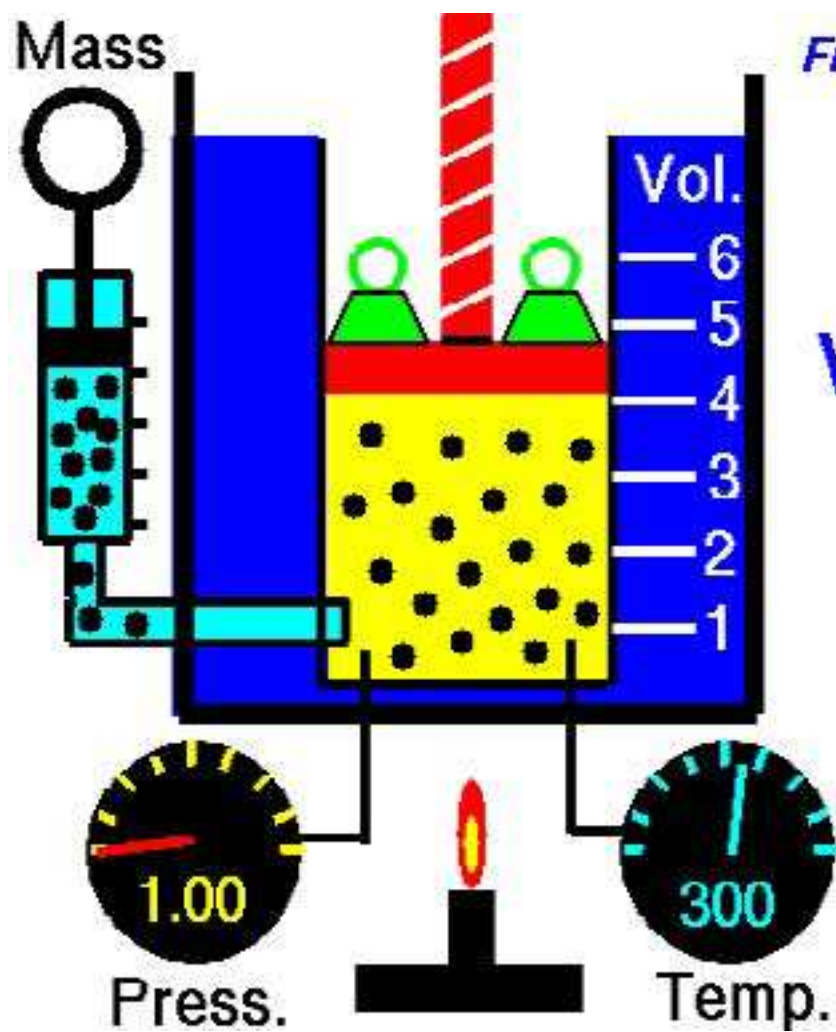
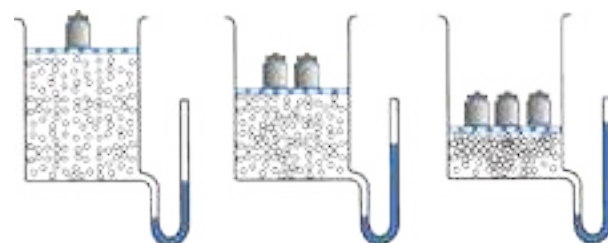


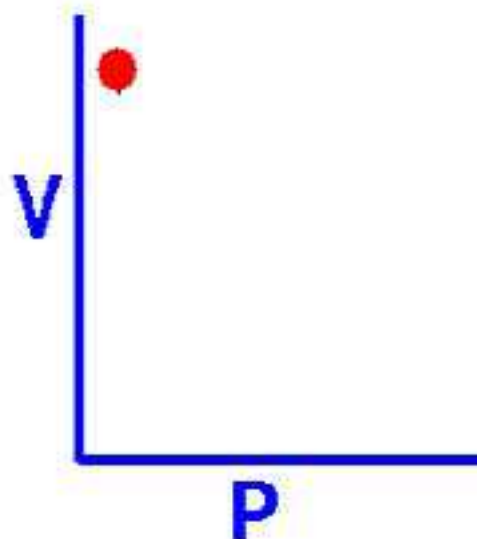
CHAPTER

3

GASES



Frozen: Mass & Temp.



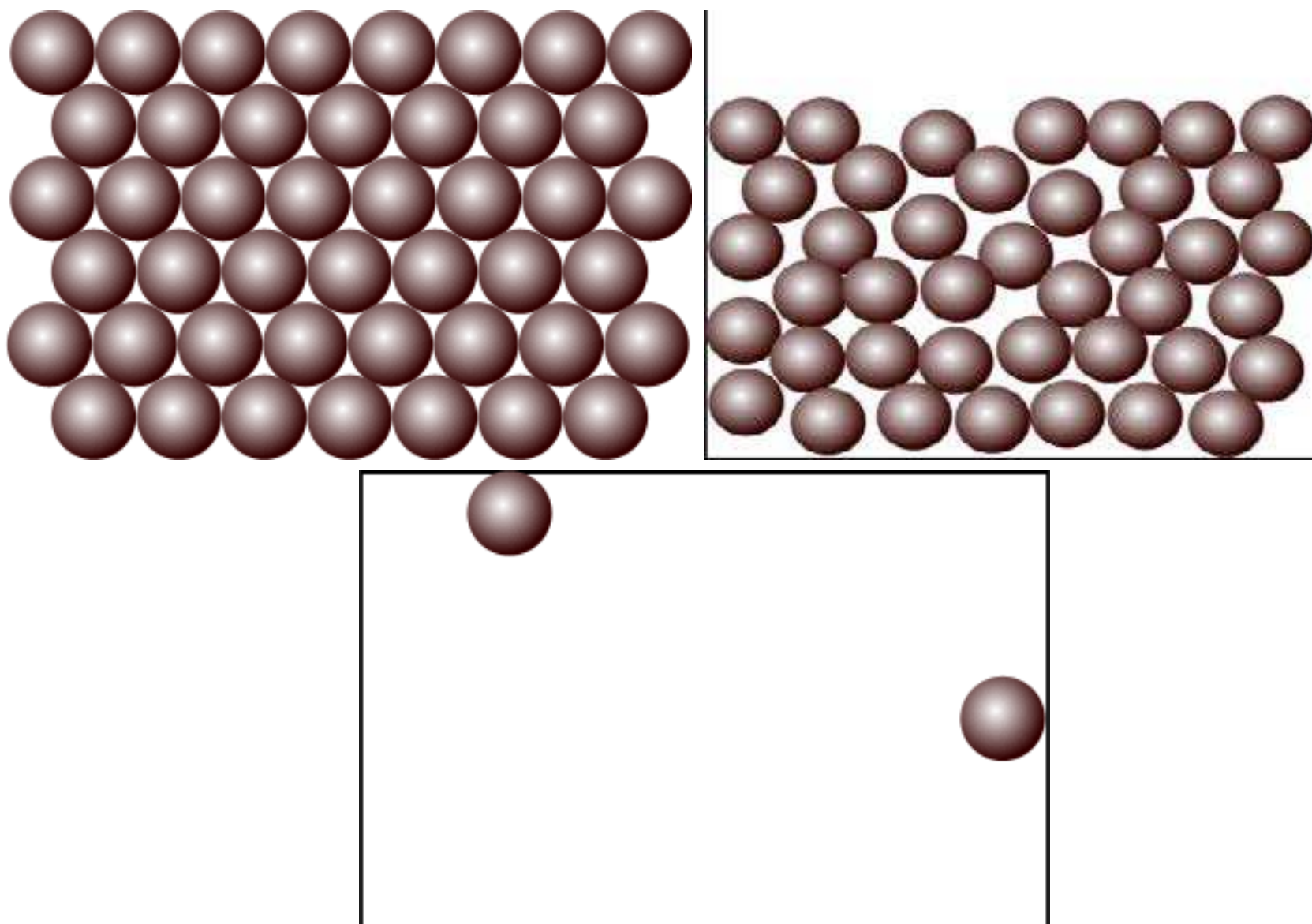
Animation 3.1: Boyle's Law
Source & credit: wikipedia

3.1 STATES OF MATTER

Matter exists in four states i.e., solid, liquid, gas and plasma. The simplest form of matter is the gaseous state and most of matter around us is in the solid state.

Liquids are less common than solids, gases and plasmas. The reason is that the liquid state of any substance can exist only within a relatively narrow range of temperature and pressure.

Let us look at the general properties of gases, liquids and solids. Kinetic molecular theory of gases can help us understand their properties.



Animation 3.2.: States of Matter

Source & Credit: knockhardy

3.1.1 Properties of Gases

1. Gases don't have a definite volume and occupy all the available space. The volume of a gas is the volume of the container.
2. They don't have a definite shape and take the shape of the container just like liquids.
3. Due to low densities of gases, as compared to those of liquids and solids, the gases bubble through liquids and tend to rise up.
4. Gases can diffuse and effuse. This property is negligible in solids but operates in liquids as well.
5. Gases can be compressed by applying a pressure because there are large empty spaces between their molecules.
6. Gases can expand on heating or by increasing the available volume. Liquids and solids, on the other hand, do not show an appreciable increase in volume when they are heated.
7. When sudden expansion of gases occurs cooling takes place, it is called Joule Thomson effect.
8. Molecules of gases are in a constant state of random motion They can exert a certain pressure on the walls of the container and this pressure is due to the number of collisions.
9. The intermolecular forces in gases are very weak.

3.1.2 Properties of Liquids

6. Liquids don't have a definite shape but have a definite volume. Unlike solids they adopt the shape of the container.
7. Molecules of liquids are in a constant state of motion. The evaporation and diffusion of liquid molecules is due to this motion.
8. The densities of liquids are much greater than those of gases but are close to those of solids.
9. The spaces among the molecules of liquids are negligible just like solids.
10. The intermolecular attractive forces in liquids are intermediate between gases and solids. The melting and boiling points of gases, liquids and solids depend upon the strength of such forces.
11. Molecules of liquids possess kinetic energy due to their motion. Liquids can be converted into solids on cooling i.e., by decreasing their kinetic energy. Molecules of liquids collide among themselves and exchange energy but those of solids can not do so.

3.1.3 Properties of Solids

1. The particles present in solid substances are very close to each other and they are tightly packed. Due to this reason solids are non-compressible and they cannot diffuse into each other.
2. There are strong attractive forces in solids which hold the particles together firmly and for this reason solids have definite shape and volume.
3. The solid particles possess only vibrational motion.

3.1.4 Units of Pressure:

The pressure of air that can support 760 mmHg column at sea level, is called one atmosphere. It is the force exerted by 760mm or 76cm long column of mercury on an area of 1cm^2 at 0°C . It is the average pressure of atmosphere at sea level $1\text{mmHg}=1\text{torr}$. The S.I. unit of pressure is expressed in Nm^{-2} . One atmospheric pressure i.e 760 torr is equal to 101325 Nm^{-2} .

$1\text{pascal}=1\text{ Nm}^{-2}$. So, $760\text{ torr} = 101325\text{Pa} = 101.325\text{ kilopascals}$ (kpa is another unit of pressure)

The unit pounds per square inch (psi) is used most commonly in engineering work, and $1\text{ atm} = 760\text{ torr}=14.7\text{ pounds inch}^{-2}$. The unit millibar is commonly used by meteorologists.

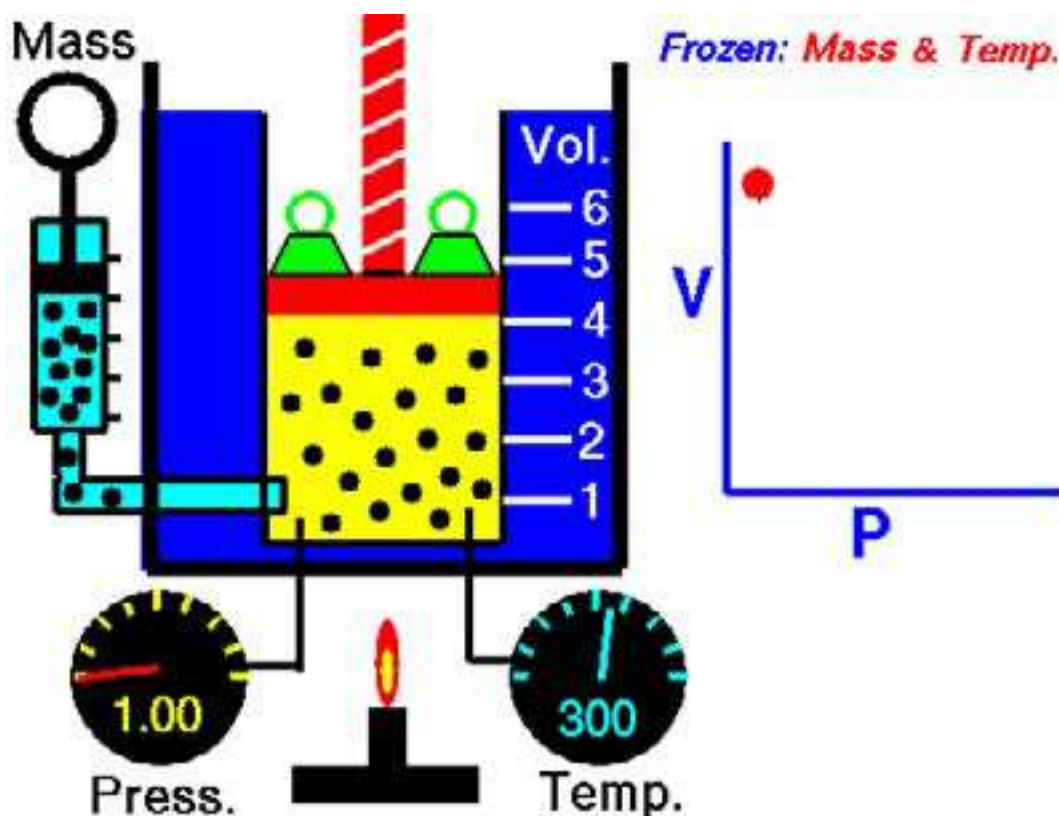
3.2 GAS LAWS

It is a matter of common observation that when external conditions of temperature and pressure are changed, the volume of a given quantity of all gases is affected. This effect is nearly the same irrespective of the nature of the gas. So gases show a uniform behaviour towards the external conditions. The gas laws describe this uniform behaviour of gases. The relationships between volume of a given amount of gas and the prevailing conditions of temperature and pressure are called the gas laws. Different scientists, like Boyle, Charles, Graham and Dalton have given their laws relating to the properties of gases.

3.2.1 Boyle's Law

In Boyle's law the pressure and volume are variables while the temperature and quantity of a gas remains constant. Boyle's law is stated as follows:-

The volume of a given mass of a gas at constant temperature is inversely proportional to the pressure applied to the gas.



Animation 3.3: Boyle's Law
Source & credit: wikipedia

So

$V \propto 1/P$ (when the temperature and number of moles are constant)

or $V = k/p$

$PV = k$ (when T and n are constant) (1)

'k' is proportionality constant. The value of k is different for the different amounts of the same gas. According to the equation (1), Boyle's law can also be defined as **The product of pressure and volume of a fixed amount of a gas at constant temperature is a constant quantity.**

So $P_1V_1 = k$ and $P_2V_2 = k$

Hence $P_1V_1 = P_2V_2$

P_1V_1 are the initial values of pressure and volume, while P_2V_2 are the final values of pressure and volume.

3.2.2 Experimental Verification of Boyle's Law

The following diagram Fig. (3.1) indicates that at constant temperature say at 25°C , the volume of a given quantity of a gas is reduced in proportion to the increase in pressure. Let us take a gas in a cylinder having a moveable piston.

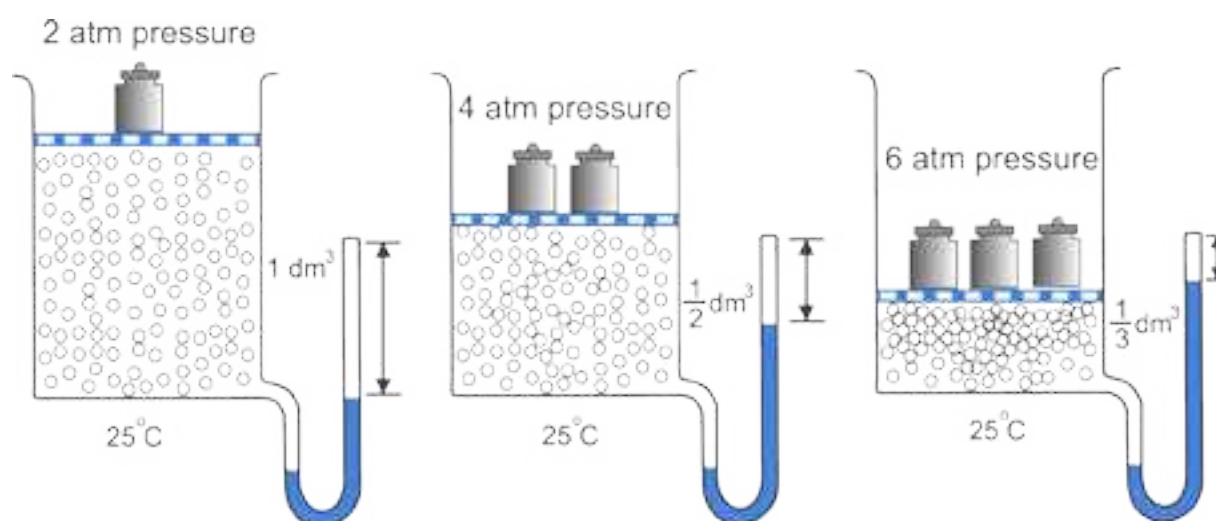


Fig (3.1) Verification of Boyle's Law

The cylinder is also attached with a manometer to read the pressure of the gas directly. Let the initial volume of gas is 1 dm^3 and its pressure is 2 atmospheres when the piston has one weight on it. When the piston is pressed twice with the help of two equal weights, the pressure becomes four atmospheres.

Similarly, when the piston is loaded with a mass three times greater, then the pressure becomes six atmospheres. The initial volume of the gas at two atmospheres is 1 dm^3 it is reduced to $1/2 \text{ dm}^3$ and then $1/3 \text{ dm}^3$ with increase of weights, respectively Fig (3.1).

$$\begin{aligned}
 P_1V_1 &= 2 \text{ atm} \times 1 \text{ dm}^3 = 2 \text{ dm}^3 \text{ atm} = k \\
 P_2V_2 &= 4 \text{ atm} \times 1/2 \text{ dm}^3 = 2 \text{ dm}^3 \text{ atm} = k \\
 P_3V_3 &= 6 \text{ atm} \times 1/3 \text{ dm}^3 = 2 \text{ dm}^3 \text{ atm} = k
 \end{aligned}$$

Hence Boyle's law is verified.

The value of k will remain the same for the same quantity of a gas at the same temperature.

Example 1

A gas having a volume of 10 dm³ is enclosed in a vessel at 0°C and the pressure is 2.5 atmospheres. This gas is allowed to expand until the new pressure is 2 atmospheres. What will be the new volume of this gas, if the temperature is maintained at 273 K.

Solution

Initial volume of gas (V_1)	= 10 dm ³
Initial temperature (T_1)	= 0°C + 273 K = 273 K
Initial pressure (P_1)	= 2.5 atm
Final pressure (P_2)	= 2 atm
Final temperature (T_2)	= 273 K
Final volume (V_2)	= ?

Since the temperature is constant ($T_1 = T_2$) Boyle's law is applicable

$$P_1 V_1 = P_2 V_2 \text{ (when } T \text{ and } n \text{ are constant)}$$

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

$$V_2 = \frac{2.5 \text{ atm} \times 10 \text{ dm}^3}{2 \text{ atm}}$$

$$= 12.5 \text{ dm}^3 \text{ Answer}$$

3.2.3 Graphical Explanation of Boyle's Law

Let us take a particular amount of a gas at a constant temperature say 0°C and enclose it in a cylinder having a piston in it. When the pressure of the gas is varied, its volume changes. Increase in pressure decreases the volume. If a graph is plotted between pressure on the x-axis (abscissa) and volume on the y-axis (ordinate), then a curve is obtained as shown in the Fig (3.2). This curve is called isotherm 'iso' means same, "therm" means heat. Now increase the temperature of the gas to 25°C.

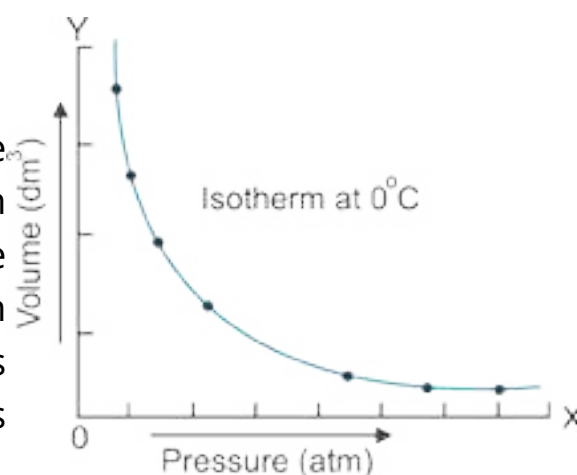


Fig (3.2) Isotherm of a gas at 0 °C.

Keep this temperature constant and again vary the pressure and volume, and plot the isotherm. It goes away from both the axes. Fig (3.3). The reason is that at higher temperature, the volume of the gas has increased. Similarly, if we increase the temperature further, make it constant and plot another isotherm, it further goes away from the axis.

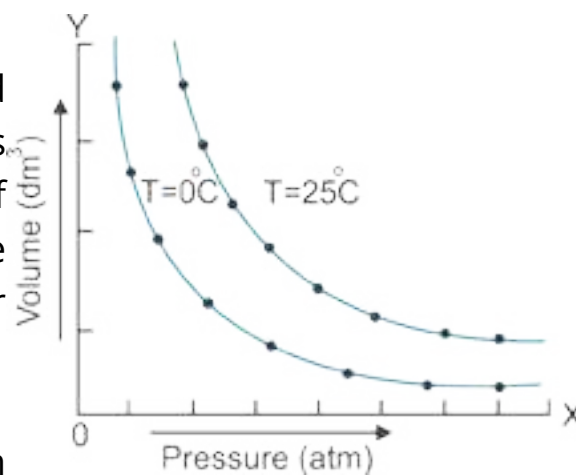
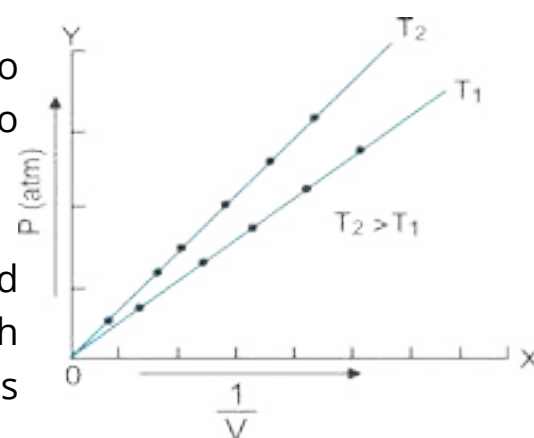


Fig (3.3) Isothermes of a gas at different temperatures.

If a graph is plotted between $1/V$ on x-axis and the pressure P on the y-axis then a straight line is obtained as shown in the Fig (3.4). This shows that the pressure and inverse of volume are directly proportional to each other. This straight line will meet at the origin which means that when the pressure is very close to zero, then the volume is so high that its inverse is very close to zero.



By increasing the temperature of the same gas from T_1 to T_2 and keeping it constant, one can vary pressure and volume. The graph of this data between P and $1/V$ will give another straight line. This straight line at T_2 will be closer to the pressure-axis Fig (3.4).

Now, plot a graph between pressure on x-axis and the product PV on Y-axis. A straight line parallel to the pressure axis is obtained Fig(3.5).

This straight line indicates that 'k' is a constant quantity.

At higher constant temperature, the volume increase and value of product PV should increase due to increase of volume at same pressure, but PV remains constant at this new temperature and a straight line parallel to the pressure axis is obtained. This type of straight line will help us to understand the non-ideal behaviour of gases. Boyle's law is applicable only to ideal gases.

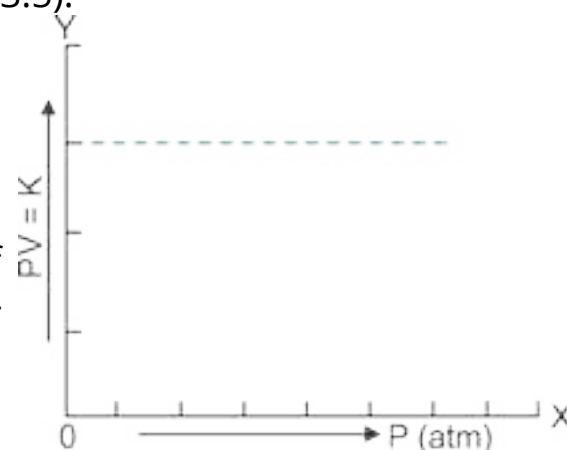


Fig (3.5) A plot between pressure and product of PV

3.2.4 Charles's Law

It is a quantitative relationship between temperature and volume of a gas and was given by French scientist J.

Charles in 1787. According to this law, **the volume of the given mass of a gas is directly proportional to the absolute temperature when the pressure is kept constant.**

$$V \propto T \text{ (when pressure and number of moles are constant)}$$

$$V = kT$$

$$V/T = k$$

If the temperature is changed from T_1 to T_2 and volume changes from V_1 to V_2 , then

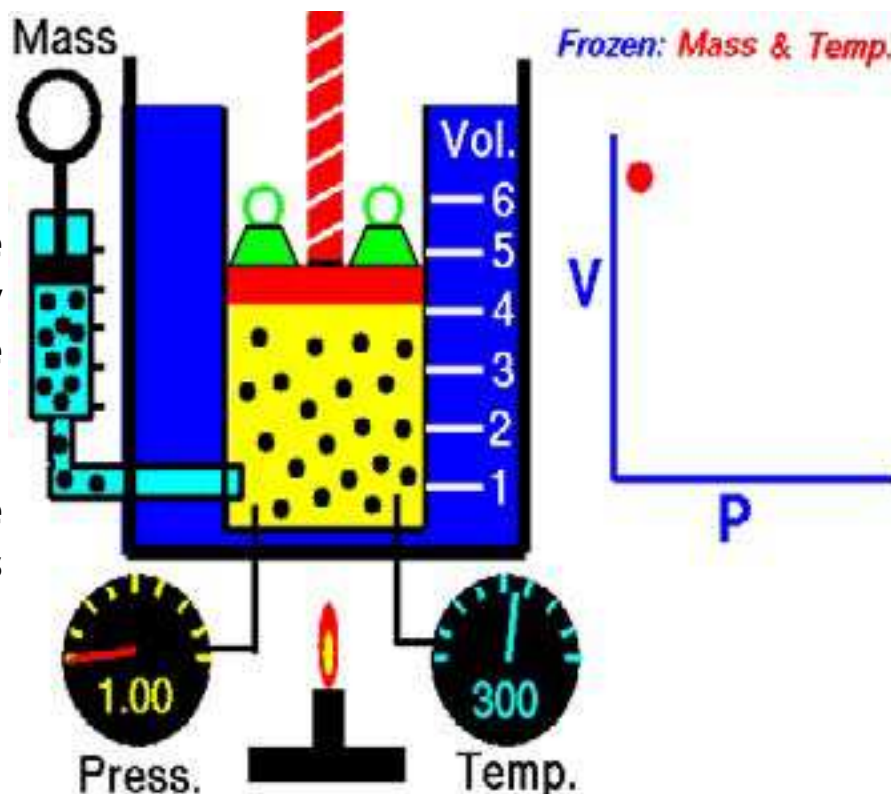
$$V_1/T_1 = k \text{ and } V_2/T_2 = k$$

So, $V_1/T_1 = V_2/T_2$ (2)

The ratio of volume to temperature remains constant for same amount of gas at same pressure.

3.2.5 Experimental Verification of Charles's Law

Let us consider a certain amount of a gas enclosed in a cylinder fitted with a movable piston. The volume of the gas is V_1 and its temperature is T_1 . When the gas in the cylinder is heated both volume and the temperature of the gas increase.



Animation 3.4: Charles's Law
Source & Credit: docsity

The new values of volume and temperature are V_2 and T_2 respectively Fig(3.6). Experiment shows that

$$V_1/T_1 = V_2/T_2$$

Hence Charles's law is verified.

Example 2

250 cm³ of hydrogen is cooled from 127°C to -27°C by maintaining the pressure constant Calculate the new volume of the gas at low temperature.

Solution

Pressure has been kept constant so this gas is obeying the Charles's law.

Initial volume (V_1) = 250 cm³ = 0.25 dm³

Initial temperature (T_1) = 127 °C + 273 K = 400 K

Final temperature (T_2) = -27 °C + 273K = 246 K

Final volume (V_2) = ?

According to Charles's law

$$V_1/T_1 = V_2/T_2 \text{ (when pressure and number of moles are constant)}$$

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

$$V_2 = \frac{0.25 \text{ dm}^3 \times 246\text{K}}{400 \text{ K}} = 0.153 \text{ dm}^3 = 153 \text{ cm}^3 \text{ Answer}$$

So by decreasing the temperature the volume of the gas has decreased at constant pressure.

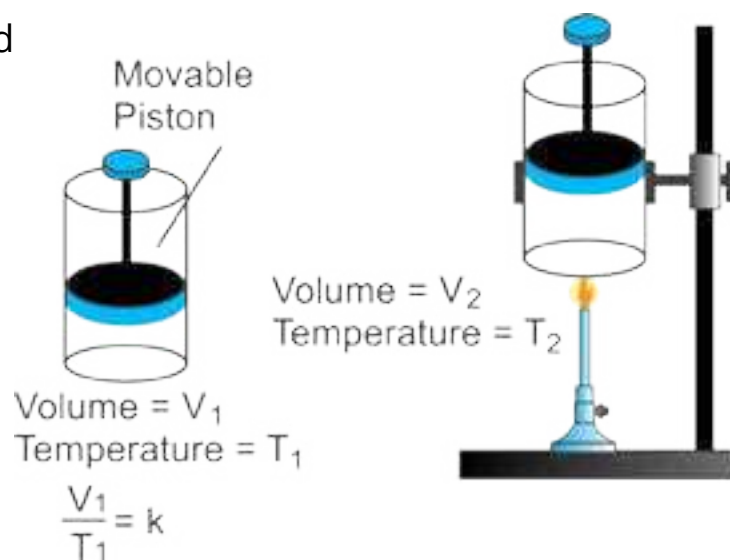


Fig (3.6) Verification of Charles's law

3.2.6 Derivation of Absolute Zero

In order to derive absolute zero of temperature, consider the following quantitative definition of Charles's law.

At constant pressure, the volume of the given mass of a gas increases or decreases by $\frac{1}{273}$ of its original volume at 0°C for every 1°C rise or fall in temperature respectively.

In order to understand the above statement, look at the Table (3.1) of temperature volume data of a hypothetical gas. At 0°C the volume of the gas taken is 546 cm^3 . It is twice 273 cm^3 , and is being supposed for the sake of convenience of understanding. At 273°C , the volume of the gas has doubled (1092 cm^3) and it should become practically zero at -273°C . The general equation to know the volumes of the gas at various temperatures is

$$V_t = V_o \left(1 + \frac{t}{273}\right) \dots\dots\dots (3)$$

Where V_t = volume of gas at temperature T

V_o = Volume of gas at 0°C

t = Temperature on centigrade or celsius scale

If a gas is warmed by 1°C , it expands by $\frac{1}{273}$ of its original volume at 0°C . Since original volume is 546 cm^3 , so, for 1°C rise in temperature, 2 cm^3 increase in volume will take place. 2 cm^3 is the $\frac{1}{273}$ of 546 cm^3 . Similarly, for 100°C rise in temperature, a change of 200 cm^3 will take place. The

Table (3.1) shows that the volume does not increase corresponding to increase in temperature on celsius scale. For example, the increase in temperature from 10°C to 100°C , increases the volume from 566 cm^3 to 746 cm^3 .

Applying Charles's law

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

$$\frac{566}{10} \neq \frac{746}{100}$$

The two sides of equation are not equal. So, Charles's law is not being obeyed when temperature is measured on the Celsius scale.

For this reason a new temperature scale has been developed. It starts from 273°C (more precisely -273.16°C) which is called zero Kelvin or zero absolute. Let us now explain how the new temperature scale has been developed. The best way is to plot a graph between the variables of Charles's law.

Table(3.1) volume-Temperature data for a given amount of a gas at constant pressure

Volumes (cm ³)	CelsiusTemperature (°C)	Temperature (K)	$\frac{V}{T} = k = \text{cm}^3 \text{K}^{-1}$
1092	273	546	2
846	150	423	2
746	100	373	2
646	50	323	2
566	10	283	2
548	1	274	2
546	0	273	2
544	-1	272	2
526	-10	263	2
400	-73	200	2
346	-100	173	2
146	-200	73	2
0	-273	0	

Graphical Explanation

If we plot a graph between temperature on x-axis and the volume of one mole of an ideal gas on y-axis, we get a straight line which cuts the temperature axis at -273.16°C . This can be possible only if we extrapolate the graph upto -273.16°C . This temperature is the lowest possible temperature, which would have been achieved if the substance remains in the gaseous state Fig (3.7). Actually, all the gases are converted into liquids above this temperature.

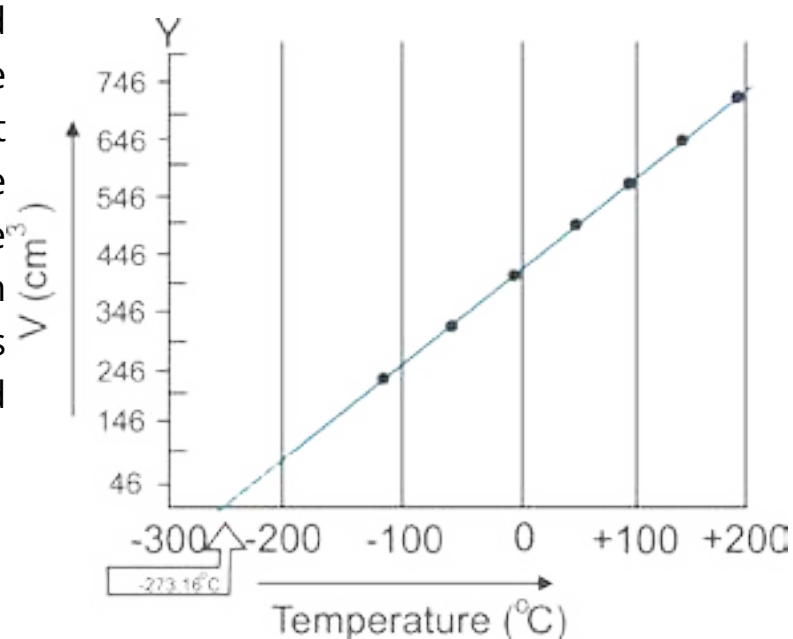


Fig (3.7) The graph between volume and temperature for a gas according to Table (3.1).

Charles's law is obeyed when the temperature is taken on the Kelvin scale. For example, at 283 K (10 °C) the volume is 566 cm³, while at 373 K (100 °C) the volume is 746 cm³ Table (3.1). According to Charles's law.

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

$$\frac{566}{283} = \frac{746}{373} = 2 = K$$

Greater the mass of gas taken, greater will be the slope of straight line. The reason is that greater the number of moles greater the volume occupied. All these straight lines when extrapolated meet at a single point of -273.16 °C (0 Kelvin). It is apparent that this temperature of -273.16 °C will be attained when the volume becomes zero. But for a real gas the zero volume is impossible which shows that this temperature can not be attained for a real gas. This is how we recognize that -273.16 °C must represent the coldest temperature.

3.2.7 Scales of Thermometry

There are three scales of thermometry which are used for temperature measurements.

(a) Centigrade Scale: It has a zero mark for the temperature of ice at one atmospheric pressure. The mark 100°C indicates the temperature of boiling water at 1 atmospheric pressure. The space between these temperature marks is divided into 100 equal parts and each part is 1°C.

(b) Fahrenheit Scale: The melting point of ice at 1 atmospheric pressure has a mark 32°F and that of boiling water is 212 °F. The space between these temperature marks is divided into 180 equal parts and each part is 1 °F.

(c) Absolute or Kelvin Scale: The melting Point of ice at 1 atmospheric pressure is 273K. The water boils at 373K or more precisely at 373.16K.

Temperature on Kelvin scale = Temperature °C + 273.16

Following relationships help us to understand the interconversion of various scales of temperatures.

$$K = °C + 273.16$$

$$°C = 5/9[°F-32]$$

$$°F = 9/5(°C)+32$$

3.3 GENERAL GAS EQUATION

While describing Boyle's and Charles's laws, some of the variables are held constant during the changes produced in the gases. According to Boyle's law.

$$V \propto \frac{1}{P} \text{ (when 'n' and 'T' are held constant)}$$

According to Charles's law

$$V \propto T \text{ (when n and P are held constant)}$$

It is a well known fact that volume of the given gas at constant temperature and pressure is directly proportional to the number of moles (Avogadro's law).

$$V \propto n \text{ (when P and T are held constant)}$$

If we think for a moment that none of the variables are to be kept constant then all the above three relationships can be joined together.

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

$$V = \text{Constant} \frac{nT}{P}$$

The constant suggested is R which is called general gas constant.

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

$$PV = nRT \text{ (4)}$$

The equation (4) is called an ideal gas equation. It is also known as general gas equation. This equation shows that if we have any quantity of an ideal gas then the product of its pressure and volume is equal to the product of number of moles, general gas constant and absolute temperature. This equation is reduced to Boyle's law, Charles's law and Avogadro's law, when appropriate variables are held constant.

$$PV = nRT, \text{ when T and n are held constant, } PV = k \text{ (Boyle's law)}$$

$$V = R \frac{nT}{P}, \text{ when P and n are held constant, } V = kT \text{ (Charles's law)}$$

$$V = R \frac{nT}{P}, \text{ when P and T are held constant } V = kn \text{ (Avogadro's law)}$$

For one mole of a gas, the general gas equation is

$$PV = RT \text{ or } \frac{PV}{T} = R$$

It means that ratio of PV to T is a constant quantity (molar gas constant)

Hence

$$\frac{P_1V_1}{T_1} = R \quad \frac{P_2V_2}{T_2} = R$$

Therefore,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \dots\dots\dots (5)$$

3.3.1 Ideal Gas Constant R

The values and units of R can be calculated by Avogadro's principle very easily. Its value depends upon the units chosen for pressure, volume and temperature. The volume of one mole of an ideal gas at STP (one atmospheric pressure and 273.16 K) is 22.414 dm³.

Putting these values in the general gas equation will give the value of R.

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

Putting their values, alongwith units

$$R = \frac{1 \text{ atm} \times 22.414 \text{ dm}^3}{1 \text{ mole} \times 273.16 \text{ K}}$$

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

When the pressure is in atmospheres, volume in dm³, then the value of R, used should be 0.0821 dm³ atm K⁻¹ mol⁻¹

The physical meanings of this value is that, if we have one mole of an ideal gas at 273.16 K and one atmospheric pressure and its temperature is increased by 1 K, then it will absorb 0.0821 dm³-atm of energy, dm³-atm is the unit of energy in this situation. Hence, the value of R is a universal parameter for all the gases. It tells us that the Avogadro's number of molecules of all the ideal gases have the same demand of energy.

If the pressure is expressed in mm of mercury or torr and the volume of the gas in cm^3 then values of R are,

$$\begin{aligned} R &= 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \\ &= 0.0821 \times 760 \text{ dm}^3 \text{ mm Hg K}^{-1} \text{ mol}^{-1} \\ &= 62.4 \text{ dm}^3 \text{ mm Hg K}^{-1} \text{ mol}^{-1} \text{ Since, (1 mm of Hg = 1 torr)} \\ &= 62.4 \text{ dm}^3 \text{ torr K}^{-1} \text{ mol}^{-1} \\ &= 62400 \text{ cm}^3 \text{ torr K}^{-1} \text{ mol}^{-1} \text{ As, (1 dm}^3 = 1000 \text{ cm}^3) \end{aligned}$$

Using SI units of pressure, volume and temperature in the general equation, the value of R is calculated as follows. The SI units of pressure are Nm^{-2} and of volume are m^3 . By using Avogadro's principle

$$\begin{aligned} 1 \text{ atm} &= 760 \text{ torr} = 101325 \text{ Nm}^{-2} \\ 1 \text{ m}^3 &= 1000 \text{ dm}^3 \\ n &= 1 \text{ mole} \\ T &= 273.16 \text{ K} \\ P &= 1 \text{ atm} = 101325 \text{ Nm}^{-2} \\ V &= 22.414 \text{ dm}^3 = 0.022414 \text{ m}^3 \\ \text{Putting their values, alongwith units.} \end{aligned}$$

$$R = \frac{PV}{nT} = \frac{101325 \text{ N m}^{-2} \times 0.022414 \text{ m}^3}{1 \text{ mol} \times 273.16 \text{ K}}$$

$$R = 8.3143 \text{ Nm K}^{-1} \text{ mol}^{-1} = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1} \text{ (1 Nm = 1J)}$$

Since $1 \text{ cal.} = 4.18 \text{ J}$

$$\text{so } R = \frac{8.3143}{4.18} = 1.989 \text{ cal K}^{-1} \text{ mol}^{-1}$$

Keep in mind that, wherever the pressure is given in Nm^{-2} and the volume in m^3 , then the value of R used must be $8.3143 \text{ JK}^{-1} \text{ mol}^{-1}$.

3.3.2 Density of an ideal Gas

For calculating the density of an ideal gas, we substitute the value of number of moles (n) of the gas in terms of the mass (m), and the molar mass (M) of the gas.

$$n = \frac{m}{M}$$

$$PV = \frac{m}{M} RT \dots\dots\dots (6)$$

Equation (6) is another form of general gas equation that may be employed to calculate the mass of a gas whose P, T, V and molar mass are known. Rearranging equation (6)

$$PM = \frac{m}{V} RT$$

$$PM = d RT \quad \left(d = \frac{m}{V}\right)$$

$$d = \frac{PM}{RT} \quad \dots\dots\dots (7)$$

Hence the density of an ideal gas is directly proportional to its molar mass. Greater the pressure on the gas, closer will be the molecules and greater the density. Higher temperature makes the gases to expand, hence density falls with the increase in temperature. With the help of equation (7), one can calculate the relative molar mass (M) of an ideal gas if its temperature, pressure and density are known.

Example 3

A sample of nitrogen gas is enclosed in a vessel of volume 380 cm³ at 120 °C and pressure of 101325 Nm⁻². This gas is transferred to a 10 dm³ flask and cooled to 27°C. Calculate the pressure in Nm⁻² exerted by the gas at 27°C.

Solution

All the three parameters of this gas have been changed, so we can solve this problem

by using the general gas equation of the form $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

Preferably, convert the volume to dm³ and temperature to Kelvin scale.

Initial volume of the gas (V ₁)	= 380 cm ³ = 0.38 dm ³
Initial temperature (T ₁)	= 120 °C + 273 K = 393 K
Initial pressure (P ₁)	= 101325 N m ⁻²
Final temperature (T ₂)	= 27°C + 273 K = 300 K
Final volume (V ₂)	= 10 dm ³
Final pressure (P ₂)	= ?

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

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

$$P_2 = \frac{101325 \text{ Nm}^{-2} \times 0.38 \text{ dm}^3 \times 300 \text{ K}}{393 \text{ K} \times 10 \text{ dm}^3}$$

$$= 2938.4 \text{ Nm}^{-2} \text{ Answer}$$

Example 4

Calculate the density of CH_4 (g) at 0°C and 1 atmospheric pressure. What will happen to the density if (a) temperature is increased to 27°C , (b) the pressure is increased to 2 atmospheres at 0°C .

Solution

Temperature of the gas	= $0^\circ\text{C} + 273 \text{ K} - 273 \text{ K}$
Pressure of the gas	= 1 atm
Molecular mass of the gas	= 16 g mol^{-1}
Gas constant (R)	= $0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$
Formula for density of a gas at any temperature and pressure	

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

$$\text{Putting values } d = \frac{1 \text{ atm} \times 16 \text{ g mol}^{-1}}{0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 273 \text{ K}}$$

$$\text{Simplifying the units } d = \frac{1 \times 16}{0.0821 \times 273} \text{ g dm}^{-3}$$

$$d = \boxed{0.7138 \text{ g dm}^{-3}} \text{ Answer}$$

It means that under the given conditions 1 dm^3 of CH_4 gas has a mass of 0.7138 g.

(a) Density at 27 °C

Temperature = 27 + 273 = 300 K

Putting values in the equation of density and simplifying the units.

$$d = \frac{PM}{RT} = \frac{1 \text{ atm} \times 16 \text{ g mol}^{-1}}{0.0821 \text{ dm}^3 \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 300 \text{ K}} = 0.649 \text{ g dm}^{-3}$$

So, by increasing the temperature from 0°C to 27°C the density of gas has decreased from 0.7138 g dm⁻³ to 0.649 g dm⁻³. The increase of temperature makes the molecules of a gas to move away from each other.

(b) Density at 2 atmospheric pressure and 0°C

$$T = 0 + 273 = 273 \text{ K}$$

$$P = 2 \text{ atm}$$

Putting values in the equation and simplifying the units.

$$d = \frac{PM}{RT} = \frac{2 \text{ atm} \times 16 \text{ g mol}^{-1}}{0.0821 \text{ dm}^3 \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 273 \text{ K}} = 1.427 \text{ g dm}^{-3}$$

The increase of pressure has increased the density of CH₄. The density has almost doubled by doubling the pressure. The reason is that increase of pressure makes the molecules to come close to each other.

Example 5

Calculate the mass of 1 dm³ of NH₃ gas at 30 °C and 1000 mm Hg pressure, considering that NH₃ is behaving ideally.

Solution

$$\text{Pressure of the gas} = 1000 \text{ mm Hg} = \frac{1000}{760} = 1.315 \text{ atm}$$

$$\text{Volume of the gas} = 1 \text{ dm}^3$$

$$\text{Temperature of the gas} = 30^\circ\text{C} + 273 \text{ K} = 303 \text{ K}$$

$$\text{Molecular mass of the gas} = 17 \text{ g mol}^{-1}$$

General gas equation $PV = \frac{m}{M} RT$ can be used to calculate the mass (m) of the gas.

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

Putting values along with units

$$\text{Mass of NH}_3 = \frac{1.315 \text{ atm} \times 1 \text{ dm}^3 \times 17 \text{ g mol}^{-1}}{0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 303 \text{ K}}$$

Simplifying the units

$$\text{Mass of NH}_3 = \frac{1.315 \times 1 \times 17 \text{ g}}{0.0821 \times 303} = \boxed{0.907 \text{ g}} \text{ Answer}$$

This is the mass of 1 dm³ of NH₃ under the given conditions. In other words, it is the density of NH₃, if it is acting as an ideal gas.

3.4 AVOGADRO'S LAW

According to this law, **“equal volumes of all the ideal gases at the same temperature and pressure contain equal number of molecules”**. This statement is indirectly the same as has been used for evaluating the general gas constant R i.e., one mole of an ideal gas at 273.16K and one atm pressure has a volume of 22.414 dm³. Since one mole of a gas has Avogadro's number of particles, so 22.414 dm³ of various ideal gases at S T P will have Avogadro's number of molecules i.e. 6.02 x 10²³. 22.414 dm³ of a gas at 273.16 K and one atmospheric pressure has number of molecules = 6.02 x 10²³.

In other words, if we have one dm³ of each of H₂, He, N₂, O₂, and CO in separate vessels at STP, then the number of molecules in each will be 2.68 x 10²². This is obtained by dividing 6.02 x 10²³ with 22.414 dm³.

Similarly, when the temperature or pressure are equally changed for these four gases, then the new equal volumes i.e. 1dm³ each will have the same number of molecules i.e. 2.68 x 10²².

No doubt, one dm³ of H₂ at STP weighs approximately 0.0899 grams and one dm³ of O₂ at STP weighs 1.4384 g, but their number of molecules are the same. Although, oxygen molecule 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 neighbour at room temperature.

3.5 DALTON'S LAW OF PARTIAL PRESSURES

John Dalton studied the mixtures of gases and gave his law of partial pressures. According to this law, **the total pressure exerted by a mixture of non-reacting gases is equal to the sum of their individual partial pressures**. Let the gases be designated as 1, 2, 3, and their partial pressures are p_1, p_2, p_3 . The total pressure (P) of the mixture of gases is given by

$$P_t = p_1 + p_2 + p_3$$

The partial pressure of a gas in a mixture of gases is the pressure that it would exert on the walls of the container, if it were present all alone in that same volume under the same temperature.

Let us have four cylinders of same volume, i.e., 10 dm^3 each and three gases H_2 , CH_4 and O_2 are separately enclosed in first three of them at the same temperature. Let their partial pressures be 400 torr, 500 torr and 100 torr respectively.

All these gases are transferred to a fourth cylinder of capacity 10 dm^3 at the same temperature. According to Dalton's law

$$P_t = p_{\text{H}_2} + p_{\text{CH}_4} + p_{\text{O}_2} = (400 + 500 + 100) \text{ torr}$$

$$P_t = 1000 \text{ torr}$$

These three non-reacting gases are behaving independently under the normal conditions. The rapidly moving molecules of each gas in a mixture have equal opportunities to collide with the walls of the container. Hence, each gas exerts a pressure independent of the pressure of other gases. The total pressure is the result of total number of collisions per unit area in a given time.

Molecules of each gas move independently, so the general gas equation ($PV = nRT$) can be applied to the individual gases in the gaseous mixture.

$$\begin{array}{lll}
 p_{\text{H}_2} V = n_{\text{H}_2} RT & p_{\text{H}_2} = n_{\text{H}_2} \frac{RT}{V} & p_{\text{H}_2} \propto n_{\text{H}_2} \\
 p_{\text{CH}_4} V = n_{\text{CH}_4} RT & p_{\text{CH}_4} = n_{\text{CH}_4} \frac{RT}{V} & p_{\text{CH}_4} \propto n_{\text{CH}_4} \\
 p_{\text{O}_2} V = n_{\text{O}_2} RT & p_{\text{O}_2} = n_{\text{O}_2} \frac{RT}{V} & p_{\text{O}_2} \propto n_{\text{O}_2}
 \end{array}$$

$\frac{RT}{V}$ is a constant factor for each gas.

All these gases have their own partial pressures. Since volumes and temperatures are the same, so their number of moles will be different and will be directly proportional to their partial pressures. Adding these three equations

$$\begin{aligned}
 P_t &= p_{H_2} + p_{CH_4} + p_{O_2} \\
 P_t &= (n_{H_2} + n_{CH_4} + n_{O_2}) \frac{RT}{V} \\
 P_t &= n_t \frac{RT}{V} \quad \text{where } n_t = n_{H_2} + n_{CH_4} + n_{O_2} \\
 P_t V &= n_t RT \quad \dots\dots\dots (8)
 \end{aligned}$$

According to equation (8), the total pressure of the mixture of gases depends upon the total number of moles of the gases.

3.5.1 Calculation of Partial Pressure of a Gas

The partial pressure of any gas in a mixture of gases can be calculated, provided one knows the mass of that gas or its number of moles alongwith the total pressure and the total number of moles present in the mixture.

In order to have a relationship, let us suppose that we have a mixture of gas A and gas B. This mixture is enclosed in a container having volume (V). The total pressure is one atm.

The number of moles of the gases A and B are n_A and n_B respectively. If they are maintained at temperature T, then

$$\begin{aligned}
 P_t V &= n_t RT \quad \dots\dots\dots \text{(equation for the mixture of gases)} \\
 p_A V &= n_A RT \quad \dots\dots\dots \text{(equation for gas A)} \\
 p_B V &= n_B RT \quad \dots\dots\dots \text{(equation for gas B)}
 \end{aligned}$$

Divide the first two equations

$$\begin{aligned}
 \frac{p_A V}{P_t V} &= \frac{n_A RT}{n_t RT} \\
 \frac{p_A}{P_t} &= \frac{n_A}{n_t} \quad \dots\dots\dots (9)
 \end{aligned}$$

$$p_A = \frac{n_A}{n_t} P_t \quad \dots\dots\dots (10)$$

$$p_A = x_A P_t \quad (x_A \text{ is mole fraction of gas A})$$

$$p_B = x_B P_t$$

Similarly

Partial pressure of a gas is the mole fraction of that gas multiplied by the total pressure of the mixture. Remember that mole fraction of anyone of the gases in the mixture is less than unity. Moreover, the sum of mole fractions is always equal to unity.

Example 6

There is a mixture of hydrogen, helium and methane occupying a vessel of volume 13 dm^3 at 37°C and pressure of 1 atmosphere. The masses of H_2 and He are 0.8 g and 0.12 g respectively. Calculate the partial pressures in torr of each gas in the mixture.

Solution

Volume of the mixture of gases = 13 dm^3
 Temperature of the mixture = $37 + 273 = 310 \text{ K}$
 Pressure of the mixture = 1 atm

First calculate the total number of moles present in the mixture of gases by applying the general gas equation. Since

$$PV = nRT$$

or
$$n = \frac{PV}{RT}$$

Putting values along with the units and simplifying

$$n = \frac{1 \text{ atm} \times 13 \text{ dm}^3}{0.0821 \text{ dm}^3 \text{ atm} \cdot \text{K}^{-1} \text{ mol}^{-1} \times 310 \text{ K}} = 0.51 \text{ moles}$$

So, the total number of moles of H_2 , He and $\text{CH}_4 = 0.51 \text{ moles}$

$$\begin{aligned}
 \text{Mass of H}_2 &= 0.8 \text{ g} \\
 \text{Number of moles of H}_2 &= \frac{\text{mass of H}_2}{\text{molar mass}} = \frac{0.8 \text{ g}}{2.0 \text{ g mol}^{-1}} = 0.40 \\
 \text{Mass of He} &= 0.12 \text{ g} \\
 \text{Number of moles of He} &= \frac{\text{mass of He}}{\text{molar mass}} = \frac{0.12 \text{ g}}{4 \text{ g mol}^{-1}} = 0.03 \\
 \text{Number of moles of CH}_4 &= \text{total moles} - \text{moles of H}_2 - \text{moles of He} \\
 &= 0.51 - 0.396 - 0.03 \\
 &= 0.084 \\
 \text{Mole fraction of H}_2 (X_{\text{H}_2}) &= \frac{\text{no of moles of H}_2}{\text{total number of moles}} = \frac{0.40}{0.51} = 0.784 \\
 \text{Mole fraction of He} (X_{\text{He}}) &= \frac{\text{no of moles of He}}{\text{total number of moles}} = \frac{0.03}{0.51} = 0.058 \\
 \text{Mole fraction of CH}_4 (X_{\text{CH}_4}) &= \frac{\text{no of moles of CH}_4}{\text{total number of moles}} = \frac{0.084}{0.51} = 0.164
 \end{aligned}$$

(Being a ratio mole fraction has no units.)

$$\begin{aligned}
 \text{Partial pressure of H}_2 (p_{\text{H}_2}) &= X_{\text{H}_2} P \\
 &= 0.776 \times 1.00 = 0.776 \text{ atm} \\
 &= 0.776 \times 760 = 589.76 \text{ torr} \\
 \text{Partial pressure of He} (p_{\text{He}}) &= X_{\text{He}} P \\
 &= 0.058 \times 1.00 = 0.058 \text{ atm} \\
 &= 0.058 \times 760 = 44.08 \text{ torr} \\
 \text{Partial pressure of CH}_4 (p_{\text{CH}_4}) &= X_{\text{CH}_4} P \\
 &= 0.164 \times 1.00 = 0.164 \text{ atm} \\
 &= 0.164 \times 760 = \boxed{124.64 \text{ mm of Hg}} \text{ Answer}
 \end{aligned}$$

The sum of individual pressures i.e. 589.76, 44.08 and 124.64 is almost 760 mm of Hg, i.e. total pressure of the mixture.

3.5.2 Applications of Dalton's Law of Partial Pressures

Following are the four important applications of Dalton's Law of partial pressures.

1. Some gases are collected over water in the laboratory. The gas during collection gathers water vapours and becomes moist. The pressure exerted by this moist gas is, therefore, the sum of the partial pressures of the dry gas and that of water vapours.

The partial pressure exerted by the water vapours is called aqueous tension.

$$P_{\text{moist}} = p_{\text{dry}} + p_{\text{w.vap}}$$

$$P_{\text{moist}} = p_{\text{dry}} + \text{aqueous tension}$$

$$p_{\text{dry}} = P_{\text{moist}} - \text{aqueous tension}$$

While solving the numericals the aqueous tension is subtracted from the total pressure (P_{moist}).

2. Dalton's law finds its applications during the process of respiration. The process of respiration depends upon the difference in partial pressures. When animals inhale air then oxygen moves into lungs as the partial pressure of oxygen in the air is 159 torr, while the partial pressure of oxygen in the lungs 116 torr. CO_2 produced during respiration moves out in the opposite direction, as its partial pressure is more in the lungs than that in air.

3. At higher altitudes, the pilots feel uncomfortable breathing because the partial pressure of oxygen in the un-pressurized cabin is low, as compared to 159 torr, where one feels comfortable breathing.

4. Deep sea divers take oxygen mixed with an inert gas say He and adjust the partial pressure of oxygen according to the requirement. Actually, in sea after every 100 feet depth, the diver experiences approximately 3 atm pressure, so normal air cannot be breathed in depth of sea. Moreover, the pressure of N_2 increases in depth of sea and it diffuses in the blood.

3.6 DIFFUSION AND EFFUSION

Diffusion

According to the kinetic molecular theory of gases, the molecules of the gases move haphazardly. They collide among themselves, collide with the walls of the vessel and change their directions. In other words the molecules of gases are scattered after collisions.

This spontaneous intermingling of molecules of one gas with another at a given temperature and pressure is called diffusion.

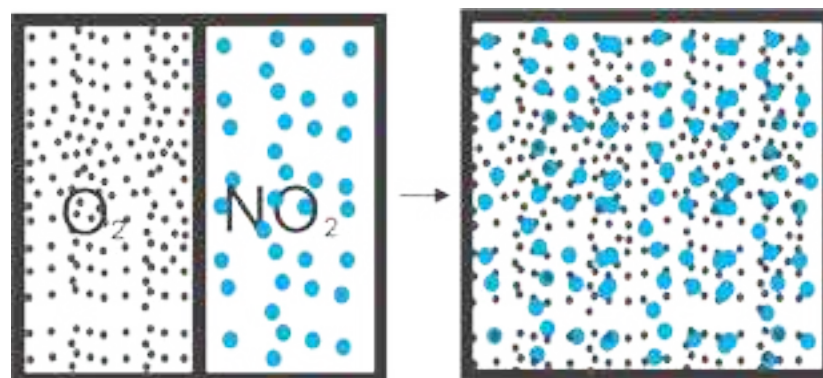


Fig (3.8) Diffusion

The spreading of fragrance of a rose or a scent is due to diffusion. When two gases diffuse into each other, they wish to make their partial pressures same every where. Suppose NO_2 , a brown coloured gas and O_2 , a colourless gas, are separated from each other by a partition Fig (3.8). When the partition is removed, both diffuse into each other due to collisions and random motion.

A stage reaches when both gases generate a homogeneous mixture and partial pressures of both are uniform throughout the mixture.

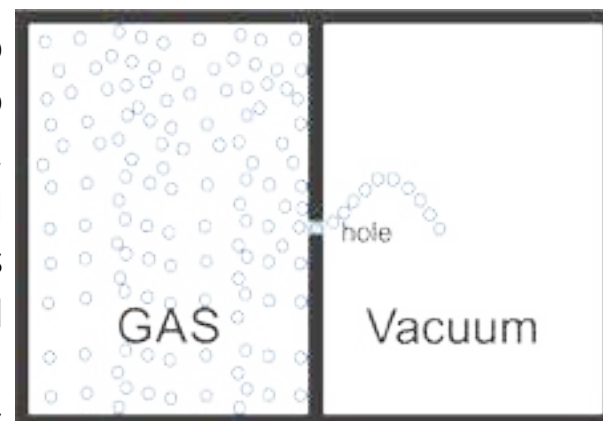


Fig (3.9) Escape of gas molecules through a hole is effusion.

Effusion

The effusion of a gas is its movement through an extremely small opening into a region of low pressure. This spreading of molecules is not due to collisions, but due to their tendency to escape one by one. Actually, the molecules of a gas are habitual in colliding with the walls of the vessel. When a molecule approaches just in front of the opening it enters the other portion of the vessel. **This type of escape of molecules is called of effusion Fig(3.9).**

3.6.1 Graham 's Law of Diffusion

Thomas Graham (1805 -1869), an English scientist, found that the rate of diffusion or effusion of a gas is inversely proportional to the square root of its density at constant temperature and pressure.

$$\text{Rate of diffusion} \propto \frac{1}{\sqrt{d}} \quad (\text{at constant temperature and pressure})$$

$$\text{Rate of diffusion} = \frac{k}{\sqrt{d}}$$

$$\text{Rate of diffusion} \times \sqrt{d} = k$$

$$\text{or Rate} \times \sqrt{d} = k$$

The constant k is same for all gases, when they are all studied at the same temperature and pressure. Let us have two gases 1 and 2, having rates of diffusion as r_1 and r_2 and densities as d_1 and d_2 respectively. According to Graham's law

$$r_1 \times \sqrt{d_1} = k$$

$$r_2 \times \sqrt{d_2} = k$$

Divide the two equations and rearrange

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} \quad \dots\dots\dots (11)$$

Since the density of a given gas is directly proportional to its molecular mass. Graham's law of diffusion can also be written as follows.

$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \quad \dots\dots\dots (12)$$

Where M_1 and M_2 are the molar masses of gases.

Demonstration of Graham's Law

This law can also be very easily verified in the laboratory by noting the rates of diffusion of two gases in a glass tube, when they are allowed to move from opposite ends Fig (3.10). Two cotton plugs soaked in HCl and NH_3 solutions are introduced in the open ends of 100 cm long tube simultaneously. HCl molecules travel a distance of 40.5 cm while NH_3 molecules cover 59.5 cm in the same duration. They produce dense white fumes of ammonium chloride at the point of junction. So

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

$$\frac{59.5}{40.5} = \frac{\sqrt{36.5}}{\sqrt{17}}$$

$$1.46 = 1.46$$

Hence the law is verified.

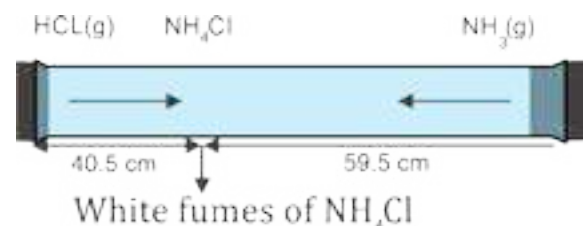


Fig (3.10) Verification of Graham's law of diffusion

Example 7

250 cm³ of the sample of hydrogen effuses four times as rapidly as 250 cm³ of an unknown gas. Calculate the molar mass of unknown gas.

Solution

Let the unknown gas is given the symbol X

$$\text{Rate of effusion of unknown gas } (r_x) = 1$$

$$\text{Rate of effusion of hydrogen gas } (r_{H_2}) = 4$$

$$\text{Molar mass of } H_2 \text{ gas } (M_{H_2}) = 2 \text{ g mol}^{-1}$$

$$\text{Molar mass of unknown gas } (M_x) = ?$$

$$\frac{r_{H_2}}{r_x} = \sqrt{\frac{M_x}{M_{H_2}}}$$

$$\frac{4}{1} = \sqrt{\frac{M_x}{2}}$$

$$\frac{M_x}{2} = \frac{16}{1}$$

$$M_x = 16 \times 2 = \boxed{32 \text{ g mol}^{-1}} \text{ Answer}$$

3.7 KINETIC MOLECULAR THEORY OF GASES

The behaviour of gases has already been discussed in gas laws. These laws were based on experimental observations quite independent of nature of a gas. In order to illustrate the behaviour of gases quantitatively, Bernoulli (1738) put forward kinetic molecular theory of gases. This theory lead Clausius (1857) to derive the kinetic equation and deduced all the gas laws from it. The theory was later on elaborated and extended by Maxwell, who gave the law of distribution of velocities. According to this law, molecules are in the form of groups having definite velocity ranges. Boltzmann also Contributed and studied the distribution of energies among the gas molecules. Among some other names Van der Waal is the prominent scientist in this field.

Following are the fundamental postulates of this kinetic theory of gases.

1. Every gas consists of a large number of very small particles called molecules. Gases like He, Ne, Ar have monoatomic molecules.
2. The molecules of a gas move haphazardly, colliding among themselves and with the walls of the container and change their directions.
3. The pressure exerted by a gas is due to the collisions of its molecules with the walls of a container. The collisions among the molecules are perfectly elastic.
4. The molecules of a gas are widely separated from one another and there are sufficient empty spaces among them.
5. The molecules of a gas have no forces of attraction for each other.
6. The actual volume of molecules of a gas is negligible as compared to the volume of the gas.
7. The motion imparted to the molecules by gravity is negligible as compared to the effect of the continued collisions between them.
8. The average kinetic energy of the gas molecules varies directly as the absolute temperature of the gas.

Keeping in view the basic assumptions given above, R.J. Clausius deduced an expression for the pressure of an ideal gas. Actually, pressure on the walls of the vessel is due to collisions. Whenever the molecules move they collide among themselves and with the walls of the container. Due to these collisions, a force is exerted on the walls of the container. This force when divided by the area of the vessel gives force per unit area, which is called pressure. In this way, the final form of kinetic equation is as follows.

$$PV = \frac{1}{3} mN\bar{c}^2 \quad \dots\dots\dots (13)$$

Where,

P = pressure

V = volume

m = mass of one molecule of the gas

N = number of molecules of gas in the vessel

\bar{c}^2 = mean square velocity

The idea of the mean square velocity is important. All the molecules of a gas under the given conditions don't have the same velocities. Rather different velocities are distributed among the molecules. To understand it study Maxwell's law of distribution of velocities. If there are n_1 molecules with velocity c_1 , n_2 molecules with velocity c_2 , and so on then,

$$\overline{c^2} = \frac{c_1^2 + c_2^2 + c_3^2 + \dots}{n_1 + n_2 + n_3 + \dots} \quad \dots \quad (14)$$

In this reference $n_1 + n_2 + n_3 + \dots = N$

$\overline{c^2}$ is the average of the squares of all the possible velocities. When we take the square root of this $\overline{c^2}$, then it is called root mean square velocity (C_{rms}). So, $(C_{rms}) = \sqrt{\overline{c^2}}$

The expression for the root mean square velocity deduced from the kinetic equation is written as follows.

$$C_{rms} = \sqrt{\frac{3RT}{M}} \quad \dots \quad (15)$$

Where, C_{rms} = root mean square velocity

M = molar mass of the gas

T = temperature

This equation (15) is a quantitative relationship between the absolute temperature and the velocities of the gas molecules. According to this equation, higher the temperature of a gas, greater the velocities. Kinetic equation can be used to explain gas laws.

3.7.1 Explanation of Gas Laws from Kinetic Theory of Gases

Kinetic theory of gases gives birth to kinetic equation of gases, which can be employed to justify the gas laws. In other words, it proves that gas laws get their explanation from kinetic theory of gases

(a) Boyle's Law

According to one of the postulates of kinetic theory of gases, the kinetic energy is directly proportional to the absolute temperature of the gas. The kinetic energy of N molecules is $\frac{1}{2} mN\overline{c^2}$

SO

$$\frac{1}{2} mN\overline{c^2} \propto T$$

$$\frac{1}{2} mN\overline{c^2} = kT \quad \dots \quad (16)$$

Where k is the proportionality constant. According to the kinetic equation of gases

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

Multiplying and dividing by 2 on right hand side

$$PV = \frac{2}{3} \left(\frac{1}{2} mN\overline{c^2} \right) \dots\dots\dots (17)$$

Putting equation (16) into equation (17).

$$PV = \frac{2}{3} kT \dots\dots\dots (18)$$

If the temperature (T) is constant then right hand side of equation (18) $\frac{2}{3} kT$ is constant. Let that constant be k' .

So, $PV = k'$ (which is Boyle's law)

Hence at constant temperature and number of moles, the product PV is a constant quantity.

(b) Charles's law

Consider the equation (18) which has just been derived

Or

$$PV = \frac{2}{3} kT$$

$$V = \frac{2}{3} \frac{kT}{P} = \left(\frac{2k}{3P} \right) T$$

At constant pressure,

Therefore,

$$\frac{2k}{3P} = k'' \text{ (a new constant)}$$

or

$$V = k'' T$$

$$\frac{V}{T} = k'' \text{ (which is Charles's law)}$$

(c) Avogadro's Law

Consider two gases 1 and 2 at the same pressure P and having the same volume V . Their number of molecules are N_1 and N_2 , masses of molecules are m_1 and m_2 and mean square velocities are $\overline{c_1^2}$ and $\overline{c_2^2}$ respectively.

Their kinetic equations can be written as follows:

$$PV = \frac{1}{3} m_1 N_1 \overline{c_1^2} \quad \text{for gas(1)}$$

$$PV = \frac{1}{3} m_2 N_2 \overline{c_2^2} \quad \text{for gas(2)}$$

$$\text{Equalizing } \frac{1}{3} m_1 N_1 \overline{c_1^2} = \frac{1}{3} m_2 N_2 \overline{c_2^2}$$

$$\text{Hence, } m_1 N_1 \overline{c_1^2} = m_2 N_2 \overline{c_2^2} \quad \dots\dots\dots (19)$$

When the temperature of both gases is the same, their mean kinetic energies per molecule will also be same, so

$$\frac{1}{2} m_1 \overline{c_1^2} = \frac{1}{2} m_2 \overline{c_2^2}$$

$$m_1 \overline{c_1^2} = m_2 \overline{c_2^2} \quad \dots\dots\dots (20)$$

Divide equation (19) by (20)

$$N_1 = N_2$$

Hence equal volumes of all the gases at the same temperature and pressure contain equal number of molecules, which is Avogadro's law.

(d) Graham's Law of Diffusion

$$PV = \frac{1}{3} m N \overline{c^2} \quad \dots\dots\dots (13)$$

Applying the kinetic equation

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

If we take one mole of a gas having Avogadro's number of molecules ($N = N_A$) then the equation (13) can be written as:

$$PV = \frac{1}{3} M \overline{c^2} \quad (M = m N_A) \quad \dots\dots\dots (21)$$

or

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

where M is the molecular mass of the gas

Taking square root

$$\sqrt{c^2} = \sqrt{\frac{3PV}{M}}$$

$$\sqrt{c^2} = \sqrt{\frac{3P}{M/V}} = \sqrt{\frac{3P}{d}} \quad \left(\frac{M}{V} = d\right)$$

' V ' is the molar volume of gas at given conditions. Since the root mean square velocity of the gas is proportional to the rate of diffusion of the gas.

so

$$\sqrt{c^2} \propto r$$

$$r \propto \sqrt{\frac{3P}{d}}$$

At constant pressure

$$r \propto \sqrt{\frac{1}{d}}$$

which is Graham's law of diffusion

3.8 KINETIC INTERPRETATION OF TEMPERATURE

According to kinetic molecular theory of gases the molecules of a gas move randomly. They collide among themselves, with the walls of the vessels and change their directions. The collisions are elastic and the pressure of the gas is the result of these collisions with the walls of the container.

Let us rewrite the kinetic equation of gases (13) as already mentioned

$$PV = \frac{1}{3} mN\overline{c^2} \quad \dots\dots\dots (13)$$

Here m is the mass of one molecule of the gas, N is the number of molecules in the vessel and $\overline{c^2}$ is their mean square velocity. The average kinetic energy associated with one molecule of a gas due to its translational motion is given by the following equation.

$$E_k = \frac{1}{2} m \overline{c^2} \quad \dots\dots\dots (22)$$

Remember that E_k is the average translational kinetic energy of gas molecules. Equation (13) can be rewritten as:

$$PV = \frac{2}{3} N \left(\frac{1}{2} m \overline{c^2} \right) \quad \dots\dots\dots (23)$$

Putting equation (22) into (23)

So
$$PV = \frac{2}{3} N E_k \quad \dots\dots\dots (24)$$

Equation (24) gives an important insight into the meaning of temperature. To understand it, consider one mole of a gas.

So
$$N = N_A$$

$$PV = \frac{2}{3} N_A E_k \quad \dots\dots\dots (25)$$

According to the general gas equation for 1 mole of a gas

$$PV = RT \quad \dots\dots\dots (4)$$

Comparing equation (4) and (25)

$$\frac{2}{3} N_A E_k = RT \quad \dots\dots\dots (26)$$

$$E_k = \frac{3R}{2N_A} T \quad \dots\dots\dots (27)$$

The equation (27) gives a new definition of temperature according to which the kelvin temperature of a gas is directly proportional to the average translational kinetic energy of its molecules. This suggests that a change in temperature means change in the intensity of molecular motion. When heat flows from one body to another, the molecules in the hotter body give up some of their kinetic energy through collisions to molecules in the colder body. This process of flow of heat continues until the average translational kinetic energies of all the molecules become equal. This equalises the temperature of both bodies.

In gases and liquids, temperature is the measure of average translational kinetic energies of molecules. In solids, where molecules cannot move freely temperature becomes a measure of vibrational kinetic energy.

Keeping in view this kinetic interpretation of temperature, we have a way of looking at absolute zero of temperature. It is that temperature at which the molecular motions cease. The absolute zero is unattainable. Anyhow, current attempts have resulted in temperature as low as 10^{-5} K.

3.9 LIQUEFACTION OF GASES

3.9.1 General Principle of Liquefaction

The conversion of a gas into a liquid requires high pressure and low temperature. High pressure brings the molecules of a gas close to each other. Low temperature deprives the molecules from kinetic energy and attractive forces start dominating.

For every gas there exists a temperature above which the gas cannot be liquefied, no matter how much pressure is applied. **The highest temperature at which a substance can exist as a liquid, is called its critical temperature (T_c).** There is a corresponding pressure which is required to bring about liquefaction at this critical temperature (T_c). This is called critical pressure (P_c).

The critical temperature and the critical pressure of the substances are very important for the workers dealing with the gases. These properties provide us the information about the condition under which gases liquefy. For example, O_2 has a critical temperature 154.4 K (-118.75 °C). It must be cooled below this temperature before it can be liquefied by applying high pressure. Ammonia is a polar gas. Its critical temperature is 405.6 K (132.44 °C), so it can be liquefied by applying sufficient pressure close to room temperature.

Table (3.2) shows the critical parameters of some common substances. Non-polar gases of low polarizability like Ar have a very low critical temperature. The substances like H₂O vapours and NH₃ gas are among the polar gases and they have better tendencies to be liquefied. CO₂ can not be liquefied above 31.1 °C, no matter how much the pressure is applied. Anyhow, if temperature of CO₂ is maintained below 31.1 °C, then lower pressure than critical pressure is required to liquefy it. The value of the critical temperature of a gas depends upon its size, shape and intermolecular forces present in it.

When a gas is measured at its critical temperature and critical pressure, then at that stage volume of 1 mole of gas is called critical volume which is represented by V_c. The critical volume of O₂ is 74.42 cm³ mol⁻¹, of CO₂, is 95.65 cm³ mol⁻¹ and that of H₂ is 64.51 cm³ mol⁻¹.

Table (3.2) Critical Temperatures and Critical Pressures of Some Substances

Substance	Critical Temperature T _c (K)	Critical Pressure P _c (atm)
Water vapours, H ₂ O	647.6 (374.44 °C)	217.0
Ammonia, NH ₃	405.6 (132.44 °C)	111.5
Freon-12, CCl ₂ F ₂	384.7 (111.54 °C)	39.6
Carbon dioxide, CO ₂	304.3 (31.142 °C)	73.0
Oxygen, O ₂	154.4 (-118.75 °C)	49.7
Argon, Ar	150.9 (-122.26 °C)	48
Nitrogen, N ₂	126.1 (-147.06 °C)	33.5

3.9.2 Methods of Liquefaction of Gases

There are various methods to liquefy a gas. One of them is Linde's method. It is based on Joule-Thomson effect.

Joule Thomson Effect

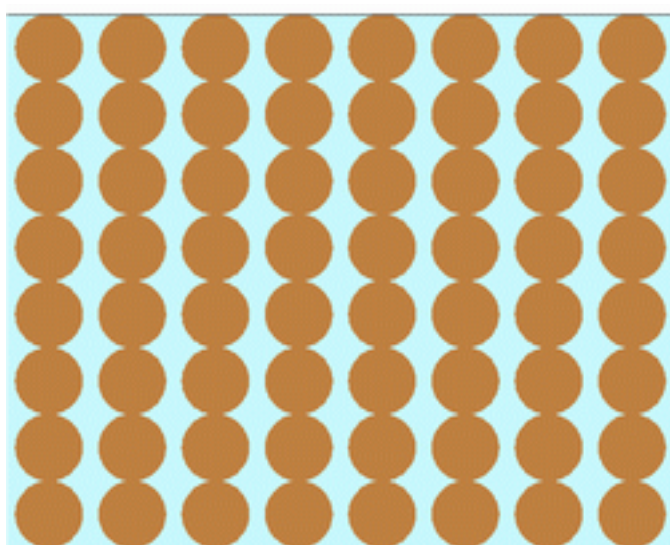
Low temperature can be achieved by Joule-Thomson effect, according to which when a compressed gas is allowed to expand into a region of low pressure it gets cooled.

The molecules of the compressed gas are very close to each other and appreciable attractive forces are present among them. When a gas is allowed to undergo sudden expansion through the nozzle of a jet, then the molecules move apart. In this way energy is needed to overcome the intermolecular attractions. This energy is taken from the gas itself, which is cooled.

Linde's Method of Liquefaction of Gases

Linde has employed Joule-Thomson effect as the basis for liquefaction. The apparatus designed for this purpose is shown in the Fig (3.11).

For the liquefaction of air, it is compressed to about 200 atmospheres, and then passed through a water cooled pipe where the heat of compression is removed. It is then allowed to pass through a spiral pipe having a jet at the end. When the air comes out of the jet the expansion takes place from 200 atm. to 1 atm. In this way, considerable fall of temperature occurs.



Animation 3.5: Liquefaction
Source & Credit: wikipedia

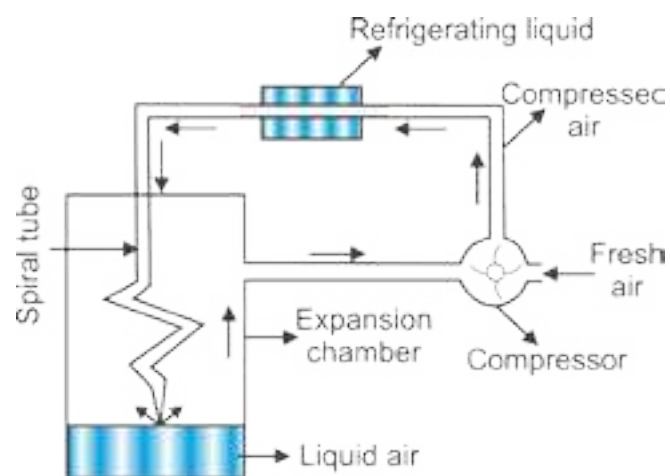


Fig (3.11) Linde's method for the liquefaction of air

This cooled air goes up and cools the incoming compressed air. It returns to the compression pump. This process is repeated again and again. The liquid air is collected at the bottom of the expansion chamber. All gases except H_2 , and He can be liquefied by the above procedure.

3.10 NON-IDEAL BEHAVIOUR OF GASES

Whenever, we discuss gas laws it is proposed that ideal gases obey them. Particularly an ideal gas obeys Boyle's law, Charles's law and the general gas equation under all conditions of temperature and pressure. Let us try to understand the behaviour of a few real gases like H_2 , He, N_2 and CO_2 at $^{\circ}C$. keeping in view the variation of the pressure on the gas and consequently the change in its volume.

For this purpose, first of all plot a graph between pressure on x-axis and the $\frac{PV}{nRT}$ on Y-axis for an ideal gas.

The factor $\frac{PV}{nRT}$ is called the compressibility factor. Its value is unity under all conditions for an ideal gas. Since the increase of pressure decreases the volume in such a way that $\frac{PV}{nRT}$ remains constant at a constant temperature, so a straight line is obtained parallel to the pressure axis. This is shown in the Figs (3.12 a, b). All the real gases have been found to show marked deviations from this behaviour. It is observed that the graph for helium gas goes along with the expected horizontal dotted line to some extent but goes above this line at very high pressures.

It means that at very high pressure the decrease in volume is not according to general gas equation and the value of $\frac{PV}{nRT}$ has increased from the expected values. With this type of behaviour, we would say that the gas is non-ideal.

In the case of H_2 the deviation starts even at low pressure in comparison to He. N_2 shows a decrease in $\frac{PV}{nRT}$ value at the beginning and shows marked deviation even at low pressure than H_2 . CO_2 has a very strange behaviour as it is evident from the graph.

The extent of deviation of these four gases shows that these gases have their own limitations for obeying general gas equation. It depends upon the nature of the gas that at which value of pressure, it will start disobeying.

When we study the behaviour of all these four gases at elevated temperature i.e., $100^\circ C$ then the graphs come closer to the expected straight line and the deviations are shifted towards higher pressure. This means that the increase in temperature makes the gases ideal Fig (3.12 b).

This discussion on the basis of experimental observations, convinces us that

- (i) Gases are ideal at low pressure and non-ideal at high pressure
- (ii) Gases are ideal at high temperature and non-ideal at low temperature.

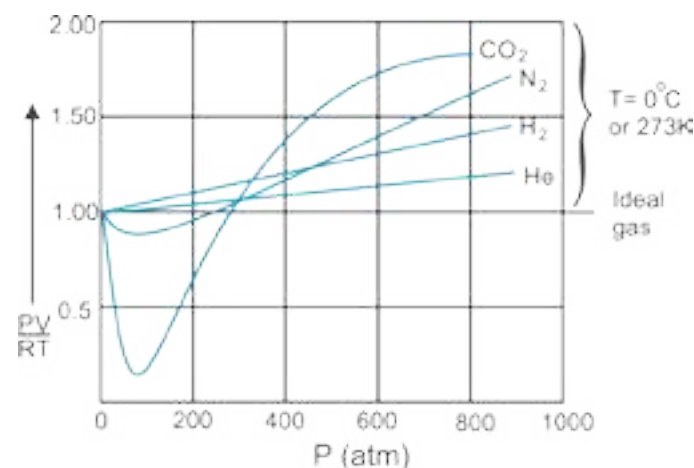


Fig (3.12 a) Non-ideal behaviour of gases at $0^\circ C$

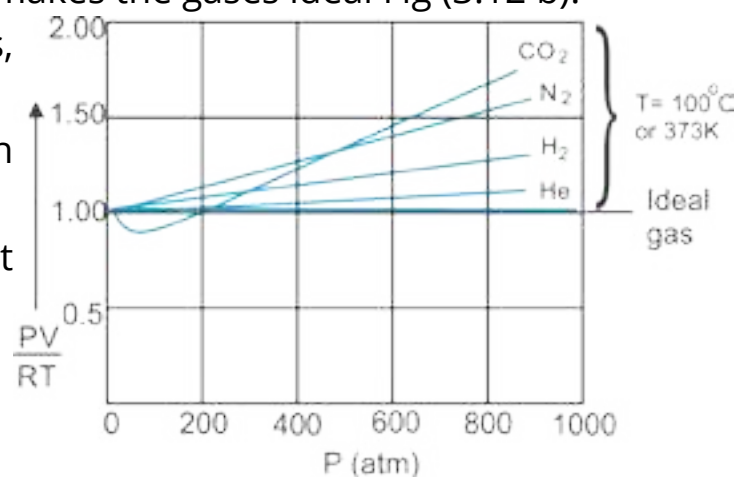


Fig (3.12 b) Non-ideal behaviour of gases at $100^\circ C$.

3.10.1 Causes for Deviations from Ideality

It was van der Waals (1873) who attributed the deviation of real gases from ideal behaviour to two of the eight postulates of kinetic molecular theory of gases.

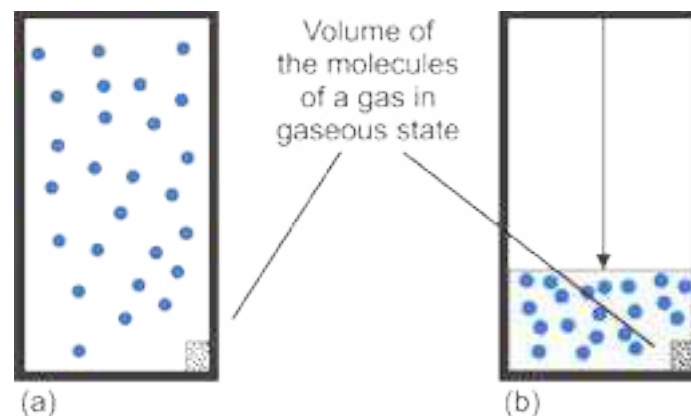
These postulates are as under.

(i) There are no forces of attraction among the molecules of a gas.

(ii) The actual volume of gas molecules is negligible as compared to the volume of the vessel.

When the pressure on a gas is high and the temperature is low then the attractive forces among the molecules become significant, so the ideal gas equation $PV = nRT$

does not hold. Actually, under these conditions, the gas does not remain ideal. The actual volume of the molecules of a gas is usually very small as compared to the volume of the vessel and hence it can be neglected. This volume, however, does not remain negligible when the gas is subjected to high pressure. This can be understood from the following Figs (3.13 a, b).



Fig(3.13.a) A gas at low pressure when actual volume is negligible.

Kig(3.13.b) A gas at high pressure when actual volume is not negligible.

3.10.2 van der Waals Equation for Real Gases

Keeping in view the above discussion, van der Waals pointed out that both pressure and volume factors in ideal gas equation needed correction in order to make it applicable to the real gases.

Volume Correction

When a gas is compressed, the molecules are pushed so close together that the repulsive forces operate between them. When pressure is increased further it is opposed by the molecules themselves. Actually the molecules have definite volume, no doubt very small as compared to the vessel, but it is not negligible. So van der Waals postulated that the actual volume of molecules can no longer be neglected in a highly compressed gas. If the effective volume of the molecules per mole of a gas is represented by b , then the volume available to gas molecules is the volume of the vessel minus the volume of gas molecules.

$$V_{free} = V_{vessel} - b \quad \dots\dots\dots (28)$$

V_{free} is that volume which is available to gas molecules. The factor b is termed as the excluded volume which is constant and characteristic of a gas. Its value depends upon the size of gas molecules. Table (3.3) shows the b values for some important gases. It is interesting to know that the excluded volume b is not equal to the actual volume of gas molecules. In fact, it is four times the actual volume of molecules.

$$b = 4V_m$$

Where V_m is the actual volume of one mole of gas molecules, ' b ' is effective volume or excluded volume of one mole of gas. It is that volume of gas which is occupied by 1 mole of gas molecules in highly compressed state, but not in the liquid state.

Pressure Correction

A molecule in the interior of a gas is attracted by other molecules on all sides, so these attractive forces are cancelled out. However, when a molecule strikes the wall of a container, it experiences a force of attraction towards the other molecules in the gas. This decreases the force of its impact on the wall. Consider the molecule "A" which is unable to create pressure on the wall due to the presence of attractive forces due to 'B' type molecules Fig (3.14). Let the observed pressure on the wall of the container is P . This pressure is less than the actual pressure P_i , by an amount P' , so

$$P = P_i - P'$$

P_i is the true kinetic pressure, if the forces of attractions would have been absent. P' is the amount of pressure lessened due to attractive forces. Ideal pressure P_i is

$$P_i = P + P'$$

It is suggested that a part of the pressure P for one mole of a gas used up against intermolecular attractions should decrease as volume increases. Consequently, the value of P' in terms of a constant ' a ' which accounts for the attractive forces and the volume V of vessel can be written as

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

How to prove it

P' is determined by the forces of attraction between molecules of type A, which are striking the wall of the container and molecules of type B, which are pulling them inward. The net force of attraction is proportional to the concentrations of A type and B type molecules.

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

Let n is the number of moles of A and B separately and total volume of both types of molecules is 'V'. The n/V is moles dm^{-3} of A and B, separately.

$$P' \propto \frac{n}{V} \cdot \frac{n}{V}$$

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

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

('a' is a constant of proportionality)

If, $n = 1$ (one mole of gas)

then $P' = \frac{a}{V^2}$ (29)

Greater the attractive forces among the gas molecules, smaller the volume of vessel, greater the value of lessened pressure P' .

This 'a' is called co-efficient of attraction or attraction per unit volume. It has a constant value for a particular real gas. Thus effective kinetic pressure of a gas is given by P_i , which is the pressure if the gas would have been ideal.

$$P_i = P + \frac{a}{V^2} \text{ (30)}$$

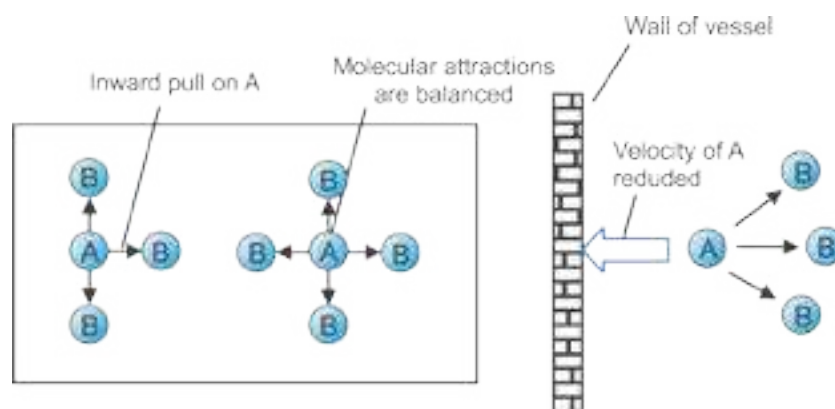


Fig (3.14) Forces of attraction and pressure correction

Once the corrections for pressure and volume are made, the kinetic equation for one mole of a gas can be constructed by taking pressure as $(P + \frac{a}{V^2})$ and volume as $(V - b)$ for one mole of a gas.

$$(P + \frac{a}{V^2})(V - b) = RT \quad \dots\dots\dots (31)$$

For 'n' moles of a gas $(P + \frac{n^2 a}{V^2})(V - nb) = nRT \quad \dots\dots\dots (32)$

This is called van der Waal's equation, 'a' and 'b' are called van der Waal's constants.

Units of 'a'.

Since,

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

So

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

$$a = \frac{\text{atm} \times (\text{dm}^3)^2}{(\text{mol})^2}$$

$$a = \text{atm dm}^6 \text{ mol}^{-2}$$

In S.I. units, pressure is in Nm^{-2} and volume in m^3

or $a = \frac{\text{Nm}^{-2} \times (\text{m}^3)^2}{(\text{mol})^2}$

or $a = \text{Nm}^4 \text{ mol}^{-2}$

Units of 'b': b' is excluded or incompressible volume /mol⁻¹ of gas. Hence its units should be dm³ mol⁻¹ or m³ mol⁻¹

The values of 'a' and 'b' can be determined by knowing the values of P, V and T of a gaseous system under two different conditions. Following Table (3.3) gives the values of 'a' and 'b' for some common gases.

Table(3.3) van der Waals Constant for Some Common Gases

Gas	'a' (atm dm ⁶ mol ⁻²)	'b' (dm ³ mol ⁻¹)
Hydrogen	0.245	0.0266
Oxygen	1.360	0.0318
Nitrogen	1.390	0.0391
Carbon dioxide	3.590	0.0428
Ammonia	4.170	0.0371
Sulphur dioxide	6.170	0.0564
Chlorine	6.493	0.0562

The presence of intermolecular forces in gases like Cl₂ and SO₂ increases their 'a' factor. The least value of 'a' for H₂ is due to its small size and non-polar character. The 'b' value of H₂ is 0.0266 dm³ mol⁻¹. It means that if 2.016g (1mole) of H₂ is taken, then it will occupy 0.0266 dm³ or 266cm³ of volume at closest approach in the gaseous state.

Example 8

One mole of methane gas is maintained at 300 K. Its volume is 250 cm³. Calculate the pressure exerted by the gas under the following conditions.

- (i) when the gas is ideal
- (ii) when the gas is non-ideal

$$a = 2.253 \text{ atm dm}^6 \text{ mol}^{-2}, \quad b = 0.0428 \text{ dm}^3 \text{ mol}^{-1}$$

Solution

(i) When the gas is ideal, general gas equation is applied i.e.,

$$PV = nRT$$

$$V = 250 \text{ cm}^3 = 0.25 \text{ dm}^3 \quad 1 \text{ dm}^3 = 1000 \text{ cm}^3$$

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

$$T = 300 \text{ K}$$

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

$$P = \frac{nRT}{V}$$

Putting the values alongwith units

$$P = \frac{1 \text{ mol} \times 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{0.25 \text{ dm}^3}$$

$$P = \boxed{98.5 \text{ atm}} \text{ (Answer)}$$

If CH_4 gas would have been ideal, under the given conditions, 98.5 atm. pressure would have been exerted.

(ii) When the gas is behaving as non-ideal, we should use the van der Waals equation

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = n R T$$

By rearranging the equation and taking the pressure on L.H.S.

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

or

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

Substituting the following values (ignore the units for sake of simplicity)

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

$V = 0.25 \text{ dm}^3$, $T = 300 \text{ K}$, $a = 2.253 \text{ dm}^6 \text{ atm mol}^{-2}$, $b = 0.0428 \text{ dm}^3 \text{ mol}^{-1}$

$$\frac{1 \times 0.0821 \times 300}{0.25 - 1(0.0428)} - \frac{1 \times 2.253}{(0.25)^2} = \frac{24.63}{0.207} - \frac{2.253}{0.0625}$$

$$P = 118.985 - 36.048 = 82.85 \text{ atm.}$$

In the non-ideal situation the pressure has lessened upto

$$98.5 - 82.85 = \boxed{15.65 \text{ atm.}} \text{ Answer}$$

Conclusion:

The difference of these two pressures shows that this gas is non-ideal. Actually CH_4 is thought to be ideal near 1 atm, but around 100 atmospheres, it develops non-ideal attitude. This difference of ideal and non-ideal pressure goes on decreasing when gas is considered at low pressures.

3.11 PLASMA STATE

What is plasma?

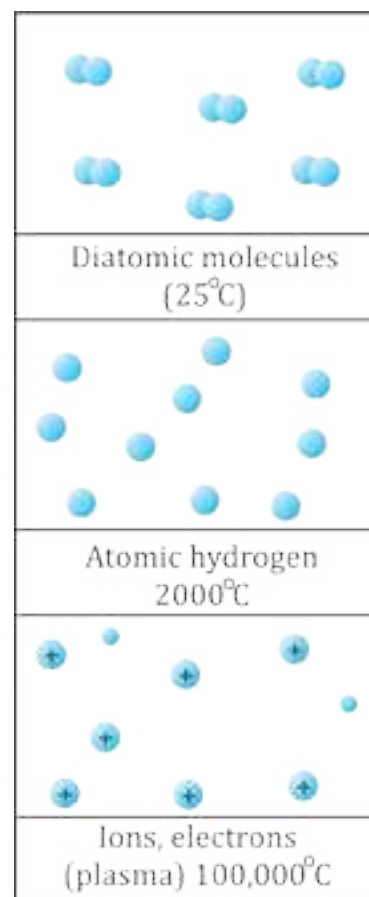
Plasma is often called the “fourth state of matter”, the other three being solid, liquid and gas. Plasma was identified by the English scientist William Crookes in 1879. In addition to being important in many aspects of our daily life, plasmas are estimated to constitute more than 99 percent of the visible universe. Although, naturally occurring plasma is rare on earth, there are many man-made examples.

Inventors have used plasma to conduct electricity in neon signs and fluorescent bulbs. Scientists have constructed special chambers to experiment with plasma in laboratories. It occurs only in lightning discharges and in artificial devices like fluorescent lights, neon signs, etc. It is everywhere in our space environment.

How is Plasma formed ?

When more heat is supplied, the atoms or molecules may be ionized. An electron may gain enough energy to escape its atom. This atom loses one electron and develops a net positive charge. It becomes an ion. In a sufficiently heated gas, ionization happens many times, creating clouds of free electrons and ions. However, all the atoms are not necessarily ionized, and some of them may remain completely intact with no net charge. This ionized gas mixture, consisting of ions, electrons and neutral atoms is called plasma.

It means that a plasma is a distinct state of matter containing a significant number of electrically charged particles a number sufficient to affect its electrical properties and behaviour.



Natural and Artificial Plasma

Artificial plasma can be created by ionization of a gas, as in neon signs. Plasma at low temperatures is hard to maintain because outside a vacuum low temperature plasma reacts rapidly with any molecule it encounters. This aspect makes this material, both very useful and hard to use. Natural plasma exists only at very high temperatures, or low temperature vacuums.

Natural plasma on the other hand do not breakdown or react rapidly, but is extremely hot (over 20,000°C minimum). Their energy is so high that they vaporize any material they touch.

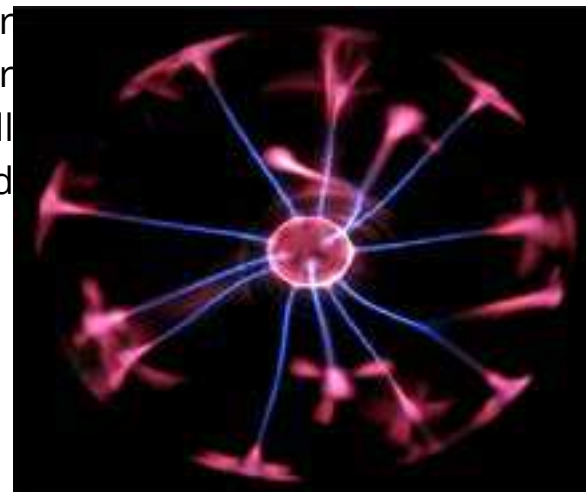
Characteristic of Plasma:

1. A plasma must have sufficient number of charged particles so as a whole, it exhibits a collective response to electric and magnetic fields. The motion of the particles in the plasma generate fields and electric currents from within plasma density. It refers to the density of the charged particles. This complex set of interactions makes plasma a unique, fascinating, and complex state of matter.
2. Although plasma includes electrons and ions and conducts electricity, it is macroscopically neutral. In measurable quantities the number of electrons and ions are equal.

Where is Plasma found ?

Entire universe is almost of plasma. It existed before any other forms of matter came into being. Plasmas are found in everything from the sun to quarks, the smallest particles in the universe.

As stated earlier plasma is the most abundant form of matter in the universe. It is the stuff of stars. A majority of the matter in inner-stellar space is plasma. All the stars that shine are all plasma. The sun is a 1.5 million kilometer ball of plasma, heated by nuclear fusion.



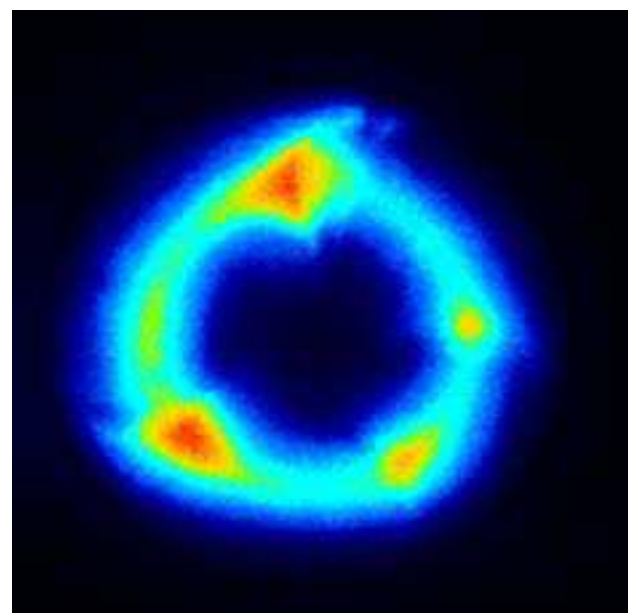
Animation 3.6: Plasma ball
source & Credit: giphy

One arth it only occurs in a few limited places, like lightning bolts, flames, auroras, and fluorescent lights. When an electric current is passed through neon gas, it produces both plasma and light.

Applications of Plasma:

Plasma has numerous important technological applications. It is present in many devices. It helps us to understand much of the universe around us. Because plasmas' are conductive respond to electric and magnetic fields and can be efficient sources of radiation, so they can be used in innumerable applications where such control is needed or when special sources of energy or radiation are required.

1. A fluorescent light bulb is not like regular light bulbs. Inside the long tube is a gas. When the light is turned on, electricity flows through the tube. This electricity acts as that special energy and charges up the gas. This charging and exciting of the atoms creates a glowing plasma inside the bulb.
2. Neon signs are glass tubes filled with gas. When they are turned on then the electricity flows through the tube. The electricity charges the gas, possibly neon, and creates a plasma inside the tube. The plasma glows with a special colour depending on what kind of gas is inside.
3. They find applications such as plasma processing of semiconductors, sterilization of some medical prodjucts, lamps, lasers, diamond coated films, high power microwave sources and pulsed power switches.
4. They also provide the foundation for important potential applications such as the generation of electrical energy from fusion pollution control and removal of hazardous chemicals.
5. Plasma light up our offices and homes, make our computers and electronic equipment work.
6. They drive lasers and particle accelerators, help to clean up the environment, pasteurize foods and make tools corrosion-resistant.



Animation 3.7.:Application of Plasma
Source & Credit: pag

Future Horizons:

Scientists are working on putting plasma to effective use. Plasma would have to be low energy and should be able to survive without instantly reacting and degenerating. The application of magnetic fields involves the use of plasma. The magnetic fields create low energy plasma which create molecules that are in what scientist call a metastable state. The magnetic fields used to create the low temperature plasma give the plasma molecules, which do not react until they collide with another molecule with just the right energy. This enables these metastable molecules to survive long enough to react with a designated molecule. These metastable particles are selective in their reactivity. It makes them a potentially unique solution to problems like radioactive contamination. Scientist are currently experimenting with mixtures of gases to work as metastable agents on plutonium and uranium, and this is just the beginning.

KEY POINTS

1. The behaviour of a gas is described through four variables i.e., pressure, volume, temperature and its number of moles. The relationships between gas variables are known as the simple gas laws. Boyle's law relates pressure of a gas with its volume, while Charles's law relates gas volume with temperature. Avogadro's law is concerned with volume and amount of a gas. The important concept of absolute zero of temperature originates from the simple gas laws.
2. By combining the above mentioned three laws, a more general equation about the behaviour of gas is obtained i.e., $PV = nRT$. This equation can be solved for any one of the variables when values for others are known. This equation can be modified for the determination of molar masses and the density of the gas.
3. Dalton's law of partial pressures can be used to calculate the partial pressures of gases.
4. The processes of diffusion and effusion are best understood by Graham's law of diffusion.
5. Kinetic molecular theory of gases provides a theoretical basis for various gas laws. With the help of this theory a relationship is established between average molecular kinetic energy and kelvin temperature. The diffusion and effusion of the gases can be related to their molar masses through the kinetic molecular theory of gases.
6. The real gases show ideal behaviour under specific conditions. They become non-ideal at high pressure and low temperature. The non-ideal behaviour results chiefly from intermolecular attractions and the finite volume occupied by the gas molecules.
7. Gases can be liquified by applying sufficient pressure but temperature should either be critical or below it.
8. To calculate the pressure or volume of a real gas under the non-ideal conditions, alternative kinetic equation has been developed. This is known as the van der Waal's equation.
9. The plasma, a fourth state of matter, consists of neutral particles, positive ions and negative electrons, 99% of the known universe is in the plasma state.

Excercise

Q 1: Select the correct answer out of the following alternative suggestions.

- (i) Pressure remaining constant, at which temperature the volume of a gas will become twice of what it is at 0°C.
- a. 546°C b. 200°C c. 546K d. 273K
- (ii) Number of molecules in one dm³ of water is close to
- a. $\frac{6.02}{22.4} \times 10^{23}$ b. $\frac{12.04}{22.4} \times 10^{23}$ c. $\frac{18}{22.4} \times 10^{23}$ d. $55.6 \times 6.02 \times 10^{23}$
- (iii) Which of the following will have the same number of molecules at STP?
- a. 280 cm³ of CO₂ and 280 cm³ of N₂O
b. 11.2 dm³ of O₂ and 32 g of O₂
c. 44 g of CO₂ and 11.2 dm³ of CO
d. 28 g of N₂ and 5.6 dm³ of oxygen
- (iv) If absolute temperature of a gas is doubled and the pressure is reduced to one half, the volume of the gas will
- a. remain unchanged b. increase four times
c. reduce to 1/4 d. be doubled
- (v) How should the conditions be changed to prevent the volume of a given gas from expanding when its mass is increased?
- a. Temperature is lowered and pressure is increased.
b. Temperature is increased and pressure is lowered.
c. Temperature and pressure both are lowered.
d. Temperature and pressure both are increased.
- (vi) The molar volume of CO₂ is maximum at
- a. S TP b. 127°C and 1 atm c. 0°C and 2 atm d. 273°C and 2 atm
- (vii) The order of the rate of diffusion of gases NH₃, SO₂, Cl₂, an CO₂ is:
- a. NH₃ > SO₂ > Cl₂ > CO₂ b. NH₃ > CO₂ > SO₂ > Cl₂
c. Cl₂ > SO₂ > CO₂ > NH₃ d. NH₃ > CO₂ > Cl₂ > SO₂
- (viii) Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of total pressure exerted by oxygen is
- a. 1/3 b. 8/9 c. 1/9 d. 16/17

- (ix) Gases deviate from ideal behaviour at high pressure. Which of the following is correct for non-ideality?
- At high pressure, the gas molecules move in one direction only.
 - At high pressure, the collisions between the gas molecules are increased manifold.
 - At high pressure, the volume of the gas becomes insignificant.
 - At high pressure, the intermolecular attractions become significant.
- (x) The deviation of a gas from ideal behaviour is maximum at
- 10°C and 5.0 atm
 - 10 °C and 2.0 atm
 - 100 °C and 2.0 atm
 - 0 °C and 2.0 atm
- (xi) A real gas obeying van der Waals equation will resemble ideal gas if
- both 'a' and 'b' are large
 - both 'a' and 'b' are small
 - 'a' is small and 'b' is large
 - 'a' is large and 'b' is small

Q2: Fill in the blanks

- The product PV has the S.I. unit of _____
- Eight grams each of O₂ and H₂, at 27 °C will have total K.E in the ratio of _____
- Smell of the cooking gas during leakage from a gas cylinder is due to the property of _____ of _____ gases.
- Equal _____ of ideal gases at the same temperature and pressure contain _____ number of molecules.
- The temperature above which a substance exists only as a gas is called _____.

Q3: Label the following sentences as True or False.

- Kinetic energy of molecules of a gas is zero at 0°C.
- A gas in a closed container will exert much higher pressure at the bottom due to gravity than at the top.
- Real gases show ideal gas behaviour at low pressure and high temperature.
- Liquefaction of gases involves decrease in intermolecular spaces.
- An ideal gas on expansion will show Joule-Thomson effect.

- Q4 . a. What is Boyle's law of gases? Give its experimental verification.
- What are isotherms? What happens to the positions of isotherms when they are plotted at high temperature for a particular gas.
 - Why do we get a straight line when pressures exerted on a gas are plotted against inverse of volumes? This straight line changes its position in the graph by varying the temperature. Justify it.
 - How will you explain that the value of the constant k in the equation $PV = k$ depends upon
 - the temperature of a gas
 - the quantity of a gas

- Q5.a. What is the Charles's law? Which scale of temperature is used to verify that $V/T = k$ (pressure and number of moles are constant)?
- b. A sample of carbon monoxide gas occupies 150.0 mL at 25.0°C. It is then cooled at constant pressure until it occupies 100.0 mL. What is the new' temperature? (Ans: 198.8K or -74.4 °C)
- c. Do you think that the volume of any quantity of a gas becomes zero at - 273.16 °C. Is it not against the law of conservation of mass? How do you deduce the idea of absolute zero from this information?
- Q6 . a. What is Kelvin scale of temperature? Plot a graph for one mole of an a real gas to prove that a gas becomes liquid, earlier than -273.16 'C.
- b. Throw some light on the factor 1/273 in Charles's law.
- Q7. a. What is the general gas equation? Derive it in various forms.
- b. Can we determine the molecular mass of an unknown gas if we know the pressure, temperature and volume along with the mass of that gas.
- c. How do you justify from general gas equation that increase in temperature or decrease of pressure decreases the density of the gas?
- c. Why do we feel comfortable in expressing the densities of gases in the units of g dm^{-3} rather than g cm^{-3} , a unit which is used to express the densities of liquids and solids.
- Q8 . Derive the units for gas constant R in general gas equation:
- a. when the pressure is in atmosphere and volume in dm^3 .
- b. when the pressure is in N m^{-2} and volume in m^3 .
- c. when energy is expressed in ergs.
- Q9. a. What is Avogadro's law of gases?
- b. Do you think that 1 mole of H_2 and 1 mole of NH_3 at 0 °C and 1 atm pressure will have Avogadro's number of particles?
- c. Justify that 1 cm^3 of H_2 and 1 cm^3 of CH_4 at STP will have same number of molecules, when one molecule of CH_4 is 8 times heavier than that of hydrogen.

- Q10. a. Dalton's law of partial pressures is only obeyed by those gases which don't have attractive forces among their molecules. Explain it.
- b. Derive an equation to find out the partial pressure of a gas knowing the individual moles of component gases and the total pressure of the mixture.
- c. Explain that the process of respiration obeys the Dalton's law of partial pressures.
- d. How do you differentiate between diffusion and effusion? Explain Graham's law of diffusion.
- Q11. a. What is critical temperature of a gas? What is its importance for liquefaction of gases? Discuss Linde's method of liquefaction of gases.
- b. What is Joule-Thomson effect? Explain its importance in Linde's method of liquefaction of gases.
- Q12. a. What is kinetic molecular theory of gases? Give its postulates.
- b. How does kinetic molecular theory of gases explain the following gas laws:
- | | |
|----------------------|--------------------------------|
| (i) Boyle's law | (ii) Charles's law |
| (iii) Avogadro's law | (iv) Graham's law of diffusion |
- Q13. a. Gases show non-ideal behaviour at low temperature and high pressure. Explain this with the help of a graph.
- b. Do you think that some of the postulates of kinetic molecular theory of gases are faulty? Point out these postulates.
- c. Hydrogen and helium are ideal at room temperature, but SO_2 , and Cl_2 are nonideal. How will you explain this?
- Q14. a. Derive van der Waal's equation for real gases.
- b. What is the physical significance of van der Waals' constants, 'a' and 'b'? Give their units.
- Q15 Explain the following facts
- a. The plot of PV versus P is a straight line at constant temperature and with a fixed number of moles of an ideal gas.
- b. The straight line in (a) is parallel to pressure-axis and goes away from the pressure axis at higher pressures for many gases.
- c. Pressure of NH_3 gas at given conditions (say 20 atm pressure and room temperature) is less as calculated by van der Waals equation than that calculated by general gas equation.
- d. Water vapours do not behave ideally at 273K.
- e. SO_2 is comparatively non-ideal at 273K but behaves ideally at 327 °C.

Q16 Helium gas in a 100 cm^3 container at a pressure of 500 torr is transferred to a container with a volume of 250 cm^3 . What will be the new pressure

- a. if no change in temperature occurs (Ans: 200 torr)
b. if its temperature changes from 20°C to 15°C ? (Ans: 196.56 torr)

Q17

a. What are the densities in kg/dm^3 of the following gases at STP ($P = 101325 \text{ Nm}^{-2}$, $T = 273 \text{ K}$, molecular masses are in kg mol^{-1})
(i) methane, (ii) oxygen, (iii) hydrogen

b. Compare the values of densities in proportion to their mole masses.

c. How do you justify that increase of volume upto 100 dm^3 at 27°C of 2 moles of NH_3 will allow the gas behave ideally, as compared to S.T.P conditions.

(Ans: $\text{CH}_4=0.714\text{kgm}$, $\text{O}_2=1.428\text{kgm}^{-3}$, $\text{H}_2=0.089\text{kgm}^{-3}$)

Q18 A sample of krypton with a volume of 6.25 dm^3 , a pressure of 765 torr and a temperature of 20°C is expanded to a volume of 9.55 dm^3 and a pressure of 375 torr. What will be its final temperature in $^\circ\text{C}$?

(Ans: $T = -53.6^\circ\text{C}$)

Q19 Working at a vacuum line, a chemist isolated a gas in a weighing bulb with a volume of 255 cm^3 , at a temperature of 25°C and under a pressure in the bulb of 10.0 torr. The gas weighed 12.1 mg. What is the molecular mass of this gas?

(Ans: 87.93 g mol^{-1})

Q20 What pressure is exerted by a mixture of 2.00g of H_2 and 8.00g of N_2 at 273K in a 10 dm^3 vessel?

(Ans: $P = 2.88 \text{ atm}$)

Q21. a. The relative densities of two gases A and B are 1:1.5. Find out the volume of B which will diffuse in the same time in which 150 dm^3 of A will diffuse?

(Ans: 122.47 dm^3)

b. Hydrogen (H_2) diffuses through a porous plate at a rate of 500 cm^3 per minute at 0°C . What is the rate of diffusion of oxygen through the same porous plate at 0°C ?

(Ans: 125 cm^3)

c. The rate of effusion of an unknown gas A through a pinhole is found to be 0.279 times the rate of effusion of H_2 gas through the same pinhole. Calculate the molecular mass of the unknown gas at STP.

(Ans: $= 25.7 \text{ g mol}^{-1}$)

Q22 Calculate the number of molecules and the number of atoms in the given amounts of each gas

- (a) 20 cm³ of CH₄ at 0 °C and pressure of 700 mm of mercury (Ans: 4.936 x 10²⁰, 24.7 x 10²⁰)
(b) 1 cm³ of NH₃ at 100 °C and pressure of 1.5 atm (Ans: 2.94 x 10¹⁹, 1.177 x 10²⁰)

Q23 Calculate the masses of 10²⁰ molecules of each of H₂, O₂, and CO, at STP. What will happen to the masses of these gases, when the temperature of these gases are increased by 100 °C and the pressure is decreased by 100 torr.

(Ans: 3.3 x 10⁻⁴g; 5.31 x 10⁻³g; 7.30 x 10⁻³g)

Q24 a. Two moles of NH₃ are enclosed in a 5 dm³ flask at 27 °C. Calculate the pressure exerted by the gas assuming that

(i) it behaves like an ideal gas

(ii) it behaves like a real gas

$$a = 4.17 \text{ atm dm}^6 \text{ mol}^{-2}$$

$$b = 0.0371 \text{ dm}^3 \text{ mol}^{-1}$$

(Ans: 9.85 atm)

b. Also calculate the amount of pressure lessened due to forces of attractions at these conditions of volume and temperature. (Ans: 0.51 atm)

c. Do you expect the same decrease in the pressure of two moles of NH₃ having a volume of 40 dm³ and at temperature of 27 °C.