Chapter Two

Gases

2.1 Definition of gases

The gaseous state is the simplest of the three states of matter, in which the arrangement of molecules at any given time is random or irregular. There are fundamental variables that play a role in the nature of a gas, namely pressure, temperature and volume, which were defined earlier in the first lecture. There are two types of gases:

First (Ideal gases):

These are gases that obey the laws of gases, namely Boyle's law, Charles's law, Avogadro's law, Graham's law of diffusion, and Dalton's law of molecular pressures. A gas behaves ideally when the pressure is low and the temperature is high.

Since there is an inverse relationship between volume (V) and pressure (P) (V α $\frac{1}{P}$), when the pressure is low, the volume increases and collisions decrease because the gas particles will be far apart from each other, and the gas will behave ideally. That is, its volume is small relative to the volume of the container.

Second: Non-ideal or real gases:

These are gases that deviate from ideal behavior and do not obey the laws that ideal gases obey. Gases behave realistically when the pressure is high and the temperature is low.

When the pressure increases, the gas molecules move closer to each other and collide, generating additional pressure. The gas then deviates from ideal behavior and behaves as a real gas at low temperatures.

In this chapter, we will learn about the laws of ideal gases and Van der Waals equation for real gases.

2.2 Ideal gas laws

2.2.1 Boyle's law

When the temperature is constant, the volume of a given quantity of gas (V) is inversely proportional to the pressure (P) and can be represented by the following equation:

$$V \ \alpha \ \frac{1}{P}$$

Boyle's law is used to deduce the pressure of a gas when its volume changes, and vice versa. If we assume that the initial values of the pressure and volume of the gas are P_1V_1 and the final values are P_2V_2 , we will have

$$P_1V_1 = P_2V_2$$

2.2.2 Charles's Law

This law states that the volume of a given quantity of gas is directly proportional to the temperature when the pressure is constant. It can be represented by the following equation:

2.2.3 Avogadro's Law

This law states that the volume of a gas at a constant temperature and pressure is directly proportional to the number of moles of the gas. It can be represented by the following equation:

$$V = n * constant$$

Where represents the number of moles and is a constant value.

The number of moles = weight/molecular weight. As the number of moles increases, the volume increases.

Through the three laws mentioned above, we can derive the universal law of ideal gases (ideal gas equation). This law is defined as follows:

$$V \; \alpha \; \frac{n \, T}{P}$$

$$V = R \frac{nT}{P}$$

$$PV = nRT$$

Where:

P= represents pressure

V= represents volume

n= represents the number of moles

T= represents temperature in Kelvin

R= represents the gas constant and is mathematically defined as $R = \frac{PV}{nT}$

Gas constants are measured in the following units:

- 1) R=0.082 lit.atm.mol⁻¹ k⁻¹
 2) R=8.314×10⁷ erg.mol⁻¹ k⁻¹
- 3) R=8.314 Joul.mol⁻¹ k⁻¹
- 4) R=2.0 cal. mol⁻¹ k⁻¹ 1cal=4.18 Joul

Note: If we have one mole called 'molar volume' and there are formulas used for molar volume

$$PV = mRT$$

$$\overline{V} = \frac{V}{m} \implies m=1$$

$$P\overline{V} = RT$$

Density (ρ) = weight / volume

$$\begin{split} \rho &= \frac{W}{V} \\ P &= \frac{W}{V} {\times} \frac{RT}{M} \Longrightarrow P = \rho {\times} \frac{RT}{M} \end{split}$$

Where represents the molecular weight of gases. The units of measurement are:

pressure	Volume
atm	M^3
mm/Hg	Lit
cm/Hg	cm ³ (ml)

Example (1): Assuming one mole of an ideal gas under standard conditions, calculate the gas constant R.

S.T.P
$$\begin{cases} T = 273 \,\mathrm{K}^{\mathrm{o}} \\ P = 1 \,\mathrm{atm} \\ 0 \,\mathrm{C}^{\mathrm{o}} \end{cases}$$

$$R = \frac{PV}{nT}$$
=\frac{1 \text{ atm*22.4 L}}{1 \text{ mol*273 K}^{\text{o}}}
=0.082 \text{ lit.atm.mol}^{-1} \text{ K}^{-1}

H.W: What volume does (2.7 gm) of H_2 gas occupy? If the molar volume of an ideal gas under the same standard conditions of temperature and pressure is equal to (22.4 dm³/mol). Note that the molar mass of H_2 is equal to (2.016 gm/mol).

Example (2): (2 mol) of ideal ammonia gas (NH₃) occupies a volume of (5) liters at (27 c) Calculate the pressure of the gas measured in

(a) atmospheres (b) newtons per square meter (Nm⁻²).

(a) atmospheres

$$PV = nRT$$

 $P \times 5 = 2 \times 0.082 \times (27 + 273)$
 $P = 9.84$ atm

(b) newtons per square meter (Nm⁻²).

 $P \times 5 \times 10^{-3} = 2 \times 8.314 \times 300 \implies \text{(joul = N.m., } 1\text{M}^3 = 1000 \text{ lit.)} \implies p \times \text{M}^3 = \text{mol} \times \text{N. m. mol}^{-1} \times \text{K}^{-1}.\text{K}$ $P = 9.98 \times 10^5 \, \text{Nm}^{-2}$

Example (3): Calculate the volume in cubic meters occupied by (10 g) of nitrogen gas (N2) under standard conditions (S.T.P) at a pressure of 1 atm and a temperature of

273 K (note that the atomic weight of nitrogen = 14).

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

$$1 \times V = \frac{10}{28} \times 0.082 \times 273$$

$$V = 7.99 \text{ lit}$$

$$V = 7.99 \times 10^{-3} \text{M}^3$$

2.2.4 Graham's Law of Diffusion

This law states that the diffusion rate of any gas is inversely proportional to the square root of the molecular weight of that gas. It can be represented by the following equation:

$$r = \frac{1}{\sqrt{M}}$$

The following law is used to find the molecular weights of unknown gases if their speeds are known.

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

Diffusion: The flow of gas from an area of high pressure to an area of low pressure through a porous barrier or a narrow tube with a very small diameter.

Example (4): If the diffusion rate of a certain gas $(r_1=10\,\mathrm{cm^3min^{-1}})$ and its molecular weight are unknown, and the diffusion rate of oxygen under the same conditions is

(r_{O_2} =14 cm³min⁻¹), calculate the molecular weight of the unknown gas, knowing that the atomic weight of oxygen is 16.

M.Wt for $O_2=16\times2=32$

$$\frac{r_{1}}{r_{2}} = \sqrt{\frac{M_{2}}{M_{1}}}$$

$$\frac{10}{14} = \sqrt{\frac{32}{M_1}}$$

$$(0.7143)^2 = \frac{32}{M_1}$$

$$0.5102 = \frac{32}{M_1}$$

$$M_1 = 62.72 \, g.mol^{-1}$$

Example (5): Arrange the following gases in order of increasing diffusion rate under standard conditions.

M.Wt for
$$SO_2 = 32 + (16 \times 2) = 64$$

M.Wt for
$$N_2 = 14 \times 2 = 28$$

M.Wt for
$$CO_2 = 12 + 32 = 44$$

M.Wt for
$$CH_4 = 12 + 4 = 16$$

M.Wt for
$$H_2S = 2 + 32 = 34$$

M.Wt for
$$Cl_2 = 35.5 \times 2 = 71$$

$$CH_4 < N_2 < H_2S < CO_2 < SO_2 < Cl_2$$

Increase in molecular weight (M.wt) and decrease in diffusion rate

2.2.5 Dalton's Law of Partial Pressures

This law states that the sum of the partial pressures of the components of a gas is equal to the total pressure. The total pressure law is defined as follows:

Suppose we have three gases, A, B, and C, and that

m_A equals the number of moles of gas A

 $m_{\mbox{\scriptsize B}}$ equals the number of moles of gas B

 $m_{\mbox{\scriptsize C}}$ equals the number of moles of gas C

m equals the total sum

$$\begin{aligned} p_T &= \left[m_A + m_B + m_C \right] \times \frac{RT}{V} \\ m_T &\times \frac{RT}{V} = m_A \times \frac{RT}{V} + m_B \times \frac{RT}{V} + m_C \times \frac{RT}{V} \\ &\therefore P &= m \times \frac{RT}{V} \\ &\therefore P_A = m_A \times \frac{RT}{V} \\ P_T &= P_A + P_B + P_C \end{aligned}$$

By division $\frac{P_A}{P_T}$ (because the fractional part (X) equals ($\rm X = \frac{P_A}{P_T}$)

$$\frac{P_{A}}{P_{T}} = \frac{m_{A} \times \frac{RT}{V}}{m_{T} \times \frac{RT}{V}}$$
$$= \frac{m_{A}}{m_{T}}$$
$$= X$$

Where X represents the mole fraction (which is unitless).

Therefore, the partial pressure of any gas is mathematically defined as: the mole fraction of that gas × total pressure. That is $^{P_A}=XP_T$

The same applies to gases B and C.

Example (6): Add (0.2 mol) of helium (He) gas at a temperature of (27 c) to a flask containing (10 gm) of N2 gas, noting that the volume of the gas (N2, He) is (7.99 L) and the atomic weight of nitrogen gas is (14).

- (a) Calculate the partial pressures PT, P_{He} , and P_{N2} .
- (b) Calculate the mole fraction (X) of He gas.

(a)

$$\begin{aligned} P_{N_2} &= m_{N_2} \times \frac{RT}{V} \\ &= \frac{10}{28} \times \frac{0.082 \times 300}{7.99} \\ &= 0.36 \times 3.08 \\ &= 1.11 \text{ atm} \end{aligned}$$

Thermodynamics (Theoretical)

New and Renewable Energy Department

Lecture 2

$$\begin{split} P_{He} &= m_{He} \times \frac{RT}{V} \\ &= 0.2 \times \frac{0.082 \times 300}{7.99} \\ &= 0.2 \times 3.08 \\ &= 0.62 \text{ atm} \end{split}$$

$$P_{T} = P_{N_{2}} + P_{He}$$

= 1.11 + 0.62
= 1.73 atm

(b)

$$\begin{split} P_{He} &= X_{He} P_T \\ X_{He} &= \frac{P_{He}}{P_T} = \frac{0.62}{1.73} = 0.36 \end{split}$$

$$m_{T} = m_{N_{2}} + m_{He}$$

= 0.36+ 0.2
= 0.56

$$X_{He} = \frac{m_{He}}{m_T} = \frac{0.2}{0.56} = 0.36$$

2.3 The kinetic theory of ideal gases

These are the laws that govern the properties of gases explained above, which were arrived at through experimentation rather than theoretical justification. This theory is based on some basic assumptions, which are:

- **1-** Each gas consists of a very large number of small solid particles known as molecules, and the gas molecules themselves are identical in all respects. That is, they have the same mass, shape and size, but differ from other gas molecules.
- **2-** The gas molecules inside the container are in rapid motion in all directions and move in straight lines until they collide with other molecules or with the walls of the container, at which point their direction of motion changes.
- **3-** The pressure of a gas on any surface is the result of the number of collisions of its atoms or molecules with the walls of the container that contains it. The reason for the increase in pressure can be easily explained by the decrease in the volume of the container, as the collisions become more numerous, leading to an increase in pressure.
- 4- There is no tangible force of attraction between gas molecules.
- **5-** The absolute temperature of a gas is a measure of the kinetic energy of all its particles and is directly proportional to it. That is, an increase in temperature leads to an increase in the speed of the atoms or molecules

that make up the gas, which leads to an increase in pressure, provided that the volume remains constant.

- 6- Gravity does not affect the motion of gas molecules.
- **7-** These particles obey Newton's laws of motion in mechanics during their movement.

According to the above assumptions, the kinetic model of an ideal gas can be conceived with properties that are approximately similar to those of a real gas.