



# 4

## GASES



After completing this lesson, you will be able to:

This is 10 days lesson  
(period including homework)

- List the postulates of Kinetic Molecular Theory.
- State the values of standard temperature and pressure (STP). Relate
- Define pressure and give its various units.
- Explain the significance of absolute zero, giving its value in degree Celsius and Kelvin.
- State and explain the significance of Avogadro's Law.
- Derive Ideal Gas Equation using Boyle's, Charles' and Avogadro's law.
- Explain the significance and different units of ideal gas constant.
- Distinguish between real and ideal gases.
- Derive new form of Gas Equation with volume and pressure corrections for real gases.
- State and use Graham's Law of Diffusion.
- State and use Dalton's Law of Partial Pressures.
- Explain Lind's method for the liquefaction of gases.
- Define and explain plasma formation.
- Describe the motion of particles of a gas according to Kinetic Theory.
- Related temperature to the average kinetic energy of the particles in a substance
- Use Kinetic Theory to explain gas pressure.
- Describe the effect of change in pressure on the volume of gas.
- Describe the effect of change in temperature on the volume of gas.
- Define and describe the properties of Plasma
- Describe some of the implications of the Kinetic Molecular Theory, such as the velocity of molecules and Graham's Law.
- Explain why real gases deviate from the gas laws.

### INTRODUCTION

Matter consists of three fundamental states, the gas, liquid and solid. Besides these three states, the fourth one is Plasma state (a partially ionised gas at very high temperature).

The word gas is derived from chaos. This is because the gaseous particles have chaotic (random) motion. The molecules travel in a straight line until they collide with each other or with the walls of the container. This type of motion of the molecules is called **Brownian Movement** (Robert Brown 1827).

A gas at a given temperature has neither a definite shape nor a definite volume. It will



take up the shape of any container into which it is placed.

All gases diffuse to fill the space available to them. The rates of diffusion are different for different gases. When diffusion takes place between a liquid and a gas, it is known as "intimate mixing".

The earth's atmosphere is a mixture of gases. Oxygen (21%) and Nitrogen (78%) are its two major components, both support life. In fact, the earth's atmosphere is an immense system of gases where many chemical reactions occur. For example, photo-synthesis, combustion etc. Natural gas, the major component of which is methane, is used to heat homes in winter, to cook food and to drive vehicles etc.

### 4.1 KINETIC MOLECULAR THEORY OF GASES

The behaviour and properties of gases can be theoretically explained using the kinetic molecular theory. This theory is a model that explains the behaviour of gases using generalization about random moving molecules within a gas.

The kinetic molecular theory was first postulated by Daniel Bernoulli, a Swiss mathematician. The Kinetic theory of gases was elaborated and extended by a number of well-known physicist such as James Maxwell (1859) and Boltzmann in (1870). In 1857, Clausius derived the kinetic equation and deduced all the gas laws from it.

Physical theories are often given in terms of postulates, the basic statements from which all conclusions or prediction of theory is deduced.

#### 4.1.1 Postulates of Kinetic Theory

The kinetic molecular theory of gases is based upon the following postulates:

1. Gases are considered to be composed of minute discrete particles called molecules.
2. The molecules move randomly in straight lines until they collide with one another or with the walls of container.
3. The collisions among the molecules are perfectly elastic i.e. the total kinetic energy remains constant.
4. The molecules of a gas are thought to be of the same mass and size but are different from gas to gas.
5. The pressure is produced due to the collisions of the molecules.
6. The average kinetic energy of a molecule is directly proportional to the absolute temperature. It means that the higher the temperature, greater will be the molecular kinetic energy.
7. At relatively low pressure, the average distances between molecules are large as compared with molecular diameters.
8. There are no attractive or repulsive forces between the molecules.
9. The volume occupied by the molecules is negligible as compared to the total volume of the container.

R.J. Clausius deduced an equation for the pressure of an ideal gas from the postulates of kinetic theory. This equation is called **kinetic equation**.

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

Where P = Pressure  
 V = Volume  
 m = mass of one molecule of the gas  
 N = number of particles of the gas  
 $c^2$  = mean square velocity of gas molecules

Since the molecules of a gas under the given conditions do not have the same velocity, so mean square velocity is considered. If  $n_1$  molecules have velocity  $c_1$ ,  $n_2$  molecules have velocity  $c_2$  etc, then

$$c^2 = \frac{n_1 c_1^2 + n_2 c_2^2 + \dots}{n_1 + n_2 + \dots}$$

Where  $c^2$  is the average of squares of all the possible velocities. The square root of  $c^2$  is called root mean square velocity ( $c_{rms}$ ).

#### 4.1.1.3 Kinetic Energy of Particles in a Gas

According to the kinetic molecular theory, the gaseous molecules are always in a state of haphazard motion. As a result due to their motion, they will have certain kinetic energy. The increase or decrease of temperature will increase or decrease their motion. In gases, the molecular motion is of three types:

- i. Translational Motion.
- ii. Rotational Motion.
- iii. Vibrational Motion.

A mono atomic molecule (e.g. He) will show only translational motion while a diatomic ( $H_2$ ) and polyatomic molecules ( $CO_2$ ,  $NH_3$  etc.) will undergo, in addition to translational motion, the rotational and vibrational motions too.

##### i. Translational Motion:

The motion imparted to the gaseous molecules due to their motion in all possible directions is called translational motion and the energy as kinetic translation energy. In this case the entire molecules move from place to place.

##### ii. Rotational Motion:

The motion imparted to the gaseous molecules as a result of net angular momentum about their centre of gravity is called rotational motion and the energy as kinetic rotational energy. In this case the molecule spins like a propeller.

##### iii. Vibrational Motion:

The motion imparted to the gaseous molecules due to the oscillations is called vibrational motion and the energy as kinetic vibrational energy. In this case the molecules vibrate back and forth about the same fixed location.

In such an oscillating system, there is a continuous interchange between vibrational kinetic energies and potential energies. As a result both K.E and P.E is possessed by the gaseous molecules. Thus, Total E(Vib.) = K.E (Vib.) + P.E (Vib.)

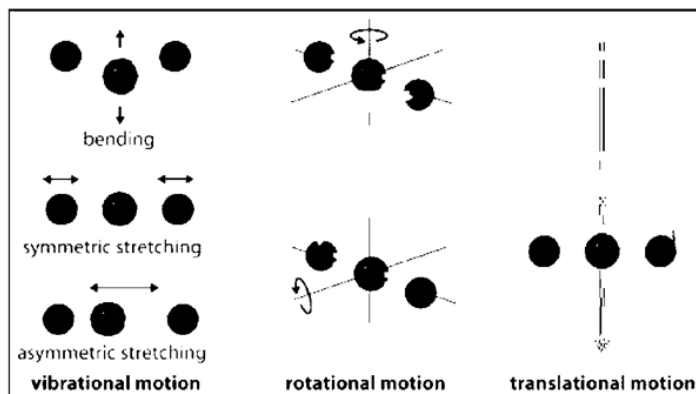


Figure 4.4: Different motions of molecules

The vibrational motions in polyatomic molecules (like  $\text{CO}_2$ ,  $\text{NH}_3$  etc.) are quite complicated.

## 4.2 ABSOLUTE TEMPERATURE SCALE ON THE BASIS OF CHARLE'S LAW

The Charle's Law states that the volume of a given mass of a gas increases or decreases by  $1/273$  times of its original volume at  $0^\circ\text{C}$  and reduces to zero at  $-273.15^\circ\text{C}$ . Actually at this temperature a gas does not remain in gaseous state but changes into the liquid or a solid.

Lord Kelvin (1824-1907) succeeded in measuring temperature of the gas with the help of a new scale called the Absolute Kelvin temperature scale or the Kelvin temperature scale. According to this scale,  $-273.15^\circ\text{C}$  is the starting point of the scale. On comparing with the Celsius scale, (which starts with  $0^\circ\text{C}$ ), the two scales are related as

$$K = ^\circ\text{C} + 273$$

Example 4.1

Convert the following Celsius temperatures to Kelvin temperatures:

- (a)  $-132^\circ\text{C}$  (b)  $96^\circ\text{C}$  (c)  $0^\circ\text{C}$  (d)  $-12^\circ\text{C}$  (e)  $148^\circ\text{C}$

**Solution**

Using the formula:  $K = ^\circ\text{C} + 273$

- (a)  $K = -132 + 273 = 141 \text{ K}$  (b)  $K = 96^\circ\text{C} + 273 = 369 \text{ K}$   
 (c)  $K = 0^\circ\text{C} + 273 = 273 \text{ K}$  (d)  $K = -12^\circ\text{C} + 273 = 261 \text{ K}$   
 (e)  $K = 148^\circ\text{C} + 273 = 421 \text{ K}$

Example 4.2

Convert the following Kelvin temperatures to Celsius degree centigrade temperatures.

- (a) 340 K (b) 200 K (c) 10K (d) 405 K

**Solution:**

Using the formula:  $t^\circ\text{C} = K - 273$

- (a)  $t^\circ\text{C} = 340 - 273 = 67^\circ\text{C}$  (b)  $t^\circ\text{C} = 200 - 273 = -73^\circ\text{C}$   
 (c)  $t^\circ\text{C} = 10 - 273 = -263^\circ\text{C}$  (d)  $t^\circ\text{C} = 405 - 273 = 132^\circ\text{C}$

### 4.2.1 Kinetic Energy of Gases: Derivation of the Average Kinetic Energy of Molecules in a Gas

The temperature of a gas depends upon kinetic energy of the molecules. The increase of temperature increases the average kinetic energy of the molecules and vice versa.

#### Derivation of relationship between Kinetic Energy and Temperature

The average kinetic energy of the gaseous molecules is re-distributed with rise or fall of temperature. It can be explained with the help of kinetic equation of gases.

According to kinetic equation of gases,

$$PV = \frac{1}{3} m N \overline{c^2} \quad \dots\dots\dots (1)$$

and  $K.E = \frac{1}{2} m \overline{c^2}$  \dots\dots\dots (2)

Again we consider  $PV = \frac{1}{3} m N \overline{c^2}$

$$= \frac{2}{3} N \left( \frac{1}{2} m \overline{c^2} \right)$$

$$= \frac{2}{3} N (K.E) \quad \dots\dots\dots (3)$$

Now consider one mole of gas. It will possess Avogadro's number ( $N_A$ ) of molecules,

Then  $N = N_A$

Therefore  $PV = \frac{2}{3} N_A (K.E)$  \dots\dots\dots (4)

According to the General Gas Equation

$$PV = nRT \quad \dots\dots\dots (5)$$

For one mole of a gas,  $n = 1$  then  $PV = RT$

Comparing equations (4) & (5) we get,

$$\frac{2}{3} N_A (K.E) = RT \quad \dots\dots\dots (6)$$

$$2N_A (K.E) = 3RT$$

$$K.E = \frac{3RT}{2N_A}$$

$$K.E = kT, \text{ where } \frac{3R}{2N_A} = k, \text{ a constant quantity.}$$

or  $K.E \propto T$

#### Conclusion

The Kelvin Temperature of a gas is actually the measure of average translational K.E of its molecules.

In gases and liquids, the temperature explains the average translational energy of the molecules. In solids where molecules cannot move freely, temperature becomes a measure of vibrational K.E.

### 4.2.2 The Pressure of a Gas: Kinetic Molecular Theory

According to the Kinetic molecular theory, gas molecules are in constant random motion. They move in straight line until they collide with another molecule or the walls of the container. The pressure of a gas in a container is due to the force exerted by its molecules on the walls of the container. The average kinetic energy of gas molecules is directly proportional to the Kelvin



temperature. So the average kinetic energy of a collision when a gas molecule collides with the walls of a container will not change at constant temperature.

#### Gaseous pressure and its various units

When a balloon is inflated, its walls expand. The balloon walls tend to collapse due to the squeezing of air trapped inside. However this must be counterbalanced by a force exerted by the trapped gas. This force is called Pressure.

So a **force being exerted over a unit area is called Pressure.**

So,  $P = \frac{F}{A}$  where P is measured in Pascal, Force in Newton and the area in  $m^2$ .

**A Pascal (Pa) is defined as the force of one Newton (N) spread over an area of  $1m^2$ .**

#### Units of Pressure:

##### SI Units:

SI unit for pressure is Pascal (Pa), in S.I. system, unit of force is Newton (N) and the unit of area is metre square ( $m^2$ ). Thus Pascal is one  $Nm^{-2}$ .

1 atm	= 101325Pa = 101325 $Nm^{-2}$
1 atm	= 14.7 Psi (Pounds per square inch)
1 atm	= 101.325 kPa
1atm	= 760 torr = 760mm of Hg
1 J	= 1Nm = $10^7$ ergs = $kgm^2s^{-2}$
1 Cal	= 4.18J
1 atm	= 1.01325 bar

#### Interconversion of Pressure in Pascals, Kilo Pascals and atmosphere

##### Example 4.3

Convert 10 Pascals into (i) Kilo Pascals (ii) atmosphere

##### Solution:

(i) One Kilo Pascal = 1000 Pascals  
or 1000 Pascals = one Kilo Pascal  
 $10 Pa = \frac{1}{1000} \times 10 = 0.01$  Kilo Pascal

(ii) One atmosphere = 101325 Pa  
or 101325 Pa = one atm  
 $10 Pa = \frac{1}{101325} \times 10 = 0.000098$  atm



#### Self Check Exercise 4.1

**Example:** Convert 35 Psi into (i) Pascal (ii) Kilo Pascal (iii) Atmosphere

#### 4.2 Boyle's Law: Relationship between Pressure and Volume of a Gas ( $P \propto \frac{1}{V}$ at $T = \text{const}$ )

In the middle of the 17<sup>th</sup> century, Robert Boyle (1627-1691) and his assistant Robert Hooke (1635-1702) made many investigations about the relationship between Pressure and Volume of a gas. In 1662, Robert Boyle reported that with increase in pressure on a gas, its volume

decreases. This was stated as Boyle's Law. **It states that the pressure of a fixed amount of a gas varies inversely with its volume, the temperature is maintained constant.**

Mathematically,  $P \propto \frac{1}{V}$  or  $P = k \times \frac{1}{V}$  where  $k$  is proportionality constant. The value of  $k$  is different for different amounts of the same gas.

Again  $P = k \times \frac{1}{V}$  or  $PV = k$ , thus the product of volume and Pressure remains constant provided the temperature is kept constant.

$$P_1 V_1 = k \quad (\text{For gas at pressure } P_1)$$

$$P_2 V_2 = k \quad (\text{For gas at pressure } P_2)$$

Therefore  $V_1 P_1 = V_2 P_2$  where  $V_1$  and  $P_1$  are initial volume and Pressure while  $P_2$  and  $V_2$  are their final Pressure and volume.

When the Pressure of a gas is plotted against volume at different temperatures, we get a family of curves as shown in the figure 4.7. Each curve is a hyperbola with different values of  $k$ . Each curve is known as Isotherm (constant temperature plot). As the temperature is increased, the Isotherm goes away from both the axis. This is because at higher temperature, the volume of the gas is increased.

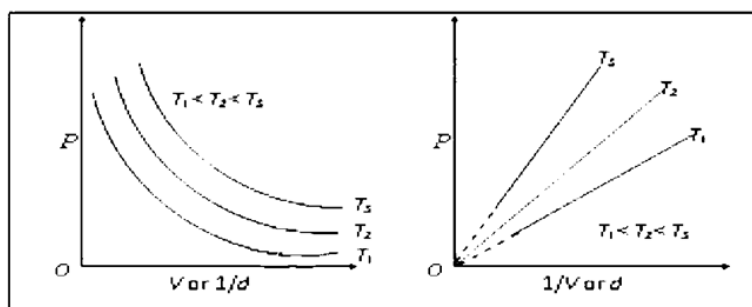


Figure 4.7: Graphical representation of different forms of Boyle's Law

#### Example 4.4

An ideal gas occupies a volume of  $0.300 \text{ dm}^3$  at a pressure of  $1.80 \times 10^5 \text{ Pa}$ . What is the volume of the gas maintained at the same temperature if the pressure is reduced to  $1.15 \times 10^5 \text{ Pa}$ .

#### Solution

$$V_1 = 0.300 \text{ dm}^3 \quad V_2 = ?$$

$$P_1 = 1.80 \times 10^5 \text{ Pa} \quad P_2 = 1.15 \times 10^5 \text{ Pa}$$

According to the Boyle's Law

$$V_1 P_1 = V_2 P_2$$

$$\text{or } V_2 = \frac{V_1 P_1}{P_2}$$

$$= \frac{0.300 \text{ dm}^3 \times 1.80 \times 10^5 \text{ Pa}}{1.15 \times 10^5 \text{ Pa}}$$

$$= \frac{0.300 \times 1.80}{1.15} \text{ dm}^3 = 0.469 \text{ dm}^3$$

Example 4.5

At sea level, where the pressure was 755 torr, the gas in a balloon occupied  $2\text{m}^3$ . What volume will the balloon expand when it has risen to an altitude where the pressure is

- (a) 100 torr (b) 10 torr temperature remains constant

Solution

(a)  $P_1 = 755\text{torr}$   $P_2 = 100\text{torr}$   
 $V_1 = 2\text{m}^3$   $V_2 = ?$

According to the Boyle's Law

$$V_1 P_1 = V_2 P_2$$

$$2\text{m}^3 \times 755\text{torr} = V_2 \times 100\text{torr}$$

or  $V_2 = \frac{2\text{m}^3 \times 755\text{torr}}{100\text{torr}}$

$$V_2 = \frac{2 \times 755}{100} \text{m}^3 = 15.10\text{m}^3$$

(b)  $V_1 = 2\text{m}^3$   $V_2 = ?$   
 $P_1 = 755\text{torr}$   $P_2 = 10\text{torr}$

According to the Boyle's law

$$V_1 P_1 = V_2 P_2$$

$$2\text{m}^3 \times 755\text{torr} = V_2 \times 10\text{torr}$$

or  $V_2 = \frac{2\text{m}^3 \times 755\text{torr}}{10\text{torr}}$   
 $= \frac{2 \times 755}{10} \text{m}^3 = 151\text{m}^3$



Self Check Exercise 4.2

$375\text{cm}^3$  of a given gas has a pressure of 770mm of Hg. What will be the volume if the pressure is reduced to 750mm of Hg? (Ans:  $385\text{cm}^3$ )

4.2.2 Effect of Change in Temperature on the Volume of a Gas (Charles's Law)

The thermal expansion of gases was studied by Jacques Charles (1746-1823). He derived the relationship between volume of a gas and temperature in 1787. This relationship is known as Charles's law. **It states that at constant pressure, the volume of a given mass of a gas varies linearly with the absolute temperature of the gas.** Charles's law can also be stated as "at constant pressure the volume of given mass of gas increases or decreases by  $\frac{1}{273}$  times of its original volume at  $0^\circ\text{C}$  for every  $1^\circ\text{C}$  rise or fall in temperature respectively."



From his preliminary investigations, Charles observed that the gases such as  $H_2$ ,  $CO_2$ ,  $O_2$  etc. expanded equally on heating from  $0^\circ C$  to  $80^\circ C$  at constant pressure.

#### Derivation of critical form of Law

Suppose the volume of a gas at  $0^\circ C = V_0$

$$\text{Volume at } 1^\circ C = V_0 + V_0 \frac{1}{273}$$

$$\text{Volume at } 2^\circ C = V_0 + V_0 \frac{2}{273}$$

$$\text{Volume at } t^\circ C = V_0 + V_0 \frac{t}{273}$$

$$V_t = V_0 \left[ 1 + \frac{t}{273} \right]$$

$$= V_0 \left[ \frac{273 + t}{273} \right]$$

Where  $t^\circ C + 273 = T$  (Absolute temperature)

$$= V_0 \left[ \frac{T}{273} \right]$$

$$V_t = \frac{V_0}{273} T$$

Thus the Law states that the volume of a definite quantity of a gas at constant pressure is directly proportional to the absolute temperature.

Again  $V \propto T$  or  $V = kT$ , where  $T$  is the temperature on absolute scale. Thus the temperature on degree centigrade or Celsius scale can be converted to the absolute scale or Kelvin scale (after the name lord Kelvin 1824-1907) by adding 273.15.

Thus  $K = t^\circ C + 273.15$

Now  $V = kT$  or  $\frac{V}{T} = k$

Thus the Law may also be defined as, "the ratio between volume and temperature is always a constant quantity."

$$\text{So } \frac{V_1}{T_1} = k \quad \text{and} \quad \frac{V_2}{T_2} = k$$

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

Where  $V_1$  and  $T_1$  are initial volume and absolute temperature.  $V_2$  and  $T_2$  are final volume and absolute temperature.

The equation for Charles's Law gives a straight line proved by plotting a graph between volume and temperature. Different straight lines are obtained with different pressures, which are a constant quantity. Each constant pressure line is called an "Isobar".

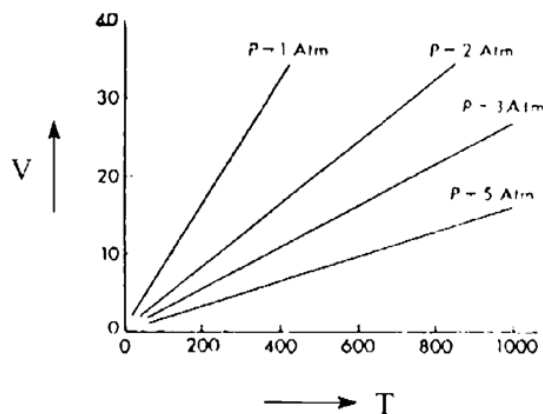


Figure 4.9: Graphical verification of Charles law

4.7 Charles's Law

According to critical definition of Charles's Law, at constant pressure, the volume of given mass of a gas increases or decreases by  $\frac{1}{273}$  of its original volume at 0°C by 1°C rise or fall of temperature, respectively.

Let the volume of an ideal gas at 0°C is  $V_0 \text{ cm}^3$

$$\text{Volume at } -1^\circ\text{C} = V_0 - \frac{1}{273} V_0$$

$$\text{Volume at } -273^\circ\text{C} = V_0 - \frac{273}{273} V_0 = 0$$

Thus exactly at  $-273^\circ\text{C}$ , the volume of a given mass of a gas reduces to zero. A graph between volume and temperature gives a straight line and cuts the temperature axis at  $-273.15^\circ\text{C}$ .

Thus the **hypothetical temperature at which the given volume of a gas reduces to zero is called Absolute zero**. For this reason a new temperature scale has been developed. This new scale is called Absolute or Kelvin scale. It starts from  $-273.15^\circ\text{C}$  which is marked as zero Kelvin.

$$-273.15^\circ\text{C} = \text{Zero Kelvin}$$

This is applicable for all other gases as well and is the lowest possible temperature in the gaseous state but actually it does not happen because all the gases liquify or solidify before they reach this temperature ( $-273.15^\circ\text{C}$ ). This temperature is considered as the lowest possible temperature.

Example 4.6

If  $50 \text{ cm}^3$  of a gas in a syringe at  $15^\circ\text{C}$  is heated to  $50^\circ\text{C}$  and the piston of syringe is allowed to move outwards against constant atmospheric pressure, calculate the new volume of the hot gas.

**Solution**

$$V_1 = 50 \text{ cm}^3 \quad V_2 = ?$$

$$T_1 = 15^\circ\text{C} + 273 = 288\text{K} \quad T_2 = 50^\circ\text{C} + 273 = 323\text{K}$$

According to Charles's Law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{or} \quad \frac{50 \text{ cm}^3}{288\text{K}} = \frac{V_2}{323} \quad \text{or} \quad V_2 = \frac{50 \times 323}{288} \times \frac{\text{cm}^3 \times \text{K}}{\text{K}}$$

$$= 56 \text{ cm}^3$$

Therefore the new volume of the hot gas =  $56 \text{ cm}^3$ .

Example 4.7

At  $17^\circ\text{C}$ , a sample of  $\text{H}_2$  gas occupies  $125 \text{ cm}^3$ . What would be the volume at  $100^\circ\text{C}$ ? (Pressure remains constant)

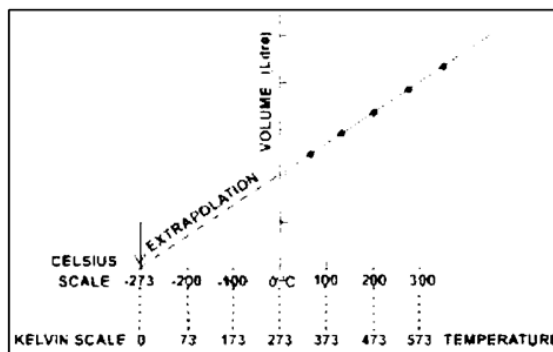


Figure 4.11: Effect of decrease of temp on a definite volume of a gas at constant pressure

**Solution**

$$V_1 = 125 \text{ cm}^3$$

$$T_1 = 17^\circ\text{C} + 273 \\ = 290 \text{ K}$$

$$V_2 = ?$$

$$T_2 = 100^\circ\text{C} + 273 \\ = 373 \text{ K}$$

According to Charles's Law

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

$$\frac{125 \text{ cm}^3}{290 \text{ K}} = \frac{V_2}{373 \text{ K}} \quad \text{or} \quad V_2 = \frac{125 \times 373 \text{ cm}^3 \times \cancel{\text{K}}}{290 \cancel{\text{K}}}$$

$$= 160.78 \text{ cm}^3$$

Thus the new volume will be  $160.78 \text{ cm}^3$

**Self Check Exercise 4.3**

A Volume-Temperature experiment which was performed on a sample of  $\text{H}_2$  gas produced the Charles's Law relationship  $V = 0.167T$  ( $V$  is in  $\text{dm}^3$ ). At what temperature in degree Celsius would this sample of gas occupy  $50 \text{ dm}^3$ , if the pressure remains constant? **(Ans:  $26.40^\circ\text{C}$ )**

**4.3 AVOGADRO'S LAW**

An Italian Physicist Amedes Avogadro (1776-1856) in 1811 proposed that a given volume of any gas at fixed temperature and pressure must contain the same number of independent units (particles). These particles may be atoms, molecules or both.

This means that if we take equal volumes of two gases at a fixed temperature and pressure, the number of molecules of both gases will always be the same. It means volume is directly proportional to the number of molecules, where  $v$  is volume of the gas and  $n$  are number of molecules, the independent entities.

**Avogadro's Law states that equal volumes of all gases at the same temperature and pressure must contain equal number of molecules.**

Mathematically  $V \propto n$  or  $V = K \times n$

**4.3.1 Avogadro's Number ( $6.022 \times 10^{23}$ )**

The exact number of particles (atoms, molecules) has been calculated in one mole of a substance with the help of spectrometer and may be called as Avogadro's number, after the name of Avogadro. It is numerically equal to  $6.022 \times 10^{23}$  particles per mole. It was confirmed by Joseph Loschmidt (1821-1895). In the case of mono-atomic gases, it should be  $6.022 \times 10^{23}$  atoms  $\text{mole}^{-1}$  and  $6.022 \times 10^{23}$  molecules  $\text{mole}^{-1}$  in the case of di- and poly-atomic molecules.

e.g. 1 mole of Hydrogen atom is equal to 1.008 g.

It contains  $6.022 \times 10^{23}$  atoms of hydrogen. However one mole of  $\text{H}_2$  gas having molecular mass as 2.016g will contain  $6.022 \times 10^{23}$  molecules.



Now it has been calculated that if we have one  $\text{dm}^3$  of  $\text{H}_2$ , its mass will be 0.09g at S.T.P.

$$\therefore 0.09\text{gH}_2 \text{ at S.T.P} = 1\text{dm}^3$$

$$2.016\text{gH}_2 \text{ (one mole) at S.T.P} = \frac{1}{0.09} \times 2.016\text{dm}^3 = 22.4\text{dm}^3$$

Thus 1gram molecule or one mole of  $\text{H}_2$  will have  $22.4\text{dm}^3$  at S.T.P. This volume of  $22.4\text{dm}^3$  at S.T.P is called Molar volume.

Generally one mole of any gas at S.T.P. occupies a volume of  $22.4\text{dm}^3$ . But one mole of the same gas will contain  $6.022 \times 10^{23}$  molecules. Other examples are as following:

$$1 \text{ mole of } \text{N}_2 \text{ (28 g) at S.T.P.} = 22.4\text{dm}^3 = 6.022 \times 10^{23} \text{ molecules}$$

$$1 \text{ mole of } \text{Cl}_2 \text{ (71 g) at S.T.P.} = 22.4\text{dm}^3 = 6.022 \times 10^{23} \text{ molecules}$$

$$1 \text{ mole of } \text{O}_2 \text{ (32 g) at S.T.P.} = 22.4\text{dm}^3 = 6.022 \times 10^{23} \text{ molecules}$$

$$1 \text{ mole of } \text{CO}_2 \text{ (44 g) at S.T.P.} = 22.4\text{dm}^3 = 6.022 \times 10^{23} \text{ molecules}$$

The standard temperature is  $0^\circ\text{C}$  and pressure is one atmosphere.

#### Example 4.8

Calculate the (i) number of molecules and atoms (ii) Number of mole (iii) Volume in  $\text{dm}^3$  of 10g of ammonia at S.T.P.

Solution:

#### (i) Number of molecules and atoms

According to Avogadro's Law, one mole of any gas at S.T.P. contains  $6.022 \times 10^{23}$  molecules in case of di-atomic and poly-atomic molecules. For example, in the case of ammonia one mole of it contains  $6.022 \times 10^{23}$  molecules.

$$\text{Now mass of } \text{NH}_3 = 10\text{g}$$

$$\text{Number of moles of } \text{NH}_3 = \frac{\text{mass}}{\text{molecular mass}} = \frac{10}{17} = 0.588 \text{ moles}$$

$$\text{One mole of } \text{NH}_3 \text{ at S.T.P.} = 6.022 \times 10^{23} \text{ molecules.}$$

$$\begin{aligned} 0.588 \text{ moles of } \text{NH}_3 \text{ at S.T.P.} &= 0.588 \times 6.022 \times 10^{23} \text{ molecules} \\ &= 3.54 \times 10^{23} \text{ molecules} \end{aligned}$$

$$\text{Now number of atoms} = \text{no of molecules} \times \text{atomicity (Number of atoms in one molecule of } \text{NH}_3)$$

$$= 3.54 \times 10^{23} \times 4$$

$$= 14.16 \times 10^{23} \text{ atoms}$$

#### (ii) Volume in $\text{dm}^3$

We know that

$$22.414\text{dm}^3 \text{ of any gas at S.T.P} = 1 \text{ mole}$$

$$22.414\text{dm}^3 \text{ of } \text{NH}_3 \text{ at S.T.P} = 17\text{g}$$

$$\text{or } 17\text{g } \text{NH}_3 = 22.4\text{dm}^3$$

$$10\text{g } \text{NH}_3 = \frac{22.414}{17} \times 10 = 13.184 \text{ dm}^3$$



#### Self Check Exercise 4.4

Calculate the number of molecules in (i) 1dm<sup>3</sup> of oxygen (ii) 2dm<sup>3</sup> of Hydrogen (iii) 2.5dm<sup>3</sup> of nitrogen All gases are at S.T.P.

(Ans: (i)  $2.7 \times 10^{22}$  (ii)  $5.4 \times 10^{22}$  (iii)  $6.75 \times 10^{22}$ )

### 4.4 IDEAL GAS EQUATION OR EQUATION OF STATE FOR AN IDEAL GAS

An equation that shows the effects of simultaneous changes in pressure and temperature on the volume of given amount of a gas is called ideal gas equation or equation of state for an ideal gas.

*What is the equation of state for an ideal gas?*

The ideal Gas Equation is a combination of three Laws:

1. Boyle's Law
2. Charles's Law
3. Avogadro's Law

Now according to Boyle's Law

$$V \propto \frac{1}{P} \quad (\text{at constant } \dots T \text{ and } n) \quad (1)$$

According to Charles's Law

$$V \propto T \quad (\text{at constant } \dots P \text{ and } n) \quad (2)$$

According to Avogadro's Law

$$V \propto n \quad (\text{at constant } \dots P \text{ and } T) \quad (3)$$

Where  $n$  is the number of moles of the gas.

Combining equations (1), (2) and (3), we get

$$V \propto \frac{1}{P} nT \quad V \propto \frac{nT}{P} \quad V = R \frac{nT}{P}$$

or

$$PV = nRT$$

Where  $R$  is a constant called general gas constant. This equation is called general gas equation or ideal gas equation.

If  $n = 1$  Then  $PV = RT$  or  $\frac{PV}{T} = R$

So  $\frac{P_1 V_1}{T_1} = R$  (For first condition of gas)

and  $\frac{P_2 V_2}{T_2} = R$  (For second condition of gas)

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



### 4.1.1 Standard temperature and pressure

Ideal gas equation enables us to calculate the effect of a change in temperature and pressure on the volume of a gas. One cannot compare volumes unless they are stated at the same temperature and pressure. Gas volumes are usually compared at 0°C (273K) and 1 atm. These conditions are referred to as standard temperature and pressure (STP).

#### Example 4.9

A certain mass of a gas occupies 1000 cm<sup>3</sup> at 57°C and 726 mm of Hg. What will be the volume at S.T.P?

#### Solution

$$\begin{array}{ll} V_1 = 1000 \text{ cm}^3 & V_2 = ? \\ P_1 = 726 \text{ mm of Hg} & P_2 = 760 \text{ mm of Hg} \\ T_1 = 57^\circ\text{C} + 273 & T_2 = 273\text{K} \\ = 330\text{K} & \end{array}$$

Now apply the general gas equation

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

$$\frac{726 \text{ mm of Hg} \times 1000 \text{ cm}^3}{330\text{K}} = \frac{760 \text{ mm of Hg} \times V_2}{273\text{K}}$$

$$V_2 = \frac{726 \text{ mm of Hg} \times 1000 \text{ cm}^3}{330\text{K}} \times \frac{273\text{K}}{760 \text{ mm of Hg}}$$

$$V_2 = \frac{726 \times 1000 \times 273}{330 \times 760} \frac{\text{mm of Hg} \times \text{cm}^3 \times \text{K}}{\text{K} \times \text{mm of Hg}}$$

$$V_2 = 790.3 \text{ cm}^3$$

So the volume of the gas at S.T.P = 790.3 cm<sup>3</sup>



#### Self Check Exercise 4.5

- Q.1** A given mass of a gas occupies 850 cm<sup>3</sup> at 320K and 0.92 × 10<sup>5</sup> Nm<sup>-2</sup> pressure. Calculate the new volume of the gas at S.T.P. (Ans: 658.410 cm<sup>3</sup>)
- Q.2** A container contains 2.5 m<sup>3</sup> of Helium gas at 15°C and 98 Nm<sup>-2</sup> pressures. What volume would this gas occupy at S.T.P? (Ans: 2.3 × 10<sup>-3</sup> m<sup>3</sup>)

### 4.4.3 Determination of Molecular Mass, Equilibrium and Diffusion of Gases

With the help of the Ideal Gas equation, we can determine:

- (a) Molecular mass of the gas. (b) Density of the gas.

(i) **Molecular Mass of the Gas:**

According to the general gas equation  $PV = nRT$  ..... (1)

But  $n$  (no of moles) =  $\frac{W}{M}$  Where  $W$  = mass of the gas  $M$  = molecular mass of the gas

Putting the value of  $n$  in equation-1

$$PV = \frac{W}{M} RT$$

$$MPV = WRT$$

$$\text{or } M = \frac{WRT}{PV}$$

So molecular mass ( $M$ ) can be calculated if  $P$ ,  $V$ ,  $W$  and  $T$  are known.

(ii) **Density of the gas ( $\text{g dm}^{-3}$ ):**

According to the General Gas Equation,  $PV = nRT$  ..... (1)

but  $n = \frac{W}{M}$ , Therefore  $PV = \frac{W}{M} RT$  or  $MP = \frac{W}{V} RT$

as  $\frac{W}{V} = d$  (density),

$$\text{so } MP = d RT$$

$$\text{or } d = \frac{MP}{RT} \text{ ..... (2)}$$

So knowing the values of  $P$ ,  $T$  and  $M$ , the density can be calculated.

**Calculation of  $R$ :**

The value of  $R$  can be calculated in different ways as shown below:

- (i) If one mole of a gas is taken at S.T.P (273 K, 1 atm), then the volume occupied by it is  $22.4 \text{ dm}^3$ . Now according to the general gas equation.

$$PV = nRT$$

Where  $V = 22.4 \text{ dm}^3$   $P = 1 \text{ atm}$   $n = 1 \text{ mole}$   $T = 273 \text{ K}$  Then  $R = ?$

From the equation

$$PV = nRT$$

$$R = \frac{PV}{nT} = \frac{22.4 \text{ dm}^3 \times 1 \text{ atm}}{1 \text{ mole} \times 273 \text{ K}}$$

$$R = \frac{22.4 \times 1}{1 \times 273} \text{ dm}^3 \times \text{atm mole}^{-1} \text{ K}^{-1}$$

$$R = 0.0821 \text{ dm}^3 \text{ atm mole}^{-1} \text{ K}^{-1}$$

- (ii) If pressure is measured in mm of Hg or torr and  $V$  in  $\text{cm}^3$  then

$$R = 0.0821 \text{ dm}^3 \times \text{atm mole}^{-1} \text{ K}^{-1}$$

$$= 0.0821 \text{ dm}^3 \times 760 \text{ mm of Hg mole}^{-1} \text{ K}^{-1}$$

$$= 62.4 \text{ dm}^3 \text{ mmHg mole}^{-1} \text{ K}^{-1}$$

$$= 62.4 \text{ dm}^3 \text{ torr mole}^{-1} \text{ K}^{-1} \text{ (one mm of Hg = one torr)}$$

$$= 62.4 \times 1000 \text{ cm}^3 \text{ torr mole}^{-1} \text{ K}^{-1}$$

$$= 62400 \text{ cm}^3 \text{ torr mole}^{-1} \text{ K}^{-1}$$

(iii) In SI Units, pressure is expressed in  $\text{Nm}^{-2}$  and volume in  $\text{m}^3$ , then

$$V = 0.0224\text{m}^3 \quad (1\text{dm}^3 = 10^{-3}\text{m}^3)$$

$$P = 101325\text{Nm}^{-2}$$

$$n = 1 \text{ mole}$$

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

$$R = ?$$

$$R = \frac{VP}{nT}$$

$$= \frac{0.0224\text{m}^3 \times 101325\text{Nm}^{-2}}{1\text{mole} \times 273\text{K}}$$

$$= \frac{0.0224 \times 101325}{1 \times 273} \text{m}^3 \text{Nm}^{-2} \text{mole}^{-1} \text{K}^{-1}$$

$$R = 8.3143 \text{ Nm mole}^{-1} \text{K}^{-1}$$

Now we know that  $1 \text{ Nm} = 1 \text{ J}$

$$\text{So, } R = 8.3143 \text{ J mole}^{-1} \text{K}^{-1}$$

Example 4.10

Calculate the average molar mass of air at sea level and  $0^\circ\text{C}$  if the density of air is  $1.29 \text{ kgm}^{-3}$ .

**Solution:**

At sea level the pressure may be taken equal to 1 atm or 101325 Pa. We know that

$$d = \frac{MP}{RT} \quad \text{or} \quad M \text{ (average molar mass)} = \frac{dRT}{P} \quad (1)$$

$$\text{Where } d = 1.29 \text{ kgm}^{-3}$$

$$R = 8.3143 \text{ Nm mole}^{-1} \text{K}^{-1}$$

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

$$P = 101325 \text{ Nm}^{-2}$$

Now putting the values of these in equation (1)

$$M = \frac{1.29 \text{ kgm}^{-3} \times 8.3143 \text{ Nm mole}^{-1} \text{K}^{-1} \times 273\text{K}}{101325 \text{ Nm}^{-2}}$$

$$= \frac{0.0289 \text{ kgm}^{-3} \times \text{Nm mole}^{-1} \text{K}^{-1} \text{K}}{\text{N.m}^{-2}}$$

$$M = 0.0289 \text{ kg mole}^{-1}$$

Example 4.11

A certain gas occupies a volume of  $6 \text{ dm}^3$  under a pressure of 720 mm of Hg at  $25^\circ\text{C}$ . What volume will this gas occupy under standard conditions of Temperature and Pressure (S.T.P)?



**Solution**

$$\begin{aligned}
 V_1 &= 6 \text{ dm}^3 & V_2 &= ? \\
 P_1 &= 720 \text{ mm} & P_2 &= 760 \text{ mm} \\
 T_1 &= 25^\circ\text{C} + 273 & T_2 &= 273 \text{ K} \\
 &= 298 \text{ K}
 \end{aligned}$$

According to the General Gas Equation

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

$$V_2 = \frac{720 \text{ mm} \times 6 \text{ dm}^3 \times 273 \text{ K}}{298 \text{ K} \times 760 \text{ mm}}$$

$$V_2 = 5.2 \text{ dm}^3$$

**Example 4.12**

Four grams of  $\text{CH}_4$  at  $27^\circ\text{C}$  and a pressure of  $2.5 \text{ atm}$  occupies a volume of  $2.46 \text{ dm}^3$ . Calculate the value of  $R$ .

**Solution**

$$\text{No of moles of } \text{CH}_4 = \frac{\text{Mass}}{\text{Molecular mass}}$$

$$n = \frac{4}{16} = 0.25 \text{ moles}$$

$$T = 27^\circ\text{C} + 273 = 300 \text{ K}$$

$$P = 2.5 \text{ atm}$$

$$V = 2.46 \text{ dm}^3$$

$$R = ?$$

According to the General Gas Equation,

$$VP = nRT$$

$$\text{or } R = \frac{VP}{nT} \quad \dots\dots\dots (1)$$

$$= \frac{2.46 \text{ dm}^3 \times 2.5 \text{ atm}}{0.25 \text{ mole} \times 300 \text{ K}}$$

$$R = 0.0821 \text{ dm}^3 \text{ atm mole}^{-1} \text{ K}^{-1}$$

**Example 4.13**

Find the density of ammonia gas at  $100^\circ\text{C}$  when confined by a pressure of  $1600 \text{ mm}$  of Hg.

**Solution**  $d = ?$

$$T = 100^{\circ}\text{C} + 273 = 373\text{K}$$

$$P = 1600 \text{ mm of Hg} = \frac{1600}{760} \text{ atm} = 2.105 \text{ atm}$$

$$M_{\text{NH}_3} = 17 \text{ g mole}^{-1}$$

$$R = 0.0821 \text{ dm}^3 \text{ atm mole}^{-1} \text{ K}^{-1}$$

Now according to the General Gas Equation,  
 $MP = dRT$  (Derived from General Gas Equation)

or  $d = \frac{MP}{RT} = \frac{17 \text{ g mole}^{-1} \times 2.105 \text{ atm}}{0.0821 \text{ dm}^3 \text{ atm mole}^{-1} \text{ K}^{-1} \times 373 \text{ K}}$

$$= \frac{17 \times 2.105}{0.0821 \times 373}$$

$$= 1.169 \text{ g dm}^{-3}$$

### 4.5 DEVIATION FROM IDEAL GAS BEHAVIOUR:

A gas which obeys the general gas equation ( $VP = nRT$ ) and all the gas laws especially Boyle's Law and Charles's Law is called an Ideal gas. No such gas is known. In reality no gas is ideal because they show deviations at low temperature and high pressure. The gases which do not obey general gas equation and all the gas laws strictly are called non-ideal gases. All known gases are found to be real under certain conditions.

*What happens when temperature is low and pressure is high?*

The following table shows the volumes of hydrogen gas at different pressures and at constant temperature. Do you think this data verifies Boyle's law?

Pressure (in atm)	Volume (in dm <sup>3</sup> )	PV
0.1	224.1	22.41
50	0.4634	23.71
1000	0.384	38.34

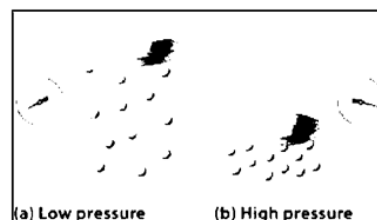
The result (PV) is quite different, temperature remains constant.

The real gases show deviation from ideal behaviour at low temperature and high pressure. Van der Waals attributed the deviation of real gases from ideal behaviour due to two **faulty assumptions** in kinetic molecule theory of gases.

- (i) **Inter molecular Forces of attraction:**  
There are no attractive or repulsive forces between the gas molecules.
- (ii) **Volume**  
The volume of the gas molecules is negligible as compared to the volume of the container.

**Explanation of deviations:**

- (i) **At lower temperature:**  
At high temperature the kinetic energy of the gaseous molecules is very high. As a result the attractive forces between them are negligible. But when temperature is



**Fig. 4.15:** Effect of pressure on volume of one mole of a gas

decreased, the kinetic energy of the molecules decreases. The intermolecular forces become significant. It means that the molecules come close to each other. At a certain very low temperature the gases change into the liquid state. Therefore attractive forces between the gas molecules become significant near liquefying temperature. That is why the ideal gases deviate from their original behaviour at low temperature e.g.  $\text{SO}_2$  liquefies at  $-10^\circ\text{C}$  while  $\text{H}_2$  at  $-252.7^\circ\text{C}$ . Therefore attractive forces between  $\text{SO}_2$  molecules cannot be considered negligible at room temperature. For this reason  $\text{SO}_2$  gas shows non-ideal behaviour at room temperature as compared to  $\text{H}_2$  gas.

(ii) **At high pressure**

At low pressure actual volume of gas molecules is very small as compared to the volume of the container. However, this volume does not remain negligible at high pressure. This can be understood from the following figure.

When pressure is one atm, individual volume of one mole of gas molecules say  $32\text{cm}^3$  is negligible as compared to the total volume of gas  $22400\text{cm}^3$ . But if it is subjected to a pressure of  $100\text{atm}$ , the volume of the gas is reduced to  $224\text{cm}^3$ . Under this pressure, individual volume of gas molecules ( $32\text{cm}^3$ ) is not negligible as compared a volume of the gas ( $224\text{cm}^3$ ).

**Graphical Representation**

For one mole of a gas, if a graph is plotted between  $\frac{PV}{RT}$  and pressure, then for an ideal gas, it must give a straight line (the temperature remains at  $0^\circ\text{C}$ ). But actually it is seen that the gases do not give a straight line. They deviate from their ideal behaviour as shown in the figure.

Actually, when the pressure is initially increased, it pushes the molecules closer and increases the intermolecular forces. Due to these forces, the volume of the gas shrinks more than that predicted from the gas laws. (i.e. Boyle's Law). This will decrease the value of  $\frac{PV}{RT}$ . That is why the gases do not show a straight line.  $\frac{PV}{RT}$  is called **compressibility**

**factor**. For ideal gases it should be one, whereas for real gases it is not equal to one.

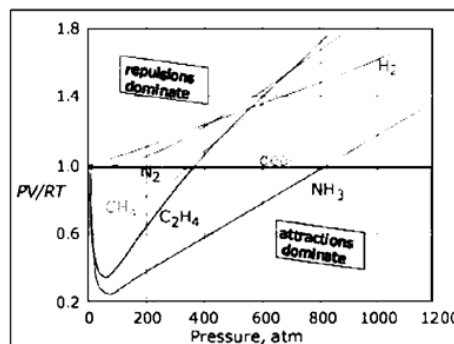


Fig. 4.16: Deviations from ideal behaviour

## 4.6 VAN DER WAALS EQUATION

### (CORRECTION FACTORS TO IDEAL GAS EQUATION)

The general gas equation is not applicable to real gases at all temperatures and pressures. In order to make it applicable to real gases, a Dutch Scientist Van der Waals in 1873 made correction in volume and pressure of the gases and derived an equation known as Van der Waals equation. Both those assumptions are not true at high pressure and low temperature.

**Volume Correction**

Van der waal thought that, when a gas is compressed the molecules are pushed so close together the repulsive forces operate between them. When pressure is further increased, it is opposed by the molecules themselves. This is because the molecules have definite volume, no doubt very small as compared to the volume of vessel, but it is not negligible. So Vander Waal's postulated that the actual volume of the molecules per mole of gas is represented by b, then the volume available to gas molecules is the volume of vessel minus the volume of gas molecules.

$$V = V_{\text{vessel}} - V_{\text{molecule}}$$

V is free volume

$$V_{\text{molecule}} = nb$$

where b is individual volume of one mole of the gas molecules and 'n' is total no. of moles of the gas molecules. It is interesting to note that b is not equal to the actual volume of gas. In fact it is four times the actual volume of molecules ( $b=4V_m$ )

So  $V = V_{\text{vessel}} - nb$  ..... (1)

**Pressure correction**

A molecule in the interior of a gas is attracted by other molecules on all sides, so these attractive forces are cancelled out. However, when a molecule is about to strike the walls of the container, it experiences a force of attraction towards the other molecules of the gas, so the molecules cannot hit the walls of the vessels with that much force with which they should have been hitting in the absence of these attractive forces.

It means that the pressure being observed on the walls of the vessels is a little bit lesser than the ideal pressure.

Therefore,  $P_{\text{observed}} = P_{\text{ideal}} - P_{\text{lessened}}$

If the ideal pressure is denoted by  $P_1$  and the pressure lessened due to molecular attractions is denoted by  $P'$  then

$$P_{\text{observed}} = P - P'$$

and  $P = P_{\text{observed}} + P'$

$P'$  is determined by the forces of attraction between molecules which are striking the walls of the container ( say type A) and molecules which are pulling them inward (say type B). The net force of attraction is proportional to the concentration of type A and type B molecules.

$$\therefore P' \propto C_A \cdot C_B$$

Let n is the number of moles of A and B type molecules separately and total volume of both types of molecules is V. So,

$$P' \propto \frac{n}{V} \cdot \frac{n}{V}, \quad P' = \frac{an^2}{V^2}$$

$$P' \propto \frac{n^2}{V^2}$$

Where 'a' is constant of proportionality and is called as co-efficient of attraction per unit volume. It has a constant value for a particular real gas.

$$P_1 = P + \frac{an^2}{V^2}$$

After the correction of volume and pressure,  $PV = nRT$  becomes

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

For 1 mole of gas,  $n = 1$ , then

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

This is the Van der Waals equation for an ideal gas.

#### Units of 'a'

$$\begin{aligned} \text{As } P' &= \frac{n^2 a}{V^2} \text{ or } a = \frac{P' V^2}{n^2} \\ &= \frac{\text{atm} \cdot (\text{dm}^3)^2}{\text{mole}^2} \\ &= \text{atm} \cdot \text{dm}^6 \text{ mole}^{-2} \end{aligned}$$

#### Units of 'b'

As  $b$  is incompressible volume per mole of a gas, its units should be  $\text{dm}^3 \text{ mole}^{-1}$

#### Van der Waals' Constants for Some Gases

Substance	a (dm <sup>6</sup> atm mole <sup>-2</sup> )	b (dm <sup>3</sup> mole <sup>-1</sup> )
H <sub>2</sub>	0.0247	0.0266
He	0.0034	0.0237
N <sub>2</sub>	0.1408	0.0391
O <sub>2</sub>	0.1378	0.0318
Cl <sub>2</sub>	0.6579	0.0562
Ar	0.1355	0.0322
Kr	0.2349	0.0398
CO	0.1505	0.0399
NO	0.1358	0.0279
CO <sub>2</sub>	0.3640	0.0427
HCl	0.3716	0.0408
SO <sub>2</sub>	0.6803	0.0564
H <sub>2</sub> O	0.5536	0.0305
NH <sub>3</sub>	0.4225	0.0371
CH <sub>4</sub>	0.2283	0.0428
CCl <sub>2</sub> F <sub>2</sub>	0.1066	0.0973

#### Example 4.14

One mole of methane gas is maintained at 300K. Its volume is 250cm<sup>3</sup>. Calculate the pressure exerted by the gas under the following conditions.

- When the gas is ideal
- When the gas is non-ideal, and  
 $a = 0.2283 \text{ dm}^6 \text{ atm mole}^{-2}$   
 $b = 0.0428 \text{ dm}^3 \text{ mole}^{-1}$

**Solution:**

- When the gas is ideal  
 General gas Equation is applied here.  
 (a) Gas = Methane:  
 $n = 1 \text{ mole}$   
 $T = 300\text{K}$   
 $V = 250\text{cm}^3 = 0.25\text{dm}^3$   
 $R = 0.0821 \text{ dm}^3 \text{ atm Mole}^{-1} \text{K}^{-1}$   
 $P = ?$

Now applying the General Gas Equation,

$$\begin{aligned}
 PV &= nRT, \\
 P &= \frac{nRT}{V} \\
 &= \frac{1 \text{ mole} \times 0.0821 \text{ dm}^3 \text{ atm mole}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{0.25 \text{ dm}^3} \\
 &= \frac{1 \times 0.0821 \times 300 \cdot \cancel{\text{mole}} \times \cancel{\text{dm}^3} \text{ atm} \cdot \cancel{\text{mole}^{-1}} \cdot \cancel{\text{K}^{-1}} \times \text{K}}{0.25 \cdot \cancel{\text{dm}^3}} \\
 &= 98.52 \text{ atm}
 \end{aligned}$$

(ii) When the gas is non-ideal (Here Van der Waals' equation is applied)

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

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

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

Putting the following values in this equation.

$$n = 1 \text{ mole}, \quad R = 0.0821 \text{ dm}^3 \text{ atm mole}^{-1} \text{ K}^{-1}$$

$$V = 0.25 \text{ dm}^3, \quad T = 300 \text{ K}, \quad a = 0.2283 \text{ dm}^6 \text{ atm mole}^{-2}, \quad b = 0.0428 \text{ dm}^3 \text{ mole}^{-1}$$

$$P = \frac{1 \text{ mole} \times 0.0821 \text{ dm}^3 \text{ atm mole}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{0.25 \text{ dm}^3 - (1 \text{ mole} \times 0.0428 \text{ dm}^3 \text{ mole}^{-1})} - \frac{1 \text{ mole}^2 \times 0.2283 \text{ dm}^6 \text{ atm mole}^{-2}}{(0.25 \text{ dm}^3)^2}$$

$$= \frac{24.63 \text{ dm}^3 \text{ atm}}{0.25 \text{ dm}^3 - 0.0428 \text{ dm}^3} - \frac{0.2283 \text{ dm}^6 \text{ atm}}{0.0625 \text{ dm}^6}$$

$$= \frac{24.63 \text{ dm}^3 \text{ atm}}{0.2072 \text{ dm}^3} - 3.6528 \text{ atm}$$

$$= 115.2178 \text{ atm}$$

## 4.7 DALTON'S LAW OF PARTIAL PRESSURE AND ITS APPLICATIONS

An English Chemist John Dalton (1766-1844) showed in 1801 that “**The total pressure exerted by a gaseous mixture is equal to the sum of partial pressures of each gas present in the mixture.**” The law is only obeyed, if the component gases do not chemically react with each other. Moreover the gases must behave ideally. The partial pressure is the pressure exerted by one component of the gaseous mixture.

$$\text{Total Pressure } (P_t) = P_A + P_B + P_C$$

Whereas  $P_A$ ,  $P_B$  and  $P_C$  are the partial pressures of individual gases.

### Particular Example

Air is a mixture of non-reacting gases. Percentage of each gas in the gaseous mixture is  $\text{N}_2$  (78.08%),  $\text{O}_2$  (20%), Ar (0.93%),  $\text{CO}_2$  (0.03%). Traces of Ne, He, Kr,  $\text{H}_2$ , along with various

amounts of water vapours and pollutant (which can pollute the atmosphere) gases such as oxides of sulphur and Nitrogen are also found in air. The total pressure exerted by the air will be the sum of partial pressure of each gas.

(i) **Relationship between pressure and no. of moles of a gas:**

If  $n_A$ ,  $n_B$  and  $n_C$  are the number of moles of the gases and  $P_A$ ,  $P_B$  and  $P_C$  be their partial pressures respectively.

Then, according to the general gas equation.

$$PV = nRT$$

$$\text{For gas A, } P_A = \frac{n_A RT}{V} \quad \dots\dots\dots (1)$$

$$\text{For gas B, } P_B = \frac{n_B RT}{V} \quad \dots\dots\dots (2)$$

$$\text{For gas C, } P_C = \frac{n_C RT}{V} \quad \dots\dots\dots (3)$$

$$P_t = \frac{n_t RT}{V} \quad \dots\dots\dots (4)$$

Where  $n_t$  (total no. of moles of all the gases) =  $n_a + n_b + n_c$

Dividing equation (1) by (4)

$$\frac{P_A}{P_t} = \frac{n_A RT}{V} \div \frac{n_t RT}{V}$$

$$\frac{P_A}{P_t} = \frac{n_A \cancel{RT}}{\cancel{V}} \times \frac{\cancel{V}}{n_t \cancel{RT}}$$

$$\frac{P_A}{P_t} = \frac{n_A}{n_t} \quad P_A = \frac{n_A}{n_t} \times P_t$$

Similarly  $P_B \propto n_B$  and  $P_C \propto n_C$

In general

$$\text{Partial Pressure of any gas} = \frac{\text{No of moles of that gas}}{\text{Total no of moles of all gases}} \times \text{Total Pressure}$$

(ii) **Relationship between pressure and mole fraction of a gas:**

We know that

$$\frac{\text{Partial Pressure of any gas}}{\text{Total Pressure of all gases}} = \frac{\text{No of moles of that gas}}{\text{Total no of moles of all gases}}$$

$$\frac{P_i}{P_t} = \frac{n_i}{n_t} \text{ or } P_i = \frac{n_i}{n_t} \times P_t$$

but  $\frac{n_i}{n_t} = X_i$  where  $X_i$  is called mole fraction of the component

$$\text{so, } P_i = P_t X_i$$

Thus the **partial pressure of any component is equal to the product of total pressure of all the components and mole fraction of that component.**

### Applications of the Law of Partial Pressure

**i. Collection of gases over water:**

The Dalton's Law is particularly useful when a gas is generated and subsequently collected over water provided the gas is insoluble in water. The total pressure consists of the pressure of the water vapours in addition to the pressure of the gas that is generated. The pressure due to water vapour is called aqueous tension.

$$\text{Thus } P_{\text{Total}} = P_{\text{gas}} + P_{\text{Water vap}} \quad \text{or} \quad P_{\text{gas}} = P_{\text{Total}} - P_{\text{Water vap}}$$

The gas contaminated with water may be called a moist gas.

**ii. Respiration at higher altitudes:**

The respiration process in living things depends upon the differences in partial pressure e.g. partial pressure of  $O_2$  in the outside air is higher (159 mmHg) than in the lungs where the partial pressure of  $O_2$  is lower (116 mmHg). However at high altitudes, the pressure of oxygen decreases and the pilots may have un-comfortable breathing in a non-pressurized cabin where the partial pressure of  $O_2$  is about 150 mmHg.

**iii. Respiration by deep sea divers:**

Deep sea divers breathe air under increased pressure. At a depth of 40 metres, the pressure increases 5 times than the normal pressure. Therefore regular air cannot be used in diver's tanks because the partial pressure of  $O_2$  would be 795 mm of Hg ( $159 \times 5 = 795$  mm of Hg) in that case. Therefore deep sea divers use to breathe a mixture of 96% He and 4%  $O_2$  (Heliox) in the respiration tank, the scuba.

A scuba (self-contained breathing apparatus having oxygen used by divers underwater) contains compressed air to breath. As diver returns to the surface, it becomes hazardous for him if not handled properly. As the diver comes up, the pressure of the surrounding water drops. Consequently, the compressed air in the lungs expands. Surfacing must be done very slowly so that the compressed air may escape out from the lungs without causing damage to them.

**iv. How deep sea divers respire on return from sea:**

The percentage of  $N_2$  in air is about 80%. If  $N_2$  is present in diver's tank, the solubility of  $N_2$  in blood can increase with increase in pressure in very deep sea. And blood of a diver may be saturated with  $N_2$  during a dive. If the diver returns quickly and relatively at low pressure at the surface, he will face life threatening condition called the "bends". Deep sea divers must either use different solutions of gases such as He in  $O_2$  or spend many hours in a decompression chamber after a dive. The pressure in a decompression chamber is slowly lowered over many hours. Nitrogen gas comes out of the blood and disposed off safely for normal breathing.

**DO YOU KNOW**

The mixture of oxygen and helium used in sea diver's tanks is called heliox. It is also used in hospital to facilitate patients suffering from Asthma.

**Example 4.15**

At  $27^\circ\text{C}$  a volume of  $500\text{cm}^3$  of  $H_2$  measured under a pressure of 400 mm of Hg and  $1000\text{cm}^3$  of  $N_2$  measured under a pressure of 600 mm of Hg are introduced into an evacuated  $2\text{dm}^3$  flask. Calculate the resulting pressure.



**Solution**

We will apply Boyle's Law, as the temperature is constant.

For  $H_2$

$$V_1 = 500 \text{ cm}^3 = \frac{500}{1000} = 0.5 \text{ dm}^3$$

$$V_2 = 2 \text{ dm}^3$$

$$P_1 = 400 \text{ mm Hg}$$

$$P_2 = ?$$

According to Boyle's law

$$P_1 V_1 = P_2 V_2$$

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

$$P_2 = \frac{400 \text{ mm Hg} \times 0.5 \text{ dm}^3}{2 \text{ dm}^3}$$

$$= 100 \text{ mm Hg}$$

For  $N_2$

$$V_1 = 1000 \text{ cm}^3 = 1 \text{ dm}^3$$

$$V_2 = 2 \text{ dm}^3$$

$$P_1 = 600 \text{ mm Hg}$$

$$P_2 = ?$$

According to Boyle's law

$$P_1 V_1 = P_2 V_2$$

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

$$P_2 = \frac{600 \text{ mm of Hg} \times 1 \text{ dm}^3}{2 \text{ dm}^3}$$

$$= 300 \text{ mm Hg}$$

$$\text{Hence Total Pressure} = p_{H_2} + p_{N_2}$$

$$= 100 \text{ mm Hg} + 300 \text{ mm Hg}$$

$$= 400 \text{ mm Hg}$$

**Example 4.16**

Find the total pressure exerted by 2g of ethane and 3g of  $CO_2$  contained in a  $5 \text{ dm}^3$  vessel at  $50^\circ\text{C}$ .

**Solution**

$$44 \text{ g of } CO_2 = 1 \text{ mole}$$

$$3 \text{ g } CO_2 = \frac{1}{44} \times 3 = 0.068 \text{ mole}$$

$$\text{Number of moles of } CO_2 = 0.068 \text{ mole}$$

$$V = 5 \text{ dm}^3 \quad T = 50^\circ\text{C} + 273 = 323 \text{ K} \quad R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mole}^{-1}$$

Now according to the General Gas Equation

$$PV = nRT \text{ or } P_{CO_2} V = n_{CO_2} RT \text{ or } P_{CO_2} = \frac{n_{CO_2} RT}{V}$$

$$P_{\text{CO}_2} = \frac{0.068 \text{ mole} \times 0.0821 \times \text{dm}^3 \text{ atm} \cdot \text{K}^{-1} \text{ mole}^{-1} \times 323 \text{ K}}{5 \text{ dm}^3}$$

$$= \frac{0.068 \times 0.0821 \times 323}{5} = 0.361 \text{ atm}$$

30g Ethane ( $\text{C}_2\text{H}_6$ ) = 1mole

$$2 \text{ g Ethane } (\text{C}_2\text{H}_6) = \frac{1}{30} \times 2 = 0.067 \text{ mole}$$

$$V = 5 \text{ dm}^3 \quad n = 0.067 \text{ moles} \quad T = 50^\circ\text{C} + 273 = 323 \text{ K}$$

$$R = 0.0821 \text{ dm}^3 \text{ atm} \cdot \text{K}^{-1} \text{ mole}^{-1}$$

$$PV = nRT \quad \text{or}$$

$$P_{\text{C}_2\text{H}_6} = \frac{n_{\text{C}_2\text{H}_6} RT}{V}$$

$$P = \frac{nRT}{V} = \frac{0.067 \text{ moles} \times 0.0821 \text{ dm}^3 \text{ atm} \cdot \text{K}^{-1} \text{ mole}^{-1} \times 323 \text{ K}}{5 \text{ dm}^3} = 0.355 \text{ atm}$$

$$\begin{aligned} \text{Total Pressure} &= P_{\text{CO}_2} + P_{\text{C}_2\text{H}_6} \\ &= 0.361 \text{ atm} + 0.355 \text{ atm} \\ &= 0.716 \text{ atm.} \end{aligned}$$

Example 4.17

1.00 mole of  $\text{N}_2$  and 3.00 moles of  $\text{H}_2$  are enclosed in a container of volume  $10.0 \text{ dm}^3$  at  $298 \text{ K}$ . What are the partial pressures and the total pressure?

**Solution**

No of moles of  $\text{N}_2$  ( $n_1$ ) = 1.00 mole

No of moles of  $\text{H}_2$  ( $n_2$ ) = 3.00 mole

Total number of moles ( $n_{\text{Total}}$ ) = 1 + 3 = 4 mole

$V = 10.0 \text{ dm}^3$

$T = 298 \text{ K}$ ,  $R = 0.0821 \text{ dm}^3 \text{ atm} \cdot \text{K}^{-1} \text{ mole}^{-1}$

According to the General Gas Equation,  $PV = nRT$

$$\begin{aligned} \text{or } P_{\text{Total}} &= \frac{n_{\text{Total}} RT}{V} = \frac{4 \times 0.0821 \times 298}{10} \cdot \frac{\text{dm}^3 \text{ atm} \cdot \text{K}^{-1} \text{ mole}^{-1} \times \text{K}}{\text{dm}^3 \text{ mole}^{-1}} \\ &= \frac{4 \times 0.0821 \times 298}{10} \text{ atm} \\ &= 9.77 \text{ atm} \end{aligned}$$

$$P_{\text{N}_2} = \frac{n_{\text{N}_2}}{n_{\text{Total}}} \times P_{\text{Total}} = \frac{1}{4} \times 9.77 = 2.44 \text{ atm}$$

$$P_{\text{H}_2} = \frac{n_{\text{H}_2}}{n_{\text{Total}}} \times P_{\text{Total}} = \frac{3}{4} \times 9.77 = 7.33 \text{ atm}$$

**Example 4.18**

A certain mass of  $H_2$  gas collected over water at  $6^\circ C$  and 765 mm Hg pressure occupied a volume of  $35cm^3$ .

Calculate its dry volume at S.T.P. (V.P. of water at  $6^\circ C$  = 7mm of Hg)

**Solution:**

$$V_1 = 35cm^3, \quad V_2 = ? \quad P_1 = 765-7mmHg = 758mmHg \quad P_2 = 760mmHg.$$

$$T_1 = 6 + 273 = 279K, \quad T_2 = 273K$$

Applying the Gas Equation,

$$\frac{V_1 P_1}{T_1} = \frac{V_2 P_2}{T_2} \quad \text{or} \quad V_2 = \frac{V_1 P_1 T_2}{T_1 P_2} = \frac{35cm^3 \times 758mmHg \times 273K}{279K \times 760mmHg} = 34.2cm^3$$

**Self Check Exercise 4.6**

A gas was collected over water at  $10^\circ C$  and 803mm of Hg. If the gas occupies  $73cm^3$ , calculate the volume of dry gas at S.T.P. (aqueous tension at  $10^\circ C$  = 9.2mmHg).

(Ans: =  $73.55cm^3$ )

**Diffusion:**

The spontaneous intermixing of molecules of one gas with another at a given temperature and pressure is called Diffusion. **Diffusion** is the random movement of a gas from an area of higher concentration to an area of lower concentration.

e.g. (i) Fragrance of rose.

(ii) Intermixing of  $NH_3$  and  $HCl$  to gives dense white fumes of  $NH_4Cl$ .



(iii) Reddish brown bromine ( $Br_2$ ) gas taken in a test tube will combine with air taken in another test tube. Red colouration of  $Br_2$  gas will spread in the test tube containing air.

(iv) If liquid ink is left in the bottom of test tube containing water, it will spread evenly throughout the water.

**Effusion**

The movement of gaseous molecules through extremely small pores in a region of low pressure is called Effusion. This escaping of molecules is not due to collisions but due to their tendency to escape one by one.

**4.8 GRAHAM'S LAW OF DIFFUSION AND EFFUSION**

An English Scientist, Thomas Graham in 1831 (1805-1869), measured the rates at which equal volumes of various gases escaped from an apparatus at the same temperature and pressure. Graham found that the less dense a gas was (the lighter its particles), the faster the gas escaped.

**Graham's Law of diffusion and effusion of gases:**

In 1831 Graham showed that "**Rate of diffusion or effusion of a gas is inversely proportional to the square root of its density**". Later in 1848 he himself showed that "**The rate of diffusion or effusion of a gas is inversely proportional to the square root of its molar mass.**"

Mathematically it can be shown as

$$r \propto \frac{1}{\sqrt{d}} \quad \text{(i)} \qquad \text{and} \qquad r \propto \frac{1}{\sqrt{M}} \quad \text{.....(ii)}$$

where  $r$  = rate of diffusion,  
 $d$  = density of the gas, and  $M$  = Molar mass of the gas

From equation (i)  $r \propto \frac{1}{\sqrt{d}}$  or  $r = k \times \frac{1}{\sqrt{d}}$  .....(iii)

and from equation (ii)  $r \propto \frac{1}{\sqrt{M}}$  or  $r = k \frac{1}{\sqrt{M}}$  .....(iv)

where  $k$  = constant of proportionality.

Let us have two gases with  $r_1$  and  $r_2$  as their rates of diffusion and  $d_1, d_2, M_1, M_2$  be their densities and molar masses respectively.

For two different gases, equation (iii) can be written as

$$r_1 = \frac{k}{\sqrt{d_1}} \quad \text{.....(v)} \qquad \text{and} \qquad r_2 = \frac{k}{\sqrt{d_2}} \quad \text{.....(vi)}$$

Dividing equation (v) by (vi),

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \quad \text{and may also be written as} \quad \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \quad \text{because } d \propto M$$

$$\text{Thus} \quad \frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

Example 4.19

Equal volumes of HCl and  $\text{SO}_2$  are confined in a porous container. What would be the comparative rates of diffusion of these gases through the porous walls? The molecular masses of HCl and  $\text{SO}_2$  are 36.5 and 64 respectively.

**Solution**

Molecular mass of HCl ( $M_1$ ) = 36.5 amu

Molecular mass of  $\text{SO}_2$  ( $M_2$ ) = 64 amu

Rate of diffusion of HCl ( $r_1$ ) = ?

Rate of diffusion of  $\text{SO}_2$  ( $r_2$ ) = ?

According to the Graham's Law of Diffusion:

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{64}{36.5}}$$

$$r_1(\text{HCl}) : r_2(\text{SO}_2)$$

$$1.33 : 1$$

Hence rate of diffusion of HCl will be 1.33 times the rate of diffusion of  $\text{SO}_2$ .



**Self Check Exercise 4.7**

If  $465\text{cm}^3$  of  $\text{SO}_2$  can diffuse through porous partition in 30 seconds. How long will  $620\text{ cm}^3$  of  $\text{H}_2\text{S}$  take to diffuse through the same partition (H = 1, S = 32, O = 16)

**(Ans: 29.15 sec)**

## 4.9 LIQUEFACTION OF GASES

### Principle

The gases can be liquefied by **Joule-Thomson's effect**. The liquefaction of a gas requires high pressure and low temperature. When a highly compressed gas is allowed to escape out through a throttle (small hole), the temperature falls to such an extent that it changes into the liquid form.

At high pressure, the gaseous molecules come close to each other with the result that the molecular attractions increase. When it is allowed to escape through a nozzle (small hole) into a region of low pressure, the molecules move apart. In doing so, energy is needed to overcome the intermolecular attractions. This energy is taken from the molecules themselves. Therefore the gas is cooled. This process is repeated for many times until the gas completely changes into the liquid form.

### 4.9.1 Linde's Method (1895)

According to Joule-Thomson's effect **"When a highly compressed gas is allowed to escape out through a throttle the temperature of the gas falls to such an extent, that it changes into the liquid form"**. This is the basic principle of the adiabatic expansion which is thermally isolated from its environment.

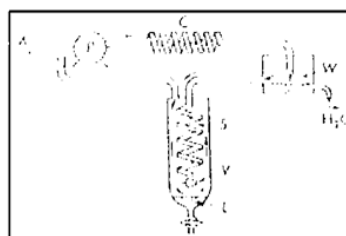


Figure 4.19: Linde's method for liquefaction of air

### Working Steps

- Air is compressed to 200 atm approx.
- Most of the water in the air condenses and is removed.
- The heat generated as a result of compression is removed by passing the gas through coils C. (Figure 4.19)
- The dry gas is then passed through a copper spiral coil S.
- It is then expanded to almost atmospheric pressure through a controlled valve V.
- When the air comes out of the valve the expansion takes place from 200atm to 1atm. In this way fall of temperature occurs. This cold air goes up and cools the incoming compressed air.
- The cycle is repeated several times.
- The temperature of the expanding gas finally drops and the remaining air is liquefied.
- The liquid air collects in the chamber L and can be drawn off.
- Any uncondensed air is re-circulated.

### Uses of Linde's Method

#### i. Construction of appliances:

The construction of appliances such as refrigerators, heat pumps and air conditioners all work on the principle of Joule-Thomson's effect.

In a refrigerator a compressor compresses a gas such as Freon.

Thus an increase in temperature takes place. The hot Freon gas moves to a condenser on the outside of the refrigerator. Air at room temperature cools the gas down and as a result condenses into liquid.

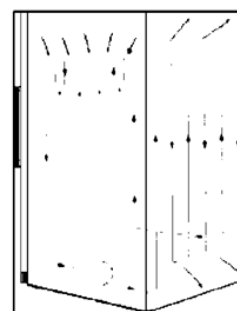


Figure 4.20 Cooling gas path in a refrigerator

The liquid Freon, now at room temperature, is then passed through a small hole in a restriction valve into the low pressure tubes which are inside the refrigerator. There, the Freon liquid vaporises rapidly. The heat of vaporisation needed to do this is drawn from the kinetic energy of the Freon molecules becoming very cold. This cold gas absorbs heat from the refrigerator and its contents, thereby cooling. Then the Freon gas is once again fed into the compressor and the cycle starts over again.

ii. Self cooling pop can (container)

A small container holding liquid CO<sub>2</sub> is built right into the can. When the can is opened, the liquid CO<sub>2</sub> vaporises and escapes out of the top of the can. The heat absorbed by the vaporising CO<sub>2</sub> can lower the temperature of the POP by about 16°C in a few seconds. Thus the temperature is lowered considerably.



Figure 4.21

### Applications of Kinetic Molecular Theory

i. Velocity of molecules:

The equation for the root mean square velocity deduced from kinetic equation is

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

$C_{rms}$  = root mean square velocity

$M$  = molecular mass of the gas

$T$  = absolute temperature.

This equation gives a quantitative relationship between the absolute temperature and the velocities of gas molecules. Higher the temperature of a gas, greater would be the velocities of the molecules.

ii. Graham's Law of diffusion of gases:

According to the postulates of Kinetic Molecular Theory, the Kinetic Energy of the particles is proportional to the Absolute Temperature.

$$\text{As, } E_k = \frac{1}{2}mv^2 \Rightarrow \frac{2E_k}{m} = v^2 \Rightarrow v = \sqrt{\frac{2E_k}{m}} \Rightarrow v = \sqrt{\frac{1}{m}} \sqrt{2E_k}$$

as at constant temperature K.E will remain constant so  $\sqrt{2E_k} = \text{Constant}$

$$\text{Therefore } v \propto \sqrt{\frac{1}{m}}$$

Thus the kinetic molecular theory predicts that the average speed depends upon the molecular mass ( $m$ ). Further the average speed of the particles is inversely proportional to the square root of their molecular mass.



#### Self Check Exercise 4.8

1. A person can inhale a maximum of 0.115 moles of air per breath. Calculate the maximum volume of air, a person can inhale in one breath if the atmospheric pressure is 100kPa and the person's body temperature is 37°C. (Ans: 2.96 dm<sup>3</sup>)
2. 130 cm<sup>3</sup> of a gas exerts a pressure of 750 mm of Hg at 20°C. Calculate its pressure if its volume is increased to 150 cm<sup>3</sup> at 35°C. (Ans: 683.28 mm)

### 4.10 FOURTH STATE OF MATTER – THE PLASMA

Plasma is the fourth state of matter. It was identified by William Crooks in 1879. He obtained it by heating molecular gas changing into atomic form and then to ionic form at higher temperature. (Molecular gas  $\rightarrow$  Atomic gas  $\rightarrow$  Ions)

At a higher temperature of 10000K to 100000K (10eV to 100eV) electrons are removed from the atoms to form ions. Plasma is composed of a mixture of un-ionized gas, free electrons and positively charged particles. Most of the universe contains matter in the Plasma state (about 99%). All shining stars and interstellar space is filled with plasma. On our planet earth, plasma does not exist. Plasma is fourth state of matter because of unique physical properties, distinct from solids, liquids and gases.

#### DO YOU KNOW

Black holes which are not directly visible are thought to be fuelled by accreting ionizing matter i.e. plasma

#### 4.10.1 Properties of plasma

It is a substance in which many of the atoms or molecules are ionised effectively allowing charges to flow freely. It takes place at very high temperature. Plasma has the following properties:

- Plasma consists of neutral particles, positive ions and free electrons.
- Plasma is strongly influenced by both magnetic and electric force.
- Plasma shows a characteristic glow depending upon the gas present in the discharge tube e.g. oxygen gives a red glow, hydrogen green and Nitrogen purple or pink glow.

#### References for additional information

- Thomas J. Green Bowe, Jeffrey Pribyl and K. A. Burke, Chemistry an Experimental Science.
- Graham Hill and John Holmar, Chemistry in context.
- John C. Kotz, Paul M. Treichel and Gabriela C. Weaver, Chemistry and chemical reactivity.



#### 4.10.2 Questions

##### 1. Choose the correct answer (MCQs)

- When compressed hydrogen is allowed to expand rapidly, it causes;
  - Cooling
  - Heating
  - Liquefaction
  - Solidification
- 760 torr is equal to \_\_\_\_\_ Pascal.
  - 760 Pascal
  - 101325 Pascal
  - 1.01325 Pascal
  - One Pascal.
- The number of molecules in 4 g H<sub>2</sub> are \_\_\_\_\_ number of molecules of 56 g of N<sub>2</sub>.
  - Equal to
  - less than
  - Greater than
  - None of these.
- According to the Kinetic theory of gases, the molecular collisions are elastic. Such collisions cause;
  - No energy change
  - A small energy change
  - High energy change
  - None of these.
- What volume would one mole of hydrogen occupy at S.T.P?
  - 11.2 dm<sup>3</sup>
  - 22.4dm<sup>3</sup>
  - 33.6dm<sup>3</sup>
  - 44dm<sup>3</sup>

- vi. According to Graham's Law of diffusion, the rate of diffusion of  $H_2$  and  $O_2$  has the ratio;  
 (a) 1:4 (b)  $1 : \sqrt{4}$  (c) 4:1 (d) 2:32.
- vii. Deep sea diver's tank contains;  
 (a) 96%  $He$  + 4%  $O_2$  (b) 4%  $N_2$  + 96%  $O_2$   
 (c) 50%  $N_2$  + 50%  $O_2$  (d) None of these
- viii. In S.I units, the value of R is;  
 (a)  $8.3413 \text{ Nm K}^{-1} \text{ mole}^{-1}$  (b)  $8.3143 \text{ dm}^3 \text{ atm K}^{-1} \text{ mole}^{-1}$   
 (c)  $0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mole}^{-1}$  (d) None of these
- ix. According to Kinetic Molecular theory kinetic energy of molecules increases when they;  
 (a) Are mixed with other molecules at low temperature  
 (b) Are frozen into solid (c) Are condensed into liquid  
 (d) Are melted from solid to liquid state.
- x. Which gas is more ideal at S.T.P.?  
 (a)  $SO_2$  (b)  $H_2S$  (c)  $NH_3$  (d)  $H_2$
- xi. On heating direct conversion of a solid in to gas is called;  
 (a) evaporation (b) sublimation (c) diffusion (d) boiling
- xii. In which of the following are the particles the most disordered?  
 (a) water (b) steam at  $100^\circ\text{C}$  (c) impure water at  $102^\circ\text{C}$  (d) water at  $0^\circ\text{C}$
- xiii. When steam condenses, the particles;  
 (a) shrink to a smaller size (b) lose energy to their surroundings  
 (c) move further apart (a) vibrate about fixed positions.
- xiv. The particles of a gas can be described as;  
 (a) only moving outwards in direction (b) vibrating about defined position  
 (c) rising upwards (d) moving randomly in all directions.
- xv. Which of these changes would speed up the rate of diffusion the most?

a	Decrease	Decrease
b	Decrease	Increase
c	Increase	Increase
d	Increase	Decrease

- xvi. Which of the following gas has the lowest density under room conditions?  
 (a)  $CO$  (b)  $N_2$  (c)  $Ne$  (d)  $NH_2$  (e)  $O_2$
- xvii. Which statement provides the best evidence that matter may exist as tiny particles moving at "random motion"?  
 (a) Many elements conduct electricity.  
 (b) Air can be readily compressed.  
 (c) A small mass of water produces a much larger volume of steam.  
 (d) If a bottle of ether is opened, the smell is quickly detected in all parts of the room.



- xviii. Which of the following is an example of diffusion?  
(a) Bubbles rising in a beaker of boiling water.  
(b) Steam condensing on a cold window.  
(c) Water spreading out on the surface of a table.  
(d) The spreading of the smell of flowers in a garden.
- xix. Which statement explains why the compounds propane and  $\text{CO}_2$  diffuse at the same rate?  
(a) They are both gases.  
(b) Their molecules contain carbon.  
(c) They have the same relative molecular mass.  
(d) Both are denser than air.

**2 Write brief answers to the following:**

- i. What is Absolute Zero and Absolute Scale of temperature?
  - ii. What is Plasma?
  - iii. What are the different units of gas constant (R)?
  - iv. Define Pressure. How will you explain its different units?
  - v. Define Charles Law. How will you derive Absolute Zero with its help?
  - vi. Define Avogadro's Law.
  - vii. What is the difference between an ideal gas and a real gas?
  - viii. How will you derive the general gas equation with the help of Boyle's law and Charles's law?
- 3** What are the main postulates of the Kinetic Molecular theory of gases?
- 4** Relate temperature to the average K.E of the particles in a substance.
- 5** (a) What are the Standard Temperature and Pressure? (S.T.P).  
(b) What is the density in grams per  $\text{dm}^3$  of  $\text{SO}_2$  at  $25^\circ\text{C}$  and 300 mm of Hg pressure?
- 6** (a) Kinetically how will you interpret the effect of temperature on gaseous molecules?  
(b) How will you explain the gas pressure with the help of Kinetic Theory?
- 7** (a) Define pressure. Derive SI units unit of pressure.  
(b) Explain the effect of change in pressure on the volume of a gas, temperature remains constant. — Boyle's Law.  
(c) How will you verify it graphically?  
(d) A sample of air occupies  $1 \text{ dm}^3$  at room temperature and pressure. What pressure is needed to compress it so that it occupies only  $100 \text{ cm}^3$  at that temperature?  
(Ans: 10atm)
- 8** How will you explain the effect of change in temperature on the volume of the gas?  
(a) Give a graphic representation of the Charles's Law.  
(b) To what temperature must a  $1 \text{ dm}^3$  sample of a perfect gas be cooled from room temperature in order to reduce its volume to  $100 \text{ cm}^3$ ?  
(Ans: 29.8k)
- 9** (a) How will you derive the Absolute Zero?  
(b) How will you explain the Absolute Temperature scale on the basis of Charles Law?
- 10** (a) Define and Explain Avogadro's Law, How does it help to determine  
(i) Mass (ii) Volume (iii) Molecules of the gas  
(b) Can we derive the Avogadro's Law for liquids and solids?

- 11** (a) How will you derive the Ideal or General Gas Equation with the help of Boyle's Law, Charles Law and Avogadro's Law?  
 (b) How will you determine  
 (i) Molecular mass of the gas.  
 (ii) Density of the gas by Ideal Gas Equation.
- 12** (a) The value of Ideal Gas constant (R) can be calculated in three ways. Explain these three ways in detail.  
 (b) The density of air at 161.325 kPa and 298.15K is 1.59g dm<sup>-3</sup>. Assuming that the air behaves as an ideal gas, calculate its molar mass. **(Ans: 22.48g mole<sup>-1</sup>)**
- 13** (a) What is the difference between a real gas and an Ideal or perfect gas. What are the deviations in Ideal behaviour of real gases?  
 (b) What are the causes of deviations of real gases from their ideal behaviour. Explain these deviations at  
 (i) Low temperature.  
 (ii) High pressure.
- 14** How will you derive the Van der Waal's Equation keeping in view the general or ideal gas equation ( $VP = nRT$ ).
- 15** (a) Define and explain the Dalton's law of partial pressure. How does it explain the  
 (i) Relationship between pressure and mole of a gas  
 (ii) Relationship between pressure and mole fraction of component.  
 (b) Give practical applications of the Dalton's law of partial pressure.
- 16** (a) By use of the Van der Waal's equation, find the temperature at which 3 moles of SO<sub>2</sub> will occupy a volume of 10 dm<sup>3</sup> at a pressure of 15 atm.  
 $a = 0.6803 \text{ atm dm}^6 \text{ mole}^{-2}$ ,  $b = 0.0564 \text{ dm}^3 \text{ mole}^{-1}$  **(Ans: 336.43°C)**  
 (b) A certain gas occupies a volume of 6 dm<sup>3</sup> under a pressure of 720 mm of Hg at 25°C. What volume will this gas occupy under standard conditions? **(Ans: 5.2 dm<sup>3</sup>)**
- 17** (a) Define and derive the Graham's law of effusion and diffusion.  
 (b) The time required for a given volume of N<sub>2</sub> to diffuse through an orifice is 35 seconds. Calculate the molecular weight of a gas which requires 50 sec to diffuse through the same orifice under identical conditions. **(Ans: 13.72 g/mol)**
- 18** (a) Interpret phenomenon liquefaction of gases.  
 (b) How will you liquefy gases by Linde's method?