

States of Matter I: Gases

After reading this unit, the students will be able to:

- List the postulates of Kinetic Molecular Theory. (Remembering)
- Describe the motion of particles of a gas according to Kinetic Theory. (Applying)
- State the values of standard temperature and pressure (STP). (Remembering)
- Relate temperature to the average kinetic energy of the particles in a substance. (Applying)
- Use Kinetic Molecular Theory to explain gas pressure. (Applying)
- Describe the effect of change in pressure on the volume of gas. (Applying)
- Describe the effect of change in temperature on the volume of gas. (Applying)
- Explain the significance of absolute zero, giving its value in degree Celsius and Kelvin. (Understanding)
- State and explain the significance of Avogadro's law. (Understanding)
- Derive Ideal Gas Equation using Boyle's, Charles' and Avogadro's law. (Understanding)
- Explain the significance and different units of ideal gas constant. (Understanding)
- Distinguish between real and ideal gases. (Understanding)

Teaching

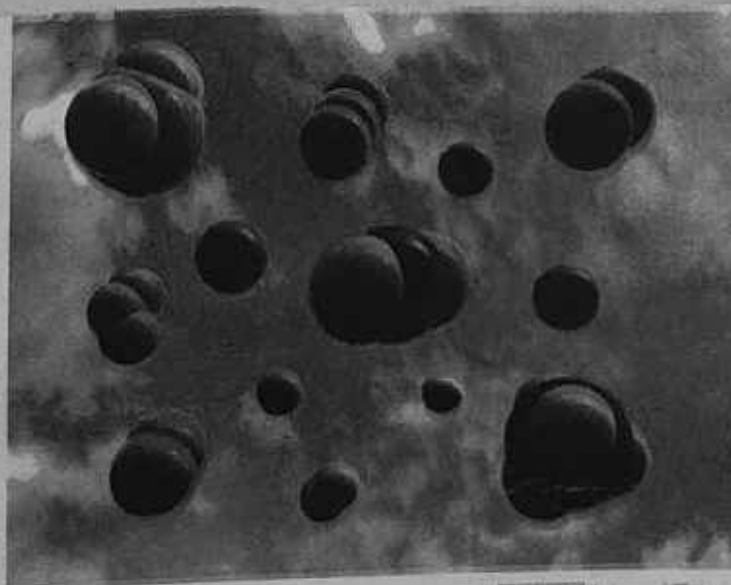
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Assessment

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- Explain why real gases deviate from the gas laws. (Analyzing)
- Define and describe the properties of Plasma. (Applying)
- Derive new form of Gas Equation with volume and pressure corrections for real gases. (Understanding)
- State and use Graham's Law of Diffusion. (Understanding)
- State and use Dalton's law of Partial Pressure. (Understanding)
- Describe some of the implications of the Kinetic Molecular Theory, such as the velocity of molecules and Graham's law. (Applying)
- Explain Linde's method for the liquefaction of gases. (Understanding)
- Define pressure and give its various units. (Remembering)
- Define and explain plasma formation. (Understanding)

Introduction

Gases, liquids and solids constitute the three principal states of matter. The gaseous state is characterized by its simplicity and uniformity of behaviour. Gases have no fixed shape or volume, because of the lack of particle intermolecular attractions. They spread out and fill the container in which it may be kept. Gases are easily compressed because of the large spaces between the particles. The rapid and random movement of the particles in all directions means that gas molecules enjoy greater freedom of motion. The overall movements of the particles in the direction from higher concentration to lower concentration make it possible to smell perfume or food when the source is at some distance from us. When the external conditions such as temperature and pressure are changed, the volume of all gases is affected to nearly the same extent, irrespective of the nature of a gas.

In the previous grades, you have learnt the gas laws but here in this unit, you will study the motion of particles of a gas according to kinetic molecular theory, use of kinetic molecular theory to explain gas pressure, the relationship between gas temperature, pressure, amount and volume. You will also study the effect of change in pressure and temperature on the volume of gas, the significance of absolute zero, real and ideal gases. You will be able to define, describe and explain the fourth state of matter, plasma.

Gases

The state of matter, which has neither definite volume nor definite shape, is called gas. It can also be defined as matter with the highest energy state due to the weak intermolecular forces present in them.

4.1 Kinetic Molecular Theory of Gases

Kinetic molecular theory of gases is based on the fundamental concept that molecules in gases are in constant movement. The kinetic molecular theory was first postulated by, Daniel Bernoulli, which was further developed by James Maxwell and Boltzmann to explain the various properties of gases.

4.1.1 Postulates of Kinetic Molecular Theory

The main postulates of this theory are,

1. All gases consist of small particles called molecules.
2. The molecules of the gas have higher kinetic energy than those of liquids and solids.
3. The molecules are far away from each other and have larger distances at ordinary conditions. That is why volume of the gas consists of mostly empty spaces.
4. The volume of a gas molecule is negligibly small as compared to the total volume occupied by the gas.
5. The attractive or repulsive forces among the gas molecules are negligible. Therefore, every gas molecule behaves independently.
6. The molecules of a gas are in constant random motion. They collide with each other as well as with the walls of the container. The pressure of gas molecules is due to the collision of molecules.
7. All the collisions of a gas molecule are elastic, because the total energy of the molecule remains constant.
8. The average kinetic energy of gas molecules is directly proportional to the absolute temperature.
9. The molecules of different gases have the same average kinetic energy at the same temperature.
10. The force of gravity has almost no effect on the gas molecules.

4.1.2 Pressure and its Units

The molecules of the gas are in constant random motion. They collide with each other as well as with any other surface, or with the walls of the container in which they are stored. Therefore, gas molecules exert pressure on any surface with which they collide. The pressure exerted by a gas depends on volume, temperature and the number of molecules present. Gases can be compressed or expanded.

Pressure is defined as *force per unit area*. It is represented by "P". Mathematically it can be written as,

$$\text{Pressure (P)} = \frac{\text{Force (F)}}{\text{Area (A)}}$$

The atmosphere is the thick blanket of air (gases) surrounding earth, which exerts pressure on the surface of earth. The atoms and molecules of the air (gases) in the atmosphere are attracted towards earth by a force called gravitational force. The force experienced by any area exposed to earth's atmosphere is equal to the weight of the column of air above it.

Tidbit

The apparatus used for measuring gas pressure is called a manometer.

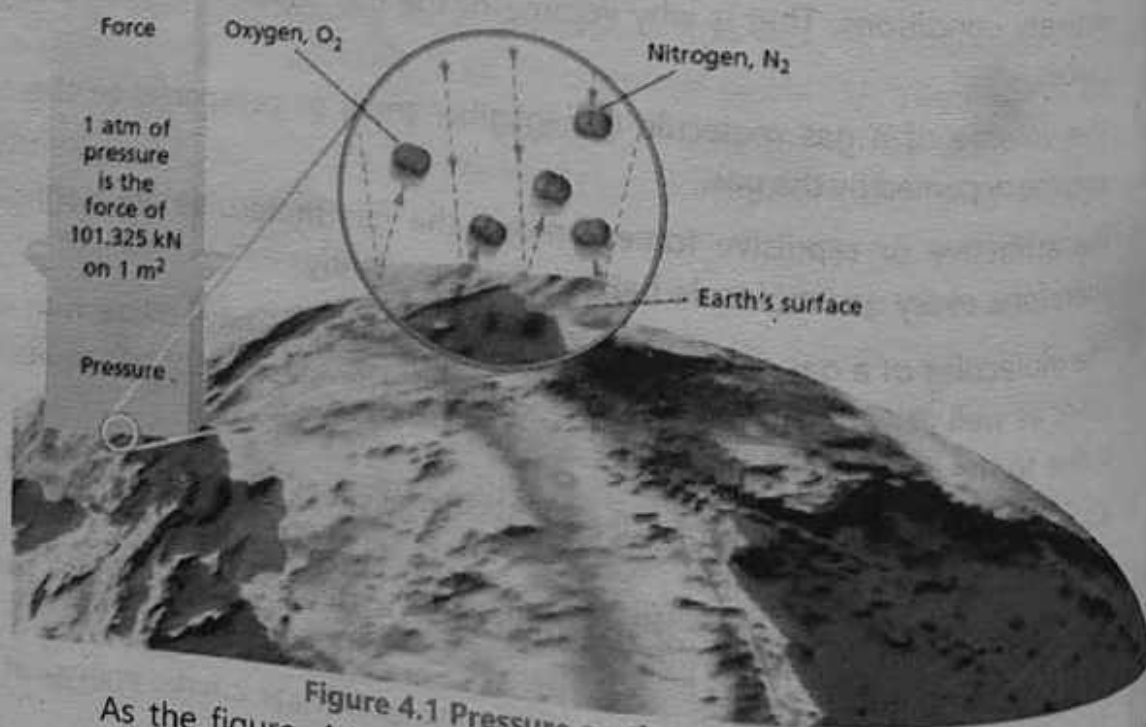


Figure 4.1 Pressure on the Surface of Earth
As the figure, 4.1 shows that atmospheric pressure at sea level is about equal to the weight of a 1.03kg mass per square centimetre of surface. The pressure of the atmosphere is the weight of the gases above it.

compose the atmosphere. Atmospheric pressure is the sum of the individual pressures of the various gases (78% nitrogen, 21% oxygen and 1% other gases, including argon and carbon dioxide) in the atmosphere. Atmospheric pressure is the pressure exerted by earth's atmosphere. The actual value of atmospheric pressure depends on location, temperature, and weather conditions.

Units of Pressure

The SI unit of force is the Newton (N), whereas the unit of area is m^2 .

$$\text{Pressure (P)} = \frac{\text{Force}}{\text{Area}} = \frac{\text{N}}{\text{m}^2} = \text{Nm}^{-2}$$

At sea level, the atmosphere exerts a pressure of 760mm Hg. This is used to define another pressure unit called atmosphere (atm). *One atmosphere is the force exerted by 76cm (760mmHg) long column of mercury on an area of 1cm^2 at 273.15K.* It is the average pressure of atmosphere at the sea level. Thus, one atmosphere can support 760mm.Hg at sea level. The mm Hg unit is also called the torr, after the Italian scientist Evangelista Torricelli, who invented the barometer. Thus, 1 atm pressure at 273K (called the standard pressure) equals to 76 cm Hg or 760 mm Hg or 760 torr.

In SI, pressure is expressed in derived units called Pascals. One Pascal (Pa) is defined as *the pressure exerted by a force of one Newton (1N) acting on an area of one square meter.*

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

In many cases, it is more convenient to express pressure in kilopascals (kPa). The standard atmosphere (1 atm) is equal to $1.01325 \times 10^5 \text{ Pa}$, or 101.325 kPa.

Example 4.1

The pressure of a gas is 49torr. Convert this pressure into both atmospheres and Pascal.

Solution

$$\text{Pressure in torr} = 49 \text{ torr}$$

$$1 \text{ atm} = 760\text{torr}$$

So,

$$49 \text{ torr} \times \frac{1 \text{ atm}}{760\text{torr}} = 0.06447 = 6.447 \times 10^{-2} \text{ atm}$$

$$\text{Pressure in atm} = 6.447 \times 10^{-2} \text{ atm}$$

$$1 \text{ atm} = 101325 \text{ pascal}$$

$$\text{So, } 6.447 \times 10^2 \text{ atm} \times \frac{101325 \text{ Pa}}{1 \text{ atm}} = 6.5327 \times 10^3 \text{ Pa}$$

4.1 Practice problem

Reading on barometer is 2.21 atm. Calculate the corresponding pressure in (a) torr and (b) Pascal.

Table 4.1 Units of Pressure

Unit	Symbol	Definition/relationship
Pascal (Newton per square meter)	Pa	SI pressure unit, $1 \text{ Pa} = 1 \text{ Nm}^{-2}$
Millimetre of mercury	mm Hg	pressure that supports a 1 mm mercury column in a Barometer
Torr	torr	$1 \text{ torr} = 1 \text{ mm Hg}$
Atmosphere	atm	average atmospheric pressure at sea level at 273.15K $1 \text{ atm} = 760 \text{ mm Hg}$ $1 \text{ atm} = 760 \text{ torr}$ $1 \text{ atm} = 101325 \text{ Pa}$ $1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$ $1 \text{ atm} = 101.325 \text{ kPa}$

$$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr} = 101325 \text{ Pa}$$

4.2 Absolute Temperature Scale on the Basis of Charles' law

4.2.1 Brief Recall of Boyle's and Charles' law

Boyle's Law

According to Boyle's law, at constant temperature, volume of a fixed mass of a gas is inversely proportional to the pressure applied on it.

Mathematically it can be written as,

$$V \propto \frac{1}{P} \text{ (at constant temperature and mass)}$$

$$V = k \times \frac{1}{P}$$

$$PV = k$$

(4.1)

(Where 'k' is called constant for Boyle's law.)

When the volume of a given mass of gas is changed from V_1 to V_2 and pressure is changed from P_1 to P_2 , then Boyle's law equation can be written as

Reading Check

Define pressure and atmospheric pressure and give the common units of pressure.

$$P_1V_1 = P_2V_2 \quad (4.2)$$

According to the above equation, the Boyle's law can also be defined as, *the product of pressure and volume of given mass of gas remains constant at constant temperature.*

Graphical Verification

If a graph is plotted between various pressures, P and the respective volume, V of fixed mass of a gas at constant temperature, a curve called isotherm is obtained as shown in figure 4.2. It indicates that V is inversely proportional to the applied P as shown.

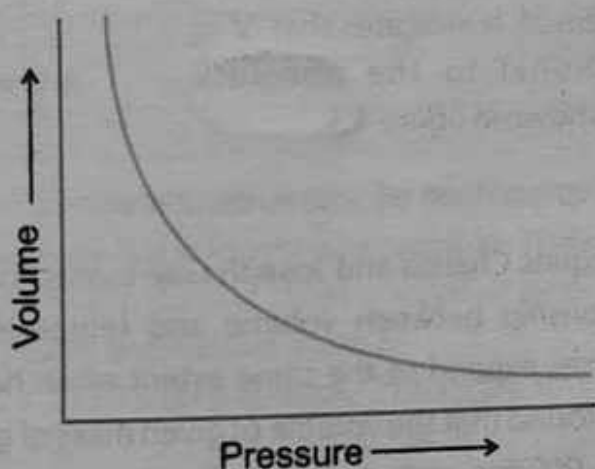


Figure 4.2 Graphical Representation of Boyle's Law

Charles' Law

This law states that, *the volume of a fixed mass of gas is directly proportional to the absolute temperature at constant pressure.*

Mathematically, it can be written as,

$$V \propto T \text{ (at constant pressure and mass)}$$

$$V = kT$$

$$k = \frac{V}{T} \quad (4.3)$$

(Where 'k' is called constant of Charles' law.)

When the volume of the fixed mass of a gas is changed from ' V_1 ' to ' V_2 ', by changing the temperature from ' T_1 ' to ' T_2 ', then the above equation will take the following form,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (4.4)$$

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From the above equation, the Charles' law can be defined as, *the ratio of volume and absolute temperature of the given mass of a gas is constant at constant pressure.*

Graphical Representation of Charles' law

If a graph is plotted between various temperature and the respective volumes of a fixed mass of a gas at constant pressure a straight line is obtained. It indicates that 'V' is directly proportional to the absolute temperature 'T' as shown in figure 4.3.

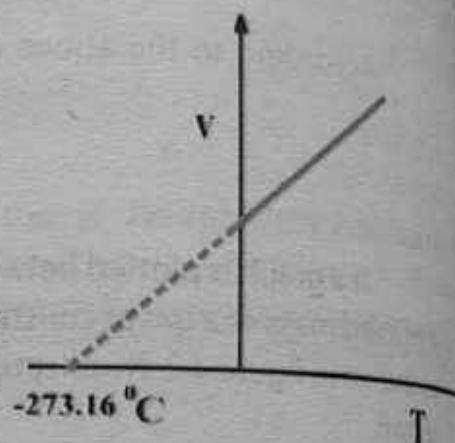


Figure 4.3 Graphical Representation of Charles' law

4.2.2 Graphical Explanation of Absolute Zero

In 1787, Jacques Charles and Joseph Gay-Lussac independently discovered quantitative relationship between volume and temperature. Their experiments showed that all gases expand to the same extent when heated through the same temperature. They found that the volume of given mass of gas changes by $\frac{1}{273}$ of the original volume at 0°C for each degree Celsius ($^{\circ}\text{C}$) rise or fall in temperature at constant pressure.

For example, raising the temperature to 1°C causes the gas volume to increase by $\frac{1}{273}$ of the volume it had at 0°C . A 2°C temperature increase causes the volume to expand by $\frac{2}{273}$ of the original volume at 0°C ; 100°C temperature increase causes the volume to expand by $\frac{100}{273}$ of the original volume at 0°C . If the temperature is increased by 273°C , the volume increases by $\frac{273}{273}$ of the original, that is, the volume of the gas becomes double.

The same regularity of volume change occurs if a gas is cooled at constant pressure. At 0°C , a 1°C decrease in temperature will decrease the original volume by $\frac{1}{273}$. At this rate of decrease in volume, a gas cooled from 0°C to -273°C would be decreased by $\frac{273}{273}$. In other words, it would have zero volume, which is not actually possible. In fact, gases cannot be cooled to -273°C . Before they reach that temperature, intermolecular forces exceed the kinetic energy of the molecules, and the gases condense to form liquids or solids.

Table 4.2 Temperature - Volume Data for a Gas Sample (at Constant Mass and Pressure)

Celsius temperature ($^{\circ}\text{C}$)	Temperature (K) $^{\circ}\text{C} + 273$	Volume (cm^3)	$\frac{V}{T}$ or k (cm^3K^{-1})
273	546	1092	2
100	373	746	2
10	283	566	2
1	274	548	2
0	273	546	2
-1	272	544	2
-73	200	400	2
-173	100	200	2
-223	50	100	2
-273	0	0	

The Kelvin temperature scale is a scale that starts at a temperature of -273.15°C . That temperature is the lowest one possible. *The temperature -273.15°C is referred to as absolute zero and is given a value of zero in the Kelvin scale.* The relation of the Kelvin scale and Celsius scale is,

$$K = ^{\circ}\text{C} + 273.15 \text{ (In this book, 273.15 are rounded off to 273)}$$

$$T = t^{\circ}\text{C} + 273 \quad (4.5)$$

It is represented by K, after Lord Kelvin who discovered it and ' $t^{\circ}\text{C}$ ' is the temperature on Celsius scale and 'T' the Kelvin temperature.

Graphical Explanation

A graph is plotted between temperature 'T' on x-axis and volume 'V' for a given mass of a gas according to table 4.4 at constant pressure, you get a straight line. When you extrapolate the graph upto 0 Kelvin (-273°C), this line cuts the temperature axis at -273°C , which is lowest possible temperature. The line breaks before reaching the temperature of a gas to -273°C . It means that at this temperature all the gases have zero volume or not in the gaseous state.

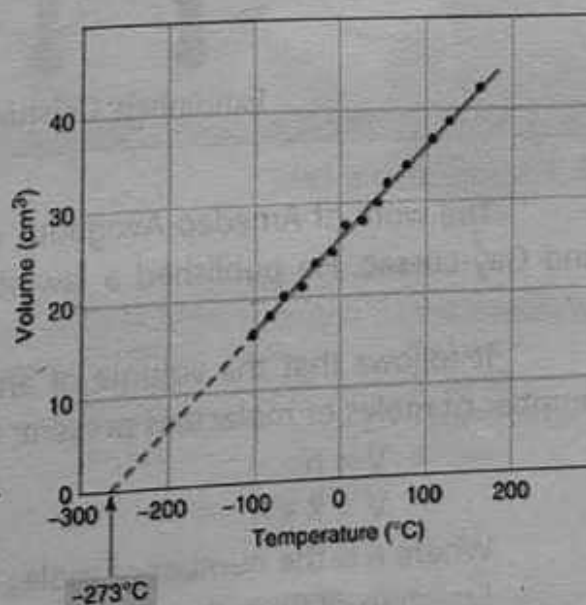


Figure 4.4 Graph between Volume and Temperature for a Gas

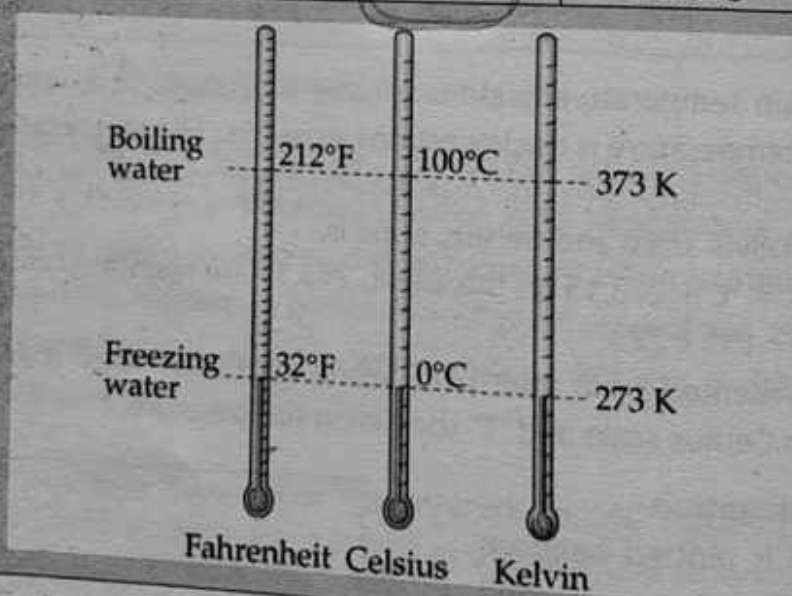
The gases are condensed and converted into the liquid or solid. Therefore, the gas laws cannot be applied on them. Actually, all the gases are converted into liquid before this temperature.

Tidbit

Absolute temperature must be used in all gas law problems involving temperature.

The boiling point, freezing point of water and absolute zero on Fahrenheit, Celsius and Kelvin are,

	Fahrenheit	Celsius	Kelvin
Boiling point of water	212°F	100°C	373K
Freezing point of water	32°F	0°C	273K
Absolute Zero	- 459°F	-273 °C	0K



4.3 Avogadro's Law

The work of Amedeo Avogadro supplements the studies of Boyle, Charles and Gay-Lussac. He published a law stating that *at the same temperature and pressure, equal volumes of different gases contain the same number of molecules*.

It follows that the volume of any given gas must be proportional to the number of moles or molecules present; that is,

$$V \propto n$$

$$V = K \times n$$

(4.6) (at constant 'P' and 'T')

(4.7)

Where n is the number of moles of gas and K is proportionality constant.

Equation (4.6) is the mathematical expression of Avogadro's law, which states that *at constant pressure and temperature, the volume of a gas is directly proportional to the number of moles of the gas present.*

As one mole of a gas has Avogadro's number of particles, so 22.414 dm^3 of various ideal gases at STP will have Avogadro's number i.e. 6.023×10^{23} molecules. One dm^3 of H_2 at STP weighs approximately 0.0899 grams and one dm^3 of O_2 at STP weighs 1.4384 grams, but their number of molecules is the same. Although oxygen molecules is 16 times heavier than hydrogen but this does not disturb the volume occupied because molecules of the gases are widely separated from each other at STP. One molecule is approximately at a distance of 300 times its own diameter from its immediate neighbour at room temperature.

Mole-Mass-Volume Relationships of Gases

One mole of any gas contains 6.022×10^{23} molecules (Avogadro's number). It has been experimentally determined that the volume occupied by a mole of any gas is 22.4 dm^3 at STP. This volume, 22.4 dm^3 , is known as the *molar volume* of a gas. *One mole of a gas occupies 22.4 dm^3 at STP.*

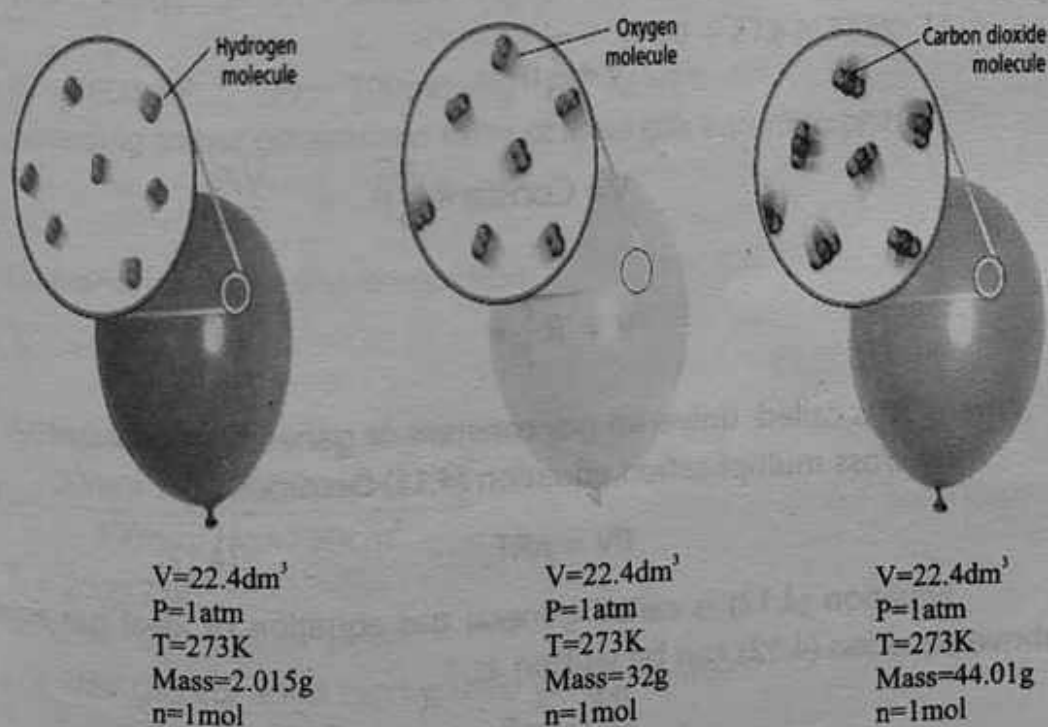


Figure 4.5 One mole of Different Gases at STP

4.4 Ideal Gas Equation or General Gas Equation

An ideal gas is a gas that behaves exactly as outlined by the assumptions of the kinetic molecular theory.

The equation that relates the pressure, volume, number of moles and temperature of an ideal gas is called ideal gas equation.

4.4.1 Derivation of Ideal Gas Equation

It is derived by combining the Boyle's law, Charles law and Avogadro's law.

According to Boyle's law, volume of the fixed mass of a gas is inversely proportional to the applied pressure at constant temperature.

$$V \propto \frac{1}{P} \text{ (at constant temperature)} \quad (4.8)$$

According to Charles law, volume of the fixed mass of a gas is directly proportional to the absolute temperature at constant pressure.

$$V \propto T \text{ (at constant pressure)} \quad (4.9)$$

According to Avogadro's law, volume of a fixed mass of a gas is directly proportional to its number of moles at constant temperature and pressure.

$$V \propto n \text{ (at constant temperature and pressure)} \quad (4.10)$$

Combining these three proportionalities equations (4.8), (4.9) and (4.10), we get,

$$V \propto \frac{T}{P} n$$

$$V = \text{Constant} \frac{T}{P} n$$

$$V = R \frac{T}{P} n \quad (4.11)$$

Where 'R' is called universal gas constant or general gas constant.

By cross multiplication equation (4.11) becomes,

$$PV = nRT \quad (4.12)$$

Equation (4.12) is called general gas equation or ideal gas equation. The above equation (4.12) can be written as,

$$\frac{PV}{T} = nR$$

Since standard moles for any gas is taken one i.e., $n = 1$, then the equation (4.12) becomes,

$$\frac{PV}{T} = R \quad (4.13)$$

For initial state: when the Pressure (P_1), Volume (V_1) and Temperature (T_1), then

$$\frac{P_1 V_1}{T_1} = R \quad (4.14)$$

For final state: Pressure (P_2), Volume (V_2) and Temperature (T_2), then

$$\frac{P_2 V_2}{T_2} = R \quad (4.15)$$

Then combining equation (4.14) and (4.15) we get,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (4.16)$$

This is the generalized form of ideal gas equation.

Example 4.2

750cm³ of a gas at 300mm Hg and 50°C is heated until the volume of gas is 2000cm³ at a pressure of 700mm Hg. What is the final temperature of the gas?

Solution

$$V_1 = 750\text{cm}^3, \quad P_1 = 300\text{mm Hg}, \quad T_1 = 50^\circ\text{C} \\ = 50 + 273 = 323\text{K}$$

$$V_2 = 2000\text{cm}^3, \quad P_2 = 700\text{mm Hg}, \quad T_2 = ?$$

According to the generalized form of ideal gas equation (4.16),

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

On rearranging the above equation,

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

Putting the values in the above equation,

$$T_2 = \frac{700\text{mm Hg} \times 2000\text{cm}^3 \times 323\text{K}}{300\text{mm Hg} \times 750\text{cm}^3}$$

$$T_2 = 2009.77\text{K}$$

4.4.2 Gas Constant and its Units

The ideal gas equation can be used to determine,

1. Value of "R" at STP
2. Value of "R" in SI unit
3. Mass of gas (m)
4. Density of gas (d)
5. Concentration of gas (c)

i. Calculation of Value of "R" at STP

According to the general gas equation (4.12), we have,

$$PV = nRT$$

On rearrangement, the above equation becomes,

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

At 0°C (273.15 K) and 1 atm pressure, many real gases behave like an ideal gas. Experiments show that under these conditions, 1 mole of an ideal gas occupies 22.414 dm³. At STP, it is known that:

$$\text{Standard temperature (T)} = 0^\circ\text{C}$$

$$= 0^\circ\text{C} + 273 = 273\text{K}$$

$$\text{Pressure (P)} = 1 \text{ atm}$$

$$\text{Amount (n)} = 1 \text{ mol}$$

$$\text{Volume (V)} = 22.4 \text{ dm}^3$$

Putting these values in equation (4.17), we get,

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

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

ii. Calculation of Value of "R" in SI Units

If the pressure is expressed in Newton's per meter square (Nm⁻²) and the Volume (V), in cubic meter (m³), so we have,

$$\text{Amount (n)} = 1 \text{ mol}$$

$$\text{Standard temperature (T)} = 0^\circ\text{C} = 0^\circ\text{C} + 273 = 273\text{K}$$

$$\text{Pressure (P)} = 1 \text{ atm} = 101325 \text{ Nm}^{-2}$$

$$\text{Volume (V)} = 22.4 \text{ dm}^3 = \frac{22.4 \text{ dm}^3}{1000} = 0.0224 \text{ m}^3 \text{ (As } 1 \text{ dm}^3 = 10^{-3} \text{ m}^3)$$

As we have equation (4.17),

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

Putting these values in equation (4.17), we get,

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

$$R = 8.313 \text{ Nm}^{-2}. \text{ m}^3. \text{ mol}^{-1}. \text{ K}^{-1}$$

Or, we get,

$$R = 8.313 \text{ Nm. mol}^{-1}. \text{ K}^{-1}$$

As, we also know that, *Newton meter (Nm) = Joule (J)*

So, we can write as,

$$R = 8.313 \text{ J K}^{-1} \cdot \text{mol}^{-1}$$

As, we also know that, $1 \text{ calorie} = 4.184 \text{ Joule}$

Then, the above values for R can be written as,

$$R = \frac{8.3143}{4.184} = 1.987 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

4.2 Practice Problems

1. What pressure will be exerted by 0.400 mol of a gas in a 5.00 dm^3 containers at 17°C ?
2. Find the values of 'R' in $\text{dm}^3 \cdot \text{mm Hg} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
3. Find the values of 'R' in $\text{dm}^3 \cdot \text{torr} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
4. Find the values of 'R' in $\text{cm}^3 \cdot \text{torr} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

iii. Calculation of Value of Mass (m) of gas

The molecular mass of the gas can be determined with the help of ideal gas equation.

According to the ideal gas equation (4.12), we have,

$$PV = nRT$$

(4.18)

As we know that,

$$\text{Mole (n)} = \frac{\text{Mass of the gas}}{\text{Molecular mass of the gas}} = \frac{m}{M}$$

Putting the value of n in equation (4.18), we get,

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

By cross multiplication,

$$PV \times M = mRT$$

By rearranging, we get,

$$m = \frac{PVM}{RT} \quad (4.19)$$

If the molecular mass of the gas (M), temperatures (T), pressure (P) and volume (V) of the gas are known then the mass of the gas can be determined by using the equation (4.19).

Example 4.3

Calculate the mass of 1 dm^3 of NH_3 gas at 30°C and 1000 mm Hg pressure, considering that NH_3 is behaving ideally?

Solution

Mass of NH_3 (m) = ?

Volume (V) = 1 dm^3

$$\begin{aligned}\text{Temperature (T)} &= 30^{\circ}\text{C} \\ &= 30 + 273 = 303\text{K}\end{aligned}$$

$$\begin{aligned}\text{Pressure (P)} &= 1000 \text{ mm Hg} \\ &= \frac{1000}{760} = 1.316 \text{ atm}\end{aligned}$$

$$\text{General gas constant (R)} = 0.0821 \text{ dm}^3 \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\text{Molecular mass of NH}_3 \text{ (M)} = 17 \text{ g} \cdot \text{mol}^{-1}$$

According to the equation (4.19)

$$m = \frac{PVM}{RT}$$

Putting the values in the above equation,

$$\begin{aligned}m &= \frac{1.316 \text{ atm} \times 1 \text{ dm}^3 \times 17 \text{ g} \cdot \text{mol}^{-1}}{0.0821 \text{ dm}^3 \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 303 \text{ K}} \\ m &= 0.8993 \text{ g}\end{aligned}$$

4.3 Practice Problem

Calculate the molecular mass of butane gas if 3.69g occupy 1.53 dm^3 at 20.0°C and 1.00 atm .

iv. Calculation of Value of Density (d) of gas

The density of a gas can be determined with the help of ideal gas equation

According to the general gas equation (4.12), we have,

$$PV = nRT \quad (4.20)$$

As we know that,

$$\text{Mole (n)} = \frac{\text{Mass of the gas}}{\text{Molecular mass of the gas}} = \frac{m}{M}$$

Putting the value of 'n' in equation (4.20) we get,

$$PV = \frac{m}{M} RT \quad (4.21)$$

By rearranging equation (4.21) becomes,

$$PM = \frac{m}{V} RT \quad (4.22)$$

Since we have,

$$\text{Density (d)} = \frac{\text{mass}}{\text{Volume}} = \frac{m}{V}$$

Putting the value of ' $\frac{m}{V}$ ' in equation (4.22) we get,

$$PM = d \times RT$$

Or
$$d = \frac{PM}{RT} \quad (4.23)$$

The density of the gas can be determined if the pressure (P), molecular mass (M), temperature (T) and universal gas constant (R) are known.

Example 4.4

What is the density in g.dm^{-3} of SO_2 at 20°C and 750mm Hg pressure?

Solution:

$$P = 750\text{mm Hg}$$

$$= \frac{750}{760} = 0.98\text{atm}$$

$$T = 20^\circ\text{C}$$

$$= 20 + 273 = 293\text{K}$$

$$\text{Molecular mass of } \text{SO}_2 = 64\text{g/mol}$$

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

$$d = ?$$

According to the general gas equation,

$$PV = nRT$$

On solving for 'd' we get,

$$d = \frac{PM}{RT}$$

Putting the values in the equation we get,

$$d = \frac{0.98\text{atm} \times 64\text{g.mol}^{-1}}{0.0821\text{dm}^3\text{atm.K}^{-1}.\text{mol}^{-1} \times 293\text{K}}$$

$$d = 2.60\text{g.dm}^{-3}$$

4.4 Practice Problem

Calculate the density in g.dm^{-3} of NH_3 at 25°C and 1.2atm.

v. Calculation of Concentration (c) of Gas

The concentration of a gas can be determined with the help of ideal gas equation.

According to the general gas equation (4.12), we have,

$$PV = nRT \quad (4.24)$$

As we know that,

$$\text{Concentration (c)} = \frac{\text{mole}}{\text{volume}} = \frac{n}{V}$$

Rearranging the equation (4.24), we get,

$$P = \frac{n}{V} RT \quad (4.25)$$

Putting the value of $\frac{n}{V}$ we get,

$$P = cRT \quad (4.26)$$

On rearranging equation (4.26), we get,

$$c = \frac{P}{RT}$$

The concentration of the gas can be determined if the pressure, temperature (T), and universal gas constant (R) are known.

Self-Assessment

1. List the physical characteristics of gases.
2. What are standard temperature and pressure (STP)?
3. Derive the ideal gas equation. Give its different units for each term in the equation.
4. Why the density of a gas is much lower than that of a liquid or solid?
5. What are the basic assumptions of the kinetic molecular theory of gases?

4.5 Deviation from Ideal Gas Behaviour

All the gas laws are based on the behaviour of an ideal gas, that is, a gas with a behaviour that is described exactly by the gas laws for all possible values of *Pressure*, *Volume*, and *Temperature*. Most real gases actually do behave very nearly like an ideal gas over a wide range of temperatures and pressures. However, when conditions are such that

the gas molecules come close together (under high pressure and/or low temperature), they show deviation from ideal behaviour. Actually, all gases deviate from gas laws to an extent that depends on the pressure, temperature, and nature of the gas. Such gases are called non-ideal or real gases.

Tidbit

A Real gas is a gas that does not behave completely according to the assumptions of the kinetic molecular theory.

4.5.1 Graphical Explanation

We will examine the experimentally observed behaviour of real gases by measuring the pressure, volume, temperature, and number of moles for a gas, noting how the quantity $\frac{PV}{nRT}$ depends on pressure. Plots of $\frac{PV}{nRT}$ versus P

shown for several gases in figure 4.6. For an ideal gas, $\frac{PV}{nRT}$ equals to 1 under all conditions. This ratio is called the compressibility factor (Z),

$$Z = \frac{PV}{nRT} \quad (4.27)$$

Compressibility factor (Z)

The extent to which a real gas departs from the ideal behaviour may be depicted in terms of a new function called the Compressibility factor, denoted by Z. It is mathematically written for 1 mole of a gas as,

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

The deviations from ideality may be shown by plotting compressibility factor $\frac{PV}{RT}$ versus pressure (P atm), as shown in the figure 4.6.

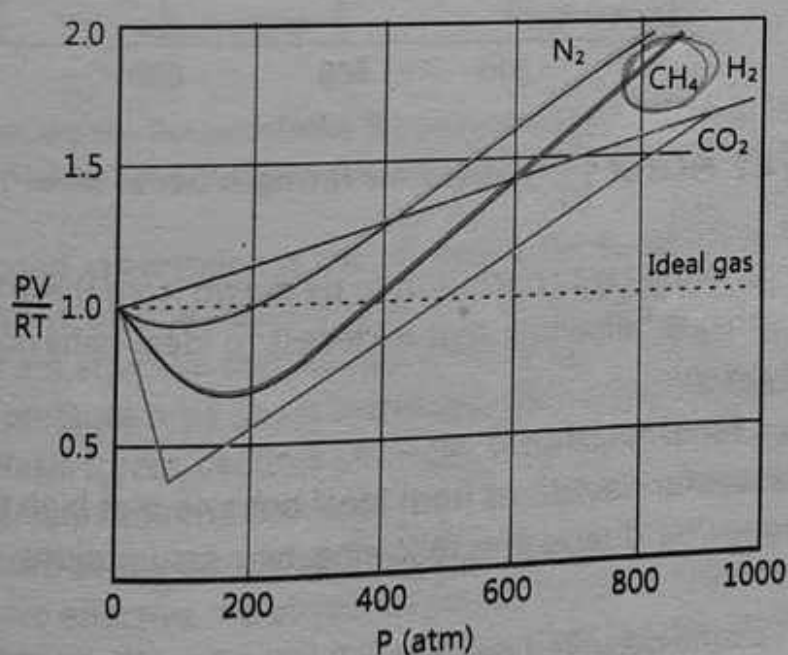


Figure 4.6 Plots of PV/RT versus P for Several Gases at 313K

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

To show the effect of temperature, $\frac{PV}{RT}$ is plotted versus P for nitrogen at several temperatures in figure 4.7. Note that the behaviour of the gas appears to become more nearly ideal as the temperature is increased.

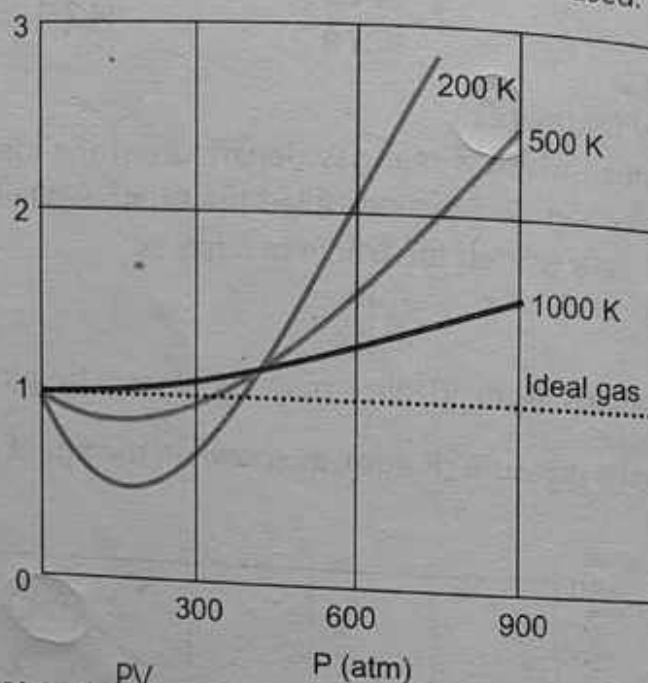


Figure 4.7 Plots of $\frac{PV}{RT}$ versus P for Nitrogen Gas at Three Temperatures

Conclusions

The most important conclusion to be drawn from these figures is that a gas typically exhibits behaviour that is closest to ideal behaviour at *low pressures and high temperatures*.

4.5.2 Causes for Deviation

The causes for deviations from ideal behaviour at high pressure or very low temperature may be due to the following two assumptions of kinetic theory of gases.

1. The volume occupied by gas molecules is negligibly small as compared to the volume occupied by the gas.
 2. The forces of attraction between gas molecules are negligible.
- The first assumption is valid only at low pressures and high temperatures when the volume occupied by the single gas molecule is negligible as compared to the total volume of the gas. However, at high pressure, the molecules of a gas come closer together, and the amount of empty space between the molecules is reduced.

At these higher pressures, the volume of the gas molecules themselves becomes considerable relative to the total volume occupied by the gas as shown in figure 4.8. The gas, therefore, becomes less compressible at these high pressures; the volumes of molecules are no more negligible as compared to the total volume of the gas.

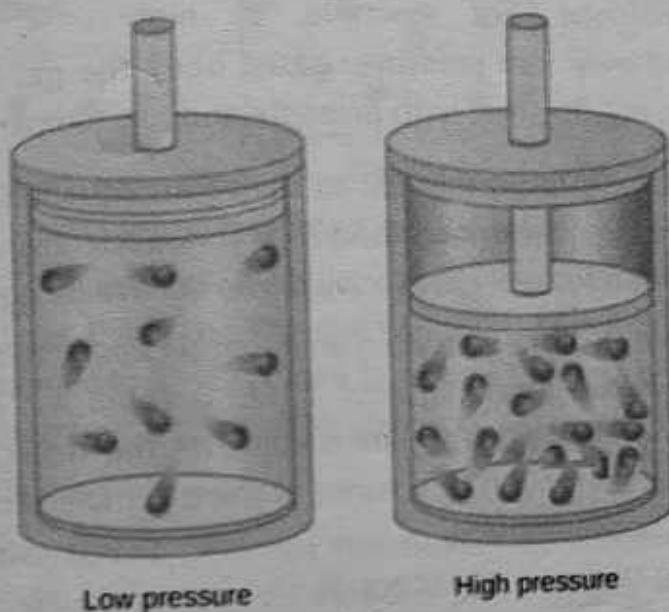


Figure 4.8 Raising the Pressure of a Gas Increases the fraction of its volume that is occupied by the gas molecules and makes the gas less compressible

The second assumption is the attractive forces, which result from attraction between electrons of one atom and nuclei of adjacent atoms, exist between all molecules, but are effective only at very short range. They are called Van der Waals forces. As the pressure on a gas is increased, molecules are forced closer together and Van der Waals forces become stronger, drawing the molecules still closer and resulting in a greater volume decrease than Boyle's law predicts. This effect is even more pronounced at low temperatures because the more slowly the molecules are moving the more effective the attractive forces become. This explanation suggests that the assumption of kinetic molecular theory that the gas molecules do not have attractive forces between them is one reason of deviation of gases from ideal behaviour. Molecules of real gases do exert force on each other, the condensation of every gas on cooling shows that attractive forces are always there among the molecules. These forces are not very important when the molecules are far apart (i.e. at low pressure and high temperature) but they become noticeable at higher pressure and low temperature.

4.6 Van der Waals Equation

An ideal gas would obey the gas laws strictly but all real gases more or less deviate from these laws. The nature and extent of deviation depend upon the conditions. For example, at high temperature and very low pressure, gases obey the gas laws almost perfectly whereas they do not do so at high pressure and low temperature.

Reading Check

Define compressibility factor.

Various attempts were made to derive an equation for non-ideal i.e. real gases to describe their behaviour. In 1873, a Dutch scientist, J.D. Van der Waals, put forward an equation for real gases, called Van der Waals equation.

The Van der Waals equation is an equation similar to the ideal gas equation but includes two constants, 'a' and 'b', to account for deviations from ideal behaviour. The Van der Waals equation improves the ideal gas law by adding two terms, one for the correction of volume of the gas molecules and another for the attractive forces between them.

According to the ideal gas equation,

$$PV = nRT$$

This equation explains the behaviour of an ideal gas consisting of volumeless entities that do not interact with each other. In contrast, a real gas consists of atoms or molecules that have finite volumes. Therefore, the volume available to a given particle in a real gas is less than the volume of the container because the particles themselves occupy some of the space. Van der Waals pointed out that both the pressure (P) and volume (V) factors in the ideal gas equation need correction in order to make it applicable to real gases.

4.6.1 Volume Correction

When a gas is compressed, the molecules become so close together that any further increase in pressure will be opposed by the molecules themselves. This is not possible when the molecules of the gas have a finite volume. The volume, V , in the ideal gas equation, $PV = nRT$, is the free volume, V in which the molecules are effectively free to move about. But when the molecules do occupy an appreciable part of the total volume, V then compressible volume V_{free} should be set equal to the difference between V and $V_{\text{molecules}}$ or b .

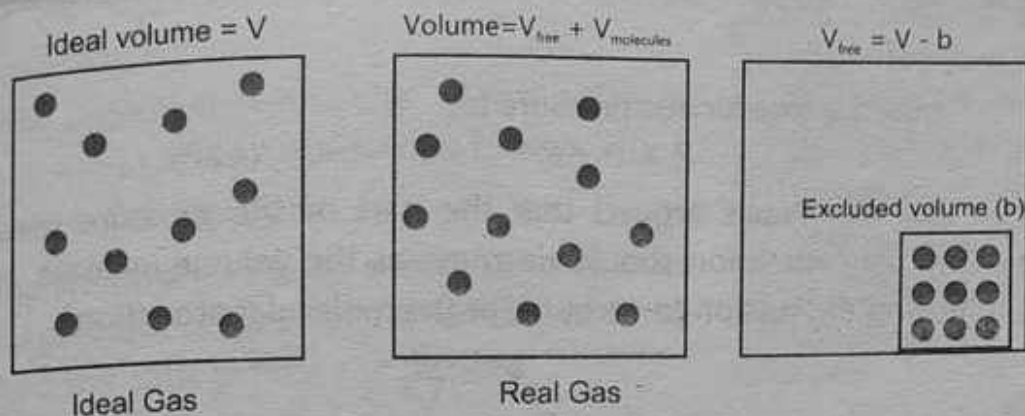


Figure 4.9 Volume of a Real Gas

For an ideal gas, $b = 0$ and Van der Waals, therefore, proposed that V in the gas equation be changed to $(V - b)$, where ' b ' is the effective molar volume of the real gas and approximately four times greater than $V_{molecules}$.

4.6.2 Pressure Correction

The attractive forces between the molecules come into play when the molecules are brought closer together by compressing the gas and become slow down by decreasing temperature. Consider a molecule A in the interior of the gas, which is completely surrounded by other gas molecules. The resultant attractive force experienced by the molecules A due to all the other molecules is zero. However, as this molecule approaches the wall of the container, it is subjected to an inward pull due to unbalanced molecular attraction. Thus, when the molecule is about to strike the wall and contribute its share to the total pressure of the gas, the other molecules in the gas exert an attractive force tending to prevent it from doing so. The observed pressure P consequently will be less than the ideal pressure, P_i by p' .

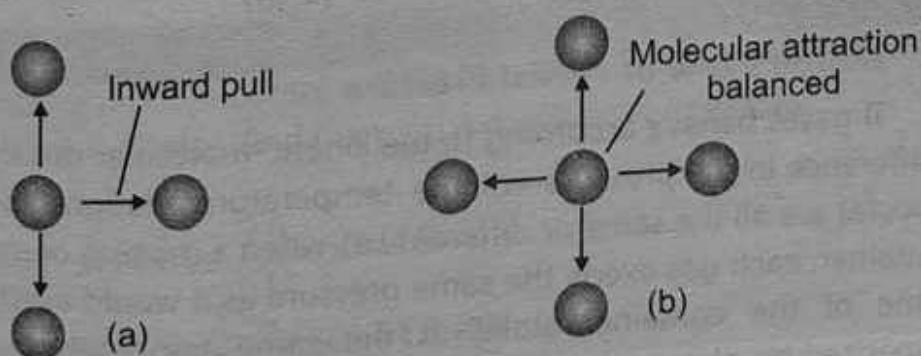


Figure 4.10

- (a) A molecule about to strike the wall has a net inward pull;
 (b) A molecule in the interior of gas has balanced attractions.

$$P = P_i - P'$$

Thus, the true kinetic pressure is,

$$P_i = P + P' \quad (4.28)$$

Van der Waals argued that the part of the pressure used up against intermolecular attraction should decrease as the volume increase. He suggested the following expression to account for the molecular attraction.

$$P' = \frac{a}{V^2}$$

Where 'a' is co-efficient of attraction i.e., attraction per unit volume and constant for a particular real gas. Thus, the effective kinetic pressure is given by,

$$P_i = P + \frac{a}{V^2}$$

Now, making correction for both the pressure and volume, the ideal gas equation for one mole of a real gas becomes,

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT \quad (4.29)$$

Kinetic pressure of a real gas free volume of a real gas

Reading Check

1. Write down two evidences to show that gases do not behave ideally under all conditions of temperature and pressure.
2. Write the Van der Waals equation for a real gas.

It represents the behaviour of real gases (non-ideal) over wide ranges of temperature and pressure more accurately than the ideal gas equation. The Van der Waals equation for 'n' moles of gas may be written as below.

$$\left(P + \frac{an^2}{V^2}\right)(V-nb) = nRT \quad (4.30)$$

4.7 Dalton's Law of Partial Pressure

If gases behave according to the kinetic-molecular theory, there should be no difference in the pressure-volume-temperature relationships whether the molecules are all the same or different i.e., when a mixture of gases is enclosed in a container, each gas exerts the same pressure as it would exert if it occupied the volume of the container alone at the same temperature. In 1803, Dalton summarized his observations as follows,

"The total pressure exerted by a mixture of gases in a container is equal to the sum of the partial pressures of all the gases present in the mixture provided"

that no chemical reaction occurs at constant temperature and volume."

This statement, known as *Dalton's law of partial pressures*, can be expressed as follows,

$$P_{\text{TOTAL}} = P_A + P_B + P_C + \dots$$

The symbols P_A , P_B , P_C , and so on, represent the partial pressure of gases in the mixture, whereas, P_{TOTAL} (P_T) is the total pressure of mixture.

Tidbit

Partial Pressure

The pressure exerted by a particular gas is hypothetical pressure of a gas when it alone occupies the same volume as the mixture.

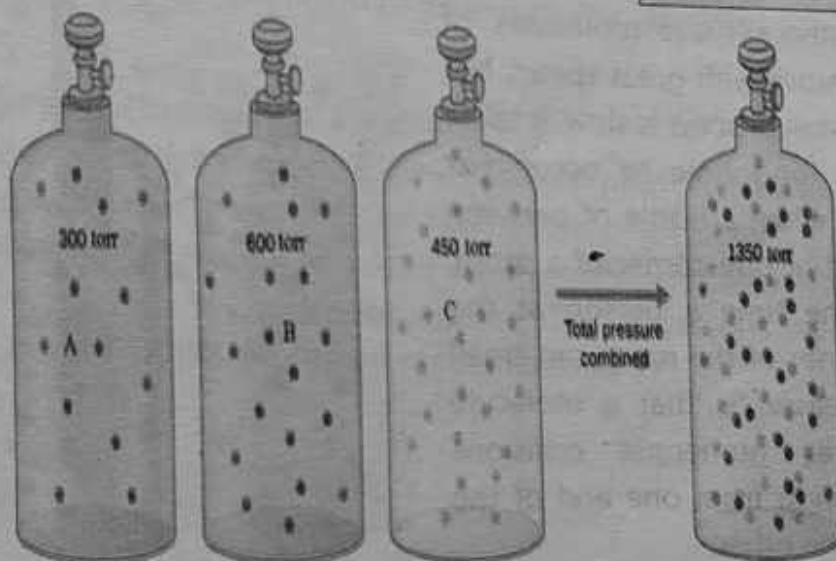


Figure 4.11 The individual Pressures of gases A, B, C and their Total Pressure

Thus, if we have a mixture of three non-reacting gases, A, B, and C, exerting partial pressures of 300 torr, 600 torr, and 450 torr, respectively, the total pressure will be 1350 torr.

$$P_{\text{total}} = P_A + P_B + P_C$$

$$P_{\text{total}} = 300 \text{ torr} + 600 \text{ torr} + 450 \text{ torr} = 1350 \text{ torr}$$

Example 4.5

A gaseous mixture contains 9.6% NH_3 and 22.6% N_2 and 67.8% H_2 gases. If its total pressure is 50 atm, find the partial pressure of each gas.

Solution

$$\text{Pressure of } \text{NH}_3 = \frac{9.6}{100} \times 50 = 4.8 \text{ atm}$$

$$\text{Pressure of } \text{N}_2 = \frac{22.6}{100} \times 50 = 11.3 \text{ atm}$$

$$\text{Pressure of } \text{H}_2 = \frac{67.8}{100} \times 50 = 33.9 \text{ atm}$$

4.8 Graham's law of Diffusion and Effusion

Gas Diffusion

Diffusion is the term used to describe the mixing of gases. Diffusion can be defined as the ability of two or more gases to mix spontaneously until they form a uniform mixture by random motion and collision (by virtue of their kinetic properties). Or

The spontaneous mixing of different non-reacting gases to form a homogenous mixture.

Although the molecules of the gas move with great speed, but the diffusion process is slow. It takes relatively long time to occur. For example, when a bottle of perfume is opened at one corner of a room, after some time a person at the other corner of the room can smell it. The reason is that a molecule experiences numerous collisions while moving from one end of the room to the other.

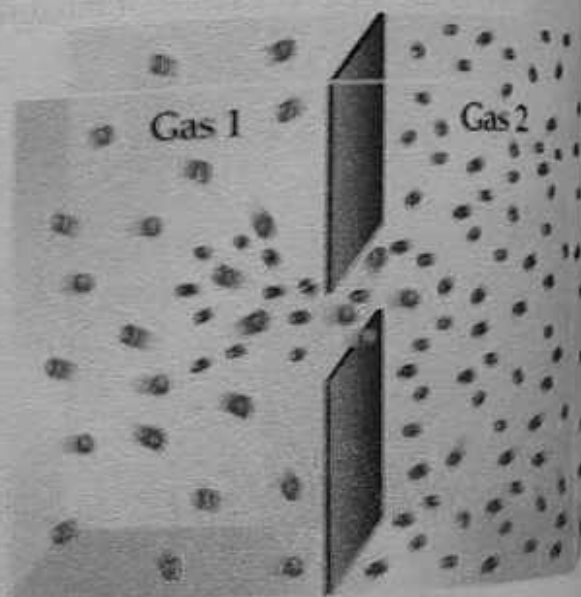


Figure 4.12 Diffusion of two Gases

Gas Effusion

Effusion is the term used to describe the passage of a gas through a tiny hole of molecular dimension, as shown in figure. 4.13. Effusion is the process by which gas molecules escape from one compartment of a container to another by passing through a small opening of molecular dimension without collision. In this process, gas molecules spread one by one without collisions to form a homogenous mixture.

A general example to differentiate between diffusion and effusion is the 'bursting' and 'puncturing' of a vehicle tyre. During

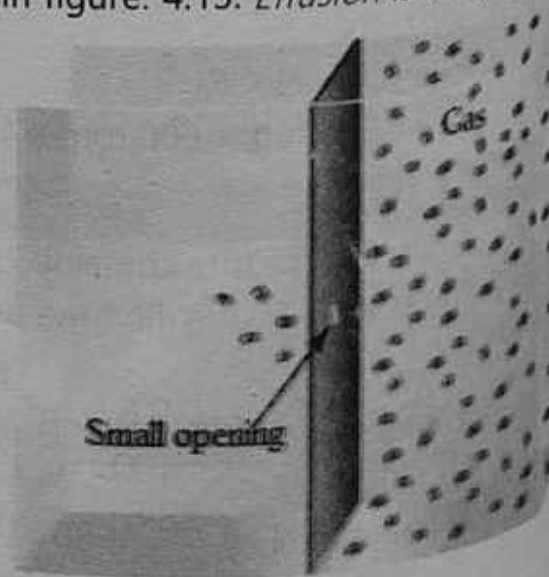


Figure 4.13 Gas Effusion

bursting, gas molecules spread suddenly. This phenomenon is called diffusion, while during puncturing, gas molecules spread by escaping through a small hole. This phenomenon is called effusion.

Rate of Diffusion or Effusion of a Gas

The distance travelled by gas molecules per unit time is called rate of diffusion or effusion of gas. Rate of diffusion of a lighter gas is greater than a heavier gas, even at the same temperature because rate of diffusion or effusion of a gas is not only directly proportional to its energy but also inversely proportional to its mass.

Graham's Law of Diffusion and Effusion

In 1832, the Scottish chemist Thomas Graham proposed his law of diffusion of gases, which states that *under the same conditions of temperature and pressure, the rates of diffusion or effusion for gases are inversely proportional to the square roots of their densities, or molecular masses*. This statement, now known as *Graham's law of diffusion*, is expressed mathematically as

$$\frac{r_A}{r_B} = \sqrt{\frac{d_B}{d_A}} \quad (4.31)$$

$$\text{Or } \frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}} \quad (4.32)$$

Where, r_A and r_B are the rate of diffusion or effusion, d_A and d_B are their densities, and M_A and M_B are molecular masses of gases A and B, respectively.

Experimental Verification of Graham's Law of Diffusion

Take a 100cm long glass tube. Plug a cotton swab soaked in hydrochloric acid $(\text{HCl})_{(\text{aq})}$ at one end and another cotton swab soaked in ammonia solution $(\text{NH}_3)_{(\text{aq})}$ at the other end simultaneously. The two gases diffuse from their solutions into air of tube and after some time react to form a white ring of ammonium chloride (NH_4Cl) . This white smoke of ammonium chloride (NH_4Cl) is 60cm from the NH_3 plug and 40cm from the HCl plug.

Let ' r_{NH_3} ', ' M_{NH_3} ' and ' v_{NH_3} ' represent rate of diffusion, molecular mass and velocity of NH_3 respectively, while ' r_{HCl} ', ' M_{HCl} ' and ' v_{HCl} ' represent the rate of diffusion, molecular mass and velocity of HCl respectively.

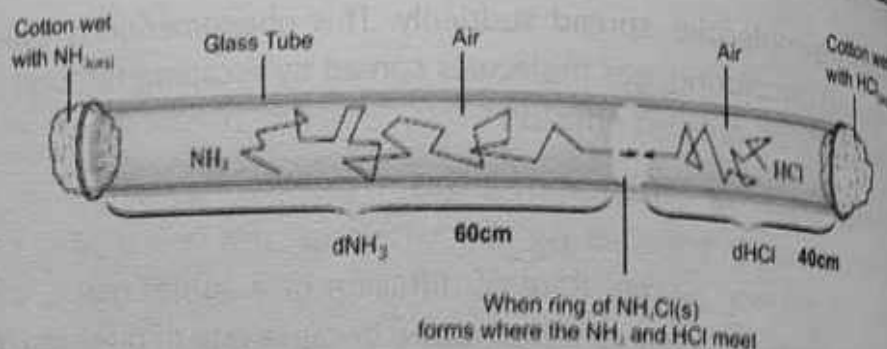


Figure 4.14 $\text{HCl}_{(\text{aq})}$ and $\text{NH}_{3(\text{aq})}$ meet in the tube, a white ring of $\text{NH}_4\text{Cl}_{(\text{s})}$ forms



Since, we know that,

$$S = vT \quad (S = \text{distance travelled by gas})$$

Or

$$v = \frac{S}{T}$$

Distance covered by $\text{NH}_3 = 60\text{cm}$

Distance covered by $\text{HCl} = 40\text{cm}$

Putting the values in the above equation,

$$\text{Velocity of } \text{NH}_3 = v_{\text{NH}_3} = \frac{60}{t} \quad (4.33)$$

and

$$\text{Velocity of } \text{HCl} = v_{\text{HCl}} = \frac{40}{t} \quad (4.34)$$

Dividing equation (4.33) by equation (4.34), we get

The ratio of velocities of two gases depends on their distance travelled the respective gases.

$$\frac{\text{Velocity of } \text{NH}_3}{\text{Velocity of } \text{HCl}} = \frac{v_{\text{NH}_3}}{v_{\text{HCl}}} = \frac{60}{t} \div \frac{40}{t}$$

$$\frac{v_{\text{NH}_3}}{v_{\text{HCl}}} = 1.5$$

But,

$$\frac{v_{\text{NH}_3}}{v_{\text{HCl}}} = \frac{r_{\text{NH}_3}}{r_{\text{HCl}}}$$

So, $\frac{r_{\text{NH}_3}}{r_{\text{HCl}}} = 1.5$ (Experimental results)

This ratio shows the relative rate of diffusion of two gases, which may be calculated on the basis of Graham's law of Diffusion.

As we have the equation,

$$\frac{\text{Rate of Diffusion of NH}_3}{\text{Rate of Diffusion of HCl}} = \sqrt{\frac{\text{Density of HCl}}{\text{Density of NH}_3}} \quad (4.35)$$

Density of HCl is 1.66 g.dm^{-3} and that of NH_3 is 0.76 g.dm^{-3} putting the values in equation (4.35) we get,

$$\frac{r_{\text{NH}_3}}{r_{\text{HCl}}} = \sqrt{\frac{1.66}{0.76}}$$

$$\frac{r_{\text{NH}_3}}{r_{\text{HCl}}} = \sqrt{2.184}$$

$$\frac{r_{\text{NH}_3}}{r_{\text{HCl}}} = 1.477 \cong 1.5 \text{ (Theoretical result)}$$

It shows that rate of diffusion of NH_3 is 1.5 times faster than the rate of diffusion of HCl.

As

$$\frac{r_{\text{NH}_3}}{r_{\text{HCl}}} = \sqrt{\frac{M_{\text{HCl}}}{M_{\text{NH}_3}}} \quad (4.32)$$

Similarly, we know that,

Molecular mass of HCl = $M_{\text{HCl}} = 36.5$

and Molecular mass of $\text{NH}_3 = M_{\text{NH}_3} = 17$

Putting the values in the equation, (4.32)

$$\frac{r_{\text{NH}_3}}{r_{\text{HCl}}} = \sqrt{\frac{36.5}{17}} = 1.465 \cong 1.5 \text{ (Theoretical result)}$$

As experimental and theoretical results are the same. Therefore, it verifies Graham's law of diffusion.

Example 4.6

Determine the relative rates of diffusion of equal volumes of H_2 and CO_2 under the same conditions of temperature and pressure.

Solution

Molecular mass of $\text{H}_2 = 2$

Molecular mass of $\text{CO}_2 = 44$

According to Graham's law of diffusion,

$$\frac{r_{H_2}}{r_{CO_2}} = \sqrt{\frac{M_{CO_2}}{M_{H_2}}}$$

Putting the values in the above equation,

$$\frac{r_{H_2}}{r_{CO_2}} = \sqrt{\frac{44}{2}} = \sqrt{\frac{22}{1}} = \frac{4.7}{1}$$

$$r_{H_2} = 4.7 r_{CO_2}$$

This means that hydrogen (H_2) molecules diffuse 4.7 times faster than carbon dioxide (CO_2) under identical conditions.

4.5 Practice problem

Calculate the relative rates of effusion of carbon dioxide (CO_2) and sulphur dioxide (SO_2), from the same container and at same temperature and pressure.

Application of Kinetic Molecular Theory of Gases

Velocity of molecules

There are different types of molecular velocities of gases. Here we will deal with root mean square velocity. It is square root of average of square velocities of gas molecules and is represented by u_{rms} .

$$u_{rms} = \sqrt{\bar{u}^2}$$

$$u_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2}{N}}$$

Where $v_1, v_2, v_3, \dots, v_n$ are velocities of N molecules of gas.

The value of the RMS of velocity, u_{rms} at a given temperature can be calculated from the kinetic gas equation given below.

$$PV = \frac{1}{3} mN\bar{u}^2 \quad (4.36)$$

Where P, V = pressure and volume of the gas

N = number of molecules

m = mass of each molecule

$\bar{u}^2$ = average (or mean) of the squares of all individual molecular velocities

Solving the equation (4.36) for $\bar{u}^2$ you will get,

$$\bar{u}^2 = \frac{3PV}{mN} \quad (4.37)$$

For one mole of gas,

Reading Check

Differentiate between effusion and diffusion gases.

$$PV = RT$$

If N = Avogadro's number, then $mN = M$, where ' M ' which is molar mass, and putting the value of PV in equation (4.37), so you get,

$$\bar{u}^2 = \frac{3RT}{M}$$

Taking the square root

$$\sqrt{\bar{u}^2} = \sqrt{\frac{3RT}{M}}$$

$$\text{As } u_{rms} = \sqrt{\bar{u}^2}$$

$$u_{rms} = \sqrt{\frac{3RT}{M}} \quad (4.38)$$

Putting the values of R , T and M , the value of u_{rms} can be determined.

Graham's Law of Diffusion of gases

According to kinetic molecular theory *at the same temperature and pressure, the molecules of different gases have the same average kinetic energy.*

Therefore, the average kinetic energies of gas molecules 'a' and 'b' at the same temperature should be equal.

Average kinetic energy of gas 'a' = Average Kinetic energy of gas 'b'

$$\frac{1}{2} m_a \bar{v}_a^2 = \frac{1}{2} m_b \bar{v}_b^2$$

$$m_a \bar{v}_a^2 = m_b \bar{v}_b^2$$

Divide the above equation by ' m_a '

$$\frac{m_a \bar{v}_a^2}{m_a} = \frac{m_b \bar{v}_b^2}{m_a}$$

$$\bar{v}_a^2 = \frac{m_b \bar{v}_b^2}{m_a}$$

Divide the above equation by ' $\bar{v}_b^2$ '

$$\frac{\bar{v}_a^2}{\bar{v}_b^2} = \frac{m_b \bar{v}_b^2}{m_a \bar{v}_b^2}$$

$$\frac{\bar{v}_a^2}{\bar{v}_b^2} = \frac{m_b}{m_a} \quad (4.39)$$

Taking square root of equation (4.39)

$$\frac{\bar{v}_a}{\bar{v}_b} = \sqrt{\frac{m_b}{m_a}} \quad \text{Or} \quad \frac{\bar{v}_a}{\bar{v}_b} = \sqrt{\frac{m_b N}{m_a N}}$$

Where N = No. of molecules of a gas
 As for one mole, mass of a gas is
 $Nm = M$

So

$$\frac{\bar{v}_a}{\bar{v}_b} = \sqrt{\frac{M_b}{M_a}} \quad (4.40)$$

It is known that,

$$\bar{v}_a \propto r_a$$

$$\bar{v}_b \propto r_b$$

Where,

r_a = rate of diffusion of gas 'a'

r_b = rate of diffusion of gas 'b'

Putting the values of ' $\bar{v}_a$ ' and ' $\bar{v}_b$ ' in equation (4.40), we get,

$$\frac{r_a}{r_b} = \sqrt{\frac{M_b}{M_a}}$$

$$\frac{r_a}{r_b} = \sqrt{\frac{M_b}{M_a}}$$

Or

$$\frac{r_a}{r_b} = \sqrt{\frac{d_b}{d_a}}$$

This is Graham's law of diffusion, which is explained by the Kinetic Molecular Theory.

4.9 Liquefaction of Gases

The process in which the gases are converted to their liquid states by lowering temperature and increasing pressure is called liquefaction of gases.

Increase in pressure on a gas causes the gas molecules to come closer to each other, while decrease in temperature decreases the kinetic energy of gas molecules. This results in development of attractive forces between molecules resulting in liquefaction of gases.

It is observed that, it is impossible to liquefy a gas by pressure alone if the required temperature is not obtained. Above this required temperature, the attractive forces are not strong enough to condense a gas into liquid. The temperature above which a gas cannot be liquefied no matter how great the pressure is called the critical temperature.

pressure is applied is called critical temperature (T_c).

The critical pressure (P_c), is the minimum pressure that is required to liquefy a gas at its critical temperature.

The critical volume (V_c), is the volume occupied by one mole of the gas at critical temperature (T_c) and critical pressure (P_c).

At critical temperature and critical pressure, the gas is in a state which is intermediate between gaseous and liquid state called **critical state**.

Table 4.3 Critical Temperature and Critical Pressure of Various Gases

S. No	Gas	T_c in $^{\circ}\text{C}$	P_c in atmosphere
1	Oxygen (O_2)	- 118.8	49.7
2	Nitrogen (N_2)	-147.1	33.5
3	Hydrogen (H_2)	-239.9	12.8

4.9.1 Joule – Thomson effect

Various methods are used for the liquefaction of gases. These methods are generally based upon Joule – Thomson effect.

Joule-Thomson effect is based on the principle that when a compressed gas is forced through a porous plug into a region of low pressure, there is appreciable cooling.

When a compressed gas is allowed to enter from region of high pressure into a region of low pressure, it expands. This sudden expansion causes cooling. This phenomenon is known as Joule-Thomson Effect.

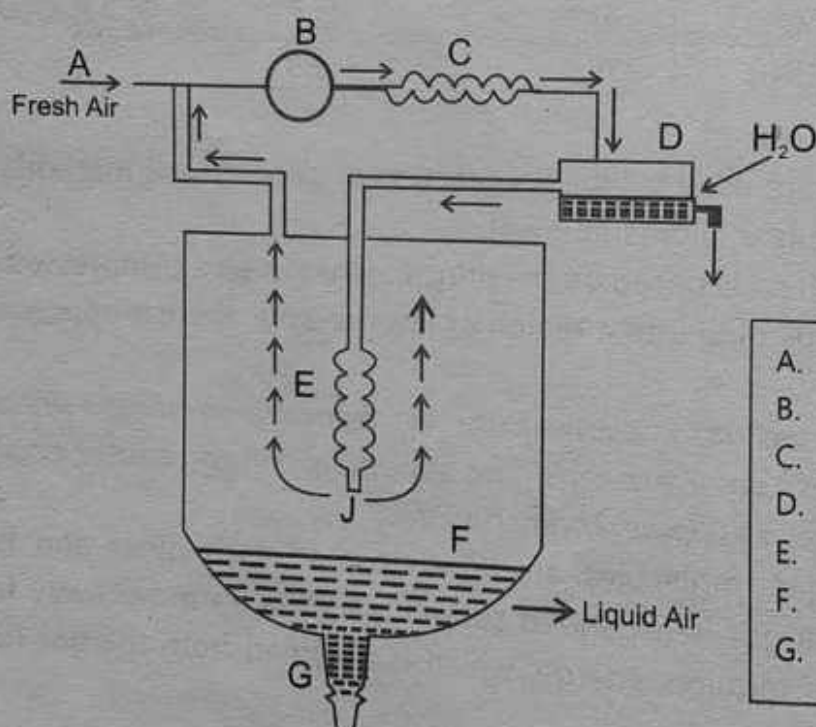
In compressed gas, molecules are very close to each other and have attractive forces. When a gas is expanded suddenly molecules move away from each other. This process requires energy, which is obtained from the gas itself, hence it is cooled.

4.9.2 Linde's Method of Liquefaction of Gases

Linde's Method is based on Joule-Thomson effect in order to liquefy gases or air. The apparatus used for the liquefaction of gas by this method is shown in figure 4.15.

- Pure air or gas is first compressed to 200 atm by passing through a compressor.
- The water in air or gas is condensed and removed.
- The heat generated as a result of compression is removed by passing the gas through spiral coils C.
- The dry gas is then passed through a copper spiral coil E having a jet J at the lower end.

- v. It is then expanded to almost 1 atm when it comes out of jet J.
- vi. When the air comes out of the jet, expansion takes place from 200 atm to 1 atm. In this way fall of temperature occurs due to Joule-Thomson Effect. The cooled air goes up and cools the incoming compressed air.
- vii. The cycle is repeated several times.
- viii. The temperature of the expanding gas finally drops and the remaining air is liquefied.
- ix. The liquid air is collected in chamber F and can be drawn off at regular intervals through outlet G.

**Reading Check**

What is liquefaction of gases?

- A. Inlet of Air
- B. Compressor
- C. Condensing Coils
- D. Receiver for Water
- E. Copper Spiral with a Jet J
- F. Liquefied Air Chamber
- G. Outlet for Liquefied Air

Figure 4.15 Linde Apparatus



Science, Technology and Society

The advantage of liquefying gases is that they can then be stored and transported in much more compact form than in the gaseous state. Liquefied gases are used for a number of purposes. Some of the most important uses are:

- Liquid natural gas is used as a fuel in vehicles in the form of liquefied natural gas (LNG).
- Liquid oxygen is used in hospitals for patients suffering from breathing problems.
- Liquid oxygen and liquid hydrogen are used in rocket engines.
- Liquid nitrogen is used by dermatologists. It is also used for low temperature

- and freezing purposes.
- Liquid oxygen and liquid acetylene can be used in welding operations.
- Liquid chlorine is used for killing the pathogens in drinking water, purification of swimming pools, sanitation of industrial waste and sewage water. It is also used for bleaching of pulp and textiles and in the preparation of different chemicals such as carbon tetra chloride (CCl_4) etc.
- Liquid air is distilled and used to obtain nitrogen, oxygen and argon.
- Liquefaction of gases is also important in the field of research known as cryogenics.
- Liquid helium is widely used for the study of behavior of matter at temperatures close to absolute zero, 0K.

4.10 Fourth State of Matter: Plasma

Solid, liquid and gas are the three fundamental states of matter. Plasma is considered the fourth state of matter.

Plasma is a Greek word which means, that 'which is diffused' that is, 'unclear or semi transparent'. Plasma is a state of matter in which it exists as a mixture of neutral particles, positive ions and negative electrons. For example, our sun is composed of plasma.

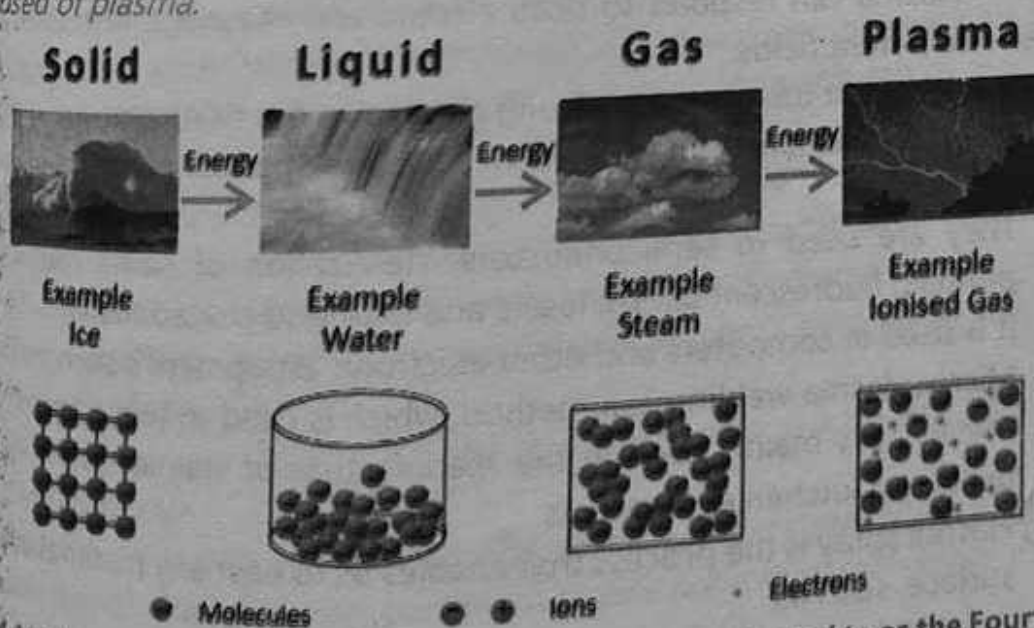


Figure 4.16 The Four States of Matter; Plasma is sometimes referred to as the Fourth State

Origin of Plasma

This term was originally applied by Irving Langmuire in 1928 to an ionized gas. Since an ionized gas cannot exist at room temperature, that is why, it was first observed for the first time in an electrical discharge at high temperature.

Plasma Formation

On heating a solid, it is converted into liquid. On further heating, the liquid is converted into vapours. Now if vapours are further heated, some of them ionize and electrons and positive ions are formed.

Plasma is a mixture of neutral particles, positive ions and free electrons. Plasma is considered a unique fourth state of matter. The properties of plasma clearly distinguish it from an ordinary gas such as it conducts electricity and responds to magnetic fields.

Occurrence of Plasma

Plasma is found in the region around sun and stars. Since sun and stars have far more matter, therefore, it is said that more matter (about 99% of the universe) is made up of plasma. On earth, plasma is limited to lightning bolts, flames and fluorescent lights, neon signs etc. when an electric current is passed through neon gas; it produces both plasma and light.

Although it contains positive ions and negative electrons but their charges are equal and hence plasma is neutral.

Applications

Plasma can respond to both electric and magnetic fields, so it has many uses in different fields.

1. A fluorescent tube consists of long glass tube. It is filled with neon gas. The neon gas in plasma form is used for lightening. The colour of plasma depends upon the gas used.
2. They are used in semiconductors, sterilization of some medical products, printers, fluorescent lamps, lasers and diamond coated films.
3. It is used in computers and other electronic equipment's such as TV etc.
4. Micro-plasma welding is a method, which is used to join paper-thin sheets of metals. It is mainly used in the manufacture of stainless steel, water storage tanks and kitchen equipments.
5. Plasma spray is the process that enables us to coat any material onto any surface, such as,
 - Metal onto metal: Titanium onto steel, to prevent corrosion
 - Metal onto non-metal: Copper onto porcelain, used in capacitors
 - Non-metal onto metal: Alumina onto stainless steel, to reduce wear and on stainless steel
 - Non-metal onto non-metal: Teflon onto ceramics, to prevent corrosion from acids.

Self-Assessment

1. State Dalton's law of partial pressures.
2. How the pressure and volume correction is made in the ideal gas equation.
3. Define Joule-Thomson effect.
4. Derive Graham's law of diffusion and effusion for molecular masses of gases.
5. Write down the experimental verification of Graham's of diffusion and effusion.
6. Differentiate between ideal and real gas.
7. What is plasma, Write down its applications?
8. Why real gases deviate from the gas laws?
9. Discuss briefly in points the Linde's method for the liquefaction of gases.
10. Define critical temperature, critical pressure and critical volume.

KEY POINTS

- Gas is the state of matter, which has neither definite volume nor definite shape. In other words, gas is the matter with the highest energy state.
- Kinetic molecular theory of gases is based on the fundamental concept that molecules in gases are in constant movement.
- Barometer, a type of manometer, is used to measure atmospheric pressure.
- One atmosphere is the force exerted by 76cm long column of mercury on an area of 1 cm^2 at 273.15 K
- One Pascal is the pressure exerted by a force of one Newton (1 N) acting on an area of one square meter. SI unit of pressure is N/m^2 , which is one Pascal.
- Charles' and Gay-Lussac experiments showed that volume changes by $1/273$ of the original volume at 0°C for each Celsius degree ($^\circ\text{C}$) rise or fall in temperature at constant pressure.
- The temperature -273.15°C is the absolute zero, and is given a value of zero in the Kelvin scale.
- Avogadro's law states that at the same temperature and pressure, equal volumes of different gases contain the same number of molecules.
- One mole of any gas contains 6.022×10^{23} molecules (Avogadro's number). One mole of a gas occupies 22.4 dm^3 at STP.
- An ideal gas is a gas that behaves exactly as outlined by the assumptions of the kinetic molecular theory.

- The conditions 0°C and 1 atm are called standard temperature and pressure (abbreviated as STP).
- Compressibility factor shows the extent to which a real gas deviate from the ideal behaviour. Real gases are non-ideal gases.
- Dalton's law states that the total pressure exerted by a mixture of gases in a container is equal to the sum of the partial pressures of all the gases present in the mixture provided that no chemical reaction occurs at constant temperature and volume.
- Diffusion is the ability of two or more gases to mix spontaneously until they form a uniform mixture by random motion and collision (by virtue of their kinetic properties). Lighter gases diffuse at higher rates than heavier gases.
- Effusion is the process by which gas molecules escape from one compartment of a container to another by passing through a small opening without collision.
- Graham's law of diffusion states that under the same conditions of temperature and pressure, rates of diffusion for gases are inversely proportional to the square roots of their densities or molecular masses.
- Liquefaction of gases is the process in which the gases are converted to the liquid state by lowering temperature and increasing pressure.
- When a compressed gas is allowed to enter from region of high pressure into a region of low pressure, it expands. This sudden expansion causes cooling. This phenomenon is known as Joule-Thomson Effect.
- Plasma is considered as the fourth state of matter. About 99% of the universe is made up of plasma.

EXERCISE

Choose the Correct Option.

1. If absolute temperature of a gas is doubled and the pressure is reduced to, one-half the volume of gas will,
a. remain unchanged
b. double
c. reduce to half
d. increase four times
2. One dm^3 of Hydrogen at STP weighs approximately
a. 0.0789g
b. 0.0799g
c. 0.0987g
d. 0.0899g
3. In a factory producing liquid air, one of the pipes carrying dry air at -80°C is blocked with a white solid. This white solid is,
a. Argon
b. Ice
c. Nitrogen
d. Carbon dioxide
4. The spreading of perfume or scent in air is due to
a. Diffusion
b. Effusion
c. Attraction with air
d. Low density
5. A gas has certain volume at 10°C . How much temperature should be raised to double its volume,
a. 566K
b. 283K
c. 293K
d. 283°C
6. The rate of diffusion of hydrogen (H_2) compared with helium (He) is,
a. 0.5 times
b. 1.4 times
c. 2 times
d. 4 times
7. The non-ideal behaviour results chiefly from
a. Intermolecular attraction and infinite volume
b. Elastic collisions and finite volume
c. Intermolecular attractions and finite volume
d. Intermolecular attraction only
8. The molar volume of helium (He) is 44.8dm^3 at,
a. 100°C and 1atm
b. 25°C and 0.25atm
c. 0°C and 0.5atm
d. 40°C and 0.5atm

9. Which statement about the behaviour of the particles in a gas is not correct?
- They are able to move at great speeds
 - The forces of attraction between the particles are negligible
 - There is large space among the particles
 - They are arranged in regular patterns
10. At the same temperature and pressure which of the following gases has the greatest density,
- CO_2
 - SO_2
 - Cl_2
 - H_2O
11. Weight of one dm^3 of O_2 at STP is
- 1.4384 g
 - 1.5394 g
 - 1.6384 g
 - 1.3384 g
12. The value of ideal gas constant in $\text{dm}^3 \cdot \text{torr} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
- 0.0821
 - 1.98722
 - 62.364
 - 8.3143
13. 760 torr is equal to,
- 760 Pascal
 - 76 Pascal
 - 101325 Pascal
 - 1.01325 Pascal
14. At 50°C a gas has 1atm pressure, and 20dm^3 volume, its volume at STP would be
- 16.94dm^3
 - 10.92dm^3
 - 3.66dm^3
 - 42.2dm^3
15. Which of the following gases will have the fastest effusion rate?
- CH_4
 - NH_3
 - CO_2
 - O_2

Short Questions

- Justify that 1cm^3 of hydrogen (H_2) and 1cm^3 of methane (CH_4) at STP will have same number of molecules although one molecule of methane (CH_4) is 8 times heavier than that of hydrogen (H_2).
- Do you think that some of the postulates of kinetic molecular theory of gases are faulty? Write down these postulates.
- Why high pressure and low temperature make the gases non-ideal?
- What is your opinion about rapid expansion of gases causes cooling?
- Why do you think that lighter gases can diffuse more rapidly than heavier ones?

Numerical Questions

1. A mass of gas is under a pressure of 760 torr and occupies volume of 525cm^3 . If the pressure is doubled, what volume would the gas now occupy? Assume the temperature is constant. (Answer: 262.5cm^3)
2. Hydrogen gas diffuses through a porous plate at a rate of 500cm per minute at 0°C . What is the rate of diffusion of oxygen gas through the same porous plate at 0°C ? (Answer: 125cm)
3. It was desired to obtain a volume of 1000cm^3 of oxygen at 100°C and 640 mm Hg. How many moles of oxygen would be required? (Answer: 0.0275mol)
4. Calculate the density of CH_4 at 0°C and 1 atmosphere. (Answer: 0.7139gdm^{-3})
5. A sample of Krypton with a volume of 6.25dm^3 and a pressure of 765 torr and a temperature of 20°C is expanded to a volume of 9.55dm^3 and a pressure of 375 torr. What will be its final temperature? (Answer: 219.64K)

Descriptive Questions

1. (a) Explain the concept of diffusion and effusion of gases.
(b) Apply the knowledge of the kinetic theory of gases and derive an expression of Graham's law of diffusion.
(c) The rate of effusion of an unknown gas through a pinhole is found to be 0.279 times the rate of effusion of H_2 through the same pinhole. Calculate the molecular mass of the unknown gas at STP. (Answer: 25.7g)
2. (a) State Dalton's law of partial pressure. Write down its mathematical form.
(b) Explain the significance of absolute zero, giving its value in degree Celsius and Kelvin.
(c) What pressure is exerted by a mixture of 2g of helium (He), 16g of oxygen (O_2) and 10g of carbon dioxide (CO_2) at 10°C in a 5dm^3 vessel? (Answer: 5.703atm)
3. (a) How would you relate temperature to the average kinetic energy of the particles in a substance?
(b) Explain Linde's method for the liquefaction of gases.
(c) Give two points of evidence to show that gases do not behave ideally under all conditions of temperature and pressure.
4. (a) Write the Van der Waals equation for a real gas. Clearly explain the meaning of the corrective terms for pressure and volume.
(b) The temperature of a real gas usually drops when it is allowed to enter into a low pressure (vacuum), Explain.
(c) Define and describe the properties of plasma.

5.
 - (a) State basic postulates of kinetic molecular theory of gases.
 - (b) Explain how Graham's law of diffusion can be derived from the Kinetic Molecular Theory.
 - (c) Explain the absolute zero on the basis of Charles' law.

PROJECT:

1. Use the daily weather reports in the newspapers or news and conduct a meteorological research to study the interrelationships among atmospheric pressure (air pressure), temperature, humidity, and other weather variables. Prepare a report of a week explaining your results and present it in the class.
2. The pressure of air in car tyres is checked regularly for safety and to prevent uneven tyre wear and tear. What units of measurement are used on a typical tyre gauge? Also, find out that how gauge pressure relates to atmospheric pressure.