a greater rate of effusion than oxygen because lighter gases travel faster than heavier and dense gases. Denser the gas, the shorter the mean free path. When density decreases the mean free path become longer as frequency of collision is less.



Diffusion

Effusion

Fig. 2.14

Diffusion: Diffusion is the gradual mixing of gases due to persistent movement of particles without any mechanical effort like stirring. Molecules keep on moving till mixing is done uniformly. Diffusion takes place in liquids and solids also but to a lesser extent.

Graham's Law

Graham's law states that the ratio of the effusion and diffusion rates of two gases is the square root of the inverse ratio of their molar masses.

Rate of effusion or diffusion $\alpha \dfrac{1}{\sqrt{M}}$

$$\frac{\text{Rate of effusion A}}{\text{Rate of diffusion B}} = \sqrt{\frac{M_B}{M_a}}$$

Hydrogen will effuse or diffuse more rapidly than helium as hydrogen has less molecular mass hence less dense. According to Graham's law all gases at same temperature have same kinetic energy. The kinetic energy of two gases with different molar masses will be

$$kE = \frac{1}{2}\frac{M_A}{N_A} V^2_{rms\ A} = \frac{1}{2}\frac{M_B}{N_B} V^2_{rms\ B}$$

Multiply both sides by 2 and rearrange

$$\frac{V^2_{rmv}\ B}{V^2_{rmv}\ A} = \frac{M_A}{M_B}$$

Take square root of both sides.

$$\frac{V_{rmv}\ B}{V_{rmv}\ A} = \sqrt{\frac{M_A}{M_B}}$$

Hence, the rate of effusion or diffusion of molecules is directly related to the speed of molecules. Graham's law shows that gaseous molecules have same average kinetic energy at same temperature.

Use of Diffusion in Enrichment of Uranium

Uranium which is used in nuclear power plants, and weapons is enriched using the process of gaseous diffusion. The uranium occuring naturally contain about 0.72% of ^{235}U. This kind of uranium is capable of sustaining nuclear fission chain reaction hence is "fissile". In nuclear reactors 2–5% ^{235}U is used and even ^{235}U with even more concentration is used in nuclear bombs. In order to enrich uranium to the desired level advantage of Graham's law is taken. In uranium enrichment plant UF_6 (the passed uranium compound that is volatile enough to work) is slowly through large cylindrical vessels called diffusers, which contain porous barriers with microscopic holes. The process used here is gaseous diffusion. The ^{235}UF have little higher average speed and diffuse through the barrier a little faster than $^{238}UF_6$ molecules. The gas after passing through the diffuser is slightly enriched in ^{235}UF and the residual gas is slightly depleted. There is a small difference is molecular masses of $^{235}UF_6$ and $^{238}UF_6$, hence about 0.4% enrichment is done in one diffuser. But by connecting many diffusers in a series (called a cascade), the desired level of enriched ^{235}UF can be obtained. This process was first used in World War II during development of first atom bomb. In this process barrier (diffuser) have tiny and uniform holes of about 10^{-6} cm in diameter were used.

Difference between Effusion and Diffusion

Effusion	*Diffusion*
1. Effusion happens when the gaseous molecules tend to escape through a pin hole of a container to the vacuum.	1. Diffusion happens when one gas tries to mix with another by random motion which result in collision between gas molecules.
2. Effusion is the ability of a gas to pass through microscopic hole.	2. Diffusion is the ability of a gases to mix, with each other evenly and uniformly in the absence of a barrier.
3. During effusion the diameter of the hole is much smaller than mean free path of the molecules.	3. The rate of diffusion depends up on the size and the kinetic energy of molecules.

4. Effusion takes place when there is difference in pressure inside and outside the container.	4. Diffusion takes place when there is a difference in concentration between to points.

Is the Rate of Effusion and Diffusion Same

Rate of diffusion depends upon surface area, difference in concentration between two points, travelling distance, and the time which is inversely proportional.

Rate of effusion depends up on size of the hole, density of the gas, and size of the molecules. Hence rate of effusion and diffusion are not equal but their ratios are same.

2.10. CHEMISTRY IN ATMOSPHERE

Chemistry in atmosphere is about chemical process which go on within earth's atmosphere. Researches in this area are critical to the improved understanding of climate forcing, air quality and interaction between atmosphere and biosphere. This field is rapidly evolving due to advances in fundamental understanding of chemical processes in the atmosphere. This involves the chemical composition of natural atmosphere and the way gases, liquids and solids in the atmosphere interact with each other and with the earth's surface and associated biota and how human activities change the chemical and physical characteristics of atmosphere. Atmosphere, for convenience is considered as composed of four layers on the basis of temperature variation as the altitude increases. The four layers according to the variation of temperature are

1. Thermosphere or Ionosphere
2. Mesosphere
3. Stratosphere
4. Troposphere

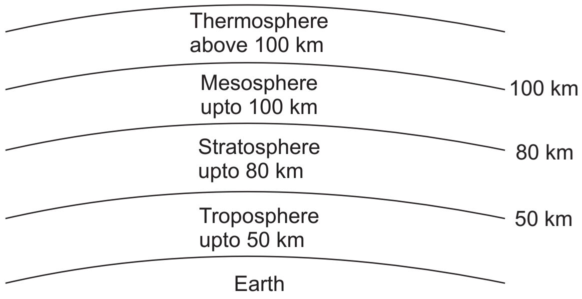


Fig. 2.15

As we go up temperature increases on increase of altitude. Temperature increases from 200 K to 500 K when we go up from 100 km to 300 km. At an altitude from 100–200 km gases are present in the form of biatomic molecules like O_2, N_2, NO etc. but at altitude higher than 200 km gases and present in atomic form H, He and O etc. The thermosphere or ionosphere is full of electrically charged ions. The ultra violet rays ionize these gases to form ions.

The reactions which take place in ionosphere are

$$O + h\nu \longrightarrow O^+ + e^-$$
$$N + h\nu \longrightarrow N^+ + e^-$$

The reactions which take place in neutral thermosphere

$$N + O_2 \longrightarrow NO + O$$
$$N + NO \longrightarrow N_2 + O$$
$$O + O \longrightarrow O_2$$

Thermosphere: Thermosphere is the outer layer of atmosphere which ranges from altitude above 100 km. Lower layer of thermosphere is neutral thermosphere or ionosphere. Above that is exosphere. These layers are favorites for space explorations, environmental studies and space sciences. Atmosphere in the outer space is more like a plasma than a gas.

Mesosphere: Mesosphere lies below thermosphere and ranges from 50 km-100 km altitude. In mesosphere temperature decreases as altitude increases. In mesosphere O_2, O_3, OH, H and NO are prominently available. The reactions which take place in mesosphere are

$$H_2O + h\nu \longrightarrow OH + H.$$
$$H_2O_2 + O \longrightarrow OH + OH$$

Stratosphere: Stratosphere is the layer below mesosphere. In stratosphere the altitude increases from 10 km-50 km. Reactions which take place in stratosphere are

$$NO_2 \longrightarrow NO + O$$
$$N_2O \longrightarrow N_2 + O$$
$$H_2 + O \longrightarrow OH + H$$
$$CH_4 + O \longrightarrow OH + CH_3$$

Upper stratosphere has a high concentration of ozone forming an ozone layer. In stratosphere air flows horizontally. Ozone layer absorbs ultraviolet rays coming from sun. Ozone is produced in stratosphere according to following reaction

$$O_2 + h\nu \rightarrow O + O$$
$$O_2 + O \rightarrow O_3$$

Weather takes place in troposphere. It is the region where air flows. The air pressure at sea level is 1 atmosphere while at the top of the troposphere it is only 0.1 atmosphere (10% of air pressure at sea level).

Tropopause is the thin buffer zone between the troposphere and the next layer (stratosphere).

Composition of Air in Stratosphere

N_2 – 78%
O_2 – 21%
Ar – 1%
CO_2 – 0.3% approx.
CH_4, H_2O, NO_2, N_2O, CO and O_3 – Variable amounts

Pollutants in the atmosphere

Atmosphere is polluted by different gases thrown in the atmosphere by industries.

Following gases pollute the atmosphere

- Nitrogen oxides such as NO, N_2O_4, NO_2 due to production of NO in engines during to internal combustion.
- Carbon dioxide produced by burning of fuel containing carbon.
- Carbon monoxide, a very toxic gas produced by automobiles.
- Ozone is produced by internal combustion engines and also formed in the ozone layer as explained earlier.
- SO_2 produced in mines and by combustion of sulphur containing fuel. SO_2 when reacts with water in the atmosphere producer H_2SO_4 and H_2SO_4 and cause **acid rains**.
- Chlorofluorocarbon (CFC) gases are used as refrigerant cause ozone layer to decrease.
- Water vapours are produced in atmosphere due to radiations from sun. Water vapours when condenses cause rains, storms, cyclones etc.

SUMMARY

- **Gas Laws.** The generalisations regarding the behaviour of gases.
- **Boyle's Law.** The volume of a fixed mass of a gas is inversely proportional to the pressure at constant temperature.
- **Charle's Law.** The volume of fixed mass of a gas is directly proportional to the temperature (in Kelvin scale) at constant pressure.
- **Gay Lussac's Law.** The pressure of fixed mass of a gas at constant volume is directly proportional to its temperature in Kelvin.
- **Avogadro's Law.** Under similar conditions equal volumes of various gases contain equal number of molecules.
- **Dalton's Law.** The pressure of the mixture of non-reacting gases is equal to the sum of their partial pressure when enclosed in the same volume under similar conditions.
- **Graham's Law of Diffusion.** The rate of diffusion of gases (V/*t*) is inversely proportional to square root of their densities under similar conditions.

EVALUATION

I. Multiple Choice Questions

1. The ratio of root mean square speed of hydrogen at 50 K and that of oxygen at 800 K is:

(a) 0.25 (b) 4

(c) 2 (d) 1

2. Which of the following sets consists of gases with same rate of diffusion?

(a) H_2, D_2, He (b) CO_2, NO_2, C_3H_8

(c) CO_2, N_2O, C_3H_8 (d) N_2, CO_2, C_2H_4.

3. The rate of diffusion of methane is twice that of X. The molecular mass of X is

(a) 64.0 (b) 32.0

(c) 40 (d) 80.

4. At what temperature, the rate of effusion of N_2 would be 1.625 times that of SO_2 at 50°C?

(a) 110 K (b) 173 K

(c) 373 K (d) 273 K.

5. The average K.E. of an ideal gas per molecule in S.I. units at 25°C will be

(a) 61.7×10^{-21} J (b) 6.17×10^{-21} J

(c) 6.17×10^{-20} J (d) 7.16×10^{-20} J

6. The density of chlorine relative to air is

(a) 2.46 (b) 3

(c) 4 (d) 5.1

7. Which of the following is not an assumption of the kinetic theory of gases?

(a) Gas particles have negligible volume

(b) Collisious of gas particles are perfectly elastic

(c) At high pressure, gas particles are difficult to compress

(d) A gas consists of many identical particles which are in continual motion.

8. When does a gas deviate the most from its ideal behaviour?

(a) At low pressure and low temperature

(b) At low pressure and high temperature

(c) At high pressure and high temperature

(d) At high pressure and low temperature

9. The root mean square velocity (rms) of N_2 molecules at certain temperature is u. If temperature is doubled and all the nitrogen molecules dissociate into nitrogen atoms, then the new rms will be:

(a) 14 u (b) 2 u

(c) $u/2$ (d) 4 u

10. Among the following, the incorrect statement is:

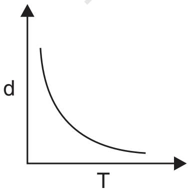
(a) At low pressures real gases show ideal behaviour.

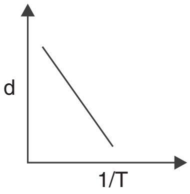
(b) At very low temperatures real gases show ideal behaviour

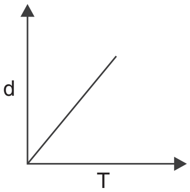
(c) At very large volume real gases show ideal behaviour

(d) At Boyle's temperature, real show should ideal behaviour.

11. Which of the following graph is correct for ideal gas?

(a)


(b)


(c)


(d) None of these

II. Descriptive Questions

1. Explain the concept of root mean square velocity.
2. What is the difference between effusion and diffusion?
3. Which are the four layers of atmosphere?
4. What do you understand by tropopause?
5. What is the composition of air in stratosphere?
6. What is the difference between ideal gas and real gas?
7. Explain the important features of Maxwell's distribution curve.
8. Is the rate of effusion and diffusion same?

III. Numerical Questions

1. Reading of mercury level in closed end arm of a manometer is 100 mm and in the arm attached to the system is 70 mm. What is the pressure of system? (**Ans.** 30 mm Hg.)
2. 200 cm^3 of a gas at 800 mn pressure is allowed to expand till the pressure is 0.9 atm keeping the temperature constant. Calculate the volume of gas. (**Ans.** 233.92 cm^3)
3. A gas occupies 100.0 mL at 50°C and 1 atm pressure. The gas is cooled to reduce volume to 50.0 mL at constant pressure. What will be the final temperature? (**Ans.** –111.57°C)
4. Calculate the pressure exerted by 56 g of an ideal gas (with molar mass 80 g mol^{-1}) enclosed in a vessel of volume 0.1 m^3 at 300 k. ($R = 8.314$ Nm mol^{-1} k^{-1}) (**Ans.** 49884 Nm^{-2})
5. A gaseous mixture containing 8 g of O_2 and 227 mL of N_2 at STP is enclosed in a flask of 5 L capacity at 0°C. Find the partial pressure of each gas and also calculate the total pressure in the vessel.
   (**Ans.** Total P = 1.16 atm, PO_2 = 1.115 atm PN_2 = 0.044 atm)