1. Gaseous State of Matter

Content

Introduction

Everything in the universe has a chemical identity. We know that the smallest particle of matter is an atom. "Study of matter and the changes that it undergoes" can simply be understood as the basic definition of chemistry. Usually matter is anything that occupies space and has mass and can be seen and touched (such as soil, water) as well as things we cannot see such as air. Based on the composition and properties, several categories such as substances, mixtures, elements as well as atoms and molecules can be identified. All substances, at least in principle, can exist in three states: solid, liquid and gas. In a solid, particles are held tightly and close together in an ordered structure with a definite shape having a small degree of motion. Particles in a liquid are close together but are not held so tightly in position and can move faster compared to that of solid. Gases differ largely from liquids and solids in the distances between the particles. In a gas, the particles are separated by distances, large compared with the size of the particles allowing them to behave freely. Therefore, the attractive forces between gas particles are very small or negligible and that allows us to consider gas particles individually and some hypotheses are easily predictable depending on the temperature and pressure changes.

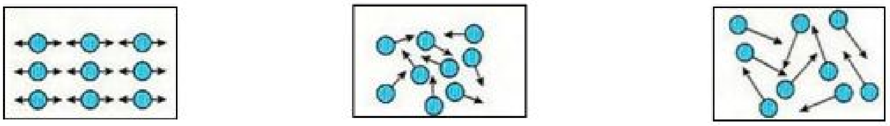
1.1 Organization of particles in three principal states and their typical characteristics

Anything that occupies space and has a mass can be called "**matter**". This could be things we can see and touch like trees or things we cannot see like the air we breathe. All matter can be classified broadly into three states **solid, liquid and gas**. Matter can be interconverted among these three states without changing the composition. For an example water in liquid state can be converted to gaseous state (steam) when heated and can be converted to a solid (ice) if cooled.

Solid (eg. nail)
Fixed shape
and volume

Liquid (eg. water)
No Fixed shape but
has fixed volume

Gas (eg. He balloons)
No fixed shape and no
fixed volume



Solid
Strong interparticle (atoms, molecules or ions) forces. Particles vibrate but cannot move around.

Liquid
Moderate interparticle (atoms, molecules or ions) forces. Particles can move around up to some extent.

Gas
Weak interparticle (atoms, molecules or ions) forces. Particles can move around.

Figure 1.1 Three states of matter

Three states of matter differ based on arrangement and movement of particles. The inter-particle distance is highest in gaseous state and lowest in solids. In liquid state, particles are relatively closer compared to gaseous state, yet not too close compared to the solid state. Therefore, a regular pattern of particles can be seen only in solid state, while both gaseous and liquid state particles show random arrangement. As a result, particles in gaseous state can move fast and freely compared to liquid state particles. However, movement of particles in solids is limited to vibrations. The arrangement and motions of particles in matter result in differences in macroscopic properties such as volume, shape, compressibility and density as indicated in the Table 1.1 below.

Table 1.1 Qualitative comparison of properties of solids, liquids and gases

Property	Solids	Liquids	Gases
Shape	Definite	Take up shape of the container but do not spread throughout the entire volume of the container	Take up the shape of the container and occupy the entire volume of the container
Volume	Definite	Definite	Occupy the volume of the container
Density (ρ)/ g cm^{-3} at 293 K	Have high values eg.: Iron (7.874 g cm^{-3})	Have moderately high values eg.: Water (0.997g cm^{-3})	Have low values eg.: Hydrogen (0.071g cm^{-3})
Compressibility	Extremely hard to compress	Extremely hard to compress	Can compress to a great extent

Note: *Here we say that a liquid takes the shape of the container and we have to think why we get these shapes. Usually, particles of any object is being pulled by a variety of forces such as intermolecular forces, and that's why it has shape. Some given amount (volume) of water in a beaker is being shaped by surface tension resulting from intermolecular forces within the liquid creating a meniscus curve at the edge of the surface, by the force of the walls of the beaker pushing up on it, and by the gravity which is greater than the surface tension, pulling it down. So, it takes the shape of the beaker, with a flat surface on the top. This happens due to the satisfaction of all those different forces. However, in the case that the surface tension is stronger than gravity, the water's surface might not lie flat by taking the shape of the container. Assume that there is no gravity, and so surface tension is very much high. As each part of the surface wants to stay as close as possible to the rest of the surface it tries to minimize the forces within. So, the shape that best allows this is a sphere, because it is the shape that has the minimal surface area for a given volume.*

Matter in one particular state can be converted to another state by heating or cooling. Increase of temperature makes particles move faster and inter-particle distance becomes greater leading to change in state. Accordingly, increase in temperature converts solid state materials to liquid and liquid state materials to gaseous state. The opposite happens with decreasing temperature. Figure 1.2 illustrates how matter can be interconverted among states.

Figure 1.2 Interconversion of states of matter

Example 1.1
In which state of matter are the particles mostly touching but arranged in a random way?

Answer
Liquid State

When we describe the properties of the three states of matter with the help of Table 1.1, motion and arrangement of particles are basically considered. Especially, thermal energy is the energy of a body arising from motion of its atoms or molecules and it is directly proportional to the temperature of the substance. Therefore, it measures the average kinetic energy of the particles of the matter and is thus responsible for movement of particles or the thermal motion.

As we already know, interparticle forces tend to keep the particles together but thermal energy of the particles tends to keep them apart. Therefore the existence of three states of matter can be regarded as a result of balance between interparticle forces and the thermal energy of the particles.

When inter molecular interactions are very weak, molecules do not tend to make liquid or solid unless thermal energy is reduced by lowering the temperature. Gases do not liquefy on compression only, although molecules come very close to each other and intermolecular forces operate to the maximum. However, when thermal energy of molecules is reduced by lowering the temperature, the gases can very easily be liquefied. These behaviours can be explained by Figure 1.3 where we can understand the reversible nature of intermolecular forces and the thermal energy acting on the three states of matter.

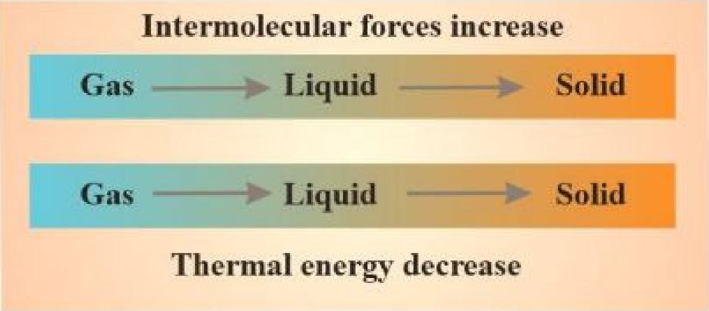


Figure 1.3 Behaviour of three states of matter against intermolecular forces and thermal energy

We have already learnt the cause for the existence of the three states of matter. Now we will learn more about the gaseous state and the laws which govern the behaviour of matter in this state.

1.2 Gaseous state

Let us now focus our attention on the behaviour of substances which exist in the gaseous state under normal conditions of temperature and pressure.

The gaseous state is characterized by the following physical properties as described in Table 1.1.

- Gases are highly compressible.
- Gases exert pressure equally in all directions.
- Gases have much lower density than the solids and liquids.
- The volume and the shape of gases are not fixed. These assume volume and shape of the container.
- Gases mix evenly and completely in all proportions without any mechanical aid.

Simplicity of gas is due to the fact that the forces between their molecules are negligible. Their behaviour is governed by same general laws (will be discussed later), which were discovered as a result of experimental studies. These laws are usually relationships between measurable properties of gases. Some of these properties like pressure, volume, temperature and amount (moles or mass) are very important because relationships between these variables describe *state of the gas* (will be defined in unit 5). Interdependence of these variables leads to the formulation of gas laws.

1.2.1 Gas laws

The gas laws that we are going to discuss are the results of experiments carried out by several scientists on the physical properties of gases. In these experiments, relations among the variables of pressure, temperature, volume and amount of gases are considered and the results provide valuable information on the gaseous state of matter in turn helping the mankind in many ways.

Ideal gas and ideal gas equation

When it is assumed that intermolecular forces do not exist among the molecules of a gas, such a gas is called an **ideal gas.** That is molecules in an ideal gas do not exhibit attraction or repulsion among them. Furthermore, the volume of ideal gas particles is considered negligible when compared to the volume of the container.

The absolute temperature (T), pressure (P), volume (V) and the amount (n, moles) of a gas are the factors that affect the behaviour of a gas. P, T, V and n are related by the expression;

$$\boxed{PV = nRT}$$

This is known as the **ideal gas equation** or **ideal gas law** where the gas constant R is same for every gases. Any gas which obeys the above relationship under any given temperature and pressure is referred to as an **ideal gas**.

The value of the constant R for one mole of an ideal gas can be calculated under the conditions of 0 °C and 1 atm as given below: (At 0 °C and 1 atm, the volume of one mole of ideal gas is 22.414 dm^3)

$$R = \frac{P\,V}{n\,T} = \frac{101325\ \text{Pa} \times\ 22.414\ \times 10^{-3}\ \text{m}^3}{1\ \text{mol}\ \times\ 273.15\ \text{K}} = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$$

We can see that the ideal gas equation is a relationship among four variables and it describes the state of any gas. Therefore, it is also called **equation of state.**

Calculations based on ideal gas equation

The ideal gas law allows us to determine any one of the quantities volume, pressure, temperature, or moles of the gas when the other three are given. If the amount of moles of the gas is known, we can also calculate its mass using its molar mass. Further it can also be used to determine the density of a gas. It is important to keep in mind that all the other quantities must be in units that match the value used for the ideal gas constant. Usually pressure can be expressed in several units such as atm, Pa, bar, torr, etc. Therefore, in solving these problems it may helpful to use pressure conversions as given in the Table 1.2.

Table 1.2 Pressure units

Pressure unit	Pa	bar	atm	torr/mmHg
1 Pa	1 N m^{-2}	10^{-5}	9.87×10^{-6}	7.5×10^{-3}
1 bar	100,000	1 bar	0.987	750.06
1 atm	101,325	1.01325	1 atm	760
1 torr/mmHg	133.32	1.3332×10^{-3}	1.3158×10^{-3}	1 torr/ 1 mmHg

Example 1.2

The volume of a gas cylinder is 0.950 dm^3. When filled, the cylinder contains liquid propane (C_3H_8) stored under pressure. When the cylinder is empty, it contains some residual propane gas molecules at atmospheric pressure and temperature.

(i) Calculate the number of moles of propane gas remaining in a cylinder when it is empty if the surrounding atmospheric conditions are 25.0 °C and 750 torr (1 torr = 133.32 Pa) (when the internal pressure equals to the external pressure).

(ii) Calculate the mass of propane remaining in the cylinder.

(iii) Calculate the density of remaining propane gas in the cylinder.

Answer

(i) First summarize the given information;

Temperature, $T = (25 + 273)\ K = 298\ K$

Pressure, $P = 750\ torr \times 133.32\ Pa/\ 1\ torr = 99990\ Pa$

Volume, $V = 0.950\ dm^3 = 0.950 \times 10^{-3}\ m^3$

Unknown is n

Using $PV = nRT$;

$$n = \frac{PV}{RT} = \frac{99990\ \text{Pa} \times 0.950\ \times 10^{-3}\ \text{m}^3}{8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}} = 0.038\ \text{mol}$$

(ii) Molar mass of propane(C_3H_8) = 44 g mol^{-1}

Mass of propane = 0.038 mol × 44 g/1 mol = 1.672 g

(iii) Density of propane = mass/volume = 1.672 g/ 0.950 dm^3 = 1.76 g dm^{-3}

When we consider the above example, there are insights into the ideal gas equation that it can be expressed in different forms to estimate mass and density of a given gas with simple modifications as shown below.

$PV = n RT$ and we can write,

$$P = \frac{n}{V} RT$$

$$\therefore \boldsymbol{P = CRT},$$

where C is the concentration

We can also write $PV = nRT$ as

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

where, m is the mass and M is the molar mass of the gas.

Also we can write the above as;

$$P = \frac{1}{M}\left(\frac{m}{v}\right) RT$$

$$\therefore \boldsymbol{P} = \frac{\boldsymbol{d\,RT}}{\boldsymbol{M}}$$

where, d is the density and $d = \frac{m}{v}$

Ideal gas law serves as the basis when deriving several other gas laws under specific conditions.

1.2.2 Boyle law (pressure – volume relationship)

That is the "*pressure of a fixed amount (mass) of gas at constant temperature inversely varies with (or proportional to) the volume of the gas*". This is known as the **Boyle Law** (1627-1691) which was named after **Robert Boyle**, an Irish scientist in the seventeenth century who studied change in volume of a gas when pressure of a gas is varied under constant temperature conditions. Mathematical form of it, is given below.

$$\boxed{P \propto \frac{1}{V} \ \ or \ \ P = \frac{k}{V} \ \ ; \text{ k is a constant}}$$

The ideal gas law can be used to derive Boyle law as follows.

$$PV = nRT$$

If the amount of the gas and temperature of the system are kept constant, then the product nT is a constant. Since R is also a constant, then the product, $nRT = k$ (a constant)

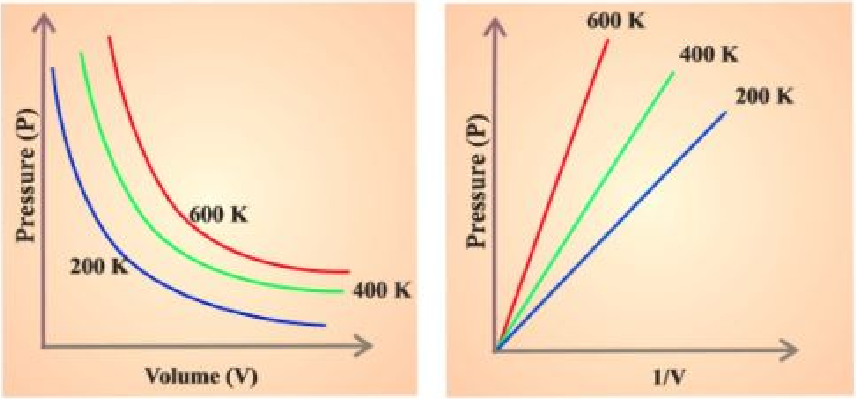
$$PV = k$$

It means that "*at constant temperature, the product of pressure and volume of a fixed amount of gas is constant*". This is another way of expressing Boyle law.

If a fixed amount of gas at constant temperature T occupying volume V_1 at pressure P_1 undergoes change, so that volume becomes V_2 and pressure becomes P_2, then according to Boyle law:

$$\boxed{\boldsymbol{P_1V_1 = P_2V_2}}$$

Figure 1.4 shows two conventional ways of graphical representation of Boyle law. Figure 1.4 (a) is the graph of $PV = k$ at different temperatures for the comparison. The value of k for each curve is different because for a given mass of gas, it varies only with temperature. Note that at higher temperatures, curves shift upwards due to the expansion of volume. It should also be noted that volume of the gas doubles if pressure is halved at a constant temperature.



(a) (b)

Figure 1.4 Changes in pressure at different constant temperatures with respect to (a) volume (*V*) changes and (b) with *1/V*

Figure 1.4 (b) represents the graph of P vs $1/V$. It is a straight line passing through the origin. These plots obtained by the experiments carried out by Boyle, show in a quantitative manner that gases are highly compressible. That is because when a given mass of a gas is compressed, the same number of molecules will occupy a smaller space. This means that gases become denser at high pressures.

Note: *We know that density (d) of a given mass (m) occupying volume (V) is given by; d = m/V. Therefore at constant temperature we can write,* $d = \left(\frac{m}{k/P}\right) = \left(\frac{m}{k}\right) P = k^{'} P$

Example 1.3

Calculate the change in pressure of a gas when the volume is doubled at constant temperature for a known amount of a gas.

Answer

$V_1 = V$, $V_2 = 2V$, $P_1 = P$, $P_2 = ?$

Applying Boyle law: $P_1V_1 = P_2V_2$

$P \times V = P_2 \times 2V$

$P_2 = P/2$

$\therefore$ New pressure is half the initial pressure.

Example 1.4

A balloon is to be filled with a known amount of hydrogen gas at room temperature. At atmospheric pressure (100 kPa), the gas occupies 2.50 dm^3 volume. What would be the volume of the balloon when the pressure inside is 20 kPa at the same temperature.

Answer

P_1 = 100 kPa, P_2 = 20 kPa, V_1 = 2.5 dm^3, V_2 = ?

Applying Boyle law: $P_1V_1 = P_2V_2$

100 kPa × 2.5 dm^3 = 20 kPa × V_2

$\therefore V_2 = 12.5\ dm^3$

The balloon is filled up to the volume of 12.5 dm^3.

1.2.3 Charles law (temperature – volume relationship)

Investigations by the scientists **Jacques Charles and Joseph Gay-Lussac** have showed that for a fixed amount (mass) of a gas at constant pressure volume of a gas increases on heating and decreases on cooling. It was also found that for each degree change (rise or fall) in temperature, volume of a gas changes (increases or decreases) by a factor of 1/273.15 of the original volume of the gas at 0 °C.

Assume that volumes of the gas at 0 °C and at t °C are V_0 and V_t respectively, then we can write,

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

At this stage, a new scale of temperature is defined such that ***t*** °C on new scale is given by

$$T_t = 273.15 + t$$

and 0 °C will be given by

$$T_0 = 273.15$$

This new temperature scale is called the **Kelvin temperature scale (K)** or **absolute temperature scale.** -273.15 °C (0 K) is also defined as the thermodynamic zero, which is the lowest theoretically reachable temperature.

By applying this temperature scale, we can rewrite the relation $V_t = V_0\left(\frac{273.15 + t}{273.15}\right)$ as,

$$V_t = V_0\left(\frac{T_t}{T_0}\right)$$

Hence,

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

For a general case when the change occurs from (V_1, T_1) to (V_2, T_2) at constant pressure

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

This can be rearranged as

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

$$\frac{V}{T} = \text{constant or } V = k\,T$$

Therefore, "*the volume of a fixed amount of gas under constant pressure is directly proportional to the absolute temperature of the gas.*" This is called **Charles law**.

Further, the ideal gas law can be used to study the effect of temperature on the volume of a gas if the pressure of the system is kept constant for a fixed amount of a gas. The ideal gas law can be rearranged as follows;

$$PV = nRT$$

$$V = nRT/P$$

When the pressure of a fixed mass of gas is constant, $\frac{nR}{P}$ is constant.

$$\therefore \boldsymbol{V \propto T} \text{ or } \boldsymbol{V = kT}$$

According to Charles law for all gases, at any given pressure, graph of volume versus, temperature (in Celsius) is a straight line and on extending to zero volume, each line intercepts the temperature axis at – 273.15 °C. Slopes of lines obtained at different pressure are different but at zero volume all the lines meet the temperature axis at – 273.15 °C or 0 K as shown in Figure 1.5.

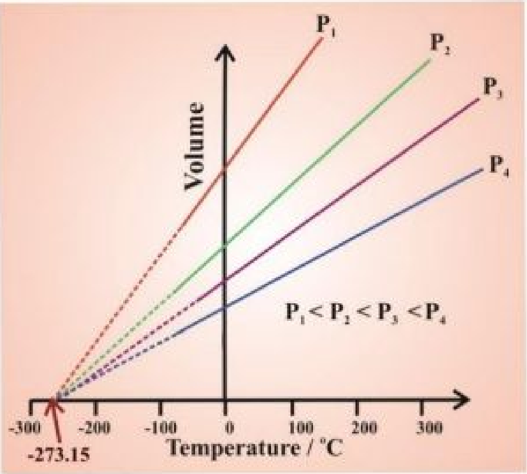


Figure 1.5 Changes in volume of a gas with respect to temperature change at different constant pressures

Example 1.5

Calculate the change in temperature of a gas when the volume is tripled at constant pressure for a known amount of gas moles.

Answer

$V_1 = V, V_2 = 3V, \ T_1 = T, T_2 = ?$

$V_1/ V_2 = T_1/T_2$

$V/3V = T/T_2$

$T_2 = 3T$

This can further be estimated directly, as the volume is directly proportional to Kelvin temperature T, the new temperature would be thrice the initial value, i.e 3T.

Let's consider the equation $V_t = V_0 \left(\frac{273.15+t}{273.15}\right)$ and substitute t = -273.15, where we get the volume of the gas equal to zero meaning that the gas will not exist. Therefore, we can understand that all the gases get liquefied before this temperature is reached. The lowest hypothetical or imaginary temperature at which gases are supposed to occupy zero volume is called **absolute zero**.

Example 1.6

A balloon is filled with a known amount of hydrogen gas resulting a volume of 2.0 dm^3 at 23 °C. Calculate the change in volume of a gas when the temperature is increased to 27 °C at the same pressure.

Answer

$T_1 = 23 + 273 = 296$ K, $T_2 = 27 + 273 = 300$ K, $V_1 = 2.0$ dm^3, $V_2 = ?$

Applying Charles law as the pressure and amount of gas constant,

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

$$\frac{2.0\ \text{dm}^3}{296\ \text{K}} = \frac{V_2}{300\ \text{K}}$$

$V_2 = 2.03\ \text{dm}^3$

Therefore, the change in volume is $0.03\ \text{dm}^3$

1.2.4 Avogadro law (amount – volume relationship)

Upon the developments of Boyle and Charles laws, in 1811 Italian scientist Amedeo Avogadro tried to combine conclusions of those with the amount and volume of a gas and postulated a new hypothesis which is now known as Avogadro law. *It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of moles* (**Avogadro Law**).

$$\text{i.e.}\quad V \propto n$$

$$\text{or we can write } V = k\,n$$

The number of molecules in one mole of a gas has been determined to be 6.022×10^{23} and also known as **Avogadro constant** (denoted as N_A or L).

Avogadro law can be easily understood with the help of the ideal gas law as follows.

$$PV = nRT$$

$$V = \frac{RT}{P} \times n$$

$$V = \frac{RT}{P} \times \frac{N}{N_A} = \frac{RT}{PN_A} \times N$$

Here, N and N_A are the number of molecules of the gas and the Avogadro constant respectively. By applying the above relationships to equal volumes of gases P and Q at the same temperature and pressure,

$$V_P = \frac{RT}{PN_A} \times N_P$$

$$V_Q = \frac{RT}{PN_A} \times N_Q$$

At constant P and T, we can write (as R and N_A are constants)

$$\boxed{V_P / V_Q = N_P / N_Q}$$

Simply it says that for a gas at constant temperature and pressure equal volumes of gases have equal number of molecules. i.e. $V \alpha N$

It is useful to understand that the gas laws discussed above can also be used to obtain the ideal gas equation for a given volume V of a gas.

$$\text{Boyel Law :}\quad V \propto \frac{1}{P} \quad ------(1)$$

$$\text{Charles Law :}\quad V \propto T \quad ------(2)$$

Avogardro Law : $V \propto n \quad ------(3)$

The only equation that fulfills (1), (2) and (3) is,

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

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

When $k = R$

$$PV = nRT$$

1.2.5 Molar volume (V_m)

Since volume of a gas is directly proportional to the number of moles we can write,

$$\boxed{V_m = \frac{V}{n}}$$

As temperature and pressure are the same, one mole of any gas should occupy the same volume V_m and that can be calculated as,

$$\boxed{V_m = \frac{RT}{P}}$$

Therefore, at temperature and standard pressure molar volume (V_m) of any gas should have the same volume. There are two sets of conditions applied for the standard value.

- *In the first set of condition; the temperature is taken as 0 °C (273.15 K) and the standard pressure as 1 atm (101325 Pa). At this standard condition molar volume of an ideal gas or a combination of ideal gases is* **22.414 dm^3 mol^{-1}**. *Molar volume under these conditions is denoted as* $\mathbf{V_m^{\theta}}$.

- *In the second set of condition; the ambient temperature is taken as 25 °C (298.15 K) and the standard pressure as 1 atm (101325 Pa). In that case, the molar volume of a gas has the value* **24.790 dm^3 mol^{-1}**.

Note: *From Avogadro law we can see that the molar mass (M) of a gas is directly proportional to its density (d).*

$V = k\,n = k\,(m/M)$,

therefore $M = k\,(m/V) = k\,d$

Example 1.7

Show that the molar volumes of 1 mole of He and 1 mole of Ne gas at 298 K temperature and 1atm pressure are the same.

Answer

P_{He} = 1 atm = 101325 Pa, T_{He} = 298 K, n_{He} = 1.00 mol, V_{He} = ?

$P_{He}V_{He} = n_{He}RT_{He}$

$V_{He} = n_{He}RT_{He} / P_{He}$

$V_{He} = (1 \text{ mol} \times 8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}) / 101325 \text{ Pa} = 24.4 \text{ dm}^3$

P_{Ne} = 1 atm = 101325 Pa, T_{Ne} = 298 K, n_{Ne} = 1.00 mol, V_{Ne} = ?

$P_{Ne}V_{Ne} = n_{Ne}RT_{Ne}$

$V_{Ne} = n_{Ne}RT_{Ne} / P_{Ne}$

$V_{Ne} = (1 \text{ mol} \times 8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}) / 101325 \text{ Pa}$

$V_{Ne} = 24.4 \text{ dm}^3$

i.e. at the same temperature and pressure, if number of moles are the same, then different gases will occupy the same volume.

1.2.6 Combined gas law

As all gases behave the same way with respect to pressure, volume, and temperature, if the amount is measured per mole, then the ideal gas expression itself can be written as a ratio useful in the events like when temperature, volume, and pressure of a fixed amount of gas vary from (T_1, V_1, P_1) to (T_2, V_2, P_2). For such an instance we can write,

for the initial condition; $nR = \frac{P_1V_1}{T_1}$

for the final condition; $nR = \frac{P_2V_2}{T_2}$

$$\boxed{\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}}$$

This is called the combined gas law.

Example 1.8

At 25 °C and 760 mm Hg pressure, a given amount of a gas occupies a volume of 600 cm^3. What will be its pressure at 10 °C when volume of the gas is 650 cm^3.

Answer

(T_1, V_1, P_1) to (T_2, V_2, P_2) we can write

P_1 = 760 mm Hg = 1 atm = 101325 Pa, V_1= 600 cm^3 = 0.600 dm^3, T_1 = 25 + 273 = 298 K

V_2 = 650 cm^3 = 0.650 dm^3, T_2 = 10 + 273 = 283 K, P_2 = ?

According to Combined gas law; $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\frac{760\text{ mm Hg} \times 600\text{ cm}^3}{298\ K} = \frac{P_2 \times 650\text{ cm}^3}{283\ K}$$

P_2 = 666.2 mmHg = 88823 Pa = 88.823 kPa

1.3 Dalton law of partial pressure

In most practical applications we encounter a mixture of gases rather than a single gas. The air we breathe has nitrogen and oxygen gases as major components and a variety of other gases in minute quantities. All of these gases contribute to the total atmospheric pressure.

Also, the pressure that a constituent gas of a mixture of gases would exert if it alone occupies the volume of the mixture at same temperature is defined as the **partial pressure** of that gas. A postulate introduced by Dalton says that *the total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases.* This is known as **"Dalton law of partial pressures".**

Accordingly, if partial pressures of individual gases in a mixture of gases A, B and C are P_A, P_B and P_C respectively, at constant temperature and constant volume the total pressure $\boldsymbol{P_T}$ of the mixture is given by the following equation.

$$\boxed{P_T = P_A + P_B + P_C}$$

The Dalton law of partial pressure can be derived using ideal gas equation as follows. Consider a mixture of gases A and B with n_A and n_B moles, respectively exerting the total pressure of P_T.

$$PV = nRT$$

For gas A, $n_A = P_AV/RT$ (P_A is the partial pressure of gas A)

For gas B, $n_B = P_BV/RT$ (P_B is the partial pressure of gas B)

For the mixture of gases, $n_T = P_TV/RT$

and $n_T = n_A + n_B$

Therefore, $P_TV/RT = (P_AV/RT) + (P_BV/RT)$

Simplification gives , $P_T = P_A + P_B$
This is the **Dalton law of partial pressures.**

1.3.1 Partial pressure in terms of mole fraction

Suppose at the temperature T, n_A moles of gas A and n_B moles of gas B, are enclosed in a container of volume V, then partial pressures exerted by gases A and B are P_A and P_B respectively while the total pressure is P_T.

Therefore, we can write, $P_A = \frac{n_A RT}{V}$ and $P_B = \frac{n_B RT}{V}$

According to Dalton law, $P_T = P_A + P_B$

Substituting from the above, $P_T = \frac{n_A RT}{V} + \frac{n_B RT}{V} = (n_A + n_B)\frac{RT}{V}$

Dividing the expressions for P_A and P_B separately by P_T, we get;

$$\frac{P_A}{P_T} = \frac{n_A RT/V}{(n_A + n_B)\,RT/V} = \frac{n_A}{(n_A + n_B)} = x_A \text{ this is the mole fraction of A}$$

Likewise,

$$\frac{P_B}{P_T} = \frac{n_B RT/V}{(n_A + n_B)\,RT/V} = \frac{n_B}{(n_A + n_B)} = x_B : \text{ this is the mole fraction of B}$$

Therefore, we can write,

$$\boxed{P_A = x_A P_T \text{ and } P_B = x_B P_T}$$

Partial pressure of the constituent gas is equal to the product of total pressure and mole fraction of the gas.

Example 1.9

(i) A mixture of gases contains 0.8 mol of nitrogen gas (N_2) and 0.2 mol of oxygen (O_2). Calculate the partial pressures of the gases if the total pressure is 1.00 atm at a certain temperature.

(ii) When the container is heated and kept at a constant temperature, N_2 gas is reacted with O_2 gas to produce NO_2 gas. At equilibrium the container has 0.7 mol of N_2 gas, 0.15 mol of O_2 gas and 0.1 mol of NO_2 gas. If the partial pressure of N_2 gas is now 0.88 atm, calculate partial pressures of O_2 gas and NO_2 gas.

Answer

(i) $X_{N_2} = \frac{n_{N_2}}{n_{N_2}+n_{O_2}} = \frac{0.8\text{ mol}}{0.8\text{ mol}+0.2\text{ mol}} = 0.8$

$P_{N_2} = X_{N_2}P_T$

$P_{N_2} = 0.8 \times 1.00\text{ atm}$

$P_{N_2} = 0.8\text{ atm}$

Similarly for O_2,

$P_{O_2} = 0.2\text{ atm}$

(ii) $X_{N_2} = \frac{n_{N_2}}{n_{N_2}+n_{O_2}+n_{NO_2}}$ therefore, $X_{N_2} = \frac{0.7\text{ mol}}{0.7\text{ mol}+0.15\text{ mol}+0.1\text{ mol}} = \frac{0.7}{0.95}$

$P_{N_2} = X_{N_2}P_T$ therefore, $P_T = P_{N_2}/X_{N_2} = \frac{0.88\text{ atm}}{0.7/0.95} = 1.19\text{ atm}$

$X_{O_2} = \frac{n_{O_2}}{n_{N_2}+n_{O_2}+n_{NO_2}}$ therefore, $X_{O_2} = \frac{0.15\text{ mol}}{0.7\text{ mol}+0.15\text{ mol}+0.1\text{ mol}} = \frac{0.15}{0.95}$

$P_{O_2} = X_{O_2}P_T$ therefore, $P_{O_2} = \frac{0.15}{0.95} \times 1.19\text{ atm} = 0.19\text{ atm}$

$X_{NO_2} = \frac{n_{NO_2}}{n_{N_2}+n_{O_2}+n_{NO_2}}$ therefore, $X_{NO_2} = \frac{0.10\text{ mol}}{0.7\text{ mol}+0.15\text{ mol}+0.1\text{ mol}} = \frac{0.10}{0.95}$

$P_{NO_2} = X_{NO_2}P_T$ therefore, $P_{NO_2} = \frac{0.10}{0.95} \times 1.19\text{ atm} = 0.12\text{ atm}$

Therefore,

$P_{N_2} = 0.88\text{ atm}$, $P_{O_2} = 0.19\text{ atm}$, $P_{NO_2} = 0.12\text{ atm}$,

$P_T = 1.19\text{ atm}$

We apply our knowledge on Dalton law for a mixture of gases assuming that they have the same properties as pure gases, provided that all gases in the mixture are ideal gases thus do not react chemically with each other. However, in practical situations such as chemical reactions involving gases, the procedure used to collect may introduce another gas. For example, a technique often used to collect gases from a chemical reaction is the displacement of water from an inverted container. In this method, a gas is collected in the container by bubbling the gas through a tube into a gas jar filled with water which is placed upside-down in a water trough. So that the gas push all the liquid out from the bottle when it is collected. Here, we assume that the gas does not dissolve in water and does not react with water. However; we do not get the gas which is in the pure state. Instead, the collected gas is a mixture of the gas generated by the reaction and some water vapour formed from evaporation. The amount of water vapour contained in the gas is most readily measured by the pressure it exerts at that temperature, called the **saturated vapour pressure**. Therefore, to determine the pressure exerted by a gas collected in this way at a specific temperature, it is necessary to subtract the vapour pressure of water from the total pressure of the mixture. Then from the partial pressure of the gas and its volume and temperature, the ideal gas law can be used to calculate the amount of the gas collected. This is illustrated in example 1.10

Example 1.10

Suppose we produce gaseous oxygen by heating $KClO_3(s)$ as shown in the following reaction:

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$

1.50 dm^3 of O_2 gas is collected over water at 27.0 °C and 760 torr. Saturated vapour pressure of water at 27.0 °C is 26.7 torr.
Calculate the number of moles of O_2 gas produced.

Answer

According to Dalton law, we can write:

$$P_{\text{total}} = P_{\text{oxygen}} + P_{\text{water}}$$

$$\therefore\ P_{\text{oxygen}} = P_{\text{total}} - P_{\text{water}} = (760 - 26.7)\text{ torr} = 733.3\text{ torr} = 97764\text{ Pa}$$

Using the ideal gas equation:

$$PV = nRT \quad \text{and } n = \frac{PV}{RT} = \frac{97764\text{ Pa} \times 1.5 \times 10^{-3}\text{ m}^3}{8.314\text{ J K}^{-1}\text{ mol}^{-1} \times 300\text{ K}} = 0.058\text{ mol}$$

1.4 Molecular kinetic theory of gases

In the above sections we have gone through and understood the laws related to gaseous state based on experimental observations (Boyle law, Charles law, etc.). By conducting such experiments we can understand how the particular system behaves under different conditions. Though, such observations are made from experiments we then have to know or understand why a system behaves that way. For example, gas laws help us to predict that pressure increases when we compress gases but we need to know what happens in the molecular level when a gas is compressed. Therefore, a theoretical model is needed to explain such events or questions where the theory should help us to understand observations. The theory that attempts to explain the behaviour of gases at the molecular level is known as **"molecular kinetic theory"**.

1.4.1 Assumptions of the molecular kinetic theory of an ideal gas

- *Gases are composed of widely separated large number of small particles (molecules or atoms).*

  Because the particles are widely separated, the actual volume of the particles is very small compared to the total volume occupied by the gas. Or in other words the actual volume of the molecules is negligible in comparison to the empty space between them. This postulate correctly predicts that the volume occupied by a gas is much larger than that of a liquid or a solid, in which the particles are much closer together. Because gas particles are so widely separated, gases have relatively low densities compared to liquids and solids. This assumption explains high compressibility of gases.

- *Each particle in a gas is in random (all possible directions), straight-line motion and undergoes perfectly elastic collisions with another particle or with the walls of the container. Different particles have different speeds.*
  Energy may be transferred from one particle to another, their individual energies may change, but there is no net loss or gain of energy. Pressure is exerted by the gas as a result of collision of the particles with the walls of the container.

- *The average kinetic energy of gas particles depends only on the absolute temperature.*
  This tells us that the gas particle (molecule or atom) has its own mass and speed because the kinetic energy (*KE*) for a given gas particle is given by the equation

$$KE = \frac{1}{2} m v^2$$

  where m is the mass of a gas particle and v is the velocity (or speed). We can see that upon heating a gas at constant volume, the pressure increases. That is because, on heating the gas, kinetic energy of the particles increases and they strike the walls of the container more frequently thus exerting more pressure. As such the relation of kinetic energy of one mole of particle with the temperature is given by the following equation.

$$KE = \frac{3}{2} RT$$

Further, we can make following notes too.

- *Particles of a gas behave independently of one another.*
  Because gas particles are widely separated, they move independently of one another unless they collide. That is, no forces of attraction or repulsion operate among gas particles. We can see that this postulate explains Dalton law of partial pressures. This postulate also explains why gases fill their containers entirely.

- *The pressure of a gas arises from the sum of the collisions of the particles with the walls of the container.*
  This postulate explains Boyle law; at a given temperature, for the same amount of gas, the smaller the volume of the container and hence more collisions occur per unit area. The average distance traveled by a gas particle before a collision is less in a smaller volume. Therefore, more collisions occur in a given area producing greater pressure.

This assumption also predicts that pressure should be proportional to the number of moles of gas particles. The more gas particles, the greater the frequency of collisions with the walls, so the greater the pressure.

1.4.2 Equation of molecular kinetic theory

The equation below is named as the equation of molecular kinetic theory.

$$\boxed{PV = \frac{1}{3}\, mN\overline{c^2}}$$

This equation now gives pressure, a macroscopic quality, in terms of molecular motion. The significance of the above relationship is that pressure is proportional to the mean-square speed of molecules in a given container at a given temperature. From the equation we can see that when molecular speed increases the pressure exerted on the container increases. $\overline{c^2}$ is defined as the mean square speed of molecules.

1.4.3 Root mean square speed and mean speed

It is worth knowing the definitions of molecular speeds in different forms as follows: When N number of molecules in a constant volume container at constant temperature travel with the different speeds of $c_1, c_2, \ldots c_N$, it can be written as shown below.

Average speed, $\bar{C} = \frac{c_1 + c_2 + \cdots c_N}{N}$

Mean square speed $\overline{c^2} = \frac{(c_1{}^2 + c_2{}^2 + c_3{}^2 \ldots + c_N{}^2)}{N}$

Root mean square speed = $\sqrt{\overline{c^2}}$

Molecular kinetic equation can be used to derive equation to show temperature dependence of the mean square speed $\overline{c^2}$. Consider the equation for having N number of particles in volume V. We know that, $P = \frac{mN\overline{c^2}}{3\,V}$ and we can write this as; $PV = \frac{mN\overline{c^2}}{3}$

Since, $N = nN_A$, where N_A is the Avogadro's constant and n is the number of moles;

$$PV = \frac{1}{3} mnN_A\overline{c^2}$$

Since, $M = m\,N_A$, then the above equation can be rearranged as, (M is the molar mass)

$$PV = \frac{1}{3} n\,M\,\overline{c^2}$$

Substitution of ideal gas law, $PV = nRT$ in the above equation gives,

$$nRT = \frac{1}{3} M\, n\, \overline{c^2}$$

$$\overline{c^2} = \frac{3RT}{M}$$

And hence we can write root mean square speed as;

$$\boxed{\sqrt{\overline{c^2}} = \sqrt{\frac{3RT}{M}}}$$

Example 1.11

Calculate the root mean square speed of H_2 and N_2 gases at 25 °C.

Answer

$T = 25\ °C = 298\ K$
$M(H_2) = 2.0\ g\ mol^{-1} = 0.002\ \ kg\ mol^{-1}$
$M(N_2) = 28.0\ g\ mol^{-1} = 0.028\ \ kg\ mol^{-1}$
$R = 8.314\ J\ K^{-1}\ mol^{-1}$

For H_2

Substituting in $\sqrt{\overline{c^2}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314\ J\ K^{-1}\ mol^{-1} \times 298\ K}{0.002\ kg\ mol^{-1}}} = 1927.8\ m\ s^{-1}$

For N_2

Substituting in $\sqrt{\overline{c^2}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314\ J\ K^{-1}\ mol^{-1} \times 298\ K}{0.028\ kg\ mol^{-1}}} = 515.2\ m\ s^{-1}$

From the above example, we can see that heavier molecules move slowly at a given temperature implying that the molecules having higher mass do not have to move as rapidly as lighter molecules to have the same kinetic energy. This kinetic energy directly related to temperature and this can be proved based on the equation of molecular kinetic theory as follows.

We have, $PV = \frac{mN\overline{c^2}}{3}$

Multiply the above equation by 2 and also divide by 2, then we can rearrange the equation as;

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

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

And also we can write $\left(\frac{1}{2}\,m\overline{c^2}\right) = \frac{3}{2}\left(\frac{Rn}{N}\right)T = \frac{3}{2}\left(\frac{R}{N_A}\right)T = \frac{3}{2}(k_B)T$

k_B is the Boltzmann constant.

We can then write these as $\frac{1}{2}\,m\overline{c^2}$ is the kinetic energy (KE)

$$\boxed{\boldsymbol{KE} = \frac{3}{2}\boldsymbol{k_B T} \text{ (per molecule)}}$$

$$KE = \frac{3}{2}(k_B)T\,N_A$$

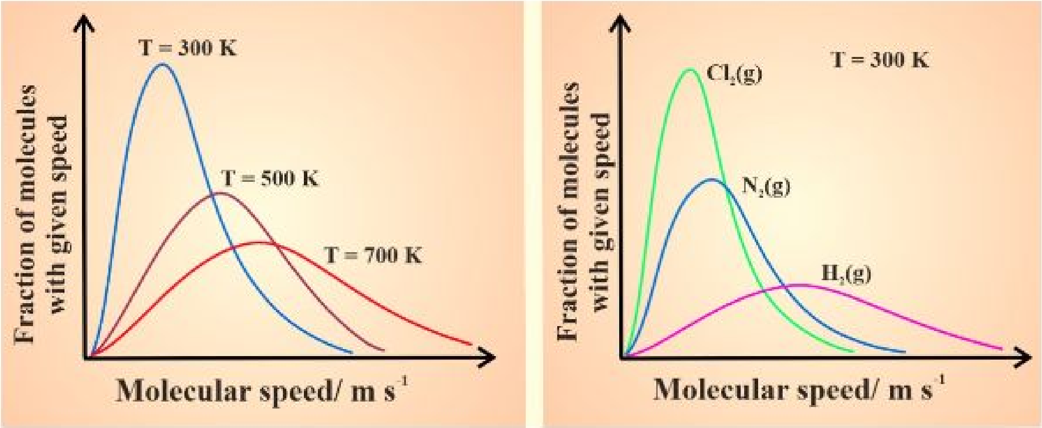
$$KE = \frac{3}{2}\left(\frac{R}{N_A}\right)T\,N_A$$

$$\boxed{\boldsymbol{KE} = \frac{\mathbf{3}}{\mathbf{2}}\boldsymbol{RT} \text{ (per mole)}}$$

This proves that the kinetic energy of a gas depends only on the Kelvin temperature.

1.4.4 Maxwell- Boltzmann distribution

Although from the above example we have calculated speed of N_2 molecule as 515 m s^{-1}, it does not mean that all the N_2 molecules travel at this speed (as the molecules move in straight line directions, that the motion has vector properties, such that the molecular speeds are expressed in relation). There is a distribution of speeds from zero to values considerably above 515 m s^{-1}. This is because as individual molecules collide and exchange energy, their speeds vary. This speed distribution can be shown as a fraction of molecules travelling with particular speeds as shown in Figure 1.6 and such a distribution is called **Maxwell- Boltzmann distribution of speeds.**

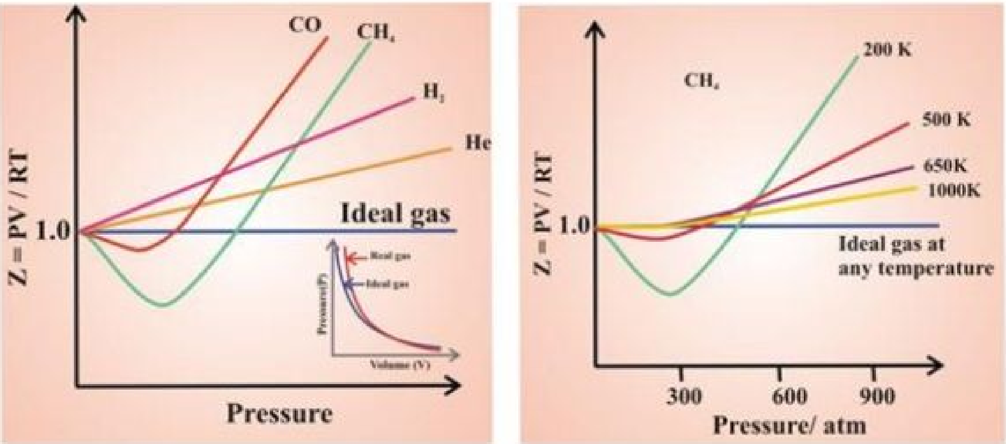


(a) (b)

Figure 1.6 (a) Maxwell- Boltzmann speed distribution for nitrogen gas at different temperatures (b) Speed distribution of three gases at 300 K

1.5 Amendments to ideal gas equation to apply for real gases

For a one mole of an ideal gas we can write $PV = RT$ or in other words $\frac{PV}{RT} = 1$ at a given temperature. When we have a real gas it actually deviates from ideal behaviour to some extent. The quantity, $Z = \frac{PV}{RT}$, called **compressibility factor (coefficient)** is used as one of the measures of this deviation. For example, for a one mole of an ideal gas if we study or analyze the variation of Z with pressure at constant temperature, PV will be constant (Boyle law) and Z *vs* P graph at all pressures will be a straight line parallel to *x*-axis (pressure - axis). Figure 1.7(a) shows such a plot for several gases at 273 K and Figure 1.7(b) for a one gas at several temperatures.



(a) (b)

Figure 1.7 Variation of compressibility factor for several gases with the comparison of an ideal gas. (a) The variation of Z with pressure at a constant temperature. Inset in (a) shows the Boyle law plot for ideal gas and real gas. (b) is the variation of Z with pressure at different temperatures for CH_4 gas.

From the plots shown in Figure 1.7 (a) it can be seen easily that at constant temperature $\frac{PV}{RT}$ *vs P (Z vs P)* plots for real gases is not a straight line parallel to the *x*-axis (pressure). There is a significant deviation from ideal behaviour. For different types of real gases, two types of curves are resulted. In the curves for hydrogen and helium, the value of *Z* increases as the pressure increases. The second type of plot is seen in the case of other gases like carbon monoxide (CO) and methane (CH_4). In these plots first there is a negative deviation from ideal behavior, the *Z* value decreases with increase in pressure and reaches to a minimum value characteristic of a gas. After that it starts increasing, crosses the line for ideal gas and increases continuously showing a positive deviation. With these observations it can be found that real gases do not follow ideal gas equation perfectly under all conditions.

This deviation from ideal behaviour can also be understood when pressure versus volume plot is considered which is drawn as an inset in the Figure 1.7(a). In that plot the pressure versus volume data of a real gas is compared with those calculated theoretically. We know that this is the plot of Boyle law (for an ideal gas) and if the real gas follows the same behaviour two plots should coincide. It is clearly apparent that at very high pressures the measured volume is more than the calculated volume and at low pressures, measured and calculated volumes approach close to each other indicating further that low pressure conditions favour the ideal behavior. Thus gases show ideal behavior when the volume occupied is large so that the volume of the molecules can be neglected in comparison to the volume of the container. In other words, the behaviour of the real gas becomes more ideal when pressure is very low and depends upon the nature of the gas and its temperature.

We can further interpret the above behaviour of real gases where Z is less than 1 ($Z < 1$) as a combination of intermolecular interactions and repulsions caused by the significant sizes of the molecules when they become crowded at high pressures. At low pressures but still high for the ideal behaviour intermolecular attractions lower the molar volume and Z value is less than 1. At sufficiently high pressures, molecules tend to become crowded and the volume of the gas particles become large compared to the situation when it would be a point mass. At high temperature (Figure 1.7(b)) intermolecular attractions become less and *PV* factor increases making *Z* values greater than one ($Z >1$). However deviation from the ideal line is less indicating that the higher temperatures favour the ideality to some extent. Therefore, we can say very low pressures and high temperatures are the favourable conditions for the ideal behaviour of real gases.

If we compare this behaviour of real gases with ideal gases considering these variations in molar volume at a given temperature and pressure, then the relation of compressibility factor Z may be understood. Assume that one mole of a real gas has the volume V_{real} and that for the ideal gas as V_{ideal}. Therefore, we can write;

$$Z = \frac{PV_{real}}{RT}$$

If the gas shows ideal behaviour under the same conditions;

$$PV_{ideal} = RT \text{ (per one mole)}$$

Substituting this in the first equation we get; $Z = \frac{PV_{real}}{PV_{ideal}}$

Therefore, $Z = \frac{V_{real}}{V_{ideal}}$

Therefore, we can see that the compressibility factor Z is the ratio of actual molar volume of a gas to the molar volume of it if it behaves as an ideal gas at that temperature and pressure.

Based on this kinds of experiments, it has been found that real gases do not follow Boyle law, Charles law and Avogadro law perfectly under all conditions. Therefore we have to understand; why gases deviate from the ideal behaviour and the conditions under which gases deviate from ideal behaviour.

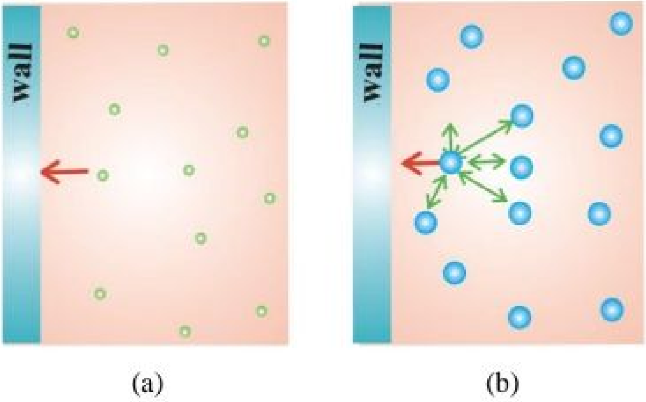
For the first one we can use the assumptions made in the molecular kinetic theory where it was assumed that; there is no force of attraction between the molecules of a gas and volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.

If there are no interactions among gas molecules, the gas will never liquefy. However, we know that gases do liquefy when cooled and compressed. Once the gases are cooled and compressed the gas molecules will come close and then form liquids. If the volume of a gas molecule is negligible then the pressure versus volume graph of real gas and that of an ideal gas should coincide (see the inset of Figure 1.7 (a) and the behavior shown in the inset help us to understand the deviation of real gases from ideality). But it does not happen therefore, the real gases deviate from ideality.

1.5.1 van der Waals equation

At the beginning of this unit, an ideal gas law, $PV = nRT$ known as **equation of state** was used to understand the behaviour of gases under different conditions with the measurable variables of P, V, T and n. From the above clarifications it can be understood that real gases show deviations from the ideal gas law due to the interactions among molecules and a significant volume of a gas molecule. Therefore, it is necessary to have another kind of equations of state to describe the behaviour of real gases as the measured pressures and volumes would not be the same as those for an ideal gas. Dutch physicist, **J. D. van der Waals** suggested the following which relates pressure and volume of a real gas to the pressure and volume of an ideal gas.

At high pressures molecules of gases are very close to each other and molecular interactions start to operate. Therefore, at high pressures, molecules cannot strike on the walls of the container with full force of impact as these are dragged back by other molecules due to the operation of these molecular attractive forces (a sketch on this behaviour is shown in Figure 1.8 comparing with an ideal gas). This affects the pressure exerted by the molecules on the walls of the container. Thus, the pressure exerted by the real gas is lower than the pressure exerted by the ideal gas under similar conditions.



(a) (b)

Figure 1.8 Comparison of the impact on the wall due to the collision of (a) an ideal gas molecule and (b) a real gas molecule.

As shown in the above figure reduction of pressure of a real gas is due to the intermolecular attractions. As it was found that the number of collisions with the wall in a given time is proportional to the density of the gas, the correction factor to pressure is proportional to the square of the gas amount and inversely proportional to the square of the volume and then the correction factor can be written as $\frac{a\,n^2}{V^2}$ where a is a constant related to magnitude of attractive forces and is independent of temperature and pressure. n and V are the number of moles of the gas and volume of the container respectively. Therefore, the pressure of the system under this condition is given by the following expression.

$$P_{ideal} = P_{real} + \frac{a\,n^2}{V^2}$$

At high pressure, repulsive forces are significant as molecules are almost in contact. Therefore, these repulsive forces cause the molecules to behave as small spheres to minimize the effect and hence results a significant volume occupied by the molecules. Now the ideal volume should be less than the measured volume because instead of moving in volume V, these are now restricted to an effective volume of

$$(V-nb)$$

nb is approximately the total volume occupied by the molecules themselves and b is a constant (volume of one molecule). Having taken into account the corrections for pressure and volume, we can rewrite the equation $PV = nRT$ as,

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

This is called **van-der Waals equation** and a and b are called **van-der Waals constants**. If we write this equation for one mole of a real gas it takes the following form.

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

1.5.2 Critical temperature and liquefaction of gases

At the beginning of the chapter the importance of the extent of the intermolecular forces to maintain a particular physical state was discussed. Matter can be interconverted between physical states supplying heat or cooling as needed to change the intermolecular distance.

For example, we may think that liquefaction of a gas can be done just by cooling and compression. Though it is correct to some extent, we need more ideas about the behaviour of real gases in accordance with their phase changes.

Note: *This is one of the topics discussed in detail in unit 12 and a little description will be given here as it is important to have a basic idea about the conditions necessary for liquefication of gases.*

For example, such kind of information on the pressure, temperature and volume relations are available for carbon dioxide where it has been found that carbon dioxide can behave as a gas, a liquid and a solid depending on the variations in pressure and temperature.

We know that high temperatures favour the ideal behaviour and a gas cannot be liquefied even at very high pressures. In the case of carbon dioxide, which exists as a gas at high temperatures starts to liquefy at 30.98 °C (304.2 K) when the pressure is below 73 atm. The temperature 30.98 °C is called **critical temperature (T_C)** of carbon dioxide. This is the highest temperature at which liquid carbon dioxide is observed and above this temperature it exists only as a gas. Therefore, we can defined the critical temperature of a substance as the temperature at and above which the vapour of the substance cannot be liquefied, no matter how much pressure is applied. The **critical pressure** of a substance is the pressure required to liquefy a vapour at critical temperature.

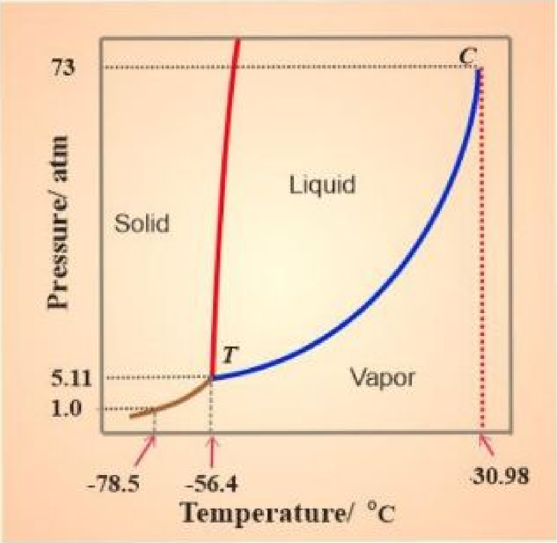


Figure 1.9 Phase diagram of CO_2

Table 1.3 A summary of equations

Gas law	Equation	Parameters kept constant
Ideal gas law	$PV = nRT$	None
Boyle law	$P = k/V$	n and T
Charles law	$V = kT$	n and P
Avogadro law	If $V_A = V_B$ then $N_A = N_B$	P and T
Molecular kinetic equation	$PV = \frac{1}{3}\, mN\overline{c^2}$	
Average speed	$\bar{C} = \frac{c_1 + c_2 + \cdots c_N}{N}$	
Mean square speed	$\overline{c^2} = \frac{(c_1{}^2 + c_2{}^2 + c_3{}^2 \ldots . + c_N{}^2)}{N}$	
Mean square speed	$\overline{c^2} = \frac{3RT}{M}$	
Dalton law of partial pressures	$P_A = x_A\, P_T$ $P_T = P_A + P_B + P_C$	
Compressibility factor	$z = \frac{PV}{RT}$	for one mole of gas
van der Waals equation	$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$	