

1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester - 1)
Module Name/Title	States of Matter: Part 3
Module Id	kech_10503
Pre-requisites	Gaseous state, Intermolecular interactions, Gas laws, Ideal gas law, Mole fraction.
Objectives	After going through this module, the learner will be able to: <ul style="list-style-type: none">• Understand Dalton's law of partial pressure.• Explain Kinetic molecular theory of gases.• Apply gas laws in various real life situations.• Explain the behaviour of real gases.
Keywords	Dalton's Law of Partial Pressure, Kinetic Molecular Theory of gases, Real gas, van der Waals equation, Compressibility factor, Boyle point.

2. Development Team

Role	Name	Affiliation
National MOOC Coordinator (NMC)	Prof. Amarendra P. Behera	CIET, NCERT, New Delhi
Program Coordinator	Dr. Mohd. Mamur Ali	CIET, NCERT, New Delhi
Course Coordinator (CC) / PI	Prof. R. K. Parashar	DESM, NCERT, New Delhi
Course Co-Coordinator / Co-PI	Dr. Aerum Khan	CIET, NCERT, New Delhi
Subject Matter Expert (SME)	Dr. Komal S. Khatri	G. B. Pant Institute of Polytechnic, Okhla Phase II, New Delhi
Review Team	Dr. Amit Kumar	Dept. of Chemistry, Dayal Singh College College, New Delhi
Language Editor	Dr. Aerum Khan Dr. Amit Kumar	CIET, NCERT Dept. of Chemistry, Dayal Singh College College, New Delhi

Table of Contents:

1. Dalton's Law of Partial Pressure
2. Kinetic Molecular Theory of Gases
3. Behaviour of Real Gases: Deviation from Ideal Gas Behaviour
4. Summary

1. **Dalton's Law of Partial Pressures:** The law was formulated by John Dalton in 1801. It states that the total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases i.e., the pressures which these gases would exert if they were enclosed separately in the same volume and under the same conditions of temperature. In a mixture of gases, the pressure exerted by the individual gas is called partial pressure (Fig. 1). Mathematically,

$$p_{\text{Total}} = p_1 + p_2 + p_3 + \dots \text{(at constant T, V)} \quad \dots 1$$

where p_{Total} is the total pressure exerted by the mixture of gases and p_1, p_2, p_3 etc. are partial pressures of gases.

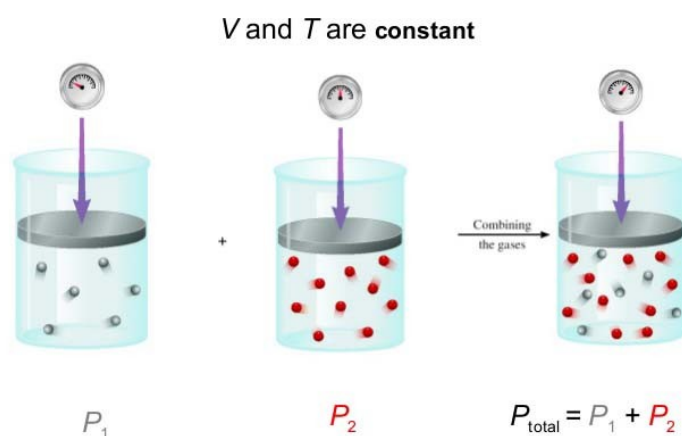


Fig. 1. Dalton's Law of Partial Pressure

(Source: <http://image.slidesharecdn.com/ch05lecture-141118105644-conversion-gate02/95/chapter-5-gases-41-638.jpg>)

Fig. 2 illustrates the Dalton's law of partial pressure in brief. The box 'a' shows the molecule of a gas, say A, at a pressure of 0.12 atm and temperature of 0 °C while the box 'b' contains another gas, say B, at a pressure of 0.12 atm and temperature of 0 °C. The box C shows mixture of A and B having pressure of 0.24 atm and temperature of 0 °C. the rapidly moving particles of each gas have an equal chance to collide with the container walls. Therefore, each gas exerts a pressure independent of that exerted by the other gases present. The total pressure is the result of the total number of collisions per unit of wall area in a given time.

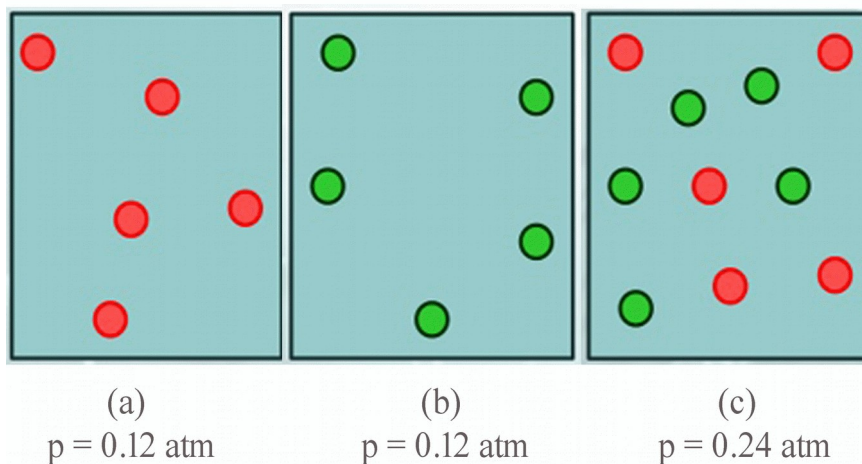


Fig. 2. Illustration of Dalton's law of Partial Pressure

(Source: <http://image.slidesharecdn.com/gaslaws-110718215802-phpapp02/95/gas-laws-diagrams-30-728.jpg>)

For example, when 0.6 mol of hydrogen gas (with partial pressure of 2.9 atm) and 1.5 mol of helium gas (with partial pressure of 7.2 atm) are mixed together, then the total pressure of the mixture is simply sum of the partial pressure of both the gases i.e. 10.1 atm (Fig. 3).

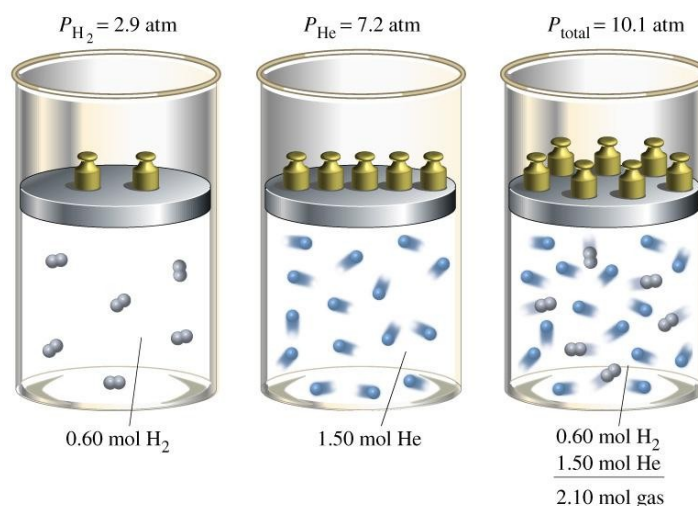


Fig. 3. Determination of pressure of the mixture of Hydrogen gas and Helium gas

(Source: https://upload.wikimedia.org/wikipedia/commons/9/9a/Presiones_parciales.JPG)

Another common example is air, the mixture of different gases. The total pressure of air is the sum of partial pressure of each of the constituent gases (Fig. 4).

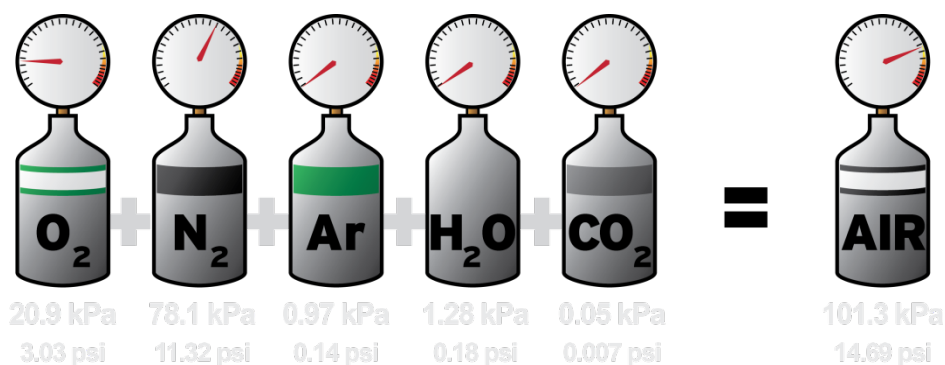


Fig. 4. Air: Example to illustrate the Dalton's law of partial pressure

(Source:

https://upload.wikimedia.org/wikipedia/commons/8/8e/Dalton's_law_of_partial_pressures.png)

Gases are generally collected over water and therefore are moist. Pressure of dry gas can be calculated by subtracting vapour pressure of water from the total pressure of the moist gas which contains water vapours also. Pressure exerted by saturated water vapour is called aqueous tension. Aqueous tension of water at different temperatures is given in Table 1.

$$p_{\text{Dry gas}} = p_{\text{Total}} - \text{Aqueous tension}$$

Table 1. Aqueous Tension of Water (Vapour Pressure) as a Function of Temperature

Temp. /K	Pressure /bar	Temp. /K	Pressure /bar
273.15	0.0060	295.15	0.0260
283.15	0.0121	297.15	0.0295
288.15	0.0168	299.15	0.0331
291.15	0.0204	301.15	0.0372
293.15	0.0230	303.15	0.0418

Partial pressure in terms of mole fraction: Suppose at the temperature T, three gases, enclosed in the volume V, exert partial pressure p_1 , p_2 and p_3 respectively. then,

$$p_1 = \frac{n_1 RT}{V} \quad \dots\dots 2$$

$$p_2 = \frac{n_2 RT}{V} \quad \dots\dots 3$$

$$p_3 = \frac{n_3 RT}{V} \quad \dots\dots 4$$

where n_1 , n_2 and n_3 are number of moles of these gases. Thus, expression for total pressure will be

$$p_{\text{Total}} = p_1 + p_2 + p_3$$

$$p_{\text{Total}} = n_1 \frac{RT}{V} + n_2 \frac{RT}{V} + n_3 \frac{RT}{V}$$

$$p_{\text{Total}} = (n_1 + n_2 + n_3) \frac{RT}{V} \quad \dots\dots 5$$

On dividing p_1 by p_{total} we get

$$\frac{p_1}{p_{\text{Total}}} = \left(\frac{n_1}{n_1 + n_2 + n_3} \right) \frac{RTV}{RTV} = \left(\frac{n_1}{n_1 + n_2 + n_3} \right) = \frac{n_1}{n} = x_1$$

where $n = n_1 + n_2 + n_3$

x_1 is called mole fraction of first gas.

Thus,

Similarly for other two gases we can write

and $p_3 = x_3 p_{\text{Total}}$

Thus a general equation can be written as

$$P_i = x_i P_{Total}$$

.....6

where p_i and x_i are partial pressure and mole fraction of i^{th} gas respectively. If total pressure of a mixture of gases is known, the equation (6) can be used to find out pressure exerted by individual gases.

Problem 1: A neon-dioxygen mixture contains 70.6 g dioxygen and 167.5 g neon. If pressure of the mixture of gases in the cylinder is 25 bar. What is the partial pressure of dioxygen and neon in the mixture ?

Solution:

$$\text{Number of moles of dioxygen} = \frac{70.6 \text{ g}}{32 \text{ g mol}^{-1}} = 2.21 \text{ mol}$$

$$\text{Number of moles of neon} = \frac{167.5 \text{ g}}{20 \text{ g mol}^{-1}} = 8.375 \text{ mol}$$

$$\text{Mole fraction of dioxygen} = \frac{2.21}{2.21 + 8.375} = \frac{2.21}{10.585} = 0.21$$

$$\text{Mole fraction of neon} = \frac{8.375}{2.21 + 8.375} = \frac{8.375}{10.585} = 0.79$$

Alternatively,

$$\text{Mole fraction of neon} = 1 - 0.21 = 0.79$$

Partial pressure of a gas = mole fraction \times total pressure

$$\Rightarrow \text{Partial pressure of oxygen} = 0.21 \times (25 \text{ bar}) = 5.25 \text{ bar}$$

$$\text{Partial pressure of neon} = 0.79 \times (25 \text{ bar}) = 19.75 \text{ bar}$$

Problem 2: The pressure of a moist gas is 750 mm Hg at 298 K. Calculate the pressure of dry gas at 298 K if aqueous tension is 13 mm Hg.

Solution: Pressure of a gas = Pressure of dry gas + Aqueous Tension

$$\text{Pressure of a dry gas} = \text{Pressure of gas} - \text{Aqueous Tension}$$

$$= (750 - 13) \text{ mm Hg}$$

$$= 737 \text{ mm Hg}$$

2. **Kinetic Molecular Theory of Gases:** So far we have learnt the laws (e.g., Boyle's law, Charles' law etc.) which are concise statements of experimental facts observed in the laboratory by the scientists. Conducting careful experiments is an important aspect of scientific method and it tells us how the particular system is behaving under different conditions. However, once the experimental facts are established, a scientist is curious to know why the system is behaving in that way. For example, gas laws help us to predict that pressure increases when we compress gases but we would like to know what happens at molecular level when a gas is compressed? A theory is constructed to answer such questions. A theory is a model (i.e., a mental picture) that enables us to better understand our

observations. The theory that attempts to elucidate the behaviour of gases is known as kinetic molecular theory.

Assumptions or postulates of the kinetic-molecular theory of gases are given below. These postulates are related to atoms and molecules which cannot be seen, hence it is said to provide a microscopic model of gases.

- Gases consist of large number of identical particles (atoms or molecules) that are so small and so far apart on the average that the actual volume of the molecules is negligible in comparison to the empty space between them. They are considered as point masses. This assumption explains the great compressibility of gases.
- There is no force of attraction between the particles of a gas at ordinary temperature and pressure. The support for this assumption comes from the fact that gases expand and occupy all the space available to them.
- Particles of a gas are always in constant and random motion. If the particles were at rest and occupied fixed positions, then a gas would have had a fixed shape which is not observed.
- Particles of a gas move in all possible directions in straight lines. During their random motion, they collide with each other and with the walls of the container. Pressure is exerted by the gas as a result of collision of the particles with the walls of the container.
- Collisions of gas molecules are perfectly elastic. This means that total energy of molecules before and after the collision remains same. There may be exchange of energy between colliding molecules, their individual energies may change, but the sum of their energies remains constant. If there were loss of kinetic energy, the motion of molecules will stop and gases will settle down. This is contrary to what is actually observed.
- At any particular time, different particles in the gas have different speeds and hence different kinetic energies. This assumption is reasonable because as the particles collide, we expect their speed to change. Even if initial speed of all the particles was same, the molecular collisions will disrupt this uniformity. Consequently the particles must have different speeds, which go on changing constantly. It is possible to show that though the individual speeds are changing, the distribution of speeds remains constant at a particular temperature.
- If a molecule has variable speed, then it must have a variable kinetic energy. Under these circumstances, we can talk only about average kinetic energy. In kinetic theory it is assumed that average kinetic energy of the gas molecules is directly proportional to the absolute temperature. It is seen that on heating a gas at constant volume, the

pressure increases. On heating the gas, kinetic energy of the particles increases and these strike the walls of the container more frequently thus exerting more pressure. Kinetic theory of gases allows us to derive theoretically, all the gas laws studied in the previous sections. Calculations and predictions based on kinetic theory of gases agree very well with the experimental observations and thus establish the correctness of this model.

3. **Behaviour of Real Gases: Deviation From Ideal Gas Behaviour:** Our theoretical model of gases corresponds very well with the experimental observations. Difficulty arises when we try to test how far the relation $pV = nRT$ reproduce actual pressure-volume-temperature relationship of gases. To test this point we plot pV vs p plot of gases because at constant temperature, pV will be constant (Boyle's law) and pV vs p graph at all pressures will be a straight line parallel to x-axis. Fig. 5 shows such a plot constructed from actual data for several gases at 273 K.

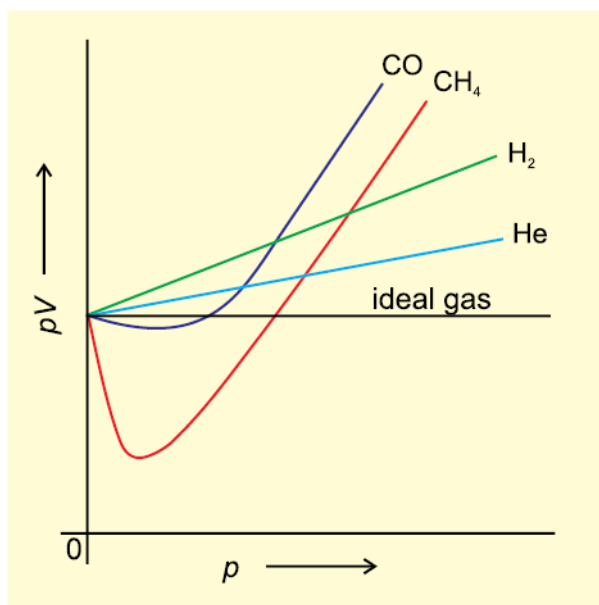


Fig. 5. Plot of pV vs p for real gas and ideal gas

(Source: Fig. 5.8, page no. 145, Class XI Textbook, NCERT)

It can be seen easily that at constant temperature pV vs p plot for real gases is not a straight line. There is a significant deviation from ideal behaviour. Two types of curves are seen. In the curves for dihydrogen and helium, as the pressure increases the value of pV also increases. The second type of plot is seen in the case of other gases like carbon monoxide and methane. In these plots first there is a negative deviation from ideal behaviour, the pV value decreases with increase in pressure and reaches to a minimum value characteristic of a gas. After that pV value starts increasing. The curve then crosses the line for ideal gas and after that shows positive deviation continuously. It is thus found that real gases do not follow ideal gas equation perfectly under all conditions.

Deviation from ideal behaviour also becomes apparent when pressure vs volume plot is drawn. The pressure vs volume plot of experimental data (real gas) and that theoretically calculated from Boyle's law (ideal gas) should coincide. Fig 6 shows these plots. It is apparent that at very high pressure the measured volume is more than the calculated volume. At low pressures, measured and calculated volumes approach each other.

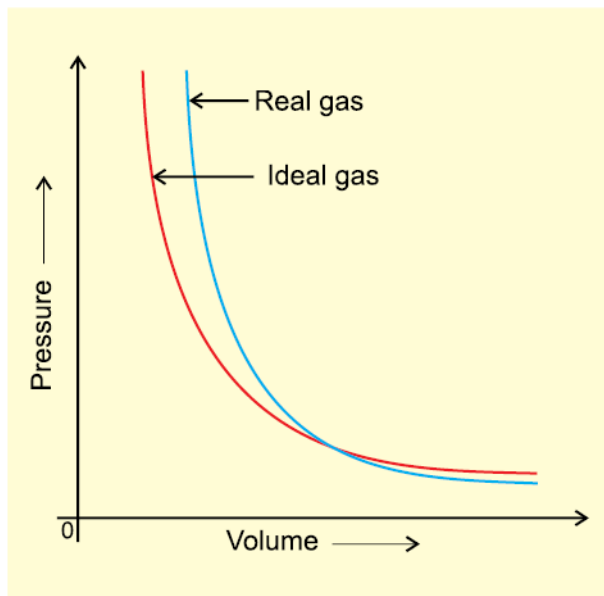


Fig. 6. Plot of pressure vs volume for real gas and ideal gas
(Source: Fig. 5.9, page no. 145, Class XI Textbook, NCERT)

It is found that real gases do not follow, Boyle's law, Charles law and Avogadro law perfectly under all conditions. Now two questions arise.

- (i) Why do gases deviate from the ideal behaviour?
- (ii) What are the conditions under which gases deviate from ideality?

We get the answer of the first question if we look into postulates of kinetic theory once again. We find that two assumptions of the kinetic theory do not hold good. These are

- (a) There is no force of attraction between the molecules of a gas.
- (b) Volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.

If assumption (a) is correct, the gas will never liquify. However, we know that gases do liquify when cooled and compressed. Also, liquids formed are very difficult to compress. This means that forces of repulsion are powerful enough and prevent squashing of molecules in tiny volume. If assumption (b) is correct, the pressure vs volume graph of experimental data (real gas) and that theoretically calculated from Boyles' law (ideal gas) should coincide. Real gases show deviations from ideal gas law because molecules interact with each other. At high pressures molecules of gases are very close to each other. Molecular interactions start operating. At high pressure, molecules do not strike the walls of the container with full impact because these are dragged back by other molecules due to molecular attractive forces.

This affects the pressure exerted by the molecules on the walls of the container. Thus, the pressure exerted by the gas is lower than the pressure exerted by the ideal gas.

$$p_{ideal} = p_{real} + \frac{an^2}{V^2} \quad \dots(7)$$

p_{real} = observed Pressure and $\frac{an^2}{V^2}$ = correction term

here, a is a constant.

Repulsive forces also become significant. Repulsive interactions are short-range interactions and are significant when molecules are almost in contact. This is the situation at high pressure. The repulsive forces cause the molecules to behave as small but impenetrable spheres. The volume occupied by the molecules also becomes significant because instead of moving in volume V, these are now restricted to volume (V-nb) where nb is approximately the total volume occupied by the molecules themselves. Here, b is a constant. Having taken into account the corrections for pressure and volume, we can rewrite ideal gas equation as

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad \dots(8)$$

Equation (8) is known as van der Waals equation. In this equation n is number of moles of the gas. Constants a and b are called van der Waals constants and their value depends on the characteristic of a gas. Value of 'a' is measure of magnitude of intermolecular attractive forces within the gas and is independent of temperature and pressure.

Also, at very low temperature, intermolecular forces become significant. As the molecules travel with low average speed, these can be captured by one another due to attractive forces. Real gases show ideal behaviour when conditions of temperature and pressure are such that the intermolecular forces are practically negligible. The real gases show ideal behaviour when pressure approaches zero.

The deviation from ideal behaviour can be measured in terms of compressibility factor Z, which is the ratio of product pV and nRT. Mathematically

$$Z = \frac{pV}{nRT} \quad \dots(9)$$

For ideal gas, Z = 1 at all temperatures and pressures because pV = nRT. The graph of Z vs p will be a straight line parallel to pressure axis (Fig. 7). For gases which deviate from ideality, value of Z deviates from unity. At very low pressures all gases shown have Z ≈ 1 and behave as ideal gas. At high pressure all the gases have Z > 1. These are more difficult to compress. At intermediate pressures, most gases have Z < 1. Thus gases show ideal behaviour when the volume occupied is large so that the volume of the molecules can be neglected in comparison to it. In other words, the behaviour of the gas becomes more ideal when pressure is very low. Up to what pressure a gas will follow the ideal gas law, depends upon nature of the gas and

its temperature. The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called Boyle temperature or Boyle point. Boyle point of a gas depends upon its nature. Above their Boyle point, real gases show positive deviations from ideality and Z values are greater than one.

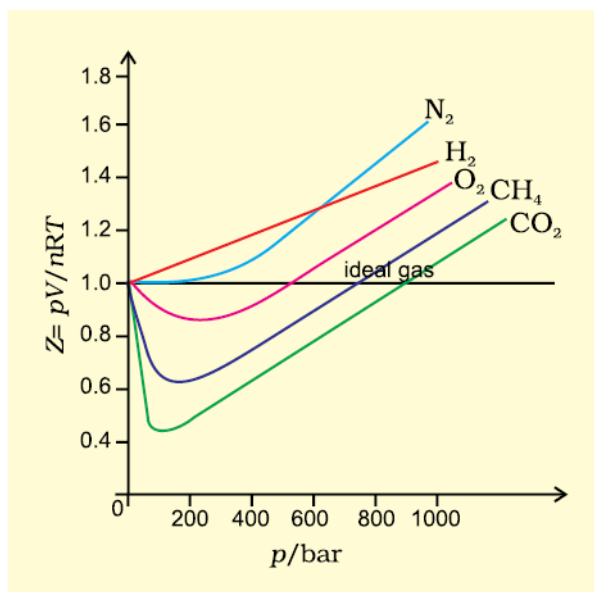


Fig. 7. Variation of compressibility factor for some gases

(Source: Fig 5.10, page no. 146, Class XI Textbook NCERT)

The forces of attraction between the molecules are very feeble. Below Boyle temperature real gases first show decrease in Z value with increasing pressure, which reaches a minimum value. On further increase in pressure, the value of Z increases continuously. Above explanation shows that at low pressure and high temperature gases show ideal behaviour. These conditions are different for different gases.

More insight is obtained in the significance of Z if we note the following derivation

$$Z = \frac{pV_{\text{real}}}{nRT} \quad \dots(10)$$

If the gas shows ideal behaviour then $V_{\text{ideal}} = \frac{nRT}{P}$. On putting this value of $\frac{nRT}{P}$ in equation (10) we have

$$Z = \frac{V_{\text{real}}}{V_{\text{ideal}}} \quad \dots(11)$$

From equation (11) we can see that compressibility factor is the ratio of actual molar volume of a gas to the molar volume of it, if it were an ideal gas at that temperature and pressure.

In the next module, we will learn that it is not possible to distinguish between gaseous state and liquid state and those liquids may be considered as continuation of gas phase into a region of small volumes and very high molecular attraction. We will also see how we can use isotherms of gases for predicting the conditions for liquifaction of gases.

4. **Summary:** This module explained Dalton's law of partial pressure which states that the total pressure exerted by a mixture of non-reacting gases is equal to the sum of partial pressures exerted by them. Thus $p = p_1 + p_2 + p_3 + \dots$. The relationship between pressure, volume, temperature and number of moles of a gas describes its state and is called equation of state of the gas. Equation of state for ideal gas is $pV = nRT$, where R is a gas constant and its value depends upon units chosen for pressure, volume and temperature. Kinetic molecular theory of gases elucidates the behaviour of the gases. It explains that a gas consists large number of submicroscopic particles such as atoms or molecules, which are in constant rapid motion. The randomness of the motion of the gas particles arises from their several collisions with each other and with the walls of the container. In spite of being very useful, an ideal gas model is only an approximation of the real nature of gases. As a consequence, the observed properties of a real gas behave differently from the properties predicted by calculations using ideal gas model. The correction terms for pressure and volume were incorporated in ideal gas equation giving rise to a new gas equation named as van der Waals equation.