# PART ONE
# GASES

Chapter 1

# GAS LAWS

## INTRODUCTION

States of matter is the function of strength of intermolecular forces. If the intermolecular forces present in a substance are so weak that room temperature is enough to break them, then that substance is referred as a gaseous substance. If the intermolecular forces are slightly strong, then the room temperature will just be enough to weaken them and the substance will be referred as a liquid substance. And if the intermolecular forces are too strong for room temperature to break or even to weaken them, the substance is referred as solid substance.

So there are three common states of matter which are gaseous state, liquid state and solid state. There is a fourth state of matter which is obtained when a substance is heated to very high temperature (above 5000°C), so that the substance become the mixture of positively charged ions and electrons (after complete ionisation of the substance) and the state is known as **plasma** which is common on the sun.

**It should be understood that:**

The three states of matter are interchangeable; for example, gases can be converted to liquids by compressing the gas at a suitable temperature.

Gases become more difficult to liquefy as the temperature increases because the kinetic energies of the particles that make up the gas also increases.

The **critical temperature** of a substance *is the temperature at and above which vapour of the substance cannot be liquefied, no matter how much pressure is applied*. It is the minimum temperature at which gas liquefaction becomes impossible. Keeping in mind that, temperature is continuous data, critical temperature can also be stated as the maximum temperature at which gas liquefaction is possible.

Gas can be liquefied at critical temperature by applying external pressure through compression which is known as critical pressure. The **critical pressure** of a substance is therefore *the pressure required to liquefy a gas at its critical temperature.*

*Critical temperature and critical pressure of a substance* are collectively known as **critical state** of the substance. *The volume occupied by one mole of a gas at its critical state* is known as **critical volume**.

## Variables of gaseous state

Physical condition of a gas is described by four properties which are pressure, volume, temperature and amount (number of moles) of the gas. The four properties are known as **variables of gaseous state** which may simply be defined as *basic properties which describe the entire condition of the gas.*

**1. Pressure (P)**

Gas exerts pressure due to collision between gas particles (molecules like oxygen gas or atoms like helium gas) and the walls of the container. The amount of pressure is therefore expected to depend on two things, namely:

- Collision frequency and
- Collision energy

**Collision frequency:** This is the number of collision of gas particles (hitting container's walls) per unit time. Greater collision frequency means higher pressure.

**Collision energy:** This is determined by kinetic energy which in turn depends on the speed of gas particles hitting the container's walls. Greater collision energy means higher pressure.

The pressure exerted by gas is actually the force exerted by gas particles hitting the wall of the container per unit area (of the wall). It is commonly expressed in millimetres of mercury (mmHg), atmosphere (atm), torr, Pascal (Pa) or kilopascal (kPa) such that:

- $1\text{atm} = 760\text{mmHg} = 101.325\text{kPa}$
- $1\text{mmHg} = 1\text{torr}$ and $1\text{kPa} = 1000\text{Pa}$

**2. Volume (V)**

Gas occupies the volume of the container in which it is enclosed. The volume is commonly expressed in litres (L), millilitres (mL), $\text{cm}^3, \text{dm}^3$ or $\text{m}^3$ such that:

- $1\text{L} = 1\text{dm}^3$ and $1\text{dm}^3 = 1000\text{cm}^3$
- $1\text{L} = 1000\text{mL}$ and $1\text{mL} = 1\text{cm}^3$
- $1\text{m}^3 = 10^6\text{cm}^3$ and 1L (or $1\text{dm}^3$ ) $=10^{-3}\text{m}^3$

Volume of the container affects the frequency of collision between gas particles and container's wall and hence it also affects the amount of pressure exerted by the gas in the container. Larger container means that each individual gas particle has to move greater distance before hitting the container's wall leading to smaller collision frequency and hence lower pressure.

**3. Temperature (T)**

Gases have temperature which is usually measured in degree of Celsius $(°\text{C})$ or Kelvin scale such that; $\text{Kelvin (K)} = \text{Celsius}(°\text{C}) + 273$.

Temperature affects both the collision frequency and the collision energy and therefore affecting amount of pressure exerted by the gas. When the temperature is increased, speed and thus kinetic energy is increased too which in turn makes collision between gas particles and container's walls more energetic and more frequent as well; leading to higher pressure.

**4. Amount of the gas (n)**

The amount of the gas present is the number of gas particles which is given as the number of moles of gas particles. The number of moles of the gas is usually calculated from measured mass of the gas by using the following formula: $\text{n} = \frac{\text{m}}{\text{M}_\text{r}}$; where m is the mass of the gas and $\text{M}_\text{r}$ is its molar mass.

When mass the gas is increased, the number of moles of gas particles is increased too leading to more frequent collisions between gas particles and container's walls and hence pressure of the gas is increased.

## MAIN GAS LAWS

Gas laws *describe the relationship between the four variables of gaseous state*. They demonstrate properties and behaviour of gases in different conditions of temperature, pressure and volume. These laws have played a crucial role in predicting the behaviour of gases in different environments, designing and optimizing chemical reactions, developing and improving technologies, and understanding the properties of gases.

There are six main gas laws which are:

- Boyle's law
- Charles's law
- Gay-Lussac's law (also known as Amontons's law)
- Avogadro's law
- Combined gas law
- Ideal gas law

Among the six laws, Boyle's law, Charles's law and Avogadro's law are fundamental from which other three gas laws can be derived.

Also the first four gas laws (Boyle's law, Charles's law, Amontons's law and Avogadro's law) are known as **specific gas laws** or **individual gas laws**. The **individual gas laws** *describe the relationship between two of the four variables of gaseous state while keeping the remaining two variables constant*. This is different to the combined gas law which connects three variables and ideal gas law which connects all four variables.

Combined gas law and ideal gas law are **merger gas laws** as *they are formed by combining (merging) two or more individual gas laws.* As we are going to witness soon, the former is the merger of two gas laws (Boyle's and Charles's law) while the latter is the merger of three gas laws (Boyle's, Charles's and Avogadro's law).

## BOYLE'S LAW

Boyle's law *is the individual gas law which describes the relationship between volume and pressure of the gas when its amount and temperature are kept constant.*

The law state that, *"Volume of fixed mass of a gas varies inversely proportional to its pressure at constant temperature"*

Thus according to Boyle's law: $V \propto \frac{1}{P}$ or $V = \frac{k}{P}$ or $PV = k$

Thus $P_1V_1 = P_2V_2 = P_3V_3 = \cdots \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. = P_nV_n$

**Note:**

Since $n = \frac{m}{M_r}$ and $M_r$ is constant, if mass of the gas is fixed (constant), number of moles of the gas (n) must be constant too.

So Boyle's law is applicable when there are constant number of moles of the gas and temperature.

**Qualitative explanation to justify Boyle's law**

If the gas volume of a given amount of gas at a given temperature is decreased (that is, if the volume of the gas container is decreased), the gas particles will have to move shorter distance before making collision with container's wall leading to increase in collision frequency and hence pressure of the gas will increase as suggested by Boyle's law.

**Real life example of Boyle's law**

**Breathing:** As the lungs expands, the volume inside the lungs increases and the pressure inside decreases in accordance with Boyle's law (this leads to the inhalation). During the exhalation, the volume inside the lungs decreases and the pressure increases (also in accordance with Boyle's law).

**Example 1**

A $120cm^3$ gas syringe containing $100cm^3$ of gas that was compressed to certain volume. After the compression, the pressure of the gas in the syringe changed to 144.75kPa. If the atmospheric pressure is 101.325kPa, and the temperature remains unchanged, what is the new volume of the gas after compression?

**Solution**

Since temperature is kept constant (remains unchanged), Boyle's law is applicable.

That is $P_1V_1 = P_2V_2$ or $V_2 = \frac{P_1V_1}{P_2}$

Where $P_1 = 101.325kPa$; $V_1 = 100cm^3, P_2 = 144.75kPa$

Substituting $V_2 = \frac{101.325kPa \times 100cm^3}{144.75kPa} = 70cm^3$

The volume is $70cm^3$.

**Example 2**

In hospital, the gas pressure in a 100L cylinder of oxygen is 405.3kPa. What volume of gas can be released slowly to a patient on releasing it to an atmospheric pressure of 1atm?

**Solution**

$$P_1 = 405.3\text{kPa} = \frac{405.3\text{kPa}}{101.325\text{kPa/atm}} = 4\text{atm (Recall: 1atm} = 101.325\text{kPa)}$$

$P_2 = 1\text{atm}$ and $V_1 = 100\text{L}$

Then by using Boyle's law:

$$P_1V_1 = P_2V_2 \text{ or } V_2 = \frac{P_1V_1}{P_2} = \frac{4\text{atm} \times 100\text{L}}{1\text{atm}} = 400\text{L}$$

The volume is 400L.

## CHARLES'S LAW

*This* is *the individual gas law which describes the relationship between volume and temperature of the gas when its amount and pressure are kept constant.*

The law state that, *"The volume of fixed mass of a gas varies directly proportional to its absolute temperature at constant pressure."*

Thus according to Charles' law: $V \propto T$ or $V = kT$ or $\frac{V}{T} = k$

Thus $\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3} = \cdots \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . \frac{V_n}{T_n}$

Experimentally it was found that the volume of the gas increase by 1/273 of its original volume for every increase of 1°C and will decrease by the same factor for every decrease of 1°C from 0°C.

- Thus if $V_o$ is initial volume of the gas at 0°C, then volume of the gas at 273°C we would expect to be: $V_f = V_o + \frac{273}{273}V_o = 2V_o$
- So the volume of the gas will be doubled at $+273°\text{C}$.
- Also the volume of the gas at $-273°\text{C}$ we would expect to be:

$$V_f = V_o - \frac{273}{273}V_o = 0$$

So the volume of the gas is expected to be zero at $-273°\text{C}$. $-273°\text{C}$ is known as **absolute zero temperature**.

This can be verified graphically as follows:

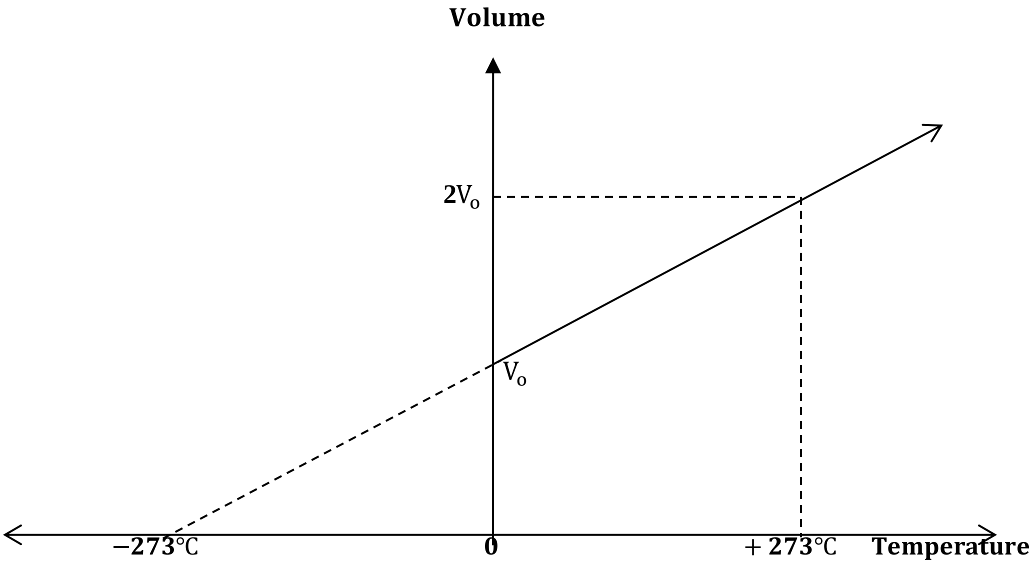



**Figure 1.1** Graph for illustrating Charles's law

**Definition of absolute zero temperature**

*This is the hypothetical temperature where by all gases were supposed to have zero volume.*

It is hypothetical because all gases become liquefied before reaching $-273$°C(0K).

**Qualitative explanation to justify Charles's law**

The basic suggests that an increase in temperature would lead to an increase in pressure of the gas by increasing both collision frequency and collision energy. The only way to stop pressure from increasing under such conditions is to increase volume, which will decrease collision frequency despite the increase of collision energy and therefore keeping pressure constant. Hence for the pressure to remain constant, the increase in temperature of given amount of the gas must be accompanied with the increase in volume as suggested by Charles's law.

**Real life example of Charles's law**

**Floating of hot-air balloon:** According to Charles's law, the air inside the balloon being hotter than the air outside, has larger volume. Larger volume implies that the air inside has smaller density and hence the balloon floats.

**Example 3**

What change in temperature (in Celsius) required to decrease 5L of a gas at 27°C to 3L at the same pressure.

**Solution**

Since pressure was the same (constant), Charles's law is applicable.

From Charles's law: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ or $T_2 = \frac{V_2 \times T_1}{V_1}$

Where: $V_1 = 5L, V_2 = 3L$ and $T_1 = 27°C = (273 + 27)K = 300K$

Substituting $T_2 = \frac{3L \times 300K}{5L} = 180K = (180 - 273)°C = -93°C$

The change required is decrease in temperature from 27°C to $-93$°C.

## COMBINED GAS LAW

Combined gas law *describes the relationship between volume, pressure and temperature of fixed amount of the gas.*

It can be stated as, *"Volume of fixed mass of a gas varies directly proportional to absolute temperature and inversely proportional to its pressure."*

That is $V \propto \frac{T}{P}$ or $\frac{PV}{T} = k$

The law can be obtained by combining Boyle's law and Charles's law as shown below:

From Boyles' law: $V \propto \frac{1}{P} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$ (i)

From Charles's law: $V \propto T \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$ (ii)

Combining (i) and (ii) gives: $V \propto \frac{T}{P}$ or $\frac{PV}{T} = k$ (Combined gas law)

Hence $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \frac{P_3V_3}{T_3} = \cdots \ldots\ldots\ldots\ldots\ldots\ldots\ldots = \frac{P_nV_n}{T_n}$

The above final result which is also known as **general gas equation** is more useful in understanding volume of the gas when both pressure and temperature are changing while mass of the gas is kept constant.

**It should be noted that:**

Boyle's and Charles's law may be deduced from general gas equation.

Boyle's law can be deduced as follows:

From $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$; when temperature is constant, $T_1 = T_2 = T$

Then $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ or $\mathbf{P_1V_1 = P_2V_2}$ which is Boyle's law.

Charles's law can be deduced as follows:

From $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$; When pressure is constant, $P_1 = P_2 = P$

Then $\frac{PV_1}{T_1} = \frac{PV_2}{T_2}$ or $\mathbf{\frac{V_1}{T_1} = \frac{V_2}{T_2}}$ which is equivalent to Charles' law

**Real life example of combined gas law**

**Helium balloon:** On the surface of the earth, the balloon filled with helium will have a specific pressure, temperature and volume. If you let go of the balloon, it will fly. The temperature and air pressure start to decrease as you get higher in the air and therefore keeping $\frac{PV}{T}$ constant in accordance with combined gas law.

**Example 4**

$50cm^3$ of a gas at 1atm and 27°C was compressed to $40cm^3$ at 37°C. Calculate the final pressure of the gas in torr.

Solution

Using combined gas law; $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

Where: $V_1 = 50cm^3, V_2 = 40cm^3$, $T_1 = 27°C = (273 + 27)K = 300K$,

$T_2 = 37°C = (273 + 37)K = 310K$ and $P_1 = 1atm = 760torr$

Substituting $\frac{760\text{torr}\times 50\text{cm}^3}{300\text{K}} = \frac{P_2\times 40\text{cm}^3}{310\text{K}}$

From which $P_2 = 981.7\text{torr}$

The final pressure is approximately 982torr

## GAY-LUSSAC'S LAW

Gay-Lussac's law (also known as **Amontons's law**) *is the individual gas law which describes the relationship between pressure and temperature of the gas when its amount and volume are kept constant.*

The law state that, *"Pressure of given mass of a gas varies directly proportional to its absolute temperature provided that the volume of the gas is constant".* The law is also simply known as **pressure law** of gases.

Thus according to pressure law:

$P \propto T$ or $P = kT$ or $\frac{P}{T} = k$ where k is the constant for proportionality

Hence $\frac{P_1}{T_1} = \frac{P_2}{T_2} = \frac{P_3}{T_3} = \cdots \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . = \frac{P_n}{T_n}$

Gay-Lussac's law can also be deduced from general gas equation as follows:

From $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$; When volume is constant, $V_1 = V_2 = V$

Then $\frac{P_1V}{T_1} = \frac{P_2V}{T_2}$ or $\mathbf{\frac{P_1}{T_1} = \frac{P_2}{T_2}}$ which is equivalent to Pressure law

**Qualitative explanation to justify Gay-Lussac's law**

When the temperature of given amount of a gas in a certain container is increased, speed and thus kinetic energy is increased too which in turn increases both collision frequency and collision energy. The increase in collision frequency and collision energy as consequence of temperature rise, makes the pressure to raise as suggested by Gay-Lussac's law.

**Real life example of Gay-Lussac's law**

**Reading of pressure gauge of the tyre:** The pressure reading of the car tyre is higher when the car is travelling over hot region than it was when the car was in the garage due to the increase in pressure as per Gay-Lussac's law.

**Example 5**

A cylinder of propane gas at 22°C exerted a pressure of 9 atm. When exposed to sunlight it warmed up to 32°C. What is the new pressure in the container?

**Solution**

Given that:

$P_1 = 9\text{ atm}, T_1 = 22°\text{C} = 295\text{K}, T_2 = 30°\text{C} = 305\text{K}$

Then by using Gay-Lussac's law;

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ or } P_2 = \frac{T_2}{T_1} \times P_1 = \frac{305\text{K}}{295\text{K}} \times 9\text{atm} = 9.3\text{atm}$$

The new pressure is 9.3atm.

# AVOGADRO'S LAW

*This* is *the individual gas law which describes the relationship between volume and amount (number of moles) of the gas when its pressure and temperature are kept constant.*

The law states, *"Volume of all gases varies directly proportional to their number of moles at constant temperature and pressure."*

Thus according to Avogadro's law:

$V \propto n$, or $V = kn$ or $\frac{V}{n} = k$ where k is the proportionality constant

Thus $\frac{V_1}{n_1} = \frac{V_2}{n_2} = \frac{V_3}{n_3} = \cdots \dots\dots\dots\dots\dots\dots\dots . = \frac{V_n}{n_n}$

If $V_1 = V_2 = V$ (Equal volume)

Then the equation $\frac{V_1}{n_1} = \frac{V_2}{n_2}$ becomes;

$\frac{V}{n_1} = \frac{V}{n_2}$ or $n_1 = n_2$ and hence Avogadro's law can alternatively be stated as follows:

*"Equal volume of different gases at constant conditions of temperature and pressure contain the same number moles (or molecules)."*

**Qualitative explanation to justify Avogadro's law**

Here the basic suggests that an increase in the number of gas particles (at constant temperature) would lead to an increase in pressure of the gas by increasing collision frequency. The only way to stop pressure from increasing under such conditions is to increase volume, which will decrease collision frequency despite the increase of amount of the gas and therefore keeping pressure constant. Hence for the pressure to remain constant, the increase in number of moles of the gas at given temperature and pressure must be accompanied with the increase in volume as suggested by Avogadro's law.

**Real life example of Avogadro's law**

**A balloon filled with helium weighs much less than an identical balloon filled with air:** Avogadro's law implies that equal volumes contain equal numbers of molecules, when pressure and temperature are held constant. Since both balloons contain the same number of molecules, and since helium atoms have lower mass than either oxygen molecules or nitrogen molecules in air, the helium balloon is lighter.

**Example 6**

A cylinder with a movable piston contains 4g of helium at room temperature. More helium was added to the cylinder and the volume was adjusted so that the gas pressure remained the same. How many grams of helium were added to the cylinder (kept at the same room temperature) if the volume was changed from 5L to 8L?

**Solution**

Since both temperature and pressure were kept constant, Avogadro's law is applicable.

Thus $\frac{V_1}{n_1} = \frac{V_2}{n_2}$ or $n_2 = \frac{V_2}{V_1} \times n_1$

$$n_1 = \frac{4g}{4g/mol} = 1mol, V_1 = 5L \text{ and } V_2 = 8L$$

Substituting $n_2 = \frac{8L}{5L} \times 1mol = 1.6mol$

Thus number of moles to be added $= n_2 - n_1 = (1.6 - 1)mol = 0.6mol$

Hence the mass of helium added is $0.6mol \times 4g/mol = 2.4g$

# IDEAL GAS LAW

Ideal gas law *describes the relationship between all four variables (volume, pressure, temperature and number of moles) of gaseous state.*

It can be stated as, *"Volume of all gases varies directly proportional to their number of moles and absolute temperature and inversely proportional to their pressure."*

Ideal gas law can be obtained by combining the three fundamental gas laws which are Boyle's law, Charles's law and Avogadro's law as shown below:

From Boyle's law: $V \propto \frac{1}{P}$; constants: n and T

From Charles's law: $V \propto T$; constants: n and P

Avogadro's law: $V \propto n$; constants: P and T

Combining the three laws: $V \propto \frac{nT}{P}$ or $V = \frac{nRT}{P}$ (All four variables of the gaseous state are changing).

Where **R** is the proportionality constant and the constant is known as **universal gas constant** or **molar gas constant**.

Hence $\mathbf{PV = nRT}$ and the result is known as **ideal gas law**. It is also more famously known as **ideal gas equation**. It is actually **the equation of state** for ideal gases because it relates all variables of gaseous state which are temperature (T), pressure (P), volume (V) and number of moles (n).

Also from the ideal gas question, $PV = nRT$; $\frac{PV}{nT} = R$

Thus; $\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$

**The value of universal gas constant, R**

When $n = 1$ at s.t.p, $V = 22.4dm^3$ (or $22.4 \times 10^{-3}m^3$), $T = 273K$,

$P = 1atm$ (or $101325\ N/m^2$)

Then from $PV = nRT$ or $R = \frac{PV}{nT}$

Substituting $P = 1atm, V = 22.4dm^3$ (22.4L), $T = 273K$, $n = 1mol$

Thus $R = \frac{1atm \times 22.4L}{1mol \times 273K} = 0.082atmLmol^{-1}\ K^{-1}$ or $0.082atmdm^3mol^{-1}\ K^{-1}$

Hence the value of $R = 0.082$ must be used when:

- Volume is in litres or $dm^3$
- Pressure is in atmospheres

Substituting $P = 101325\ N/m^2, V = 22.4 \times 10^{-3}m^3, T = 273K, n = 1mol$

Then $R = \frac{101325Nm^{-2} \times 22.4 \times 10^{-3} \times m^{-3}}{1mol \times 273K} = 8.314J\ mol^{-1}\ K^{-1}$

Hence the value of $R = 8.314$ must be used when:

- Given volume is in $m^3$
- Pressure is in Pascal (Pa) or $N/m^2$

**Remember:**

$1atm = 760mmHg$; $1torr = 1mmHg$; So $1atm = 760torr$

## Applications of ideal gas law

Ideal gas law describes the behaviour of an ideal gas under any condition of pressure, volume, and temperature. This makes it more useful than any form of gas law we have discussed so far. The law is useful indifferent ways including:

**1. Determination of molar mass of a gas**

From ideal gas equation; $PV = nRT$

But $n = \frac{m}{M_r}$ then $PV = \frac{m}{M_r} \times RT$

From which: $\mathbf{M_r = \frac{mRT}{PV}}$

Where m is the given mass of the gas in grams, g

T is the absolute temperature in Kelvin, K

P is the pressure exerted by the gas

V is **the volume of the gas = volume of the container**

R is the universal molar gas constant

And $M_r$ is the molar mass of the gas in g/mol.

**2. Determination of the density of the gas**

Density of the gas can be expressed in two different ways, namely:

- Normal density.
- Relative density (commonly is termed as vapour density)

**Normal density** of a gas is the mass per unit volume of the gas at given conditions of temperature and pressure.

That is; Normal density $(\rho) = \frac{m}{V}$

Where m is the mass of the gas

V is the volume of the gas = volume of the container.

**Relative density (or vapour density)** of a gas is the ratio of the normal density of the gas to the normal density of hydrogen gas at the given conditions of temperature and pressure.

That is, relative density $= \frac{\rho_g}{\rho_{H_2}}$

Where $\rho_g$ is the normal density of the gas

$\rho_{H_2}$ is the normal density of the hydrogen gas.

From ideal gas equation; $PV = nRT$ but $n = \frac{m}{M_r}$

Then $PV = \frac{m}{M_r} \times RT$ or $PM_r = \left(\frac{m}{V}\right) \times RT$ but $\frac{m}{V} = $ Normal density, $\rho$

Hence $\boldsymbol{\rho} = \mathbf{\frac{PM_r}{RT}}$

If $M_{H_2}$ and $M_g$ are molar masses of hydrogen gas and another gas respectively

And $\rho_{H_2}$ and $\rho_g$ are normal densities of hydrogen gas and the another gas respectively

Then $\frac{\rho_g}{\rho_{H_2}} = \frac{PM_g}{RT} \div \frac{P \times M_{H_2}}{RT} = \frac{M_g}{M_{H_2}}$

But $\frac{\rho_g}{\rho_{H_2}}$ = Relative density(vapour density) of the gas

And molar mass of hydrogen gas is 2g/mol

Hence **Relative density** $= \frac{\mathbf{M_g}}{\mathbf{2g/mol}}$

**3. Determination of molar concentration of the gas**

From ideal gas equation: $PV = nRT$ or $P = \left(\frac{n}{V}\right)RT$

But $\frac{n}{V}$ = concentration of the gas in $moldm^{-3}$ which is denoted as [ ]

Then $P = [\ \ ]RT$

Hence $[\ \ ] = \frac{\mathbf{P}}{\mathbf{RT}}$

**4. Derivation of relationship between pressure and number of moles of gas**

From ideal gas equation, $PV = nRT$ or $P = \frac{nRT}{V}$

If the volume of the container,V, is fixed at given temperature; that is V and T are constants;

Then $\frac{RT}{V}$ = constant

Thus $P = \text{constant} \times n$ or $P \propto n$

Hence we can conclude that: For fixed volume of a gas at constant temperature, pressure of the gas varies directly proportional to the number of moles (or molecules) of the gas.

Since $n = {}^{m}/_{M_r}$; and for the given gas, $M_r$ is constant; number of moles of the gas (n) varies directly proportional to the mass of the gas (m). And therefore it can also be said that: the pressure of the given volume of gas at given temperature increases as the mass of the gas increases.

**Example 7**

Calculate the molecular weight of the gas if 1.82g of the gas occupies volume of 2L at 25˚C and 737mmHg. Assume the gas behaves ideally.

**Solution**

From ideal gas equation: $PV = \frac{m}{M_r}RT$

From which: $M_r = \frac{mRT}{PV}$

Where $m = 1.82g$, $R = 0.082$, $T = 25°C = (25 + 273)K = 298K$

P = 737mmHg = $\frac{737}{760}$ atm

$M_r = \frac{1.82 \times 0.082 \times 298 \times 760}{737 \times 2}$ g/mol = 23g/mol

Hence molecular mass of the compound is 23g/mol

**Example 8**

A $1000cm^3$ bulb contains 1.197g of gas at standard pressure and temperature at 20°C. Assume the gas behaves ideally. Calculate its:

(i) Relative density
(ii) Normal density

**Solution**

(i) Relative density $= \frac{M_g}{2g/mol}$

Where $M_g$ is the molar mass of the gas

But from $PV = nRT$

Where $n = \frac{m_g}{M_g}$

So $PV = \frac{m_g}{M_g}RT$ or $M_g = \frac{m_gRT}{PV}$

Where: $m_g$ is the given mass of the gas $= 1.197g$

$P = \text{standard pressure} = 1atm$

$V = 1000cm^3 = 1L$

$T = 20°C = 293K$

$R = 0.082$

Then $M_g = \frac{1.197 \times 0.082 \times 293}{1 \times 1} g/mol = 28.76g/mol$

So relative density $= \frac{28.76g/mol}{2g/mol} = 14.38$

Hence relative density is 14.38

(ii) Normal density $= \frac{m}{V} = \frac{1.197g}{1\text{ litre}} = 1.197g/L$

Hence normal density of the gas is 1.197g/L

**Example 9**

If 6.4g of $CH_4$ has pressure of 0.5atm and volume of 2 litres. Find pressure of 9g of $C_2H_6$ having 1litre volume under constant temperature.

**Solution**

Using $n = \frac{m}{M_r}$

Number of moles of $CH_4 = \frac{6.4}{16}mol = 0.4mol$

Number of moles of $C_2H_6 = \frac{9}{30}$ mol $= 0.3mol$

From ideal gas equation: $\frac{PV}{nT} = R = \text{constant}$

Then $\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$

But $T_1 = T_2 = T$(temperature is constant)

If follows that:$\frac{P_1V_1}{n_1} = \frac{P_2V_2}{n_2}$

Substituting $\frac{05atm \times 2L}{0.4mol} = \frac{P_2 \times 1L}{0.3mol}$

From which $P_2 = 0.75atm$

Hence the pressure is 0.75 atm

# OTHER GAS LAWS

Gas laws which are going to be discussed under this heading are Dalton's law of partial pressure and Graham's law of diffusion.

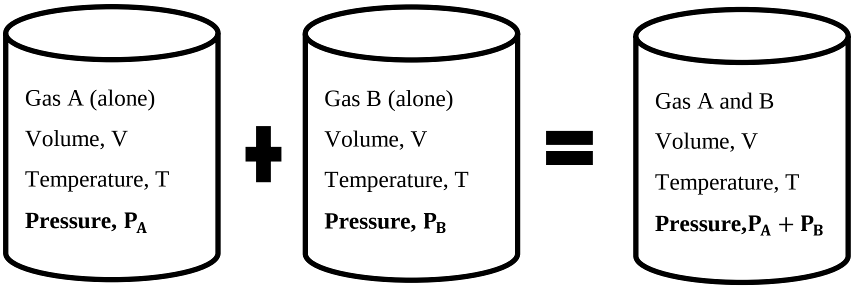
## DALTON'S LAW OF PARTIAL PRESSURE

Dalton's law of partial pressure *describes the relationship between the total pressure of a mixture of non-reacting ideal gases and the partial pressures of each individual component.* Whereas, **partial pressure** *is the pressure which would be exerted by a particular gas constituent in the gaseous mixture if the gas would be alone in the container at the same temperature.*

Dalton's law of partial pressure state that: *"The total pressure exerted in the container of the mixture of two or more gases is equal to the summation of their partial pressures provided that the gases do not react."* The law implies that the pressure depends on the total number of gas particles, not on the types of particles.

Thus if the container, have two gases say A and B with their respective partial pressures, $P_A$ and $P_B$

Then by Dalton's law of partial pressure: $P_T = P_A + P_B$




**Qualitative explanation to justify Dalton's law of partial pressure**

Gas particles are very far apart in the container. Due to this large distances between them, the particles of one gas in a mixture hit the container walls with the same frequency whether other gases are present or not, and the total pressure of a gas mixture is therefore becoming equals to the sum of the (partial) pressures of the individual gases as suggested by Dalton's law.

## Theoretical applications of Dalton's law of partial pressure

### 1. Determining total pressure exerted by gaseous mixture

This can simply be done directly from the law if the partial pressures of the components are known. For example, if the mixture consist of two gases; A and B, then $P_T = P_A + P_B$

### 2. Determining mole fraction of an individual gas in the gaseous mixture

This can be done if partial pressure of the gas and total pressure are known. To understand this, again consider the same mixture of two gases; A and B.

From the Dalton's law of partial pressure; $P_T = P_A + P_B$

But from ideal gas equation: $PV = nRT$ or $P = \frac{nRT}{V}$

Then $P_A = \frac{n_A RT}{V}, P_B = \frac{n_B RT}{V}$

Thus $P_T = \frac{n_A RT}{V} + \frac{n_B RT}{V}$

$P_T = \frac{RT}{V}(n_A + n_B)$

Then $\frac{P_A}{P_T} = \frac{n_A RT}{V} \div \frac{RT}{V}(n_A + n_B)$

$\frac{P_A}{P_T} = \frac{n_A}{(n_A+n_B)}$

But $\frac{n_A}{(n_A+n_B)} = X_A$

Where $X_A$ is the mole fraction of A

Hence $X_A = \frac{P_A}{P_T}$

**3. Determining partial pressure of a gas in the gaseous mixture from its mole composition**

This can be done if the mole fraction of the gas and the total pressure are known as shown below.

From (2) above; $X_A = \frac{P_A}{P_T}$

Then $P_A = X_A P_T$

**Be aware of this fact!**

Introducing new gas in the container with gases, does not change the partial pressures of the gases in the container because **it does both increases the total pressure in the container and decreases the mole fraction of the gases by the same proportion**.

- To understand this considers gas C is introduced in the container of volume, V, with two gases, say A and B at temperature T.

**Before addition of gas C in the container:**

$P_A = X_A P_T = \left(\frac{n_A}{n_A+n_B}\right) P_T = \left(\frac{n_A}{n_A+n_B}\right)\frac{(n_A+n_B)RT}{V} = \frac{n_A RT}{V}$

And $P_B = X_B P_T = \left(\frac{n_B}{n_A+n_B}\right) P_T = \left(\frac{n_B}{n_A+n_B}\right) \frac{(n_A+n_B)RT}{V} = \frac{n_B RT}{V}$

**After addition of gas C in the container:**

Total pressure in the container will change, say from $P_T$ to $P_{T2}$

And total number of moles of gases will change from $(n_A + n_B)$ to $(n_A + n_B + n_C)$

$P_A = X_A P_T = \left(\frac{n_A}{n_A+n_B+n_C}\right) P_{T2} = \left(\frac{n_A}{n_A+n_B+n_C}\right)\frac{(n_A+n_B+n_C)RT}{V} = \frac{n_A RT}{V}$

$P_B = X_B P_{T2} = \left(\frac{n_B}{n_A+n_B+n_C}\right) P_{T2} = \left(\frac{n_B}{n_A+n_B+n_C}\right)\frac{(n_A+n_B+n_C)RT}{V} = \frac{n_B RT}{V}$

Hence partial pressure of A and B remain unchanged even after addition of C in the container (provided that the gas has no reaction with A or B present in the container).

**Real life example of Dalton's law of partial pressure**

**Breathing problem for mountain climbers:** Percentage of oxygen in air is 21% by moles (or more commonly noted as by volume which does not change the meaning as long as you are familiar with Avogadro's law). Thus according to Dalton's law of partial pressure, oxygen also accounts for 21 percent of the atmosphere's total pressure. As one ascend to higher altitude, atmospheric pressure tends to decrease which in turn decreases partial pressure of oxygen in accordance with the Dalton's law. It is difficult for oxygen to go into the bloodstream when its partial pressure decreases. So people who climb to high altitudes experience difficulty in breathing and may experience hypoxia which is life threatening medical problem.

**Example 10**

Nitrogen gas is collected over water at 22°C, and the volume is measured as 284mL where the total pressure of the gas is 764torr. What volume would nitrogen occupy if it was dry and the pressure was 760torr? (The vapour pressure of water at 22°C us 19.8 torr)

**Solution**

By Dalton's law of partial; pressure: $P_T = P_{N_2} + P_{H_2O} = 764 \text{ torr}$

But $P_{H_2O} = 19.8\text{torr}$

Then $P_{N_2} = P_T - P_{H_2O} = (764 - 19.8)\text{torr} = 744.2 \text{ torr}$

If temperature and number of moles (mass) of $N_2$ remain constant

$P_1V_1 = P_2V_2$ (Boyle's law)

Substituting $744.2 \times 284 = 760 \times V_2$

From which $V_2 = \frac{744.2 \times 284}{760}\text{mL} = 278\text{mL}$

Hence the volume would be 278mL

**Example 11**

A mixture of helium and oxygen is used in diving tanks instead of nitrogen which at elevated pressure a large quantity is dissolved in blood producing an agonizing condition called the 'band'. For a particular dive 40litres of oxygen at 25°C and 1atm was pumped along with 12litres of helium at 25°Cand 1atmosphere into a tank with volume of 5litre. Calculate the partial pressure of each gas and the total pressure in the tank at 25°C.

**Solution**

**For oxygen gas:** $V = 40\text{L}, T = 25^\circ\text{C} = 298\text{K}$**,** P = 1atm

From $PV = nRT$

$n = \frac{PV}{RT} = \frac{1 \times 40}{0.082 \times 298}$ moles = 1.64 moles

The partial pressure of oxygen in 5L container = $\frac{nRT}{V} = \frac{1.64 \times 0.082 \times 298}{5}\text{atm} = 8\text{atm}$

Thus the partial pressure of oxygen gas, $P_{O_2}$ is 8atm

**For helium gas**

$V = 12\text{L}, T = 25^\circ\text{C} = 298\text{K}, P = 1\text{atm}$, From $n = \frac{PV}{RT}$

Then $n_{He} = \frac{1 \times 12}{0.082 \times 298}$ moles = 0.491 moles

So $P_{He} = \frac{n_{He}RT}{V} = \frac{0.491 \times 0.082 \times 298}{5}$ atm= 2.4 atm

Hence partial pressure of Helium is 2.4atm

By Dalton's law of partial pressure; total pressure, $P_T$, in the tank is given by:

$P_T = P_{O_2} + P_{He}$= (8+2.4)atm $= 10.4$ atm

Hence total pressure in the tank is 10.4 atm

**Alternative solution**

Since temperature is kept constant, Boyle's law is applicable

That is $P_1V_1 = P_2V_2$ or $P_2 = \frac{P_1V_1}{V_2}$

**For oxygen gas:** $P_1 = 1\text{atm};\ V_1 = 40\text{L}, V_2 = 5\text{L}$

Then $P_2 = \frac{1\times40}{5}\ \text{atm} = 8\text{atm}$

Hence the partial pressure of oxygen gas is 8atm

**For Helium gas:** $P_1 = 1\text{atm}, V_1 = 12\text{L}, V_2 = 5\text{L}$

Then $P_2 = \frac{1\times12}{5}\text{atm} = 2.4\text{atm}$

Hence the partial of oxygen gas is 2.4atm

By Dalton's law of partial pressure: $P_T = P_{O_2} + P_{He}$= (8+2.4) atm = 10.4atm

Hence the total pressure in the tank is 10.4atm

## GRAHAM'S LAW OF DIFFUSION OR EFFUSION

To understand the Graham's law of diffusion, we must first understand the two terms accompanied with the law: diffusion and effusion. If Graham's law of diffusion (or effusion) is the main course meal, then diffusion and effusion are delicious appetizers for our meal! Another great appetizer in the menu is the rate of diffusion and of course the rate of effusion.

Let us start with diffusion! Though diffusion and effusion are interchangeably used many times, they have actually different meaning. In gas perspective, the process through which the gas particles move from one gas to another gas is what we call diffusion. It causes significant disorder in the entire system. Diffusion is not a phenomenon which we only observe in gases; we can also observe diffusion (although at slower rates) in liquids as well. The leading cause of this phenomenon is the concentration level differences. When the particles of a material are in an area of low concentration, they tend to move to the content with a high area of concentration. A straightforward example of this process is when we use perfume in one part of the room, and then we can smell it in the entire room. Diffusion is involved in this whole scenario.

On another hand, the change in volume of diffusing gas particles over time is called the rate of diffusion. That is all about, the diffusion and its rate; let us put effusion and its rate on our dining table!

When the gaseous particles move from a tiny opening into the vacuum of space or open container, then the process is called effusion. This space can be a vacuum, any other gas or atmosphere. In this case, the molecules of material try to escape from a closed container through the aperture. The best example of you can observe effusion is in the car tyre with slow puncture whereby air in the tyre is slowly escaping from the tyre into the atmosphere until the tyre become flat. We can term this as effusion of air (gas) into the atmosphere.

On another hand, the change in volume of effusing gas particles over time is known as the rate of effusion. That is all about our appetizer! But before the main dish, let us assemble the terms together and concisely defining them.

**Diffusion of a gas** *is the spread up of gas particles throughout the space form the side of higher gas concentration to that of lower concentration.*

**Effusion of a gas** *is the escaping of the gas from the container through a tiny hole.*

**Rate of diffusion (or effusion) of a gas** *is the volume of the gas diffused (or effused) per unit time.*

So the rate of diffusion $= \frac{\text{Volume of the gas diffused (or effused)}}{\text{Time taken}}$

## Graham's law of diffusion

The Graham's law *describes the relationship between rate of diffusion (or effusion) of gases and their densities at given temperature and pressure.*

The law state that, **"***The rate of diffusion (or effusion) of gases at given temperature and pressure vary inversely proportional to the square root of their densities."*

Thus $\mathbf{R} \propto \frac{\mathbf{1}}{\sqrt{\boldsymbol{\rho}}}$

Where **R** is the rate of diffusion (or effusion).

$\boldsymbol{\rho}$ is the density of the gas.

For two gases, say A and B; $R_A \propto \frac{1}{\sqrt{\rho_A}}$ or $R_A = \frac{k}{\sqrt{\rho_A}}$

$R_B \propto \frac{1}{\sqrt{\rho_B}}$ or $R_B = \frac{k}{\sqrt{\rho_B}}$

Then $\frac{R_A}{R_B} = \frac{k}{\sqrt{\rho_A}} \div \frac{k}{\sqrt{\rho_B}}$

From which $\mathbf{\frac{R_A}{R_B} = \sqrt{\frac{\boldsymbol{\rho}_B}{\boldsymbol{\rho}_A}}}$

Since density of the gas varies directly proportional to its molar mass then $\mathbf{\frac{R_A}{R_B} = \sqrt{\frac{M_B}{M_A}}}$

Since the rate of diffusion $= \frac{\text{Volume of the gas diffused}}{\text{Time taken}}$

Then $\mathbf{\frac{R_A}{R_B} = \frac{V_A/t_A}{V_B/t_B} = \sqrt{\frac{M_B}{M_A}}}$

If $t_A = t_B = t$ (constant time)

Then $\mathbf{\frac{V_A}{V_B} = \sqrt{\frac{M_B}{M_A}}}$

If $V_A = V_B = V$

Then $\mathbf{\frac{t_B}{t_A} = \sqrt{\frac{M_B}{M_A}}}$

Since volume of a gas varies directly proportional to its number of moles (according to Avogadro's law) That is $V \propto n$ or $V = kn$

Then $\frac{V_A}{V_B} = \frac{kn_A}{kn_B} = \sqrt{\frac{M_B}{M_A}}$

Hence, $\mathbf{\frac{n_A}{n_B} = \sqrt{\frac{M_B}{M_B}}}$

**Be careful!**

The relationship between density of gases and their molar masses can be derived from either Avogadro's law or ideal gas equation when both temperature and pressure are kept constant.

- That is $\frac{\rho_A}{\rho_B} = \frac{M_A}{M_B}$ at constant temperature and pressure.
- So if temperature and pressure are not kept constant, the relationship does not hold and hence the formula $\frac{R_A}{R_B} = \sqrt{\frac{M_A}{M_B}}$ becomes **invalid.**

Below is the derivation of the appropriate formula for dealing with the case when temperature and pressure are not kept constant

- Consider the basic conclusion of the Graham's law which is $\frac{R_A}{R_B} = \sqrt{\frac{\rho_B}{\rho_A}}$

But from ideal gas equation it can be shown that; $\rho = \frac{PM_r}{RT}$

Thus $\rho_A = \frac{P_A M_A}{RT_A}$ and $\rho_B = \frac{P_B M_B}{RT_B}$

Thence $\frac{\rho_B}{\rho_A} = \frac{P_B M_B}{RT_B} \times \frac{RT_A}{P_A M_A} = \frac{P_B M_B T_A}{P_A M_A T_B}$

Therefore the equation: $\frac{R_A}{R_B} = \sqrt{\frac{\rho_B}{\rho_A}}$ becomes; $\frac{R_A}{R_B} = \sqrt{\frac{P_B M_B T_A}{P_A M_A T_B}}$

The above formula is applicable if both P and T for two gases (A and B) are different.

- If the pressure(P) is kept constant,$(P_A = P_B = P)$ while temperatures are different, the formula becomes $\frac{R_A}{R_B} = \sqrt{\frac{PM_B T_A}{PM_A T_B}} = \sqrt{\frac{M_B T_A}{M_A T_B}}$

If temperature (T) is kept constant $(T_A = T_B = T)$ while pressures are different, the formula becomes $\frac{R_A}{R_B} = \sqrt{\frac{P_B M_B T}{P_A M_A T}} = \sqrt{\frac{P_B M_B}{P_A M_A}}$

- If both temperature and pressure are kept constant $(P_A = P_B = P$ and $T_A = T_B = T)$, the formula becomes $\frac{R_A}{R_B} = \sqrt{\frac{PM_B T}{PM_A T}} = \sqrt{\frac{M_B}{M_A}}$

## Applications Graham's law

Graham's law has various uses in daily life. The main application of Graham's law is in the separation process. Different gases with different density can be separated by using this law. Also the formula of Graham's law, can be used to compare the rates of diffusion two gases and then to calculate molar mass of an unknown gas and thereafter identifying the unknown gas from the calculated molar mass. Furthermore, it can even be used to separate the isotopes of a given gas. The typical example of this process is the separation of heavy and light uranium from isotopes of uranium. In summary, Graham's law has the following applications:

1. Separation of gases with different densities.
2. Determination of densities and molar masses of gases
3. Identification of unknown gas by calculating molar mass of unknown gas.
4. Separation of isotopes of some elements (e.g. uranium isotopes).

**Example 12**

A gas diffuse through a porous plug at the rate of $1.43 cm^3/s$. Carbon dioxide diffuses through the plug at the rate of $0.43\ cm^3/s$. Calculate the molar mass of the gas.

**Solution**

By Graham's law of diffusion:

$$\frac{R_{CO_2}}{R_g} = \sqrt{\frac{M_g}{M_{CO_2}}} \text{ or } M_g = M_{CO_2}\left(\frac{R_{CO_2}}{R_g}\right)^2 = 44\left(\frac{0.43}{1.43}\right)^2 = 3.98\text{g/mol}$$

Hence molar mass of the gas is approximately 4g/mol.

**Example 13**

10.25cm$^3$ of ethane effuses through a small aperture in 40s. What is the time taken by 25 cm$^3$ of carbon dioxide?

**Solution**

From Graham's law of diffusion: $\frac{R_e}{R_{CO_2}} = \sqrt{\frac{M_{CO_2}}{M_e}}$

But the rate of diffusion $= \frac{\text{Volume diffused}}{\text{Time taken}}$

Then $\frac{R_e}{R_{CO_2}} = \frac{V_e/t_e}{V_{CO_2}/t_{CO_2}} = \frac{V_e t_{CO_2}}{V_{CO_2} t_e} = \sqrt{\frac{M_{CO_2}}{M_e}}$

Where:

$M_{CO_2} = 44\text{gmol}^{-1}, M_e = \text{molar mass of ethane } (C_2H_6) = 30\text{gmol}^{-1},\ V_{CO_2} = 25\text{cm}^3,$

$V_e = \text{volume of ethane diffused} = 10.25\text{cm}^3, t_e = \text{time taken by ethane to diffuse} = 40\text{s}$

$$\frac{10.25t_{CO_2}}{25 \times 40} = \sqrt{\frac{44}{30}}$$

From which $t_{CO_2} = 118\text{s} = 1\text{min}58\text{sec}$

Hence the time taken by $CO_2$ is 1min58 sec.

**Example 14**

A certain volume of hydrogen gas takes 2min10sec to diffuse through a porous plug and an oxide of nitrogen taken 10min23sec. What is:

(i) the molar mass of oxide
(ii) the formula of oxide of nitrogen.

**Solution**

By Grahm's law of diffusion; $\frac{t_O}{t_{H_2}} = \sqrt{\frac{M_O}{M_{H_2}}}$ or $M_O = M_{H_2}\left(\frac{t_O}{t_{H_2}}\right)^2$

Where $t_O = 10\text{min}23\text{sec} = 623\text{sec}, t_{H_2} = 2\text{min}10\text{sec} = 130\text{sec}, M_{H_2} = 2\text{g/mol}$

Thus $M_O = 2 \times \left(\frac{623}{130}\right)^2 = 46\text{g/mol}$

(i) Hence the molar mass of the oxide is 46g/mol.
(ii) Oxides of nitrogen are $\mathbf{N_2O, NO, N_2O_3, NO_2}$ and $\mathbf{N_2O_4}$

The formula of the oxide with molar mass of 46g/mol (from a mentioned oxide) is $NO_2$.

Hence the formula of oxide is $NO_2$.

# MISCELLANEOUS WORKED EXAMPLES ON GAS LAWS

**Example 15**

For each of the following, show how the final volume ($V_f$) is related to initial volume ($V_i$) for fixed mass of a gas:

(i) The pressure is decreased from 3atm to 1atm while the temperature remain constant
(ii) The temperature is risen from 200K to 300K while pressure is increased from 2atm to 3atm
(iii) The temperature is lowered from 400K to 100K while the pressure remain constant

**Solution**

(i) Since temperature is kept constant, Boyle's law is applicable.

By Boyle's law: $P_iV_i = P_fV_f$

But $P_i = 3\text{ atm}; \quad P_f = 1\text{ atm}$

Then $3V_i = 1 \times V_f$

Hence $V_f = 3V_i$

(ii) Since both pressure and temperature have been changed, general gas equation is applicable.

Using $\frac{P_iV_i}{T_i} = \frac{P_fV_f}{T_f}$ (General gas equation)

Where, $P_i = 2\text{ atm}$, $P_f = 3\text{ atm}$, $T_i$ = 200K, $T_f$ = 300K

Then $\frac{2V_i}{200} = \frac{3V_f}{300}$

Hence $V_f = Vi$

(iii) Since pressure is kept constant, Charles's law is applicable.

By Charles's law: $\frac{V_i}{T_i} = \frac{V_f}{T_f}$

Where $T_1 = 400\text{K}$ and $T_2 = 100\text{K}$

Then $\frac{V_i}{400} = \frac{V_f}{100}$

Hence $V_f = \frac{V_i}{4}$

**Example 16**

By using Avogadro's law, deduce a relationship between the molar mass and the vapour density of a substance.

**Solution**

By definition:

Vapour density (relative density of a gas) $= \frac{\text{Density of the gas}}{\text{Density of hydrogen gas}}$

$$= \frac{\text{Mass of given volume of the gas}}{\text{Mass of an equal volume of hydrogen gas}}$$

But from Avogadro's law: equal volumes of gases contain the same number of moles of gas molecules at given temperature and pressure.

That means that: Volume of one mole of the gas $=$ volume of one mole of hydrogen gas

If follows that:

Vapour density $= \frac{\text{Mass of one mole of the gas}}{\text{Mass of one mole of hydrogen gas}}$

But mass of one mole $=$ Molar mass

Then, vapour density = $\frac{\text{Molar mass of the gas}}{\text{Molar mass of hydrogen gas}} = \frac{\text{Molar mass of the gas}}{2\text{g/mol}}$

Hence vapour density = $\frac{\text{Molar mass of the gas}}{2\text{g/mol}}$

Or Molar mass of the gas $=$ Vapour density $\times$ 2g/mol

**Example 17**

A 2g sample of water is vapourised completely into 10L container at 200˚C. Calculate the pressure of vapour in this container at 200˚C

**Solution**

From ideal gas equation: $PV = nRT$

Then $P = \frac{nRT}{V} = \frac{mRT}{M_rV}$

Substituting given values

$P = \frac{2\times0.082\times473}{18\times10}$ atm= 0.43atm

Hence the pressure of vapour in the container is 0.43atm

**Example 18**

At room temperature pyridine is colourless liquid containing 75.9%C. 6.37%H and nitrogen. At 110°C and 630mmHg the density of the gas is 2.12g/L. Determine the molecular formula of pyridine.

**Solution**

$\%C + \%H + \%N = 100\%$

Substituting given value: $75.9 + 6.37 + \%N = 100$

From which $\%N = 17.73\%$

Then calculating empirical formula of the given compound as follows;

| Composition by element | C | H | N |
|---|---|---|---|
| Percentage of each by mass | 75.9 | 6.37 | 17.73 |
| Mass of each in 100g o f the compound | 75.9g | 6.37g | 17.73g |
| Number of moles of each. Using: $n = \frac{m}{M_r}$ | $\frac{75.9g}{12g/mol} = 6.325mol$ | $\frac{6.37g}{1g/mol} = 6.37mol$ | $\frac{17.73g}{14g/mol} = 1.266mol$ |
| Dividing by the smallest number of moles in each so as to get simpler ratio | $\frac{6.325mol}{1.266mol} = 5$ | $\frac{6.37mol}{1.266mol} = 5$ | $\frac{1.266mol}{1.266mol} = 1$ |

Hence t e empirical formula of the compound is $C_5H_5$ N

Calculating molar mass of the compound

From ideal gas equation: $PV = nRT$ but $n = \frac{m}{M_r}$

Then $PV = \frac{m}{M_r}RT$ or $M_r = \frac{mRT}{PV}$ but $\frac{m}{V} = \rho$

Thus $M_r = \frac{\rho RT}{P}$

Where $\rho = \frac{2.12g}{L}, R = 0.082, T = 110^{\circ}C = 383K, P = 630mmHg = \frac{630}{760}$ atm

Then $M_r = \frac{2.12 \times 0.082 \times 383 \times 760}{630} g/mol = 80g/mol$

Let molecular formula of the compound be $(C_5H_5N)_n$

Then $60n + 5n + 14n = 80$ or $79n = 80$ or $n = 1$

Hence the molecular formula of the compound is $C_5H_5N$

**Example 19**

From the ideal gas equation, deduce the following:

(i) Boyle's law
(ii) Charles's law
(iii) Pressure law
(iv) Avogadro's law
(v) Dalton's law of partial pressure

**Solution**

(i) From ideal gas equation: $PV = nRT$

For fixed mass o f a gas, n is constant

So if T (temperature) is constant, nRT must be also constant.

Thus $PV = \text{constant}$ or $V = \frac{\text{constant}}{P}$

And hence $V \propto \frac{1}{P}$ which is equivalent to Boyle's law and states that: The volume of fixed mass of a gas varies inversely proportional to its pressure at constant temperature.

(ii) From ideal gas equation: $PV = nRT$

For fixed mass of a gas, number of moles, n is constant

So if P (pressure) is constant, $\frac{nR}{P}$ must be also constant

Thus from $PV = nRT$ or $V = \left(\frac{nR}{P}\right)T$ but $\frac{nR}{P}$ constant

Then $V = \text{constant} \times T$ or $V \propto T$ which is equivalent to Charles's law and it states that: The volume of fixed mass of a gas varies directly proportional to its absolute temperature at constant pressure

(iii) From ideal gas equation: $PV = nRT$

For given mass of a gas, n is constant

So if volume, V is constant, $\left(\frac{nR}{V}\right)$ must be also constant

And from $PV = nRT$

$$P = \left(\frac{nR}{V}\right)T \text{ but } \frac{nR}{V} = \text{constant}$$

So $P = \text{constant} \times T$

or $P \propto T$ which is equivalent to pressure's law and the law states that: The pressure of given mass of a gas varies directly proportional to its absolute temperature provided that the volume of the gas is constant.

(iv) From ideal gas equation: $PV = nRT$

If P and T are constant, $\frac{RT}{P}$ must be constant also.

And from $PV = nRT$ or $V = \left(\frac{RT}{P}\right)n$ but $\frac{RT}{P}$ = constant

Then $V = \text{constant} \times n$ or $V \propto n$ which is equivalent to Avogadro's law and it states that: The volume of a gas varies directly proportional to its number of moles at constant temperature and pressure

(v) Consider three gases, say **A**, **B** and **C** are mixed in a container of volume, V at temperature, T

Total number of moles of all gases which will exert pressure in the container $= n_A + n_B + n_C$

Thus $P_TV = (n_A + n_B + n_C)RT$

Where $P_T$ is the total pressure exerted by the gaseous mixture in the container

Rewriting equation $P_TV = (n_A + n_B + n_C)RT$; $P_TV = n_ART + n_BRT + n_CRT$

From which $P_T = \frac{n_ART}{V} + \frac{n_BRT}{V} + \frac{n_CRT}{V}$

But $\frac{n_ART}{V} = P_A$, $\frac{n_BRT}{V} = P_B$, $\frac{n_CRT}{V} = P_C$

Where $P_A$, $P_B$ and $P_C$ are partial pressures of A, B and C respectively

Hence $P_T = P_A + P_B + P_C$ which is the Dalton's law of partial pressure

**Example 20**

Show that the density of gases varies directly proportional to their molar masses.

**Solution**

Using density of gas, $\rho = \frac{\text{Mass of the gas, m}}{\text{Volume Vof the gas, V}} = \frac{\text{Mass of one mole of the gas}}{\text{Volume of one mole of the gas}}$

But mass of one mole of the gas = molar mass of the gas, $M_r$

Volume of one mole of the gas = Gas molar volume, GMV or $\rho = \frac{M_r}{GMV}$

But at given temperature, GMV is constant for all gases (From Avogadro's law).

Then $\rho = \frac{M_r}{C}$ where C is constant; so $\frac{1}{C}$ gives another constant, say k

Therefore $\rho = kM_r$ and hence $\boldsymbol{\rho \propto M_r}$

**Example 21**

Oxygen can be converted to ozone according to the reaction equation: $3O_2(g) \rightarrow 2O_3(g)$

In an experiment conducted in a physical chemistry laboratory to study this conversion, a form six student used 12L of oxygen gas and all of this oxygen was converted to Ozone at s.t.p. Calculate the volume of Ozone produced.

**Solution**

From the given equation: $3O_2(g) \rightarrow 2O_3(g)$

Mole ratio of $O_2$ to $O_3$ is 3:2

But from Avogadro's law, mole ratio = volume ratio (For gases)

Thus 3L of $O_2$ produces 2L of $O_3$

Hence 12L of $O_2$ will produce $\frac{2}{3} \times 12L = 8L$

Therefore, the volume of ozone produced was 8 Litre of ozone

**Example 22**

Sulphur dioxide ($SO_2$) used in manufacturing of sulphuric acid is obtained from sulphide ores according to the following equation:

$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(g) + 8SO_2(g)$

Find the mass of oxygen in grams reacting when 75 Litres of $SO_2$ is produced at 100˚C and pressure of 1.04atm.

**Solution**

From the given equation: $4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$

8L of $SO_2$ are produced by 11L of $O_2$ (For gases: mole ratio = volume ratio)

Thus 75L of $SO_2$ will be produced by $\frac{11}{8} \times 75$L of $O_2$ = 103.125L of $O_2$

Thus 75L of $SO_2$ is produced by 103.125L of $O_2$

From ideal gas equation: $PV = \frac{m}{M_r}RT$ or $m = \frac{PVM_r}{RT}$

Where P = 1.04atm, V = 103.125L, $M_r$ = 32g/mol, $R = 0.082$

$T = 100°C = (100 + 273)K = 373K$

$m = \frac{1.04 \times 103.125 \times 32}{0.082 \times 373}$ g = 112.2g

Hence mass of oxygen is 112.2g

**Example 23**

A $2dm^3$ flask containing 4g of oxygen at 27°C;

(a) What is the pressure in the flask?
(b) When 3g of nitrogen gas is introduced in the flask (still containing oxygen gas)
  (i) What is the total pressure exerted by the gaseous mixture in the flask?
  (ii) What is the total number of molecules?
  (iii) The mixture is exploded so that nitrogen gas and oxygen gas react according to the equation. $N_2(g) + O_2(g) \rightarrow 2NO(g)$, what is the new pressure in the flask?

**Solution**

(a) From ideal gas equation: $PV = nRT$

But $n = \frac{m}{M_r}$ then $PV = \frac{m}{M_r}RT$ or $P = \frac{mRT}{VM_R}$

Where: $m = 4g, R = 0.082, T = 27°C = (27 + 273)K = 300K, M_r = 32g/mol$

$V = 2dm^3$

Then $P = \frac{4 \times 0.082 \times 300}{2 \times 32}$ atm $= 1.5375$ atm

Hence the pressure exerted by oxygen gas in the flask is 1.5375atm

(b) (i) When 3g of nitrogen gas is introduced in the flask:

By Dalton's law of partial pressure; total pressure exerted by gaseous mixture in the flask is given by; $P_T = P_{O_2} + P_{N_2}$

But from ideal gas equation: $PV = nRT$

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

Then $P_{O_2} = \frac{n_{O_2}RT}{V}$ and $P_{N_2} = \frac{n_{N_2}RT}{V}$

Thus $P_T = \frac{n_{O_2}RT}{V} + \frac{n_{N_2}RT}{V}$

$$P_T = (n_{O_2} + n_{N_2})\frac{RT}{V}$$

$$P_T = \left(\frac{m_{O_2}}{M_{O_2}} + \frac{m_{N_2}}{M_{N_2}}\right)\frac{RT}{V}$$

$$P_T = \left(\frac{4}{32} + \frac{3}{28}\right) \times \frac{0.082\times300}{2}\ \text{atm} = 2.855\text{atm}$$

Hence total pressure exerted by gaseous mixture in flask is 2.855atm

(ii) $n_{O_2} = \frac{m_{O_2}}{M_{O_2}} = 4/32\ \text{moles} = 0.125\ \text{moles.}$

$n_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{3}{28}\text{moles} = 0.107\ \text{moles}$

Using $N = nN_A$

Where N is the number of molecules of a gas

n is the number of moles of the gas

$N_A$ is the Avogadro's number (constant) = $6.02\times 10^{23}$

Hence total number of molecules $= 0.125 \times 6.02 \times 10^{23} + 0.107 \times 6.02 \times 10^{23}$

$= 1.39664\times 10^{23}$ molecules

Hence there are $1.39664\times 10^{23}$ molecules in the flask

(iii) If the mixture is allowed to explode: (Explosions occur for very fast chemical reactions which always occur between gases).

Equation for the reaction: $N_2(g) + O_2(g) \rightarrow NO(g)$

Since mole ratio of $N_2$ to $O_2$ is 1:1, oxygen gas present in excess.

Thus (0.125 – 0.107) moles = 0.018 moles of oxygen gas remains unreacted at the end of chemical reaction

From above equation; mole ratio of $N_2$ **(limited reactant)** to NO is 1:2

Thus number of moles of NO produced is $2\times 0.107\text{moles} = 0.214$ moles

So at the end of the chemical reaction (after explosion) there are:

- 0.018 moles of unreacted oxygen gas
- 0.214 moles of produced NO(g)

Then by Dalton's law of partial pressure:

$$P_T = P_{O_2} + P_{NO} = \frac{n_{O_2}RT}{V} + \frac{n_{NO}RT}{V} = (n_{O_2} + n_{NO})\frac{RT}{V}$$

$$= (0.214 + 0.018) \times \frac{0.082\times300}{2} = 2.8536\text{atm}$$

Hence the new pressure in the flask is 2.8536atm

**Example 24**

A vessel contains 8g of oxygen at 25°C and pressure of 5atm. Assume the gas behaves ideally

(a) What is the volume of the vessel?

(b) What is the final pressure when one mole of hydrogen molecules is added at 25°C without changing volume?

(c) If the mixture in (b) above is now allowed to explode and allowed to cool to 25°C, what will be the final pressure in the vessel (In your calculations; neglect vapour pressure of water)

**Solution**

(a) From $PV = nRT$, $V = \frac{nRT}{P}$

But $n = \frac{m}{M_r}$

Thus $V = \frac{mRT}{PM_r} = \frac{8\times0.082\times298}{5\times32}\,dm^3 = 1.2218dm^3$

Hence the volume of the vessel is $1.2218dm^3$

(b) By Dalton's law of partial pressure:

Total pressure, $P_T = P_{O_2} + P_{H_2} = \frac{n_{O_2}RT}{V} + \frac{n_{H_2}RT}{V} = \left(n_{O_2} + n_{H_2}\right)\frac{RT}{V}$

But $n_{O_2} = \frac{8}{32}$ moles $= 0.25$ moles

$$P_T = (1 + 0.25) \times \frac{0.082 \times 298atm}{1.2218} = 25atm$$

Thus the final pressure is 25atm.

(c) Equation for the reaction (allowing the mixture to explode means the reaction between hydrogen and oxygen is allowed to take place)

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
1mol 0.25mol

From above equation; mole ratio of oxygen to hydrogen is 1:2, thus 0.25 moles of oxygen require $(2\times 0.25)$ moles $= 0.5$moles of hydrogen.

Thus $(1 - 0.5)$ moles $= 0.5$ moles of hydrogen remains unreacted at the end of the reaction.

So the gas which remains after explosion (reaction) is only 0.5moles of hydrogen gas and this amount of the gas will account for final pressure in the vessel.

That is; $P = \frac{n_{H_2}RT}{V} = \frac{0.5\times0.082\times298}{1.2218}atm = 10atm$

The final pressure in the vessel is 10atm

**Example 25**

A closed bulb contains 0.01 moles of helium and sample of solid ammonium chloride. The pressure of helium is measured at 27°C and is found to be 114mmHg. The bulb is heated to 327°C where all ammonium chloride decomposed according to the equation:

$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$

The final pressure in the bulb after complete decomposition was found to be 908mmHg. Assume the ideal behaviour, calculate;

(i) The partial pressure of HCl(g) at 327°C
(ii) The amount of ammonium chloride originally present in the bulb

**Solution**

(i) Gases which present at 327˚C are (after decomposition of solid $NH_4Cl$):

- Helium gas
- Ammonia ($NH_3$) gas and
- Hydrogen chloride (HCl) gas

By Dalton's law of partial pressure, total pressure exerted by gaseous mixture at 327°C is given by; $P_T = P_{He} + P_{NH_3} + P_{HCl}$

But from the given equation, mole ratio of $NH_3$ to HCl is 1:1

Thus $n_{HCl} = n_{NH_3} = n$

And hence $P_{HCl} = P_{NH_3} = P$

So $P_T = P_{He} + 2P$

But $P_{He}$ at 327°C may be found by pressure law as follows;

$P_1 = 114mmHg \quad T_1 = 27^\circ C = 300K$

And $T_2 = 327^\circ C = 600K$

By pressure law (keeping volume constant): $\frac{P_2}{T_2} = \frac{P_1}{T_1}$

or $P_2 = \left(\frac{P_1}{T_1}\right)T_2 = \frac{600\times114}{300}mmHg = 228mmHg$

Thus $P_{He}$ at 327°C is 228mmHg

But $P_T = P_{He} + 2P = 908mmHg$

Then $908 = 228 + 2P$

Or $P = 340mmHg$

Hence the partial pressure of HCl at 327°C is 340mmHg

(ii)But $P_{HCl} = \frac{n_{HCl}RT}{V}$

From which: $n_{HCl} = \frac{P_{HCl}V}{RT} = \frac{340\times V}{760\times0.082\times600}$

Using $PV = nRT$ ; $V=\frac{nRT}{P}$

**But for helium:**

When $T = 300K\ (27^\circ C), n = 0.01$ moles and $P = 114mmHg$

$$V = \frac{0.01\times0.082\times300\times760}{114}dm^{-3}$$

Then substituting the value o f V in

$$n_{HCl} = \frac{340V}{760\times0.082\times600}$$

$$n_{HCl} = \frac{340 \times 0.01 \times 0.082 \times 300 \times 760}{760 \times 0.082 \times 600 \times 114} \text{ moles } = 0.0149 \text{ moles}$$

But from the given equation

$NH_4Cl(s) \rightarrow NH_3(g) + HCl\ (g)$

Moles ratio of $NH_4Cl$ to HCl is 1:1

Thus number of moles of $NH_4Cl$ originally present in the flask was also 0.0149 moles

Using $m = nM_r$

Where molar mass of $NH_4Cl$ is 53.5g

Then m = 0.0149 × 53.5g = 0.797g

Hence amount of $NH_4Cl$ was approximately 0.8g

**Example 26**

$MgCO_3$ is heated in a closed vessel of $1dm^3$; the container is at start filled with air at 1atm and 20°C. At 800°C, the compound is completely decomposed according to the equation:

$MgCO_3(S) \rightarrow MgO(s) + CO_2\ (g)$

The total pressure after reaction at this temperature (800°C) is found to be 5atm. Calculate:

(i) The partial pressure of $CO_2$.
(ii) The amount of $MgCO_3$ originally present in the vessel
(In your calculation neglect the volume of the solid and the change of volume of the container)

**Solution**

(i) From Pressure law: $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ or $P_2 = P_1\left(\frac{T_2}{T_1}\right)$

**Then for air:**

$P_1 = 1atm\ T_1 = 20°C = 293K$ and $T_2 = 800°C = 1073K$

It follows that: $P_2 = \frac{1atm \times 1073K}{293K} = 3.66atm$

Thus the partial pressure of air at 800°C is 3.66atm

By Dalton's law of partial pressure:

$P_T = P_{CO_2} + P_{air}$ or $P_{CO_2} = P_T - P_{air} = 5atm - 3.66atm = 1.34atm$

Hence the partial pressure of $CO_2$ is 1.34 atm.

(ii) Using $n_{CO_2} = \frac{P_{CO_2}V}{RT} = \frac{1.34\times1}{0.082\times1073}$ moles $= 0.0152$moles

From the given equation:

Mole ratio of $CO_2$ to $MgCO_3$ is 1:1

Thus number of moles of $CO_2 =$ number of moles of $MgCO_3 = 0.0152mol$

Using $m = nM_r$

Mass of $MgCO_3 = 0.0152 \times 84g = 1.2768g$

Hence amount of $MgCO_3$ was approximately 1.3g

**Example 27**

A sample of butane ($C_4H_{10}$) of unknown mass is introduced into a vessel of volume, V at 28°C and 560mmHg. To this vessel is introduced 8.6787g of Neon gas until the final pressure in the vessel is 1420 mmHg at the same temperature. Calculate the volume of the vessel and the mass of butane introduced (Atomic mass of Ne is 20).

**Solution**

**For Butane:**

$P_bV = n_bRT$ ……………………………………………………….. (i)

When Neon is introduced in the vessel:

$P_T = P_b + P_{Ne}$ (By Dalton's law of partial pressure)

$= \frac{n_bRT}{V} + \frac{n_{Ne}RT}{V}$ or $PV = (n_b + n_{Ne})RT$ ………….. (ii)

It follows that $\frac{(i)}{(ii)}$ gives; $\frac{P_T}{P_b} = \frac{n_b + n_{Ne}}{n_b}$

But $n_{Ne} = \frac{8.6787}{20}$ moles $= 0.434$moles

And it is given that: $P_T = 1420$mmHg, $P_b = 560$mmHg

Then $\frac{1420}{560} = \frac{n_b + 0.434}{n_b}$

From which $n_b = 0.2826$moles

But from (i); $V = \frac{n_b RT}{P_b} = \frac{0.2826 \times 0.082 \times 301 \times 760}{560} dm^3 = 9.466 dm^3$

**Hence the volume of the vessel is an approximately 9.5 dm$^{3}$.**

Using $n = \frac{m}{M_r}$ or $m = nM_r$

Thus mass of butane, $m_b = n_b M_b$

Where $n_b = 0.2826$moles, $M_b = 58 gmol^{-1}$

Then $M_b = 0.2826 \times 58g = 16.3908g$

**Hence mass of butane was approximately 16.4g**

**Alternative solution**

By Dalton's law of partial pressure; $P_T = P_{Ne} + P_b$ or $P_{Ne} = P_T - P_b$

Where $P_T = 1420$mmHg; $P_b = 560$mmHg

Thus $P_{Ne} = (1420 - 560)$ mmHg $= 860$ mmHg

But $P_{Ne} = \frac{n_{Ne}RT}{V}$ where $n_{Ne} = \frac{m_{Ne}}{M_{Ne}}$

So $P_{Ne} = \frac{m_{Ne}RT}{VM_{Ne}}$ or $V = \frac{m_{Ne}RT}{M_{Ne}P_{Ne}} = \frac{8.6787 \times 0.082 \times 301 \times 760}{20 \times 860} dm^3 = 9.5 dm^3$

Hence the volume of the vessel is 9.5 dm$^{3}$.

Then $n_b = \frac{P_b V}{RT} = \frac{560 \times 9.5}{760 \times 0.082 \times 301}$ moles $= 0.2836$moles

Then $m_b = n_b M_b = 0.2836 \times 58g = 16.4488g$

Hence mass of butane was approximately 16.4g

**Example 28**

A 600cm$^3$ flask contains a mixture of water vapour and nitrogen gas at 127°C and 950mmHg. The flask is cooled to 27°C, the new pressure is found to be 380mmHg. What are masses of water and nitrogen in the flask?

**Solution**

Given that:

Pressure at 127°C = 950mmHg

Pressure at 27°C = 380mmHg

Volume of flask = 600cm$^3$ = 0.6L

When the flask is cooled to 27°C, water vapour condenses to liquid so pressure in the flask is exerted by nitrogen gas only. Thus $P_{N_2} = 380$mmHg at 27°C or 300K

**Thus at 27°C:**

$n_{N_2} = \frac{P_{N_2}V}{RT} = \frac{380\times0.6}{760\times0.082\times300}$ moles $= 0.0122$moles

**At 127°C;** pressure is exerted by both nitrogen gas and water vapour.

Using $P_T = \frac{(n_{H_2O} + n_{N_2})RT}{V}$,

Then $\frac{950}{760} = \frac{(n_{H_2O} + 0.0122) \times 0.082 \times 400}{0.6}$

From which $n_{H_2O} = 0.011$moles

Using $m = nM_r$, where $M_r$ of $H_2O$ and $N_2$ are 18 and $28gmol^{-1}$ respectively.

Then: Mass of water = 0.011×18g = 0.198g

Mass of nitrogen gas = 0.0122×28g = 0.3416g

**Example 29**

Nickel forms a carbonyl $Ni(CO)_n$. Deduce the value of n from the fact that: Carbon monoxide diffuse 2.46 times faster than the carbony1 compound.

(Atomic mass of Ni is 59)

**Solution**

By Graham's law of diffusion:

$$\frac{R_{CO}}{R_{Ni(CO)_n}} = \sqrt{\frac{M_{Ni(CO)_n}}{M_{CO}}} \text{ or } M_{Ni(CO)_n} = M_{CO}\left(\frac{R_{CO}}{R_{Ni(CO)_n}}\right)^2 \ldots\ldots\ldots..(i)$$

But $\frac{R_{CO}}{R_{Ni(CO)_n}} = 2.46$ (CO diffuse 2.46 times faster than carbonyl compound)

And $M_{CO} = 28g/mol$.

So by substituting above values in (i) gives; $M_{Ni(CO)_n} = 2.46^2 \times 28gmol^{-1} = 169gmol^{-1}$

Then: $59 + 28n = 169$

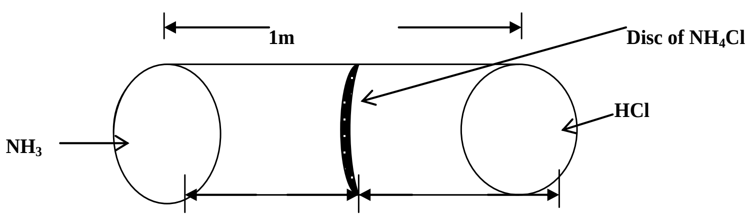
$28n = 110$ or $n = 4$.

Hence the value of n is 4.

**Example 30**

Plugs of cotton wool are soaked in concentrated ammonia solution and the other soaked in concentrated hydrochloric acid solution are inserted into opposite ends of horizontal glass tube. A disc of solid ammonium chloride forms in the tube. If the tube is 1m long, how far from the ammonia plug is the solid deposit?

**Solution**



From Graham's law of diffusion: $\frac{R_{NH_3}}{R_{HCl}} = \sqrt{\frac{M_{HCl}}{M_{NH_3}}}$

But the rate of diffusion is direct proportional to the distance travelled by the compound in the diffusion:

Thus $\frac{R_{NH_3}}{R_{HCl}} = \frac{l_{NH_3}}{l_{HCl}} = \sqrt{\frac{M_{HCl}}{M_{NH_3}}}$; Then $\frac{x}{1-x} = \sqrt{\frac{36.5}{17}}$

Solving above equation gives x = 0.59m

Hence the solid deposit is 0.59m or 59cm from the ammonia plug

**Example 31**

A mixture of carbon dioxide and carbon monoxide diffuse through a porous diaphragm in one half the time taken for the same volume of bromine vapour to diffuse through the same diaphragm. What is the composition by volume of the mixture?

**Solution**

From the Graham's law of diffusion: $\frac{t_{mixture}}{t_{Br_2}} = \sqrt{\frac{M_{mixture}}{M_{Br_2}}}$ but $t_{mixture} = \frac{1}{2}t_{Br_2}$

Then $\frac{\frac{1}{2}t_{Br_2}}{t_{Br_2}} = \sqrt{\frac{M_{mixture}}{M_{Br_2}}} = \sqrt{\frac{M_{mixture}}{160}}$

From which $M_{mixture} = \left(\frac{1}{2}\right)^2 \times 160\text{gmol}^{-1} = 40\text{gmol}^{-1}$

Thus the average molar mass of the mixture is 40g/mol

Let the percentage by volume of CO be x then the percentage of $CO_2$ will be 100 – x

Where molar masses of CO and $CO_2$ are 28g/mol and 44g/mol respectively

So $\left(\frac{28x}{100}\right) + \left(\frac{100-x}{100}\right) \times 44 = 40$

$28x + 4400 - 44x = 4000$

$16x = 400$ or $x = 25$ and $100 - x = 100 - 25 = 75$

Hence:

The percentage of CO is 25%

The percentage of $CO_2$ is 75%

**Example 32**

In 4 minutes, 16.2cm$^3$ of water vapour effuse through a small hole in the same time 8.1 cm$^3$ of the mixture of $NO_2$ and $N_2O_4$ effuse through the same hole. Calculate the percentage by volume of $NO_2$ in the mixture.

**Solution:**

By Graham's law of diffusion:

$\frac{V_{water\ vapour}}{V_{mixture}} = \sqrt{\frac{M_{mixture}}{M_{water}}}$ or $M_{mixture} = M_{water}\left(\frac{V_{water\ vapour}}{V_{mixture}}\right)^2$

Then $M_{mixture} = 18\left(\frac{16.2}{8.1}\right)^2 = 72\text{g/mol}$

Let the percentage by volume of $NO_2$ be x

Then the percentage by volume of $N_2O_4$ will be 100 – x.

Where molar mass of $NO_2$ is 46g/mol

Molar mass of $N_2O_4$ is 92 g/mol

Then $\left(\frac{46x}{100}\right) + 92\left(\frac{100 - x}{100}\right) = 72$

$46x + 9200 - 92x = 7200$

$46x = 2000$

$x = 43.5$ and $100 - x = 100 - 43.5 = 56.5$

Hence: The percentage of $NO_2$ is 43.5 %

The percentage of $N_2O_4$ is 56.5%

**Example 33**

At 27°C hydrogen is leaked through a tiny hole into a vessel for 20 minutes. Another unknown gas at the same temperature and pressure as that of hydrogen leaked through the same hole for 20 minutes. After the effusion of gases, the mixture exerts a pressure of 6 atmospheres. The hydrogen content of the mixture is 0.7 moles. If the volume of the container is 3 litres, what is the molecular weight of unknown gas?

**Solution**

By Dalton's law of partial pressure:

$P_T = P_{H_2} + P_U$

But $P_T = 6\text{atm}$ and $P_{H_2} = \frac{n_{H_2}RT}{V} = \frac{0.7 \times 0.082 \times 300}{3}\text{atm} = 5.74\text{atm}$

So $P_U = P_T - P_{H_2} = 6\text{atm} - 5.74\text{atm} = 0.26\text{atm}$

Using $n = \frac{PV}{RT}$;

So number of moles of unknown gas diffused $= \frac{0.26 \times 3}{0.082 \times 300} = 0.0317\text{moles}$

According to Avogadro's law: number of moles of gases diffused must be directly proportional to their volume diffused;

Thus $\frac{V_{H_2}}{V_U} = \frac{n_{H_2}}{n_U} = \sqrt{\frac{M_U}{M_{H_2}}}$

From which; $M_U = M_{H_2}\left(\frac{V_{H_2}}{V_U}\right)^2 = 2\left(\frac{0.7}{0.0317}\right)^2 \text{gmol}^{-1} = 975\text{gmol}^{-1}$

Hence the molecular weight of unknown gas is $975\text{gmol}^{-1}$

**Example 34**

Gas **A** of a certain volume diffuses for 580 seconds at 15 °C and 1.02atm. Find the time required for the same volume of the gas **J** to diffuse at 25°C and 1.1atm. Given that;

Molar mass of **A** = 120g/mol
Molar mass of **J** = 32g/mol

**Solution**

From Graham's law of diffusion: $\frac{R_A}{R_J} = \frac{V_A/t_A}{V_J/t_J} = \frac{V_A t_J}{V_J t_A} = \sqrt{\frac{\rho_J}{\rho_A}}$

But $V_A = V_J$ (the same volume of two gases was diffused)

It follows that; $\frac{t_J}{t_A} = \sqrt{\frac{\rho_J}{\rho_A}}$

But $\rho = \frac{PM_r}{RT}$ (from ideal gas equation)

Thus $\frac{\rho_J}{\rho_A} = \frac{P_J M_J}{RT_J} \times \frac{RT_A}{P_A M_A} = \frac{P_J M_J T_A}{P_A M_A T_J}$

Then $\frac{t_J}{t_A} = \sqrt{\frac{P_J M_J T_A}{P_A M_A T_J}}$

Substituting $\frac{t_J}{580s} = \sqrt{\frac{1.1 \times 32 \times 288}{1.02 \times 120 \times 298}}$; from which $t_J = 306s$

Hence the time required by gas J is 306 seconds

# DIGGING DEEPER EXERCISE 1

## EXERCISE 1A: BINDER QUESTIONS

**Question 1**

Explain whether you agree or you disagree with the following statement: *According to Boyle's law, equal mass of hydrogen and oxygen kept in different containers of the same volume at the same temperature exerts the same pressure.*

**Question 2**

*According to Charles's law, increasing the temperature of the gas from 10℃ to 20℃ doubles its volume.* Is this statement correct or incorrect? Explain.

**Question 3**

In the discussion of Gay-Lussac's law with her classmate, **Kipute** argued that, *"The increase of temperature from 27℃ to 327℃ doubles the pressure of a given amount of a gas provided that the volume is kept constant."* Her classmate challenged **Kipute** that her statement is wrong because Gay-Lussac's law needs the temperature to double for doubling the pressure of the gas and the increase in temperature (327℃) mentioned by **Kipute** is not twice the initial one (27℃). Do you support or oppose **Kipute's** classmate challenge? Explain.

**Question 4**

Can you use the ideal gas law for liquids? Give reason.

**Question 5**

(i) Derive an ideal gas equation.
(ii) Why the ideal gas equation is also known as equation of state?

**Question 6**

One way to state Boyle's law is; *"All other things being equal, the pressure of a gas is inversely proportional to its volume."*

(i) What is the meaning of the term "inversely proportional?"
(ii) What are the "other things" that must be equal?

**Question 7**

An alternate way to state Avogadro's law is; *"All other things being equal, the number of molecules in a gas is directly proportional to the volume of the gas."*

(i) What is the meaning of the term "directly proportional?"
(ii) What are the "other things" that must be equal?

**Question 8**

Which of the following gases diffuse more slowly than oxygen?

$$F_2,\ Ne, N_2O,\ C_2H_2,\ NO,\ Cl_2,\ H_2S$$

**Question 9**

Pressure exerted by 4g of oxygen in a container at certain temperature is twice the pressure exerted by 2g of hydrogen gas in the same container at the same temperature. With correct reasoning state whether this statement is true or false.

**Question 10**

(a) How the following are related to the amount of pressure exerted by a gas in a container?
 (i) Collision frequency
 (ii) Collision intensity
(b) How can these factors (mentioned in (a) above) be changed?

**Question 11**

Gay-Lussac's pressure law is contained in the merger of Boyle's law and Charles's law. Justify.

**Question 12**

In a flask containing 2atm of oxygen gas and 3atm of helium gas, 2mol of neon gas are added;

(i) Is there any change of amount of total pressure in the flask after the addition of neon? Explain.
(ii) What is the effect on partial pressures of oxygen and helium after the addition of neon? Explain.

# EXERCISE 1B: REAL QUESTIONS

**Question 13**

Why hot-air balloon floats in air?

**Question 14**

Propane tanks should not be kept at extreme temperatures. Explain.

**Question 15**

Air pressure in a car tyre increases during driving. Explain

**Question 16**

**Kipute** is a big funny of potato chips. One evening she went to the supermarket and bought number of bags of potato chips. She ate some of them and she found that the taste amazingly delicious. However, she was unable to finish all chips in the bags. Worrying that unconsumed potato chips would lose their wonderful flavour, she decided to store the bags of potato chips into a freezer. In the morning of the next day she taken the stored chips and started eating; surprisingly she felt disappointment-the chips are no longer delicious on the contrary to her yesterday's experience! **In terms of gas laws, offer possible explanation for this.**

**Question 17**

Sometimes leaving a bicycle in the sun on a hot day will cause a blowout. Explain.

**Question 18**

The tyres in cars are inflated to a slightly lower pressure in the summer than in the winter. Explain.

**Question 19**

A balloon filled with helium weighs much less than an identical balloon filled with oxygen.

(i) Which gas law provides better explanation of this observation?
(ii) Explain the observation by reference of the law mentioned in (i) above

**Question 20**

Bakery products like bread are fluffy. Explain why.

**Question 21**

Aerated water bottles are kept under water during summer. Explain.

**Question 22**

A flat tyre takes up less space than an inflated tyre. Explain.

**Question 23**

Account for the role of Amontons's law in the working of pressure cooker.

**Question 24**

Why a football inflated inside and then taken outdoors on a winter day shrinks slightly?

**Question 25**

Throwing an aerosol can into a fire may cause it to explode. Explain.

**Question 26**

**Kipute** is the form five student and beloved friend of yours. She learned in chemistry that according to Boyle's law, pressure and volume of the gas are inversely proportional. However, she got confusion after thinking the inflation a tyre and saw like it goes against what she learned in the chemistry. She came to you and explained her doubts; *"If you pump air into a tyre, you're increasing the pressure, and the tyre expand. Which means when the pressure is increased, the volume increases too. Isn't this a violation of Boyle's law?"* She asked. Please, assist your friend to eliminate this 'contradiction' and help her understand the inflation of the tyre in terms of gas laws.

# EXERCISE 1C: HOT QUESTIONS

**Question 27**

Consider the flask in the following diagram

(a) What are the final partial pressures of Helium and argon after the stopcock between the two flasks is opened?
(b) What is the total pressure?

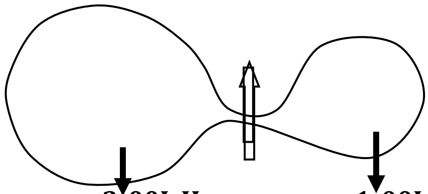



**Figure 1.3** Diagram for question 1

**Question 28**

Magnesium metal is reacted with excess HI to produce hydrogen gas. The gas is collected over water.45.82mL Of the wet hydrogen gas is collected at 30°C.The water level in the eudiometer is equalized with in another vessel before the volume of $H_2$ gas is determined. The atmospheric pressure in the laboratory is 738.72mmHg.

$$Mg(s) + 2HI(aq) \longrightarrow MgI_2(aq) + H_2(g)$$

(a) What is the vapour pressure of $H_2$ gas in the eudiometer?
(b) What mass of magnesium metal was consumed in the reaction? (Vapour pressure of water at 30°C is 31.824 mmHg).

**Question 29**

If equal amounts of the helium and argon are placed in a porous container and allowed to escape, which gas will escape faster and how much faster?

**Question 30**

What is the molecular weight of a gas which diffuses $^1/_{50}$ as fast as hydrogen?

**Question 31**

$2.278 \times 10^{-4}$ mol of an unidentified gaseous substance effused through a tiny hole in 95.7s.Under identical conditions,$1.738 \times 10^{-4}$ mol of argon takes 81.6s to effuse. What is the molar mass of the unidentified substance? (Molar mass of argon= 39.948g/mol)

**Question 32**

If a molecule of $CH_4$ diffuse a distance of 0.530m from a point sources, calculate the distance that a molecule of $N_2$ would diffuse under the same conditions for the same period of time.

**Question 33**

What is the rate of effusion for a gas that has molar mass twice that of a gas that effuses at rate of 3.62mol/min ?

**Question 34**

Given that HCl and $NH_3$ come together to form a solid $NH_4Cl$ according to the following reaction,
$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

If a 2 litre container of HCl and 5 litre container of $NH_3$ (both at stp) were connected and then allowed to react, what would the final pressure be after reaction?

**Question 35**

Suppose that 2 atm $H_2$ and 3 atm $O_2$ are put into a 10 litre container. If a spark is added and oxygen and hydrogen react to form gaseous water, calculate total pressure inside the container after reaction Assume that the temperature and volume of the container remain constant.

**Question 36**

A 10 litre container at stp is filled with both $O_2$ and $N_2$. 25% of all the atoms in the container are oxygen. Using this information, answer the following questions:

(a) What is the partial pressure of $O_2$?
(b) How many moles of $N_2$ are there in the container?
(c) What will the partial pressure of oxygen be if 2.5 mole of argon are introduced in the container?

**Question 37**

One way of making natural gas is by the so called water-gas reaction,

$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$

(a) An experiment took 20 litres of $CO_2$ reacted with 75 litres of $H_2$ at STP. How many grams of $CH_4$ would be produced?
(b) Calculate the final pressure assuming all products and reactants are ideal gases
(c) What is the mole fraction of the water in the final mixture?
(d) Explain briefly why would the final pressure in the reaction vessel mixture after reaction be much less than the prediction made in (b) above?

**Question 38**

A 2 litre tank containing oxygen at 0.5atm pressure is connected by means of a valve to a 3 litre tank containing nitrogen at 2atm at the same temperature.

(a) If the valve is opened, what will the new pressure be if the temperature remains constant?
(b) What is the partial pressure of the oxygen?
(c) What is the mole fraction of nitrogen?

**Question 39**

A 10L container has 0.3mole fraction argon. When the temperature of the container is increased by 50℃, the pressure increases by factor of 1.4. If the total number of mole of gas in the container is 1.3 moles, what was the original pressure of the argon in the container?

**Question 40**

If we open the taps given in the figure below, find the total final pressure exacted by gases.

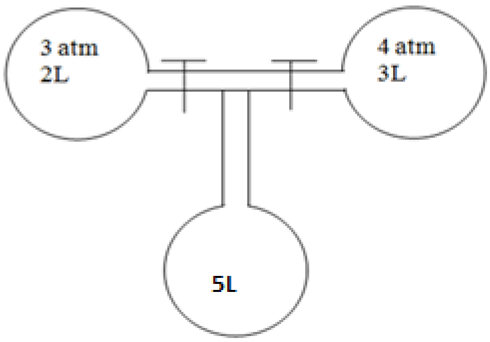



**Figure 1.4** Diagram for question 14

**Question 41**

A rigid 8.2L flask contains a mixture of 2.5moles of $H_2$, 0.5mol of $O_2$, and sufficient argon so that the partial pressure of argon in the flask in 2 atm. The temperature is 127℃.

(a) Calculate the total pressure in the flask.
(b) Calculate the mole fraction of $H_2$ in the flask
(c) Calculate the density (in $gL^{-1}$) of the mixture in the flask

The mixture in the flask is ignited by a spark and the reaction represented below occurs until one of the reactants is entirely consumed.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

(d) Give the mole fraction of all species present in the flask at the end of the reaction.

**Question 42**

$KClO_3$ is decomposed by the following reaction: $2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$

The $O_2$ produced was collected by the displacement of water at 22℃ at a total pressure of 760torr.The volume of gas collected was 1.2L and the vapour pressure of water at 22℃ is 21torr. Calculate:

(i) The partial pressure of $O_2$ in the gas collected and
(ii) The mass of $KClO_3$ in the sample that was decomposed

**Question 43**

Oxygen gas is collected over water at 22℃. If the gas was collected in a 250mL container at 740mmHg atmospheric pressure, how many grams of oxygen were collected?
Vapour pressure of water at 22℃ $= 19.8\text{mmHg}$

**Question 44**

Hydrogen gas is collected over water at 22℃. If the gas was collected at 800mmHg atmospheric pressure, what pressure of $H_2$ gas was collected?
Given that: vapour pressure of water at 15℃ is $12.8\text{mmHg}$

**Question 45**
It takes x seconds for $100\text{cm}^3$ of gas A to diffuse at certain pressure and temperature of 20℃. How long will take $200\text{cm}^3$ of gas B to diffuse at 30℃ under the same pressure?
Given that:
Molar mass of A $= 32\text{g/mol}$
Molar mass of B $= 71\text{g/mol}$

**Question 46**

*If 3atm of carbon monoxide (CO) is mixed with 2atm of oxygen in a container at 30*℃*, the total pressure in the container will be 5atm.* Is this argument correct? If it is correct, give clear reason to support your answer, and if it is not correct, calculate the correct value.

**Question 47**

A mixture of excess carbon monoxide and oxygen gas was allowed to diffuse through a porous diaphragm (after their reaction) in one half the time taken for the same volume of bromine vapour to diffuse through the same diaphragm. What is the composition by volume of the mixture?

**Question 48**

A certain dry gas is composed of 21% by volume of oxygen, 1% of argon and 78% of nitrogen. Find its density in grams per $\text{dm}^3$ at 20℃ and $98.65\text{kNm}^{-2}$ pressure.

**Question 49**

Two gas burettes, one containing $10\text{cm}^3$ of sulphur dioxide ($SO_2$) and the other containing $30\text{cm}^3$ of hydrogen sulphide ($H_2S$) both at 1 atmosphere and at 0℃ are initially separated by a stop cork. The stop cork is then opened and the two gases are allowed to mix according to the reaction:
$SO_2(g) + 2H_2S(g) \rightarrow 3S(s) + 2H_2O\ (l)$
Calculate the final pressure (in atmospheres) after the reaction has ended and the apparatus has regained its temperature of 0℃. (Assume liquid water does not exert pressure).

**Question 50**

Two glass bulbs of equal volumes joined by a narrow tube of negligible volume are containing gas at s.t.p. When one of the bulbs is lowered into a container containing melting ice and other kept in hot water, the new pressure in the bulb is 877.6mmHg. Determine the temperature of the water.

Chapter 2

# KINETIC MOLECULAR THEORY OF GASES

The gas laws that we have studied in the previous chapter, are empirical (they have been derived from experimental observations). Although these laws describe relationships that have been verified by many experiments, they do not tell us why gases follow these relationships. The **kinetic molecular theory** (KMT) is a simple model that effectively explains the gas laws.

Kinetic molecular theory of gases explains the behaviour of gases with respect to motion of its molecules (particles). It holds for ideal gases only and hence is also known as **assumptions for ideal gas law.**

## ASSUMPTIONS OF KINETIC MOLECULAR THEORY OF GASES

**Assumption 1:** A gas consists of very small particles (molecules) in a random motion of which there is a collision between gas particles themselves and the collision between gas particles and the walls of the container, thus exerting a pressure.

**Assumption 2:** Force of gravity (gravitational force) has no effect on the motion of gas particles.

**Assumption 3:** Intermolecular forces of attraction are negligible in the motion of gas particles.

**Assumption 4:** Kinetic energy of gas particles varies directly proportional to the absolute temperature

**Assumption 5:** The collision between gas particles and walls of the container is completely elastic (There is no loss in kinetic energy in the collisions).

**Assumption 6:** Volume of individual gas particles is negligible compared to the volume of the whole gas or the volume of the container.

**The reader should understand that:**

Since assumptions of KMT are based on microscopic particles found in gases, the kinetic molecular theory is sometimes known as the **microscopic model of gases**.

## DERIVATION OF KINETIC EQUATION FROM KMT

Consider N molecules of gases in the cube (container) are moving in three dimensions (directions) such that N/3 molecules are moving in each direction as shown below:

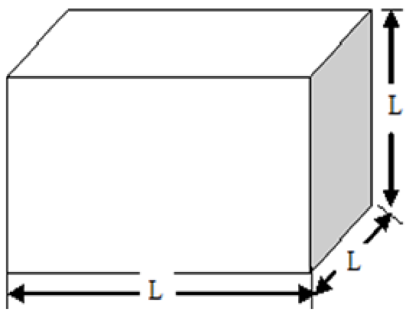



**Figure 2.1** Gas container

Consider N/3 molecules which are moving in X- direction

For a particle of mass, m moving in X- direction with root mean square speed, c;

Momentum of a particle before collision with the wall of the container = mc,

After collision, the velocity of a particle will change from c to –c as the collision is completely elastic.

Thus momentum of a particle after collision $= -\mathrm{mc}$;

So change in momentum of the particle $= mc - (-mc) = 2mc$

Force of exerted by the particle on the wall of the container, $F = \frac{\Delta mc}{t} = \frac{2mc}{t}$

Thus total force exerted on the wall of the container by $N/3$ molecules $= \frac{2Nmc}{3t}$

A particle will move a distance of 2L before making another collision.

Thus $c = \frac{2L}{t}$ or $t = \frac{2L}{c}$

Substituting $t = \frac{2L}{c}$ in $F = \frac{2Nmc}{3t}$; $F = \frac{Nmc^2}{3L}$

Using Pressure, $P = \frac{Force}{Area}$; but Area $= L^2$ and Force $= \frac{Nmc^2}{3L^2}$; then $P = \frac{Nmc^2}{3L^3}$;

But $L^3 =$ Volume of the container, V. So $P = \frac{Nmc^2}{3V}$

Hence $\mathbf{PV} = \frac{\mathbf{Nmc^2}}{\mathbf{3}}$

The final result is known as kinetic equation of gases.

## Kinetic energy of gases from kinetic equation

From the kinetic equation: $PV = \frac{Nmc^2}{3}$

But the kinetic energy of N molecules $= \frac{1}{2}Nmc^2$

Where m is the mass of one molecule and Nm is the total mass of N molecules.

So from $K.E = ½Nmc^2$, $Nmc^2 = 2K.E$

Then substituting $Nmc^2 = 2K.E$ to the above kinetic equation gives: $PV = 2/3\ K.E$

Thus $\mathbf{K.E = 3/2\ PV}$

But from ideal gas equation: $PV = nRT$

So $\mathbf{K.E} = {}^{3}/_{2}\ \mathbf{nRT}$ for n moles of gas

If n = 1 (for one mole of the gas): $\mathbf{K.E} = {}^{3}/_{2}\ \mathbf{RT}$

Since $\mathbf{R}$ is constant, $\mathbf{3/2R}$ is also constant and hence the result of kinetic energy confirm one of the assumption of kinetic theory of gases which state that: The kinetic energy of gas molecules varies directly proportional to the absolute temperature.

## Root mean square speed of a gas, c, from kinetic equation

From the kinetic equation of gases: $PV = {}^{1}/_{3}\ Nmc^2$

If $N = N_A = 6.02 \times 10^{23}$ molecules, $n = 1$ (n is the number of moles of the gas)

And $Nm = N_A m = M_r$ ($M_r$ is the molar mass of the gas)

Then $PV = \frac{M_r c^2}{3}$ but for $n = 1, PV = RT$

Then $RT = \frac{M_r c^2}{3}$ or $c^2 = \frac{3RT}{M_r}$

Hence $\mathbf{c} = \sqrt{\dfrac{\mathbf{3RT}}{\mathbf{M_r}}}$

Where c is the root mean square (r.m.s) speed or velocity of gas molecules

**Be careful!**

In the formula, $c = \sqrt{\frac{3RT}{Mr}}$ ; R must be $8.314\text{Jmol}^{-1}\text{K}^{-1}$(**not** $0.082\text{atm Lmol}^{-1}\text{K}^{-1}$) and $M_r$ must be in kg/mol(**not** g/mol) so as to give the value of c in m/s.

**The kinetic energy (K.E) can also be deduced from the above equation for the root mean square speed as follows:** From $c = \sqrt{\frac{3RT}{M_r}}$

But kinetic energy(K. E)of the gas $= \frac{1}{2}mc^2$ where m is the given mass of the gas

But $c = \sqrt{\dfrac{3RT}{M_r}}$

Then $K.E = \dfrac{1}{2}m\left(\sqrt{\dfrac{3RT}{M_r}}\right)^2 = \dfrac{3mRT}{2M_r}$

But $\dfrac{m}{M_r} = n$; So $\mathbf{K.E} = \dfrac{\mathbf{3}}{\mathbf{2}}\mathbf{nRT}$ for n moles of the gas

When $n = 1$, the equation become $\mathbf{K.E} = \dfrac{\mathbf{3}}{\mathbf{2}}\mathbf{RT}$ for 1 mole of the gas

## Derivation of Boyle's law and Charles's law from kinetic equation of gases

From the kinetic equation of gases: $PV = \frac{N}{3}mc^2$; but $K.E = \frac{1}{2}Nmc^2$ or $Nmc^2 = 2K.E$

Then $PV = \dfrac{2}{3}K.E$

From one of the assumption of kinetic theory of gases; $K.E \propto T$

Thus $K.E = kT$ where k is the constant for proportionality

Therefore; $PV = \dfrac{2}{3}kT$ ……………………………………………………..(i)

**If T is constant:**

$\dfrac{2}{3}kT$ = Constant and therefore (i) become: PV = Constant or $V = \dfrac{\text{Constant}}{P}$

Hence $\mathbf{V} \propto \dfrac{\mathbf{1}}{\mathbf{P}}$

The result is Boyle's law which states that: The volume of the fixed mass of the gas varies inversely proportional to its pressure at constant temperature.

**If P is constant:**

$\dfrac{2k}{3P}$ = Constant and therefore the equation (i)above become: V = Constant × T

Hence $\mathbf{V} \propto \mathbf{T}$

The result is Charles's law which states that: The volume of the fixed mass of the gas varies directly proportional to its absolute temperature at constant pressure.

Similarly pressure-temperature law can be deduced by keeping volume, V constant in the equation: $PV = \frac{2}{3}kT$ (On your own try to confirm this).

## Derivation of general gas equation from kinetic equation of gases

From the kinetic equation of gases; $PV = \frac{Nmc^2}{3}$

But $K.E = \frac{1}{2}Nmc^2$ or $Nmc^2 = 2K.E$

Then $PV = \frac{2}{3}K.E$

From one of the assumption of kinetic theory of gases; $K.E \propto T$

Thus $K.E = kT$ where k is the constant for proportionality

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

But $\frac{2}{3}k = \text{Constant}$; so $PV = \text{Constant} \times T$ or $\frac{PV}{T} = \text{Constant}$

Hence $\frac{\mathbf{P_1V_1}}{\mathbf{T_1}} = \frac{\mathbf{P_2V_2}}{\mathbf{T_2}} = \frac{\mathbf{P_3V_3}}{\mathbf{T_3}} = \cdots \ldots \ldots \ldots = \frac{\mathbf{P_nV_n}}{\mathbf{T_n}}$ which is general gas equation

## Derivation of Avogadro's law from kinetic equation of gases

From the kinetic equation of gases; $PV = \frac{Nmc^2}{3}$

**For two gases, say 1 and 2**

$P_1V_1 = \frac{N_1m_1{c_1}^2}{3} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots .(i)$

$P_2V_2 = \frac{N_2m_2{c_2}^2}{3} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots .(ii)$

But kinetic energy of one molecule of a gas, $K.E = \frac{1}{2}mc^2$; then $2K.E = mc^2$

Equation(i) is then become $P_1V_1 = \frac{N_1K.E_1}{3} \ldots \ldots \ldots \ldots \ldots \ldots \ldots ..(iii)$

Equation(ii) is then become $P_2V_2 = \frac{N_2K.E_2}{3} \ldots \ldots \ldots \ldots \ldots \ldots \ldots ..(iv)$

But $K.E \propto T$ or $K.E = kT$(From one of the assumption of kinetic theory of gases)

Equation (iii) is then become $P_1V_1 = \frac{2}{3}N_1kT_1 \ldots \ldots \ldots \ldots \ldots \ldots \ldots (v)$

Equation (iv) is then become $P_2V_2 = \frac{2}{3}N_2kT_2 \ldots \ldots \ldots \ldots \ldots \ldots \ldots (vi)$

For constant pressure and temperature; $P_1 = P_2 = P$ and $T_1 = T_2 = T$

The last two equations are then become:

$PV_1 = \frac{2}{3}N_1kT \ldots \ldots \ldots \ldots \ldots \ldots \ldots (vii)$

$PV_2 = \frac{2}{3}N_2kT \ldots \ldots \ldots \ldots \ldots \ldots \ldots (viii)$

$\frac{(viii)}{(vii)}$ gives: $\mathbf{\frac{V_2}{V_1} = \frac{N_2}{N_1}}$

(This is the form of **Avogadro's law** which states that: The volume of the gas varies directly proportional to its number of molecules or moles at constant temperature and pressure)

**If $V_1 = V_2$ (Equal volume of two gases)**

Then $= \frac{V_2}{V_1} = 1$, so $\frac{V_2}{V_1} = \frac{N_2}{N_1} = 1$

Hence **$N_1 = N_2$** which is more famous forms of Avogadro's law which states that: Equal volume of different gases at constant conditions of temperature and pressure contain the same number of molecules (or moles).

## Derivation of Graham's law of diffusion / effusion from kinetic equation of gases

From kinetic equation of gases: $PV = \frac{N}{3}mc^2$

But Nm is the total mass for N molecules of the gas, $m_g$;

It follows that: $PV = \frac{m_g c^2}{3}$

From which $P = \frac{m_g c^2}{3V}$

But $\frac{m_g}{V}$ density of the gas, $\rho_g$

Thus $P = \frac{\rho_g c^2}{3}$ or $c^2 = \frac{3P}{\rho_g}$

Whence $c = \sqrt{\frac{3P}{\rho_g}}$

If pressure P, is constant, $\sqrt{3P} = $ constant

Then it becomes; $c = \frac{\text{constant}}{\sqrt{\rho_g}}$ or $c \propto \frac{1}{\sqrt{\rho_g}}$

Since the speed of the gas is directly proportional to the rate of diffusion (or effusion) of the gas, it can be concluded that:

Rate of diffusion $\propto \frac{1}{\sqrt{\rho_g}}$ which is the Graham's law of diffusion

The final result is equivalent to **Graham's law of diffusion or effusion** which state that: The rates of diffusion or effusion of gases at given (constant) temperature and pressure varies inversely proportional to the square root of their densities.

## Derivation of ideal gas equation from kinetic equation of gases

From the kinetic equation of gases; $PV = \frac{Nmc^2}{3}$

But $K.E = \frac{1}{2}mc^2$ (for one molecule of the gas)

Or $mc^2 = 2K.E$; Then $PV = \frac{2}{3}N \times K.E$

But from one of the assumptions of kinetic theory of gases: $K.E \propto T$

Then $K.E = kT$ where k is constant for proportionality and $PV = \frac{2}{3}NkT$

But $\frac{N}{N_A} = n$ or $N = nN_A$ where n is the number of moles of the gas

Substituting $N = nN_A$ to $PV = \frac{2}{3}NkT$ gives $PV = \frac{2}{3}nN_AkT$

Since $N_A$ is constant, $\frac{2}{3}N_A k$ gives another constant, R

Hence **PV = nRT** this is ideal gas equation.

**Example 1**

Deduce the Dalton's law of partial pressure from kinetic equation of gases:

**Solution**

From kinetic equation of gases: $PV = \frac{Nmc^2}{3}$ or $P = \frac{Nmc^2}{3V}$

For mixture of three gases say, **A, B** and **C** with their respective number of molecules (which exert total pressure, $P_T$ in the container) $N_A$, $N_B$ and $N_C$

Thus $P_T = \frac{(N_A + N_B + N_C)mc^2}{3V} = \frac{N_A mc^2}{3V} + \frac{N_B mc^2}{3V} + \frac{N_C mc^2}{3V}$

But: $\frac{N_A mc^2}{3V} = P_A$, $\frac{N_B mc^2}{3V} = P_B$, $\frac{N_C mc^2}{3V} = P_C$

Where $P_A$, $P_B$ and $P_C$ are partial pressures of **A**, **B** and **C** respectively

Hence $\mathbf{P_T = P_A + P_B + P_C}$ which is Dalton's law of partial pressure and the law states that: "The total pressure exerted in the container of the mixture of two or more gases is equal to the summation of their partial pressures provided that the gases do not react''

**Example 2**

How long will it take a nitrogen dioxide molecule to travel 25 metres at STP?

**Solution**

Velocity (c) of the gas is given by the following equation:

$c = \sqrt{\frac{3RT}{M_r}}$ where $R = 8.314 J mol^{-1} K^{-1}, T = 273K, M_r = 46 g/mol = 4.6 \times 10^{-2} kg/mol$

Substituting $c = \sqrt{\frac{3 \times 8.314 \times 273}{4.6 \times 10^{-2}}} m/s = 384.74 m/s$

$\text{Time} = \frac{\text{Distance travelled}}{\text{Velocity}} = \frac{25}{384.74} s = 0.06498 s$

It will take 0.06498seconds

**Example 3**

Given that: PV = ⅓ $Nmc^2$, calculate the energy of 1mole of an ideal gas at 27°C.

**Solution**

Given that: $PV = \frac{Nmc^2}{3}$

But the kinetic energy of N molecules $= \frac{1}{2}Nmc^2$

Where m is the mass of one molecule and Nm is the total mass of N molecules.

So from $K.E = ½Nmc^2$, $Nmc^2 = 2K.E$

Then substituting $Nmc^2 = 2K.E$ to the above kinetic equation gives: $PV = 2/3\ K.E$

Thus $K.E = 3/2\ PV$

But from ideal gas equation: $PV = nRT$

So $K.E = {}^3/_2\ nRT$ for n moles of gas

If n = 1 (for one mole of the gas): $K.E = {}^3/_2\ RT$

$R = 8.314, T = 25°C = 298K$

$K.E = {}^3/_2 \times 8.314 \times 298 J = 3716.358 J$

Hence kinetic energy for one mole of the gas is $3716.358 J$ or $3.716358 kJ$

# DIGGING DEEPER EXERCISE 2

## EXERCISE 2A: BINDER QUESTIONS

**Question 1**

What is the kinetic theory's main foundation?

**Question 2**

What are the three main components of the kinetic molecular theory of gases?

**Question 3**

How does the concept of pressure follow from the kinetic molecular theory?

**Question 4**

What is the kinetic gas equation?

**Question 5**

Arrange the following gases in order of increasing their average molecular speed at $25°C$.

$$Cl_2, O_2, F_2, N_2$$

**Question 6**

At certain temperature, hydrogen molecules move at an average velocity of $1.84 \times 10^3 m/s$. Estimate the molar mass of a gas whose molecules have an average velocity of $311 m/s$. (molar mass of hydrogen gas $= 2.02 g/mol$).

## EXERCISE 2B: REAL QUESTIONS

**Question 7**

Observations about real gases can be explained at the molecular level according to the kinetic molecular theory of gases and ideas about intermolecular forces. Explain how each of the following observations can be interpreted according to those concepts.

(i) When a gas-filled balloon is cooled, it shrinks in volume; this occurs no matter what gas is originally placed in the balloon.
(ii) When the balloon described in (i) is cooled further, the volume does not become zero; the gas becomes a liquid or solid.

**Question 8**

When $NH_3$ gas is introduced at one end of a long tube and HCl gas is introduced simultaneously at the other end, a ring of white ammonium chloride is observed to form in the tube after a few minutes .This ring is closer to the HCl end of the tube than the $NH_3$ end. Explain.

**Question 9**

A flag waves in wind. Explain.

**Question 10**

If helium gas is cooled, will the distribution of velocities look more like that of $H_2$ or of $H_2O$? Explain your answer.

**Question 11**

It is harder to smell perfume in the cold room. Explain.

# EXERCISE 2C: HOT QUESTIONS

**Question 12**

At what temperature will the velocity of oxygen equal the velocity of hydrogen at 25℃?

**Question 13**

At what temperature does nitrogen have exactly twice velocity of chlorine gas? $N_2 = 28\text{g/mol}$ and $Cl_2 = 70.9\ \text{g/mol}$ (Assume chlorine is at 25℃)

**Question 14**

Give qualitative explanation on how Boyle's law, Charles's law and Avogadro's law agree with kinetic molecular theory of gases.

**Question 15**

Using the postulates of the kinetic molecular theory, explain why a gas uniformly fills a container of any shape.

**Question 16**

Can the speed of a given molecule in a gas double at constant temperature? Explain your answer.

**Question 17**

Describe what happens to the average kinetic energy of ideal gas molecules when the conditions are changed as follows:

(i) The pressure of the gas is increased by reducing the volume at constant temperature.
(ii) The pressure of the gas is increased by increasing the temperature at constant volume.
(iii) The average velocity of the molecules is increased by a factor of 2.

**Chapter 3**

# DEVIATION OF REAL GAS FROM IDEAL GAS LAW

Both gas laws and kinetic molecular theory we have studied so far are only compatible with ideal behaviour of gases. Those laws and theory are just 'shadow' of real truth of behaviour of gases we are experiencing in our real life. The simple truth that all gases can be liquefied, is quite opposite to what these laws and theory told us! It the no doubt evidence that there are intermolecular forces existing between gas molecules, the real truth which is completely against the 'truth shadow' we had seen in the previous chapters. Not only the presence of intermolecular forces breaks what we can call splendid gas laws and our beloved KMT theory, but there are also other real observations which altogether are going to establish new facts about how gas behave in the real world of imperfection!

In the ideal world were perfection exists, there are **ideal gases** (also known as **perfect gases**) which may be defined as *gases which obey Charles's law, Boyle's law as well as ideal gas equation and their behaviour are well explained by kinetic molecular theory of gases*.

However, in the real world where perfection does not exist, the concept of ideal gas is just hypothetical because all gases are **real** (**non- ideal),** that is, there is no gas which is totally ideal due to the following reasons:

- There are intermolecular forces of attraction existing between gas molecules.
- Individual gas molecules occupy space (have volume).
- Collision between gas molecules and container's wall is **not** perfectly elastic.

Among the four variables (P, V, n and T) of gaseous state, pressure and volume are only victims of such imperfection. Consequently, we have two types of deviations of real gas from ideal behaviour which are **pressure deviation** and **volume deviation**.

## PRESSURE DEVIATION OF REAL GASES

At high temperature, gas molecules are moving so fast that the high kinetic energy they possess tends to break any possible intermolecular attraction immediately.

- Thus the effect of the intermolecular forces of attraction in properties of gases at high temperature is negligible.

When the temperature decreases, the gas molecules move more slowly, and therefore they have small kinetic energy. This kinetic energy is not enough to break all of the intermolecular attraction between them.

- Thus at lower temperature, the intermolecular forces of attraction between gas molecules cannot be neglected and consequently the gas does not behave like ideal gas.

***How do these intermolecular attractions affect properties of real gases?***
When the intermolecular attractions between gas molecules are significant, the measured pressure of a real gas becomes less than the pressure predicted by the ideal gas equation.

That is $P_{\text{real gas}} < P_{\text{ideal gas}}$

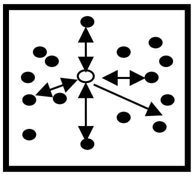
Where;

$P_{\text{real gas}}$ is the measured pressure

$P_{\text{ideal gas}}$ is the pressure calculated from the ideal gas equation with measured T and V by using $\frac{nRT}{V}$

**Digging deeper!**

To have clear understanding of why the pressure of real gas is less than the predicted pressure for ideal gas, consider a single gas molecule moving in the container with millions of gas molecules.



Where ○ represents the gas molecule in our consideration

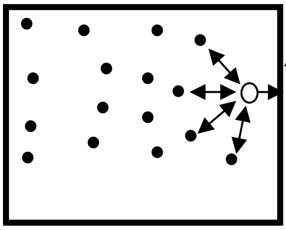
● represents other gas molecules in the container

⟷ represents intermolecular attraction between the gas molecule in our consideration and other gas molecules

⟶ represents the direction of the gas molecule in our consideration (the head of the arrow directs where the gas is going in the container).

When the gas molecule in our consideration is in the middle of the container, there is no net effect of the intermolecular attraction. It will be attracted to some extent to all the other molecules around it, but on average, those attractions will cancel out to each other as for any attraction acting upon the molecule on one direction there is corresponding attraction acting upon the molecule on opposite direction.

- So despite all the intermolecular attraction it is experiencing, our molecule will just continue to move in the same direction at the same speed. But that is different if our molecule is just about to hit the wall of the container.




From the above figure, it is clearly seen that:

- When our gas molecule is just about to hit the container wall, there is no any gas molecule in front of it and hence there is net intermolecular attraction acting backward on the molecule (the molecule is pulled backward).
- The pull (intermolecular attraction acting backward of the gas molecule) lowers the speed of the gas molecule and therefore:

**The intensity of collision between the gas molecule and the wall of the container becomes weak.** Consequently, the changes in momentum become small and hence the force exerted by the molecule on the wall becomes small too.

**The frequency of the collisions between the gas molecule and the container wall is lowered.**

The above two 'dots' explain why intermolecular forces of attraction is said to decrease the pressure of the gas.

**Extra fact you should understand!**

The decrease in speed as result of the intermolecular forces of attraction makes the collision between gas molecules and wall of the container inelastic. This is because same of kinetic energy are transformed into potential (intermolecular) energy.

- This fact is different to the one of assumptions of kinetic theory of gas which states that; the collision between gas molecules and walls of the container is perfect elastic which means that no kinetic energy is lost during the collision.

## Factors affecting extent of deviation of real gas pressure from ideal gas pressure

There are three main factors which determine the strength of intermolecular forces and therefore degree of deviation of real pressure from ideal pressure of the gas; these are;

1. Nature of the gas
2. Temperature of the gas
3. Concentration of the gas.

**1. Nature of gas**

Different gases with equal concentrations at the same conditions of temperature and pressure still have different degree of deviation of their pressure from the ideal one.

- This is because each gas has unique structure and therefore different strength of their intermolecular forces. As an example, consider the following few cases:

Ammonia gas shows greater deviation of its measured pressure (from the ideal pressure) than nitrogen gas because the ammonia ($NH_3$) has intermolecular hydrogen bonds which are stronger intermolecular forces than London dispersion forces existing between molecules of nitrogen ($N_2$).
Chlorine gas ($Cl_2$) shows greater deviation of its measured pressure than oxygen gas ($O_2$) because $Cl_2$ having larger molecular weight has stronger London dispersion forces (Van der Waals dispersion forces) than $O_2$.
Hydrogen and helium gas show smallest deviation of their measured pressure from ideal pressure. This because with only two electrons, the two gases have weakest London dispersion forces of all other gases.

- However, the two gases can be liquefied at very low temperature and pressure, justifying presence of intermolecular forces between their molecules. Among the two gases, helium being mono-atomic has weaker intermolecular forces than hydrogen gas which is diatomic (hydrogen exist as $H_2$) and therefore making electrons in $H_2$ to have more space to move around and hence stronger dispersion forces in $H_2$ than in He.

**2. Temperature of the gas**

The same gas with the same concentration show different degree of deviation at different temperature.

- As explained earlier, the lower the temperature is, the stronger intermolecular attraction there are between molecules, and the more the real gas pressure deviates from the ideal pressure.
- Gases show maximum deviation in their measured pressure (from ideal pressure) when their temperatures are very close to their boiling points (just before their liquefaction).

**3. Concentration of the gas**

The same gas at the same temperature, show different degree of deviation of its measured pressure (from the ideal pressure) if its concentration is changed.

- The higher the concentration of the gas is, the shorter the average distance between the gas molecules; and if the gas molecules are closer together, more of them will be close enough to experience significant intermolecular attraction. This greater attraction in the direction away from the wall decreases the pressure against the wall compared to that it would be if there were fewer attractions (in the low gas concentration) between the molecules.
- Therefore, although the pressure of a real gas increases as the concentration increases, it does not increase as much as it would if there were no attractions between the molecules.
- With a greater concentration of gas, there are more molecules pulling a molecule back to the centre of the container at the instant before it hits the wall.

**Very important point to understand!**

The concentration $\left(\frac{n}{V}\right)$ of a gas can be increased in two ways; either by:

1) Decreasing the volume of given amount of the gas or
2) Adding more gas to a given volume.

Thus:

The given amount of gas shows greater deviation of its measured pressure if its volume is lowered.

- The volume of the gas may be decreased by either using the container of lower volume or compressing the gas through application of higher external pressure.

With a given volume of a gas, the gas will show greater deviation to its measured pressure compared to the ideal pressure if mass (or number of moles) of gas is larger.
**Warning!**

I have personally met with students who say that;

*"Because pressure is the* ***force*** *per area, the increase in pressure will increase the intermolecular* ***forces*** *of attraction between gas molecules."* It sounds good but it is actually technically incorrect explanation! How force from external pressure is transformed to the intermolecular forces? What is the relation (if any) between the two?

The correct explanation (as explained earlier) is that;

Increase in external pressure; compress the gas and therefore decreasing its volume. Decrease in volume of the gas means its concentration is increased, decreasing the average distance between gas molecules and hence an intermolecular force of attraction is increased.

## VOLUME DEVIATION OF REAL GASES

When a gas behaves like an ideal gas, we can calculate its volume by measuring its T, P and n and then substituting them to the ideal gas equation; $V = \frac{nRT}{P}$.

- Kinetic theory of gases assumes that, the volume taken up by the gas molecules is negligible compared to the volume of the container. So if this assumption is correct, it means that; the volume calculated by the above formula$\left(V = \frac{nRT}{P}\right)$ is the volume of the container.

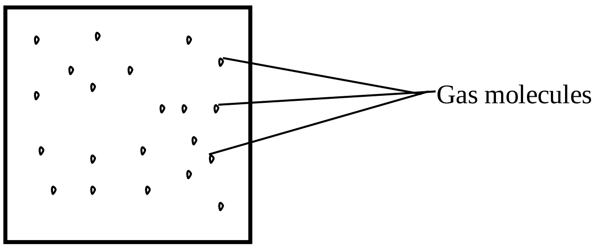



**Figure 3.1 Volume in ideal gas**

**Whole space is available for being occupied by gas molecules**

- However, for real gases, that assumption is not true. The volume of real gas (measured volume of the container) is greater than the volume that would be calculated from the ideal gas equation. The reason is that, although gas molecules are very small, **they do constitute part of its volume.**
- Thus the space in the container available for gas molecules to move around in is less than the measured volume of the container.

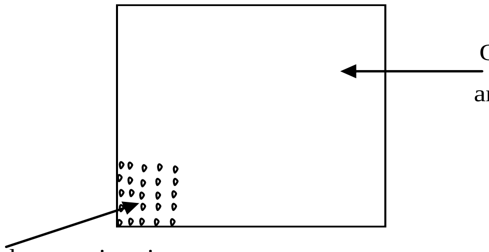



**Figure 3.2** Volume in real gas

(In the above figure; gas molecules are just intentionally kept together, just to enable you to imagine the total volume of gas molecules. But in fact, they are randomly moving in different part of the container, not settled in that ways shown in the figure).

In other words:

$$V_{\text{real gas}} \text{ or } V_{\text{container}} = V_{\text{gas molecules}} + V_{\text{empty space}}$$

Where $V_{\text{empty space}} = V_{\text{ideal gas}} = \frac{nRT}{P}$

Thus we can conclude that:

Because the gas molecules of real gas do occupy a finite volume, the real or measured volume of a gas is larger than the ideal volume calculated from ideal gas equation.

That is $V_{\text{real gas}} > V_{\text{ideal gas}}$

## Factors affecting extent of deviation of real gas volume from ideal gas volume

There are three factors for this which are:

1. Amount of the gas (number of gas molecules in the container)
2. Amount of external pressure
3. Size of gas molecules

**1. Amount of the gas**

As the mass of the gas is increased in the container, the number of gas molecules increases and therefore the percentage of the volume (of the container) occupied by the gas molecules also increases. When volume of gas molecules is increased, the volume of empty space automatically decreases; thus the increase in amount of gas increases the deviation of real gas volume from ideal gas volume by doing the following:

- It increases volume of gas molecules
- It decreases the volume of empty space (where the gas molecules can move around in)

This leads to greater difference between the measured volume of real gas and the volume ideal gas and hence greater deviation of real gas volume from the ideal volume (calculated from ideal gas equation).

**2. Amount of external pressure**

Compressing the gas through application of very high external pressure, decreases the volume of empty space and hence the percentage of the volume occupied by gas molecules increases.

Thus greater external pressure means greater deviation of real gas volume from ideal gas volume (if the compression is so high that the gas molecules are touching each other, the volume available for them to move around is zero and the deviation become maximum).

The above two factors may be combined to single factor of 'concentration of gas' but I have intentionally separated them due to difference on approach of their explanation and due to the way the factor of number of molecules (amount of the gas) appears on Van der Waals equation as we will see later.

**In one sentence:**

Application of high external pressure increases the deviation of real gas volume from ideal gas volume by decreasing the volume of empty space where the gas molecules can move around in.

**3. Size of the gas molecule (nature of the gas)**

A gas with larger molecular size, its molecules occupy greater space and therefore the gas shows greater deviation in its measured volume compared to its corresponding ideal volume because:

- Larger sized molecules occupy larger space and therefore larger volume of gas molecules.
- Large sized molecules occupy larger space and therefore smaller empty space is left in the container for gas molecules to move around in.

The molecular size is determined by two factors which are:

**Atomic size**. Greater atomic size (radius) in the molecule greater molecular size. For example $\mathrm{Cl}$ having larger atomic size than $\mathrm{F}$, $\mathrm{Cl_2(g)}$ has larger molecular size than $\mathrm{F_2}$.
**Number of atoms per one molecule**. For example $\mathrm{H_2}$ having greater number of atoms (two atoms) per molecule than He (it is mono-atomic with only one atom per molecule) has larger molecular size
**Roughly gas with molecules of large size, have large molecular weight.**

However, if the difference in the molecular weight is small, sometimes you may find the gas with lower molecular weight has larger molecular size either due to greater number of atoms per molecule or larger size of atoms which comprise the gas or both. For example $\mathrm{CH_4}$ has larger molecular size than $\mathrm{H_2O}$ although molecular weight of $\mathrm{CH_4}$(16g/mol) slight lower than that of $\mathrm{H_2O}$(18g/mol) because atomic size of C is larger than that of O and also because $\mathrm{CH_4}$ has four hydrogen atoms while $\mathrm{H_2O}$ has only two of them. So we are expecting methane gas ($\mathrm{CH_4}$ ) to show greater volume deviation from ideal volume than water vapour.
**Do you remember this fact?**
*A gas with large molecular size also has stronger dispersion intermolecular forces and therefore greater deviation of measured pressure compared to ideal gas pressure.* So we may conclude that:
The gas with large molecules deviate more from ideal behaviour because:

- Has stronger London dispersion intermolecular forces and therefore greater deviation of its measured pressure from its corresponding ideal pressure.
- Occupy larger space and therefore greater deviation of its measured volume from its corresponding ideal volume.

## VAN DER WAALS EQUATION FOR REAL GASES

The Van der Waals equation for real gases is modified equation from ideal gas equation which expresses the variation of pressure and volume of real gas with respect to variation of temperature and amount of the gas. It is the **equation of state** for real gases.

The Van der Waals equation can be written as follows:

$\left(\mathrm{P} + \mathrm{a}\left(\frac{\mathrm{n}}{\mathrm{V}}\right)^2\right)(\mathrm{V} - \mathrm{nb}) = \mathrm{nRT}$ for n moles of the real gas

But for one mole of the gas, that is n= 1, the equation become: $\left(\mathrm{P} + \frac{\mathrm{a}}{\mathrm{V}^2}\right)(\mathrm{V} - \mathrm{b}) = \mathrm{RT}$

Where: $\frac{\mathbf{a}}{\mathbf{V}^2}$ is the factor for pressure correction of real gases to ideal behaviour. It is known as **internal pressure**.

**a** is a **coefficient of attraction**, that is, attraction per unit volume. Its unit is $\mathrm{L^2atm\ mol^{-2}}$

**b** is the factor for volume correction of real gas to ideal behaviour. It is **effective volume** or **vibratory volume** of one mole of gas molecules. Its unit is $\mathrm{Lmol^{-1}}$.

Strictly speaking b does not reflect the actual volume of the gas molecule and has been theoretically shown to be roughly equal to 4 times the volume of the gas molecule and to thus b is also called **vibratory volume** or **effective volume** of the gas molecule.

**P** is the pressure of real gas

**V** is the volume of real gas

**T** is the absolute temperature in Kelvin

$P + a\left(\frac{n}{V}\right)^2$ is the pressure of a gas if the gas would be ideal i.e. $P_{\text{ideal gas}} = P_{\text{real gas}} + a\left(\frac{n}{V}\right)^2$

$V -$ nb is the volume of a gas if the gas would be ideal; i.e. $V_{\text{ideal gas}} = V_{\text{real gas}} - nb$

Also from the Van der Waals equation: $\left(P + a\left(\frac{n}{V}\right)^2\right) = \frac{nRT}{V-nb}$

But $P + a\left(\frac{n}{V}\right)^2$ is the pressure of a gas if the gas would be ideal

Hence $P_{\text{ideal}} = \frac{nRT}{V-nb}$

**Digging the Van der Waals equation!**

Below are miscellaneous facts associated with terms which appear in the Van der Waals equation;

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

- Greater strength of intermolecular forces in the gas, greater value of **a**.
- $a\left(\frac{n}{V}\right)^2$ represents deviation of real pressure from ideal pressure,

  That is the pressure deviation, $\Delta P = a\left(\frac{n}{V}\right)^2$
- Greater value of **a** (intermolecular forces) means greater the deviation as explained earlier.
- Greater value of $\mathbf{n}/\mathbf{V}$ (concentration) means greater deviation as explained earlier. (Also a greater value of **n** means greater deviation while greater **V** means smaller the deviation).
- **b** is the effective volume of **one mole** of gas molecules.
- **b** depends on the molecular size of the gas; larger molecular size means greater the value of **b**.
- **nb** is the total effective volume occupied by **n** moles of gas molecules.

Thus the volume deviation, $\Delta V = nb$

From which:

- Greater value of b (molecular size) means greater deviation as explained earlier.
- Greater value of n (number of moles of gas molecules) means greater deviation as explained earlier.

Below are Van der Waals constants for some gases (you should be able to explain the trend drawn on the constant values for **a** and **b** separately as explained in different parts of this chapter).

**Table 3.1 Van der Waals constants for some gases**

| Gas | Molar mass (g/mol) | a ($\mathbf{L^2 atm\ mol^{-2}}$) | b ($\mathbf{Lmol^{-1}}$) |
|---|---|---|---|
| Hydrogen ($H_2$) | 2 | 0.244 | 0.0266 |
| Helium (He) | 4 | 0.034 | 0.0237 |
| Methane ($CH_4$) | 16 | 2.25 | 0.0428 |
| Water ($H_2O$) | 18 | 5.46 | 0.0305 |
| Nitrogen ($N_2$) | 28 | 1.39 | 0.0391 |
| Carbon dioxide ($CO_2$) | 44 | 3.59 | 0.0427 |
| Carbon tetrachloride($CCl_4$) | 154 | 20.4 | 0.1383 |

## POSITIVE AND NEGATIVE DEVIATION OF REAL GAS FROM IDEAL BEHAVIOUR

The reader should recall that, for ideal gas; $PV = nRT$ where P and V are measured pressure and measured volume respectively.

But for real (non-ideal) gas, $PV \neq nRT$; it may be either $PV > nRT$ or $PV < nRT$

- The measure of deviation of real gas from ideal behaviour is known is **compression factor (Z)** or simply **compressibility.**

**By definition:**

**Compression factor** *is the ratio of the real (actual) volume to the volume predicted by the ideal gas equation.*

That is $Z = \frac{\text{Real volume}}{\text{Ideal volume}}$

If V represents real volume, the formula becomes: $Z = \frac{V}{\text{Ideal volume}}$

But ideal volume can be calculated from ideal gas equation with measured (actual) P, T and n

That is $V = \frac{nRT}{P}$ (From $PV = nRT$)

Where V is the ideal volume.

Then the formula $Z = \frac{V}{\text{ideal volume}}$ becomes $Z = \frac{V}{\frac{nRT}{P}} = \frac{PV}{nRT}$

Thus the **compression factor, Z** $= \mathbf{\frac{PV}{nRT}}$

Where P is the measured (real) pressure

V is the measured (real) volume

n is the measured number of moles

T is the measured temperature

But for ideal gas; $PV = nRT$

Hence $Z = 1$ for ideal gas

**Effect of the pressure deviation in the value of compression factor**

Pressure of real gas is less than the ideal pressure (Recall; $P_{ideal} = P_{real} + a\left(\frac{n}{V}\right)^2$)

- Then because $P_{real} < P_{ideal}$ ; $P_{real}V < nRT$(Neglecting effect of the volume deviaition)
- It follows that, from $Z = \frac{PV}{nRT}$ ; it is clearly understood that if: $PV < nRT$ (numerator value is less than denominator value), Z (quotient) will automatically be less than 1.
- That is $Z < 1$ due to deviation of real pressure from the ideal pressure.
- Because the compression factor is less than 1, in that situation the gas is said to deviate negatively from ideal behaviour (remember $Z = 1$ for real gas) and hence such kind of deviation is known as **negative deviation** of real gas.

**In one sentence we can conclude that:**

*Deviation of pressure of real gas from the ideal pressure leads to negative deviation of real gas from ideal behaviour.*

**Effect of the volume deviation in the value of compression factor**

Volume of real gas is larger than the ideal volume (Recall; $V_{ideal} = V_{real} - nb$)

- Thus because $V_{real} > V_{ideal}$; $PV_{real} > nRT$(Neglecting effect of the pressure deviation)

- It follows that, from $Z = \frac{PV}{nRT}$ ; it is clearly understood if $PV > nRT$, Z will be greater than 1.
- That is $Z > 1$ due to deviation of real volume from ideal volume
- Because the compression factor is greater than 1, in such situation the gas is said to deviate positively from the ideal behaviour and hence such kind of deviation is known as **positive deviation** of real gas.

**In one sentence……….!**

*Deviation of volume of real gas from the ideal volume leads to the positive deviation of real gas from ideal behaviour.*

***Have you seen the contradiction?***

The pressure deviation tries to makes $Z < 1$ whereas at the same time the volume deviation compete (with pressure deviation) to make $Z > 1$! What a result is actually observed? Is the pressure deviation more dominant such that $Z < 1$? Or, is the volume deviation more dominant such that $Z > 1$? Or, are the two factors counterbalance each other such that $Z = 1$?

- Experimentally it has been proved that pressure deviation is dominant at low pressure while volume deviation is dominant at high pressure
- Thus we can conclude that; at low pressure real gases tend to show negative deviation while at high pressure they tend to show positive deviation.

***Why do real gases show negative deviation at low pressure?***

At low pressure, volume of the gas (V) is very large such that the volume of individual molecules can be neglected compared to the volume of whole gas. Thus the deviation of real gas will only be significantly explained by the pressure deviation leading to the negative deviation.

**Digging deeper!**

From $V_{ideal} = V_{real} - nb$

When $V_{real}$ is very large (at low pressure), b become negligible and therefore;

$$V_{real} - nb \approx V_{real} = V_{ideal}$$

Then the Van der Waals equation,

$$\left(P + a\left(\frac{n}{v}\right)^2\right)(V - nb) = nRT \text{ becomes;}$$

$$\left(P + a\left(\frac{n}{v}\right)^2\right) V = nRT$$

And hence $PV < nRT$ or $\frac{PV}{nRT}(Z) < 1$(Negative deviation)

***Why do real gases show positive deviation at high pressure?***

At high pressure, the volume of the gas is small, and therefore the volume of individual gas molecules cannot be neglected while because the pressure is very large the effect of intermolecular forces can be neglected. Thus the deviation of real gas will only be significantly explained by the volume deviation leading to the positive deviation.

**Digging deeper!**

From $P_{ideal} = P_{real} + a\left(\frac{n}{v}\right)^2$

When $P_{real}$ is very large, $a\left(\frac{n}{v}\right)^2$ can be neglected and therefore;

$P_{real} + a\left(\frac{n}{v}\right)^2 = P_{real} = P_{ideal}$

Then the Van der Waals equation;

$\left(P + a\left(\frac{n}{v}\right)^2\right)(V - nb) = nRT$ becomes;

$P(V - nb) = nRT$

And hence $PV > nRT$ or $\frac{PV}{nRT}(Z) < 1$(positive deviation)

## Graphical representation of deviation of real gas from ideal behaviour

Positive and negative deviation of real gas from ideal behaviour can well be illustrated graphically and the resulting graph is known **Amagat's curve** which *is the plot of compression factor (Z) against pressure of gases.*

- For different gases say $H_2$, $N_2$ and $CO_2$ (at constant temperature), the Amagat's curve will look as follows:

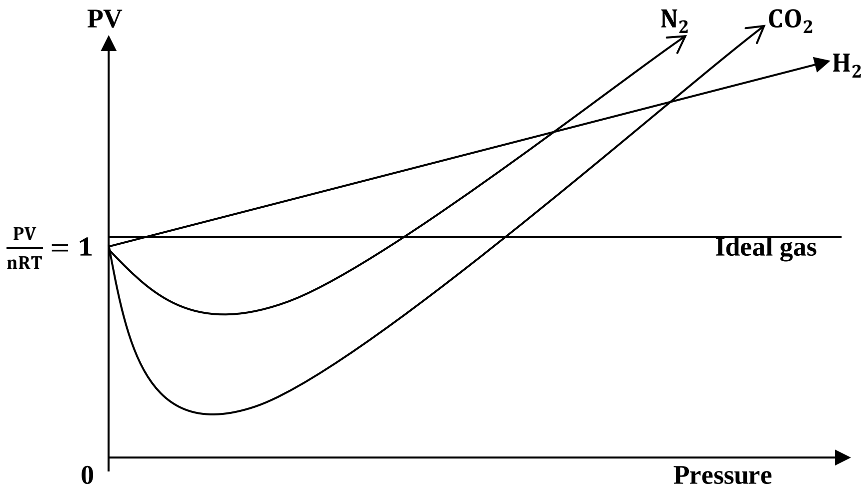



**Figure 3.3** Amagat's curve for $H_2$, $N_2$ and $CO_2$ gas

**Things to note from the graph:**

- At low pressure, gases show negative deviation (the curve pass below straight line with $Z = 1$ for ideal gas).
- At high pressure, gases show positive deviation.
- At that temperature (where data are taken), hydrogen does not show negative deviation at all. This because, $H_2$ have very small molecular weight and therefore very weak Van der Waals dispersion intermolecular forces.
- $CO_2$ shows greatest negative deviation of all gases because it has greatest molecular weight of the three gases and hence strongest Van der Waals dispersion intermolecular forces.

For the same gas at different temperatures, the Amagat's curve will look as follows:

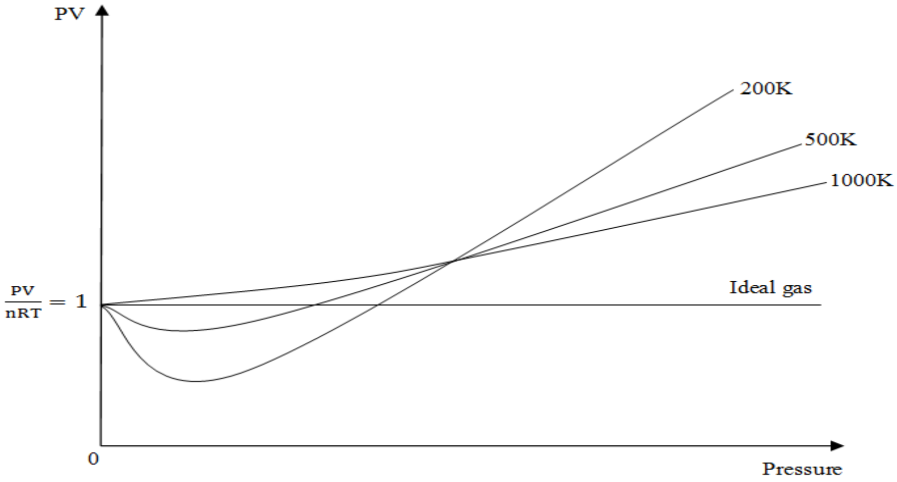



**Figure 3.4** Amagat's curve for the same gas at different temperatures

**Things to note from the graph:**

- At low pressure the gas shows negative deviation while at high pressure it shows positive deviation.
- Greatest deviation is observed at lowest temperature (200K) of the three (on your own, you should be able to explain this).
- When temperature is very large (1000K), the gas does not show negative deviation at all. (You should be able to explain this too)

## COMPARISON BETWEEN REAL GAS AND IDEAL GAS

Ideal and real gases resemble in the following ways:

- They both made of small particles that have mass
- The both constitute of mostly empty space
- They both have low density.
- They both constitute of particles which are in constant random straight line motion.

Differences between ideal and real gases are summarised in the table below.

**Table 3.2 Differences between ideal gas and real gas**

| | IDEAL GASES | | REAL GASES |
|---|---|---|---|
| 01 | Obey all gas laws under all conditions of temperature and pressure | 01 | Obey gas laws only at low pressure and high temperature |
| 02 | The volume occupied by the gas molecules is negligible as compared to the total volume occupied by the gas | 02 | The volume occupied by the gas molecules is not negligible compared to the total volume of the gas |
| 03 | The force of attraction between gas molecules are negligible | 03 | The force of attraction between the gas molecules are not negligible |
| 04 | Obey ideal gas equation, $PV = nRT$ | 03 | Obey Van der Waals equation $\left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$ |
| 05 | Collisions between gas molecules and walls of the container is elastic | 05 | Collisions between the gas molecules and walls of the container is not elastic |

**However, the reader should understand that:**

Gases become approximately ideal at the following conditions:

- High temperature
- Low pressure

At high temperature and low pressure gas molecules are more randomly moving very far apart with higher speed so that the intermolecular forces of attraction can be neglected and the gas contain the whole space of available of the container which make able to neglect the volume of the gas molecule compared to the volume of the whole gas.

**Example 1**

According to one of postulates of kinetic theory of gases, *"Gas exerts pressure in the container due to collision between gas molecules and the container's wall."* Based on this postulate, explain clearly the effect of the each of the following factors on the pressure exerted by the gas:

(i) Decreasing the volume of the container at the same temperature.
(ii) Increasing the temperature of the container.
(iii) Adding amount of the gas in the container at the same temperature

**Solution**

(i) Decreasing the volume of the container will decrease the distance between walls of the container and therefore gas molecules will hit the container's walls more frequent leading to higher pressure.
(ii) Increasing temperature, increases the speed of gas molecules and therefore making collisions between gas molecules and container's walls more energetic and more frequent and hence higher pressure.
(iii) Adding amount of the gas in the container increases the concentration of the gas leading to more frequent collision between gas molecules and container's walls and hence higher pressure.

**Example 2**

Arrange the following gases in order of increasing their magnitude of volume correction in Van-der-Waals equation.

$$CO, CO_2, He, NH_3, SF_6$$

**Solution**

The magnitude of volume correction increases as molecular size (volume) of gas increases. Gases with larger molecular size have large molecular weight. So the order is as follows:

$$SF_6 < CO_2 < CO < NH_3 < He$$

**Example 3**

(a) Under what set of experimental condition is the Van der Waals equation more applicable than the ideal gas equations?
(b) Use the Van der Waals equation: Calculate the pressure of 10moles of $NH_3$ gas in 10L vessel at 0°C 'a' $= 4.2\text{L2atm/moL}^2$, 'b' $= 0.037\ \text{L/mol}$.

**Solution**

(a) Low temperature and high pressure.
(b) From Van-der-Waals equation: $\left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$

Substituting given value: $\left(P + 4.2\left(\frac{10}{10}\right)^2\right)\left(10 - (10 \times 0.037)\right) = 10 \times 0.082 \times 273$

From which $P = 19.0461\text{atm}$

Hence the pressure of ammonia gas is 19.0461atm

**Example 4**

The Van-der-Waals equation for 'n' moles of real gas can be written as follows:

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

(i) Which single word can be used to represent the $\frac{n}{V}$?

(ii) How does the larger value of the ratio $\frac{n}{V}$ affect the pressure of the real gas?

(iii) Explain how would you make the value of the ratio, $\frac{n}{V}$ bigger?

**Solution**

(i) Concentration

(ii) Larger value of the ratio means greater pressure deviation and hence the real pressure will be much smaller compared to ideal pressure.

(iii) The ratio can be increased by decreasing the volume of fixed amount of the gas by either using the container of smaller volume or compressing the gas through the application of higher external pressure. Another way of increasing the ratio is by adding amount of the gas to the fixed volume.

# DIGGING DEEPER EXERCISE 3

## EXERCISE 3A: BINDER QUESTIONS

**Question 1**
From the standpoint of the kinetic molecular theory, explain briefly the properties of gas molecules that cause deviations from ideal behaviour.

**Question 2**
What are the shortcomings of kinetic theory for gases?

**Question 3**
At 25℃ and 1 atmosphere pressure, which of the following gases shows greatest deviation from ideal behaviour? give two reasons for your choice.

$CH_4$ $SO_2$ $O_2$ $H_2$

**Question 4**
Real gases approach ideality at low pressure, high temperature or both. Explain these observations.

**Question 5**
The concept of ideal gas is just ideal. Justify.

**Question 6**
The Van-der-Waals equation for 'n' moles of real gas can be written as follows:

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

(i) The real gas becomes more ideal with smaller value or larger value of the ratio $\frac{n}{V}$? Explain.
(ii) For given gas, is it possible to alter the value of constants 'a' and 'b'? Explain.

**Question 7**

Comment on the following statement: The molecular attraction between gas molecules is high at low temperature.

**Question 8**

*"Collision between gas particles and walls of a container is completely elastic."* What is wrong with this statement?

**Question 9**

In Van der Waals equation for real gases, the value of constant, **'a'** is larger for $NH_3$ gas than for $N_2$ gas but that of **'b'** is larger for $N_2$ gas. Explain.

**Question 10**

Predict which of the substances;

$NH_3, N_2$ $CH_2Cl_2, Cl_2, CCl_4$ has:

(i) The smallest Van der Waals **'a'** constant
(ii) The largest **'b'** constant

**Question 11**

20 moles of He is in 10L cylinder at 120atm pressure. Calculate the temperature by using:

(a) Van der Waals equation
(b) Ideal gas equation

$a = 0.0341 L^2 atm mol^{-2}, b = 0.0237 L mol^{-1}$

# EXERCISE 3B: REAL QUESTIONS

**Question 12**

It easier to liquefy ammonia gas than fluorine gas. Explain.

**Question 13**

Explain how deviation of real gas from ideal behaviour is beneficial in both gas transportation and its storage.

**Question 14**

Greater amount of investment is required in building a plant for liquefaction of helium than that of carbon dioxide. Explain.

**Question 15**

Explain how knowing compressibility factor of a gas is crucial in daily life.

**Question 16**

You have been employed in **BYAKATONDA ENERGY COMPANY**, as petroleum engineer. As one of its core activities, the company prepares liquefied natural gas (LNG). You have been visited by form six students from **MTWARA TECHNICAL SCHOOL**, who need to understand the liquefaction process as one of objectives in their study tour. Give a summary of your presentation by outlining two important steps in the process.

# EXERCISE 3C: HOT QUESTIONS

**Question 17**

When the molecular weight of a volatile liquid is calculated from the mass, volume, temperature, and pressure of a sample of the liquid when vapourised, the assumption is usually made that the gases behave ideally. In fact, at a temperature not far above the boiling point of the liquid, the liquid gas is not ideal. Explain how this would affect the results of the molecular weight determination.

**Question 18**

The Van der Waals equation of state for one mole of real gas is as follows:

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

For any given gas, the values of the constants, **'a** and '**b'** can be determined experimentally.

(a) Indicate which physical properties of molecule determine the magnitudes of the constants '**a'** and '**b'**

(b) Which of the two molecules, $H_2$ or $H_2S$ , has the higher value for **'a'** and which has the higher value for **'b'**? Explain

(c) One of the Van der Waals constants can be correlated with the boiling point of a substance. Specify which constant and how it is related to the boiling point

**Question 19**

Carbon dioxide gas (1mole) at 373K occupies 536mL of 50 atmosphere pressure. What is the calculated value of the pressure using?

(i) Ideal gas equation

(ii) Van der Waals equation

Calculate the % deviation of each value from that observed.

Given that; Van der Waals constants for carbon dioxide:

$a = 3.61L^2$ atm $mol^{-2}$ $b = 0.0428$ $Lmol^{-1}$

**Question 20**

2mol of oxygen gas in 5L container at 25℃ shows greater deviation from ideal behaviour than 1mol of the oxygen gas in the container of the same volume at the same temperature. Explain whether you agree or you disagree with this statement.

**Question 21**

Explain the following: Doubling number of moles of a real gas in a container at given temperature does not double its pressure.

**Question 22**

Pressure deviation of real gas from ideal pressure is maximum at its boiling temperature. Explain.

**Question 23**

Clearly differentiate ideality of gas at its boiling temperature and its critical temperature.

**Question 24**

Helium behave more as a gas than chlorine. Explain.

**Question 25**

Identify the postulate of the kinetic molecular theory most closely identified with the Van – der – Waals constant 'a' and explain the relationship. Repeat the procedure for the constant 'b'.

**Question 26**

The Van-der-Waals equation for 'n' moles of real gas can be written as follows:

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

(i) Which constant (a or b) is related to the gas's ability to undergo liquefaction? Give a reason to support your answer.

(ii) Does the ability of the gas to be liquefied favoured with large value or small value of the constant mentioned in (i) above? Explain.

**Question 27**

Then Van der Waals equation for real gases is: $\left(P + \frac{n^2a}{v^2}\right)(V - nb) = nRT$; where all symbols carry their usual meaning.

(i) Explain briefly the significance of the term $\frac{n^2a}{v^2}$ and nb in the equation.

(ii) The compressibility factor for one mole of a real gas at 273K and 100 atm pressure is found to be 0.5. Assuming that the volume of gas molecules is negligible, calculate Van der Waals constant. Show your work clearly including manipulation of units.

Chapter 4

# MOLAR MASS MEASUREMENT FOR VOLATILE SUBSTANCES

Volatile substances are substances which are capable of undergoing evaporation at normal temperatures and pressures. They tend to form vapour easily. One of the practical applications of gas laws is their usefulness in determining molecular mass and thus molar mass of these volatile substances.

Molecular mass is the total mass of all atoms present in one molecule of the substance while molar mass is the total mass of Avogadro's number (one mole) of molecules of the substance. One of interesting fact about molecular mass and molar mass is that, if molecular mass is given as **relative** molecular mass, then its numerical value will be equal to that of molar mass; so theoretical aspect of determining molecular mass (which is commonly given as relative molecular mass) and molar mass can be applied interchangeably.

After proper treatment of experimental results, the molar mass of a volatile liquid or solid can be calculated from measured vapour density or mass of a sample of the volatile substance by using one of the following relations:

$$\mathrm{M_r} = 2 \times \text{Vapour density or } \mathrm{M_r} = \frac{\mathrm{mRT}}{\mathrm{PV}}$$

There are various methods which may be employed in molar mass determination by using above formulae. In this book we are going to discuss two of them which are:

- Victor Meyer's method
- Duma's method

## VICTOR MEYER'S METHOD

Determination of molar mass of volatile substance by using this method is done by using by an apparatus which is known as **Victor Meyer's apparatus**.

***What Victor Meyer's apparatus consisting?***

The victor Meyer's apparatus consists of four parts:

**1. A syringe**

This is used to inject a known volume (and hence known mass if its density is known by using $m = \rho v$) of a volatile substance.

**2. A vapourisation chamber**

This is used to vapourise a sample of the volatile substance.

The vapourisation chamber is surrounded by a steam (hot vapours of water) jacket which is responsible for doing the vapourisation of the sample. So to be able to be vapourised the sample must have boiling point below 100°C; otherwise the steam would not be able to cause the vapourisation.

**3. A gas burette**

The gas burette contains water as the indicating liquid and has associated with it a side tube of the same diameter which is open to the atmosphere. It is used for measuring the volume of air displaced by the vapour of the sample formed in the vapourisation chamber.

The air displaced from the vapourisation chamber by the vapourised sample is cooled at room temperature and its volume is carefully measured by the gas burette.

Where, **volume of air displaced = volume of the vapourised sample**

(Therefore substitution of air by the actual vapour provides a means of determining the volume of the known mass of the vapour would occupy at room temperature if it could be cooled without condensation. Remember that air is still a gas at room temperature while our volatile substances condense to liquid at room temperature).

### 4. A steam generator

This is connected to the heating (steam) jacket surrounding the vapourisation chamber. It ensures constant supply of the steam for doing vapourisation in the vapourisation chamber.

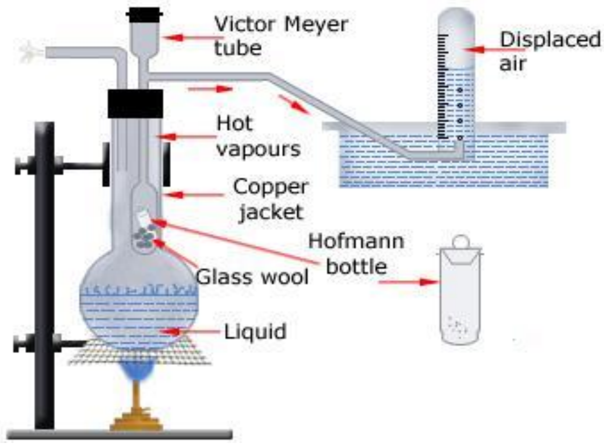



**Figure 4.1** Victor Meyer's apparatus

## DUMA'S METHOD

With this method, molar mass is calculated by measuring the mass of a known volume of a vapourised substance (liquid). The measurements are done in round flask which is known as **Duma's bulb**.

- A sample of a volatile substance is added to a pre-weighed flask (Duma's bulb).
- The flask is submerged in a boiling water bath to vapourise the substance.
- Upon heating, the vapour that is created initially pushes the air out of the flask and then the vapour begins exiting the flask until the pressure inside the flask is equal to the atmospheric pressure.
- The mass of the vapour remaining in the flask is obtained by reweighing the flask

That is; mass of the vapourised sample in the flask (Duma's bulb)

$$= \text{mass of Duma's bulb with the vapour} - \text{mass if empty Duma's bulb}$$

- Once mass of the vapourised sample has been determined, molar mass of the substance may be calculated after doing additional measurement of the pressure, temperature and the volume of the vapourised sample in the flask.

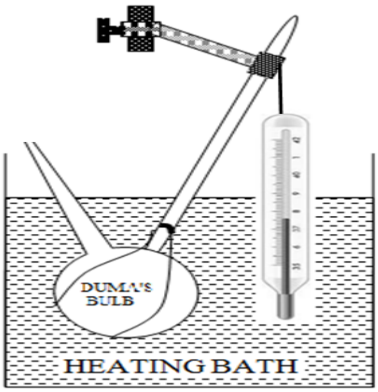



**Figure 4.2** Duma's bulb

**Example 1**

In a Victor Meyer determination; 0.292g of a substance displaced $61\text{cm}^3$ of air at 22℃ and 755mmHg. Calculate molar mass of the substance.

Given that: Vapour pressure of water at 22℃ $= 22\text{mmHg}$

**Solution**

$\text{Volume of air displaced} = \text{volume of the sample} = 61\text{cm}^3 = 0.061\text{dm}^3$

Mass of the sample $= 0.292\text{g}$

Pressure e exerted by the vapour of the sample = $\text{Total pressure} - \text{Vapour pressure of water}$

$$= (755 - 22)\text{mmHg} = 733\text{mmHg}$$

From general gas equation;

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2};\ V_2 = \frac{P_1V_1T_2}{P_2T_1}$$

Volume of the gas at $\text{stp}(T = 273, P = 760\text{mmHg})$ may be found if;

$P_1 = 733\text{mmHg}, P_2 = 760\text{mmHg}, V_1 = 0.061\text{dm}^3$

$T_1 = 295\text{K}$ And $T_2 = 273\text{K}$

Substituting $V_2 = \frac{733\times0.061\times273}{760\times295}\ \text{dm}^3 = 0.0544\text{dm}^3$

But at stp, 1mol of the gas, occupies $22.4\text{dm}^3$ and therefore mass of the gas in $22.4\text{dm}^3$ (at STP) is the molar mass of the gas

Also it is given that 0.292g of the gas occupies $0.061\text{dm}^3$(which is equivalent to $0.0544\text{dm}^3$ at STP).

Using; $n = \frac{V}{22.4\text{dm}^3/\text{mol}} = \frac{m}{M_r}$

Substituting $\frac{0.0544\text{dm}^3}{22.4\text{dm}^3/\text{mol}} = \frac{0.292\text{g}}{M_r}$

From which; $\frac{22.4}{0.0544} \times 0.292\text{g/mol}$ or $120.2\text{g/mol}$

Hence molar mass of the substance is $120.2\text{g/mol}$

**The reader should understand that:** Modern Victor Meyer's method experiment (of course in the modern Duma's method as well) uses the ideal gas law which is easier as shown below.

Using ideal gas equation, $PV = nRT$ from which it can be shown that; $M_r = \frac{mRT}{PV}$.

With:

$m = 0.292\text{g}, T = 295\text{K}, P = 733\text{mmHg}, V = 0.061\text{dm}^3$;

$$M_r = \frac{0.292 \times 0.082 \times 295}{\frac{733}{760} \times 0.061} \text{ or } 120.1\text{g/mol}$$

**Example 2**

Calculate the relative molecular mass of volatile liquid X from the following data:

Mass of Dumas bulb full of air at 10℃ and 770 mmHg $= 25.700\text{g}$

Mass of bulb sealed full of vapour of X at 100℃ and 770mmHg $= 25.759\text{g}$

Mass of bulb full of water $= 265.1\text{ g}$

Given: 1 $\text{dm}^3$ of air of s.t.p has mass of 1.293 g

**Solution**

Mass of water which fill the bulb = $(265.1 - 25.7)\text{g} = 239.4\text{g}$

Volume of bulb = volume of water $= \frac{m}{\rho} = \frac{239.4\text{g}}{1\text{g/cm}^3} = 239.4\text{cm}^3$

But at s.t.p $1\text{dm}^3$ of air contain 1.293g

$P_1 = 760\text{mmHg}, V_1 = 1\text{dm}^3, T_1 = 273\text{K}$

$P_2 = 770\text{mmHg}, T_2 = 283\text{K}, V_2 = ?$

$V_2 = \left(\frac{283}{273}\right)\left(\frac{760}{770}\right) \times 1\text{dm}^3 = 1.0232\text{dm}^3$

Thus mass of air filled in the bulb $= \frac{0.2394 \times 1.293}{1.0232} = 0.303\text{g}$

So mass of the bulb is $(25.7 - 0.303)\ \text{g} = 25.397\text{g}$

Mass of vapour of X $= (25.759 - 25.397)\ \text{g} = 0.362\text{g}$

$M_r = \frac{mRT}{PV} = \frac{0.362 \times 0.082 \times 373 \times 760}{770 \times 0.2394} = 45.6\text{g/mol}$

Hence the relative molecular mass of X is $45.6\text{g/mol}$

## ABNORMAL RESULT IN MOLAR MASS MEASUREMENT OF GASES

Sometimes measurement of molar mass of gases gives unexpected results by giving measured molar mass of either greater or smaller than the expected one. This may be either due to **dissociation** or **association**.

### Dissociation of gases

This is splitting of a large molecule into two or smaller molecules. Thus dissociation leads to increase in number of gas particles such that the observed number of gas particles (molecules) becomes greater than the expected number of gas particles.

But increase in number of gas molecules (particles) leads to increase in volume of the gas. So from the ideal gas equation which can be written as $PV = \frac{m}{M_r}RT$; it is clearly understood that the volume (V) of the gas varies inversely proportional to its molar mass ($M_r$). So **the increase in volume of the gas as the result of dissociation leads to decrease in molar mass of the gas.**

Hence the dissociation makes the measured (or observed) molar mass of the gas to be smaller than the expected one as its normal molecular formula suggests.

A fraction of gas molecules which has been dissociated is known as a **degree of dissociation, α**

Thus $\alpha = \frac{\text{Number of gas molecules dissociated}}{\text{Original number of gas molecules before dissociation}}$

A good example of dissociation is the dissociation of nitrogen tetraoxide ($N_2O_4$) into nitrogen dioxide ($NO_2$) and oxygen gas according to the following equation: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

### Association of gases

This is the combining of more than one small molecule to form one larger molecule. So association leads to decrease in number of gas molecules so that the observed number of gas molecules becomes smaller than the expected one.

The decrease in number of gas molecules leads to decrease in volume of the gas, so from the ideal gas equation; $PV = \frac{m}{M_r}RT$ where volume of the gas varies inversely proportional to its molar mass, **the molar mass of the gas must increase as result of association.** Hence association makes the measured molar mass to be greater than the expected one as its normal molecular formula suggests.

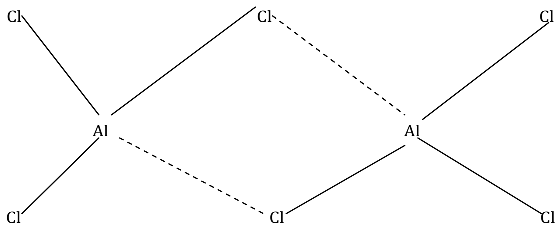
A fraction of gas molecules which has been associated is known as the **degree of association, α**

$$\text{Thus } \alpha = \frac{\text{Number of gas molecules associated}}{\text{Original number of gas molecules before association}}$$

A good example of association is the association in aluminum chloride:

In vapour phase two molecules of aluminum chloride associates (**dimerises**) to form a single larger molecule which is known as **dimer.** The process of **dimerisation** in aluminum chloride makes its observed (measured) molar mass to be twice the expected one.

This can be illustrated as follows:




**Dimer of aluminum chloride which correspond to the molecular formula of $Al_2Cl_6$**

## Calculations of degree of dissociation and association

**Degree of dissociation**

Consider one molecule of a gas $\mathbf{A_xB_y}$ which dissociate to form **a** molecules of $\mathbf{A_c}$ and **b** molecules of $B_d$ where $\mathbf{a} + \mathbf{b} = \mathrm{N}$ which is the total number of molecules formed after dissociation.

That is: $\mathbf{A_xB_y}(g) \rightleftharpoons \mathbf{aA_c(g)} + \mathbf{bB_d}(g)$

| | | | |
|---|---|---|---|
| 1 | 0 | 0 | Initial number of molecules before dissociation |
| $1 - \alpha$ | $\mathbf{a}\alpha$ | $\mathbf{b}\alpha$ | Number of molecules after dissociation |

Where α is numerically equal to degree of dissociation = fraction of the molecules dissociated.

From the above equation:

Expected number of molecules (without dissociation) = 1

Observed number of molecules (after dissociation) = $1 - \alpha + \mathbf{a}\alpha + \mathbf{b}\alpha = 1 + \alpha(\mathbf{a} + \mathbf{b} - 1)$

But $\mathbf{a} + \mathbf{b} = \mathrm{N}$

So observed number of molecules = $1 + \alpha(\mathrm{N} - 1)$

The ratio of observed number of particles to expected number of particles is known as **Vant Hoff's factor**, **i**

$$\text{Thus i} = \frac{\text{Observed number of paricles}}{\text{Expected number of particles}} = \frac{1 + \alpha(\mathrm{N} - 1)}{1} \quad \text{or i} = 1 + \alpha(\mathrm{N} - 1)$$

$$\text{Hence } \boldsymbol{\alpha} = \frac{\mathbf{i - 1}}{\mathbf{N - 1}}$$

Where **α** is the degree of dissociation

**i** is the Van't Hoff's factor

**N** is the number of molecules formed after dissociation

**It should be noted that:**

For dissociation; i > 1; because observed number of particles must be greater than the expected one.

**Degree of association**

Consider $\mathbf{N}$ molecules of $\mathbf{A_xB_y}$ associate to form one molecule of $\mathbf{A_{xN}B_{yN}}$ according to the following equation:

| $\mathbf{NA_xB_y}(g)$ | $\rightleftharpoons$ | $\mathbf{A_{xN}B_{yN}}\ (g)$ | |
|---|---|---|---|
| $\mathbf{N}$ | | $0$ | Initial number molecules before association |
| $\mathbf{N - N\alpha}$ | | $\boldsymbol{\alpha}$ | Number of molecules after association |

Where α is the degree of association

Expected number of molecules (without association) = $\mathbf{N}$

Observed number of molecules (after association) = $\mathbf{N} - \mathbf{N}\alpha + \alpha$

$$= \mathbf{N} + \alpha(1 - \mathbf{N})$$

Then $i = \dfrac{\text{Observed number of particles(molecules)}}{\text{Expected number of particles(molecules)}} = \dfrac{\mathbf{N} + \alpha(1-\mathbf{N})}{\mathbf{N}}$ or $\alpha = \dfrac{i\mathbf{N} + \mathbf{N}}{1 - \mathbf{N}}$

Dividing by N throughout the expression $\dfrac{i\mathbf{N} + \mathbf{N}}{1 - \mathbf{N}}$ gives $\boldsymbol{\alpha} = \dfrac{\mathbf{i - 1}}{\frac{\mathbf{1}}{\mathbf{N}} - \mathbf{1}}$

Hence degree of association is given by; $\boldsymbol{\alpha} = \dfrac{\mathbf{i - 1}}{\frac{\mathbf{1}}{\mathbf{N}} - \mathbf{1}}$

**It should be noted that:**

- For association, i < 1; because observed number of particles must be less than the expected one.
- If $i = 1$ then there is neither dissociation nor association.
- Degree of dissociation (or association) may be given as a fraction or percentage.

**The reader should understand that:**

From $i = \dfrac{\text{Observed number of particles}}{\text{Expected number of particles}}$:

- Since number of gas particles varies directly proportional to its volume, then:

  $i = \dfrac{\text{Observed(measured)volume of the gas}}{\text{Expected volume of the gas}}$

- As number of gas particles varies directly proportional to the pressure exerted by the gas, then:

$$i = \frac{\text{Observed(measured) pressure of the gas}}{\text{Expected pressure of the gas}}$$

- Since number of gas particles varies directly proportional to the volume of the gas which in turn varies inversely proportional to the molar mass of the gas, then:

$$i = \frac{\text{Expected molar mass}}{\text{Measured(observed) molar mass}}$$

**Example 3**

Nitrogen dioxide exists in an equilibrium mixture: $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

The relative molar mass of nitrogen dioxide at 25°C is 80. What is the percentage of molecules in the mixture is $N_2O_4$ ?

**Solution**

Expected molar mass of $N_2O_4$ is $92g/mol\ ((2 \times 14) + (4 \times 16)) = 92g/mol$

Measured molar mass of $N_2O_4$ is $80g/mol$

Using $i = \frac{\text{Expected molar mass}}{\text{Measured molar mass}} = \frac{92gmol^{-1}}{80gmol^{-1}} = 1.15$

From the equation: $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

$1 - \alpha \qquad 2\alpha$ After association N = 2

Using $\alpha = \frac{i-1}{N-1} = \frac{1.15-1}{2-1} = 0.15$ or 15%

But total number of molecules of $N_2O_4$ after dissociation:

$= 1 - \alpha + 2\alpha = (1 + \alpha)$ Molecules

$\%N_2O_4$ in the mixture $= \frac{n_{N_2O_4}}{n_T} \times 100\% = \frac{1-\alpha}{1+\alpha} \times 100\% = \left(\frac{1-0.15}{1+0.15}\right) \times 100\% = 73.9\%$

Hence the percentage of $N_2$ in the mixture is 73.9%

**Example 4**

A 10.32g of $AlCl_3$ are allowed to vapourise in $1dm^3$ vessel at 80°C a pressure of $1.7 \times 10^5\ Nm^{-2}$ develops. What is the degree of association of $AlCl_3$ into $Al_2Cl_6$.

**Solution**

An equation to show association of $AlCl_3$ into $Al_2Cl_6$

$2AlCl_3(g) \rightleftharpoons Al_2Cl_6(g);\ N = 2$

From $PV = \frac{m}{M_r}RT$ or $M_r = \frac{mRT}{PV}$

Where: $m = 10.32g$, $R = 8.314$, $T = 80°C = 353K$, $P = 1.7 \times 10^5\ Nm^{-2}$

$V = 1dm^3 = 103\ m^3$

$$M_r = \frac{10.32 \times 8.314 \times 353}{1.7 \times 10^5 \times 10^{-3}} gmol^{-1} = 178gmol^{-1}$$

$$i = \frac{\text{Expected molar mass}}{\text{Measured(observed) molar mass}}$$

But expected molar mass of $AlCl_3 = (27 + (3 \times 35.5)) = 133.5gmol$

$$i = \frac{133.5}{178} = 0.75$$

Degree of associaton, $\alpha$ is given by; $\alpha = \frac{i-1}{\frac{1}{N}-1} = \frac{0.75-1}{\frac{1}{2}-1} = 0.5\%$ or 50%

Hence degree of association of $AlCl_3$ into $Al_2Cl_6$ is 50%

**Example 5**

20.85g of phosphorous (V) chloride are allowed to vapourise in 5 $dm^3$ vessel at 175°C.A pressure of $1.04 \times 10^5$ Pa develops. Calculate the degree of dissociation of $PCl_5$ into $PCl_3$ and $Cl_2$

**Solution**

An equation to show the dissociation of $PCl_5$;

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g); N = 2$ .

From $M_r = \frac{mRT}{PV}$

Where $m = 20.85g, R = 8.314, T = 175°C = 448$ K, $P = 1.04 \times 10^5$ Pa

$V = 5dm^3 = 5 \times 10^{-3} m^3$

$$M_r = \frac{20.85 \times 8.314 \times 448}{1.04 \times 10^5 \times 5 \times 10^{-3}} gmol^{-1} = 149gmol^{-1}$$

But expected molar mass of $PCl_5$ is $208.5\ gmol^{-1}$

$$i = \frac{\text{Expected molar mass}}{\text{Measured molar mass}} = \frac{208.5}{149} = 1.4$$

Using $\alpha = \frac{i-1}{N-1} = \frac{1.4-1}{2-1} = 0.4$ or $40\%$

Hence degree of dissociation of phosphorous (V) chloride is $0.4$ or $40\%$

**Example 6**

(a) Calculate the relative molecular mass of Iron (III) chloride.
(b) Calculate another value from the following data.

When 1g of Iron (III) chloride was volatilised at 300°C, its vapour displaced $76cm^3$ of air measured at 27°C and 101 KPa (758mmHg) pressure.

Comment on your two values of parts (a) and (b) ($r.a.m. Cl = 35.5, Fe = 55$)

**Solution**

(a) Molecular mass of $FeCl_3 = 55 + (3 \times 35.5) = 161.5g/mol$

Hence molecular mass of Iron (III) chloride is $161.5g/mol$.

(b) Volume of air displaced at $27°C$ is $76cm^3$

That is $V_1 = 76cm^3, T_1 = 27°C$ or $300K$

So the volume of air at 300°C (573K) may be found by applying Charles's law as follows:

From Charles's law: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ or $V_2 = \left(\frac{T_2}{T_1}\right) V_1 = \frac{573}{300} \times 76cm^3 = 145.16cm^3$

But volume of air displaced = volume of Iron (III) chloride vapour

Thus the volume of $FeCl_3$ vapour is $145.16cm^3$

$$\text{Using } M_r = \frac{mRT}{PV} = \frac{1 \times 0.082 \times 573 \times 760}{758 \times 145.16 \times 10^{-3}} = 324.5g/mol$$

Hence molar mass of $FeCl_3$ is $324.5g/mol$

**Comment:**

The obtained molar mass in (b) is approximately twice the value obtained in (a) because in the vapour phase two molecules of Iron (III) chloride associates (dimerises) to form a dimer which corresponds to the molecular formula of $Fe_2Cl_6$

**Example 7**

The relative vapour density of a sample of ozone at a certain temperature was 18.3. What is the degree of dissociation of ozone into oxygen under these conditions? (Ozone is $O_3$, trioxygen)

**Solution**

$O_3$ dissociates according to the following equation:

$$2O_3(g) \rightleftharpoons 3O_2(g)$$

Rewriting the equation to show number of molecule of $O_2$ produced by one molecule of ozone by dividing with 2 throughout the above equation gives: $O_3(g) \rightleftharpoons {}^3/_2\, O_2(g)$

So $\mathbf{N} = {}^{\mathbf{3}}/_{\mathbf{2}} = \mathbf{1.5}$

Using $\alpha = \frac{i-1}{N-1}$ Where α is the degree of dissociation and i is the Van't Hoff's factor.

But $i = \frac{\text{Expected relative vapour density}}{\text{Observed relative vapour density}}$

Where $\text{Expected relative vapour density} = \frac{\text{Expected molar mass (of } O_3)}{2g/mol} = \frac{48g/mol}{2gmol} = 24$

Then $i = \frac{24}{18.3} = 1.31$

It follows that $\alpha = \frac{1.31-1}{1.5-1} = 0.62$

Hence the degree of dissociation is 0.62 or 62%.

# DIGGING DEEPER EXERCISE 4

## EXERCISE 4A: BINDER QUESTIONS

**Question 1**

(a) What is the role of combined gas law and Avogadro's law on determination of molecular mass of volatile substance by Victor Meyer's method?
(b) Instead of combined gas law and Avogadro's law (in (a) above), what alternative can be applied?
(c) Between the two alternatives ((a) and (b)), which one you would prefer most? Give reason(s) to support your choice.

**Question 2**

The experimentally determined molar mass of a substance is not always the same as that suggested by its molecular formula. Explain.

**Question 3**

List down at least two advantages and three advantages of employing Victor Meyer's method in the determination of molecular mass of volatile substances.

**Question 4**

What are two main assumptions in determining molecular mass of a volatile substance by the Duma's method?

**Question 5**

In the determination of molecular mass by Victor Meyer's method, 0.60 g of volatile substance expelled 123mL of air measured over water at 20 °C and 757.4 mmHg. Find the molecular mass of the substance if the vapour tension of water at 20°C is 17.4 mmHg.

**Question 6**

In the Duma's bulb technique for determining the molar mass; you vapourise the sample of a liquid that boils below 100°C in a boiling-water bath and determine the mass of vapour required to fill the bulb. From the following data, calculate the molar mass of the unknown vapour: mass of unknown vapour, 1.012 g; volume of bulb, 354 $cm^3$ pressure, 742torr; temperature, 99°C.

## EXERCISE 4B: REAL QUESTIONS

**Question 7**

Victor's Meyer method cannot be used in the determination of molar mass of table salt. Explain.

**Question 8**

Why molecular mass of methanol cannot be determined by Victor Meyer's method although it is volatile with boiling point of only 64.7℃?

**Question 9**

Determination of molecular mass of substances is crucial in the real life. How the molecular masses obtained from Duma's bulb or Victor Meyer's apparatus are useful?

**Question 10**

**Mr. Akilikubwa** is a laboratory technician at your school. He was experimentally demonstrating to you the determination of molar mass of volatile liquid by Duma's method. During the demonstration, he didn't weigh the amount of liquid initially put into the flask. Was this correct? Explain.

**Question 11**

Your beloved friend, **Kipute**, was given a homework assignment of calculating molecular mass of a substance from data that were collected in the Victor Meyer's experiment. However, she got the wrong answer of 116.56g/mol because she didn't include vapour pressure of water in her calculations. She came to your home, seeking for the help so that she can understand both correct solution of the problem and correct molar mass of the substance. Unfortunately, she forgot to carry her counter book for homework assignment, but she is still able to recall all data except that of total pressure. She told you that other data were: 0.292g of a substance displaced 61$cm^3$ of air at 22℃ and the vapour pressure of water at 22℃ was given as 22mmHg. Without seeking her to go and carry her forgotten counter book, provide the much needed help to your great friend, **Kipute**!

# EXERCISE 4C: HOT QUESTIONS

**Question 12**

What is wrong with this statement: *Dissociation of gas increases number of gas particles and therefore increasing its volume in accordance to Avogadro's law. According to Boyle's law the increase in volume as a result of dissociation leads to the decrease in pressure of the gas and hence it can be concluded that the dissociation of the gas decreases amount of the pressure exerted by the gas.*

**Question 13**

0.143g of a volatile liquid, when vapourised in a Victor Meyer apparatus displaced $30.4\text{cm}^3$ of air at $17°\text{C}$ and $99350\text{Nm}^{-2}$ (745mm Hg) pressure. Calculate

(a) The relative vapour density
(b) The relative molecular mass of the liquid
(c) The vapour pressure of water at $17°\text{C}$ is $2000\text{Nm}^{-2}$(15mmHg)

**Question 14**

In Dumas method for the estimation of nitrogen, 0.25 g of an organic compound gave 40 mL of nitrogen collected at $27°\text{C}$ temperature and 725 mmHg pressure. If the vapour pressure of water at $27°\text{C}$ is 25 mmHg, what is the percentage of nitrogen in the compound?

**Question 15**

When a glass bulb with a stop cock is evacuated, weighed, and then filled with oxygen, the weight increases by 0.25g. When the same bulb is evacuated and filled with another unknown gas under the same conditions of temperature and pressure, the mass increases by 0.5525g. If the molecular mass of oxygen is 32;

(a) Calculate the molecular mass of the unknown gas.
(b) Calculate the volume of the glass bulb assuming that it does not change appreciably with the change in pressure and temperature.

**Question 16**

A 6.19g sample of $PCl_5$ is placed in an evacuated 2L flask and is completely vapourised at $252°\text{C}$.

(a) Calculate the pressure in the flask if no chemical reaction were to occur.
(b) Actually at $252°\text{C}$, the $PCl_5$ is partially dissociated according to the following equation:

$PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$

The observed pressure is found to be 1.00atm. In view of this observation, calculate the partial pressure of $PCl_5$ and $PCl_3$ in the flask at $252°\text{C}$.

**Question 17**

The vapour density of $N_2O_4$ at certain temperature is 30.Calculate the percentage dissociation of $N_2O_4$ at this temperature.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

# EXAMINATION QUESTIONS FOR PART ONE

**Question 1**

(a) Give brief explanation to argue against or to argue for the following statement: *Liquid state of a substance cannot exist above its critical temperature.*

(b) $140cm^3$ of water vapour measured at 150°C and 100700 $Nm^{-2}$ (755mmHg) pressures have a mass of 0.071g. Show that these figures are in accordance with the formula $H_2O$ for steam.

**Question 2**

(a) In your own words, explain what will happen to the pressure when 4g of nitrogen gas stored in 1L container kept in a certain room is now stored in the new container of the 2.5L in the same room.

(b) Beryllium chloride was known to contain 11.3% of beryllium but the oxidation number of the metal was uncertain. The chloride was found to have a relative vapour density of 40. Determine the oxidation number of beryllium in the compound and hence it's relative atomic mass.

**Question 3**

(a) What is the pressure-volume law governing gas behaviour?

(b) In a diffusion experiment, the time required for water to cover the space between two marks on a tube as oxygen diffused out of it was 240 seconds. In identical conditions, the time required for another gas, X, was three and three – quarters minutes. Calculate the relative molecular mass of X

**Question 4**

(a) Based on Charles's law, justify the following statement, *"Negative Kelvin is nonsense."*

(b) A certain volume of hydrogen diffuses from an apparatus in one minute. Calculate the time required for the diffusion of the same volume of ozonide oxygen, containing 10% of ozone by volume, from the apparatus under identical conditions. (ozone is $O_3$, trioxygen)

**Question 5**

(a) Compare diffusion and effusion of gases.

(b) The relative vapour density of nitrogen dioxide at 1050°C is 24; calculate the degree of dissociation (by mass) of the gas in these conditions.

**Question 6**

(a) The critical temperature of nitrogen is 126K and that of helium is 5.3K. With reason, predict which of the gases will liquefy first?

(b) If phosphorous pentachloride is 20% dissociated at a certain temperature, calculate the relative vapour density of the equilibrium mixture of the pentachloride, trichloride and chlorine at this temperature.

**Question 7**

(a) Give your understanding on meaning of the following terms with reference to gases:
   (i) Critical temperature
   (ii) Critical volume
   (iii) Critical pressure

(b) The relative vapour density of iodine at 1 atmosphere pressure and 125°C is 87. Calculate the percentage dissociation of iodine, $I_2$ into its corresponding atoms in these conditions.

**Question 8**

(a) The Van der Waals equation of state for one mole of real gas is as follows:

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

For any given gas, the values of the constants, **'a** and '**b'** can be determined experimentally.

(i) Indicate which physical properties of molecule determine the magnitudes of the constants '**a'** and '**b'**

(ii) Which of the two molecules, $H_2$ or $H_2S$ , has the higher value for **'a'** and which has the higher value for **'b'**? Explain

(iii) One of the Van der Waals constants can be correlated with the boiling point of a substance. Specify which one.

(b) 1g of hydrogen iodide was heated to a certain temperature and the products suddenly cooled. The iodine which had been liberated required $15cm^3$ of 0.1M sodium thiosulphate for complete reaction. Calculate the percentage by mass of hydrogen iodide which remained undissociated at that temperature.

**Question 9**

(a) Predict which of the substances;

$NH_3, N_2\ CH_2Cl_2, Cl_2, CCl_4$ has:

(i) The smallest Van der Waals **'a'** constant
(ii) The largest **'b'** constant

(b) 2.5g of calcium carbonate are placed in a globe of capacity $850cm^3$. The globe is evacuated and heated to a temperature of 800℃ at which the temperature the carbon dioxide evolved exerts a pressure of $26660\ Nm^{-2}$(200mmHg). Calculate the percentage of the calcium carbonate which is decomposed.

**Question 10**

(a) From kinetic equation of gases, derive a mathematical equation of kinetic energy of one mole of a gas and hence show that the kinetic energy varies directly proportional to absolute temperature.
(b) $1\ cm^3$ of water measured at 4℃ is heated until has attained a temperature of 2500℃; if steam of this temperature is 3.98% of mass dissociated into molecules of hydrogen and oxygen, Calculate the volume the gasses should occupy. Assume that the gas laws apply at the temperature given. Pressure is 760mmHg throughout.

**Question 11**

(a)
(i) State gas law which govern breathing in human.
(ii) At what conditions the law stated in (i) above obeys strictly?

(b) What volume of 0.165M sodium thiosulphate would be required to react with iodine from 3g of hydrogen iodine? If the latter were heated to a temperature where it is 16% dissociated; what mass of hydrogen would remain uncombined?

**Question 12**

(a) Explain the concept of absolute zero of temperature.
(b) At 27℃ dinitrogen tetraoxide is 20% dissociated into nitrogen dioxide. $1dm^3$ of this mixture was heated to (i) 100℃ and (ii) 600℃. At 100℃ the dinitrogen tetraoxide is 90% dissociated and at 600℃ it is completely dissociated into nitrogen oxide and oxygen. Calculate the volume the gasses would occupy under condition (a) and (b). All measurements are made at 760 mmHg.

$$N_2O_4 \rightleftharpoons 2NO_2$$

**Question 13**

(a) Explain the effect of dissociation and association in the experimental determination of molar mass of volatile substances.
(b) At a certain temperature and under identical conditions, the volumes of oxygen and dinitrogen tetraoxide diffusing from an apparatus in a given time were in the ratio of 3 to 2. Calculate the degree of dissociation of dinitrogen tetraoxide of this temperature.

**Question 14**

(a) Show that Boyle's law and Charles's law are contained in the kinetic equation of gases.
(b) $24cm^3$ of a mixture of methane and ethane were exploded with $90cm^3$ of oxygen. After cooling to room temperature, the volume of gas was noted. It was found to decrease by $32cm^3$ when treated with KOH solution (pressure is constant throughout). Calculate the composition of the mixture.

**Question 15**

(a) Show that if kinetic equation of gases is valid, Graham's law of diffusion must be valid too.
(b) $32\ cm^3$ of a mixture of carbon monoxide, methane and hydrogen were mixed with $50\ cm^3$ of oxygen and exploded. After cooling to room temperature, the volume was noted. It was reduced by $22\ cm^3$ when exposed to KOH solution, leaving $16\ cm^3$ of excess oxygen. Calculate the composition of the mixture.

**Question 16**

(a) Which one of the following statements is correct, and which one is incorrect? For incorrect statement(s) give reason(s) to support your choice.

**Statement 1:** *Critical volume is the molar volume of a fluid at its critical temperature and critical pressure.*

**Statement 2:** *One mole of an ideal gas at room temperature and pressure occupies a volume of 22.4L.*

(b) 65 $cm^3$ of a mixture of hydrdogen, carbon monoxide and nitrogen are mixed with 50$cm^3$ of oxygen at room temperature. The mixture is exploded and allowed to cool. The residual volume is 55 $cm^3$. After absorption with KOH solution the final volume is 25 $cm^3$, calculate the percentage by volume of each gas in the original mixture (Temperature and pressure constant room values).

**Question 17**

(a) From kinetic equation of gases, derive the equation for root mean square speed (c) of a gas with molar mass, $M_r$, at absolute temperature, T, and hence deduce the mathematical equation which will enable you to calculate kinetic energy of '*n*' moles of the gas.

(b) 100 $cm^3$ of a sulphorous acid solution required 11.2 $cm^3$ of 0.05M iodine solution for complete reaction. Calculate the volume of dissolved sulphur dioxide at 15℃ and 742mmHg per $dm^3$ of the acid.

**Question 18**

(a) Duma's method is useless in the experimental determination of molar mass of glucose.

(b) The carbon dioxide in the air of a room was estimated by drawing 200 $dm^3$ of air at 14℃ and 753mmHg through potassium hydroxide bulbs of known mass. The increase in mass of bulbs was 0.157g. Calculate the percentage by volume of carbon dioxide in the air.

**Question 19**

$SO_2$ used in the air manufacture of sulphuric acid, is obtained from sulphide ores (iron pyrites):

$4FeS_2\ (s) + 11O_2\ (g) \rightarrow 2Fe_2O_3 + 8SO_2\ (s)$

The $SO_2$ is then treated with suitable reagent to produce sulphorous acid and finally sulphuric such that one mole of $SO_2$ produces one mole of sulphuric acid

(a) How many kg of iron pyrites, $FeS_2$, would be required to produce 100kg of sulphuric acid containing 98 % $H_2SO_4$?

(b) How many $m^3$ of air containing 21% of oxygen by volume and measured at 15℃ and 750 mmHg, would be required for complete combustion of pyrites in (a) above?

**Question 20**

(a) Under what conditions do real gases fail to obey Charles's and Boyle's law?

(b) 141.4$cm^3$ of an inert gas diffused through a porous plug in the same time as it took 50 $cm^3$ of oxygen to diffuse through the same plug under identical conditions. Calculate the relative atomic mass of inert gas.

**Question 21**

(a) Write down two assumptions of kinetic theory of gases that are not considered to be negligible under real gas behaviour.

(b) A quantity of 2.4g of a compound fills 934 $cm^3$ as a vapour at 298K and 740 mmHg. It contains 37.21% carbon 7.8% hydrogen and 55% chlorine. What is its molecular formula?

**Question 22**

(a) At what conditions does real gas obey the ideal gas equation?

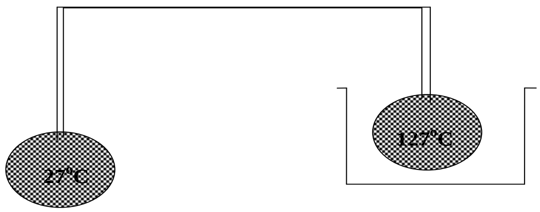
(b) Using Van der Waals equation, calculate the constant 'a' when two moles of a gas contained in a 4 litre flask exerts a pressure of 11 atmosphere at temperature of 300K. the values of b is 0.05 $Lmol^{-1}$

**Question 23**

(a) Under what conditions (s), does Dalton's law of partial pressure apply?
(b) For 10 minutes each, at 27℃, from two identical holes nitrogen and an unknown gas are leaked into a common vessel of 3L capacity. The resulting pressure is 4.18atm and the mixture contains 0.4 mole of nitrogen. What is the molar mass of unknown gas?

**Question 24**

(a) What each of the following gas laws does?
  (i) Boyle's law
  (ii) Charles's law
  (iii) Gay-Lussac's law
  (iv) Avogadro's law
(b) Two flasks of equal volumes are connected by a narrow tube of negligible volume. Initially both flasks are at 27℃ and each contains 0.35 moles of hydrogen gas at 0.5 atm. One of the flasks is then immersed in an oil bath at 127℃ as shown below:




Calculate:

  (i) The number of moles of hydrogen gas in each flask.
  (ii) The final pressure of the system.

**Question 25**

(a) "A gas consists of very small molecules in a random motion of which there is a collision between gas molecules and walls of the container"
  (i) What is the characteristics feature of that collision? (Assume the gas is ideal)
  (ii) The collision will result into important property of the gas: mention it.
  (iii) Explain clearly how, the presence of intermolecular forces in real gas, will affect facts mentioned in (i) and (ii) above
(b) Pyridine contains 75.92% C, 6.37% H and the rest being N. At 110℃ and 630mmHg the density of gaseous pyridine was $2.12gdm^{-3}$. Determine the empirical formula and molecular formula of pyridine.

**Question 26**

(a) What does each of the following say about? In each case give their corresponding mathematical equation.
  (i) Gay-Lussac's law
  (ii) Combined gas law
(b) A gaseous compound X has 46.1%C and 53.9% H; in 20 seconds, $50cm^3$ of X diffused through a porous plug and the same volume of $O_2$ diffused in 15.7 seconds. Determine the molecular mass of X. What volume of $CO_2$ would diffuse in 20 seconds under the same conditions as before?

**Question 27**

(a) A reaction mixture for combustion of $SO_2$ was prepared by opening a stop cock connecting two separate chambers, one having volume of 2.125L, filled at 0.75 atm with $SO_2$ and other having a 1.5L volume filled at a pressure of 0.5 atm with $O_2$, both gases at 80°C

  What were the:

  (i) Mole fraction of $SO_2$ in the mixture
  (ii) The total pressure
  (iii) The partial pressure of $SO_2$

(b) If the mixture was passed over a catalyst that promote the formulation of $SO_3$ and then was returned to the original connected vessels. What were the:
   (i) The mole fraction of $SO_3$ in the final mixture.
   (ii) The final total pressure.

**Question 28**

(a) State four postulates under kinetic theory of gases.
(b) At the start of an experiment one end of the U tube of 6mm glass is immersed in a concentrated ammonia solution and other end is immersed in concentrated acid solution. At the point in the tube where the vapours of $NH_3$ and HCl meet a white cloud of $NH_4Cl$ forms. At what fraction of distance along the tube from the ammonia the white clouds first forms?

**Question 29**

(a) What does each of the following law say?
   (i) Boyle's law (ii) Avogadro's law (iii) Graham's law
(b) At the top of mountain the thermometer reads 0°Cand barometer reads 710mmHg. At the bottom of the mountain the temperature is 30°C and the pressure is 760 mmHg. Compare density of the air at the top with that at the bottom.

**Question 30**

(a) What does ideal gas law say?
(b) A 15L vessel containing 5.65g of nitrogen ($N_2$) is connected by means of valve to a 6L vessel containing 5g oxygen ($O_2$). After the valve is opened and the gases were allowed to mix, what would be partial pressure of each gas and the total pressure at 27°C?

**Question 31**

(a)
   (i) State the law which governs the total pressure in the container of mixture of two or more gases.
   (ii) From kinetic equation of gases, derive the law stated in (i) above.
(b) The pressure in a vessel that contained pure oxygen dropped from 2000 torr to 1500torr in 55 minutes as the oxygen leaks through a small hole into a vacuum. When the vessel was filled with another gas, the pressure dropped from 2000 torr to 1500 torr in 85 minutes. What is the molecular weight of the second gas?

**Question 32**

(a) From the fundamental gas equation, derive an ideal gas equation.

(b) Calculate the kinetic energy of 1mol of an ideal gas at 27°C.

**Question 33**

A mixture of gases ethane, ethene and helium is contained in a container of unknown volume at 300K and 680 mmHg. The mixture is burned with excess oxygen and all the carbon is converted into carbon dioxide and hydrogen into water. The carbon dioxide is collected in a container of volume $0.25dm^3$ and found to exert a pressure of 561.3mmHg at 300K. The Helium is also collected in a separate container of volume 0.25 $dm^3$ and exerts a pressure of 187.1 mmHg at 300K.

$$C_2H_6\,(g) + 7/2\,O_2\,(g) \rightarrow 2CO_2\,(g) + 3H_2O\,(l)$$

$$C_2H_4\,(g) + 3O_2(g) \rightarrow 2CO_2\,(g) + 2H_2O(l)$$

(i) How many moles of Helium are in the original vessel?
(ii) How many moles of carbon dioxide are produced?
(iii) What is the partial pressure of Helium in the original vessel?
(iv) What is the volume of original vessel?

**Question 34**

(a) What is the physical meaning of the 'a' and 'b' constants in the Van der Waals equation?
(b) Calculate the pressure of real gases of 0.02mol occupied in 1.6L bulb at 20°C

Given that: $a = 1.34\ \text{atm}\ L^2\ \text{mol}^{-2}$ and $b = 0.32\ \text{L moL}^{-1}$

**Question 35**

(a) At 110°C and 454mmHg, 0.11g of ethanoic acid vapour occupies $63.7cm^3$. At 156°C and 458mmHg, 0.081g of ethanoic acid vapour occupies $66.4cm^3$. Calculate the molar mass of ethanoic acid in the vapour phase at each temperature.
(b) Give the interpretation of the results in 35(a) above.

**Question 36**

(a) Which of the following gases would be nearly impossible to collect over water? Why?

$$CO_2, HCl, CH_4, NH_3$$

(b) A $3.2m^3$ vessel contains a mixture of 86.2g of oxygen and 1.5 g of hydrogen at 88°C. Calculate the total pressure in the vessel.

**Question 37**

(a) What is Dalton's law of partial pressure doing?
(b) Gas A of a certain volume diffuses for 580.8s while the same volume of gas J diffuses for 300s under identical experimental conditions. Calculate the relative molecular mass of J if the relative molecular mass of gas A is 120.

**Question 38**

(a) Compressibility factor, **Z**, is used to test ideality and non-ideality of real gases:
 (i) Derive an expression for **Z**
 (ii) At what value of Z a real gas shows ideal behaviour, positive and negative deviation from ideality?
(b) A certain compound Ỵ has an approximate RMM of 207. At 80°C and in a 3 litres vessel, the vapour of this compound exerts a pressure of about 0.12atmosphere. What is the mass in grams of the vapour of this compound?

**Question 39**

(a)
 (i) State the meaning of an ideal gas.
 (ii) Derive an ideal gas equation.
(b) $267cm^3$ of a certain gas at 18°C and 100400 Pa pressure has a mass of 0.162g; calculate:
 (i) Normal density of the gas at s.t.p
 (ii) Relative density of the gas at s.t.p

**Question 40**

(a) State at least one application of each of the following:
  (i) Graham's law of diffusion
  (ii) Dalton's law of partial pressures
  (iii) Avogadro's hypothesis

(b) $200cm^3$ of oxygen gas takes 250 seconds to diffuse through a porous diaphragm. Under identical conditions, $200cm^3$ of an unknown gas T takes 177 seconds to diffuse. Calculate the relative molecular mass for unknown gas.

**Question 41**

(a) List down error free postulates of kinetic theory of gases.

(b) 1 mole of hydrogen gas was reacted with 1 mole of iodine vapour. Calculate the number of moles of hydrogen iodide formed at t seconds. After t seconds; 0.8moles for hydrogen remained.

**Question 42**

(a) Based on your knowledge of diffusion, suggest any four factors which may affect the rate of diffusion. How each factor mentioned affects the rate of diffusion?

(b) Two porous containers are filled with hydrogen and neon respectively. Under identical conditions, $^2/_3$ of hydrogen escapes in 6 hours. How long will it take for half the neon to escape? (You may use the following molar masses: $H_2 = 2.02 g/mol, Ne = 20.18 g/mol$).

**Question 43**

(a) Some compounds are said to have 'abnormal' relative densities when determination is carried out experimentally. Result can either be higher or lower than the expected from their molecular formulae.
 (i) What factor(s) lead to such abnormalities?
 (ii) For each factor, give two examples of compounds whose vapour shows such abnormalities.

(b) A container has two gases in it and one of them weighs $64\mathrm{g/mol}$. Given the following information; calculate the molecular mass of the other component.
 - The mole fraction of unknown gas is 0.35
 - The total pressure inside the 1litre container is 1.6atm
 - The density of the gaseous mixture is $3.45\mathrm{g/L}$ at 25℃

**Question 44**

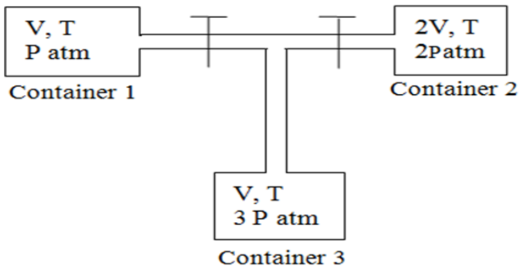
(a) By using Amagat's curves, show how $CO_2$ deviates from ideal gas behaviour.

(b) When an open flask containing air is heated from 27℃ to 87℃, what percentage of the air in the flask is expelled? Assume that the volume of the flask and atmospheric pressure are constant.

**Question 45**

(a) Aerosol cans will explode if heated. Explain.

(b) When we open the taps given in the picture below, find the final pressure exerted by gases.




**Question 46**

(a) According to Boyle's law; *pressure and volume are inversely proportional. However, when we fill air into a tyre, we are increasing both volume and pressure.* Give an explanation to eliminate this contradiction.

(b) 0.964g sample of mixture of sodium methanoate and sodium chloride is analysed by adding sulphuric acid. The equation for the reaction for sodium methanoate with sulphuric acid is shown below.

$$2\mathrm{HCOONa} + \mathrm{H_2SO_4} \longrightarrow 2\mathrm{CO} + 2\mathrm{H_2O} + \mathrm{Na_2SO_4}$$

The carbon monoxide formed measures 242mL when collected over water at 752mmHg and 22℃. Calculate the percentage of sodium methanoate in the original mixture. Given that: vapour pressure of water at 22℃ is 19.8mmHg.

**Question 47**

A mixture of hydrogen gas, oxygen gas and 2mL of liquid water is present in a 0.5L rigid container at 25℃.The number of moles of hydrogen gas and the number of moles of oxygen gas is equal. The total pressure is 1146mmHg.

The mixture is sparked, and $H_2$ and $O_2$ react until one reactant is completely consumed.

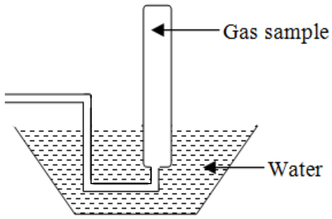
(a) Identify the reactant remaining and calculate the number of moles of the reactant remaining
(b) Calculate the total pressure in the container at the conclusion of the reaction if the final temperature is 90℃.
(c) Calculate the number of moles of water present as vapour in the container at 90℃

Given that:

- The vapour pressure of water at 25℃ is 24mmHg
- The vapour pressure of water 90℃ is 526mmHg

**Question 48**

A student collected a sample of hydrogen gas by the displacement of water as shown by the diagram below




The relevant data are given in the following table:

| GAS SAMPLE DATA | |
|---|---|
| Volume of sample | 90mL |
| Temperature | 25°C |
| Atmosphere pressure | 745mmHg |
| Vapour pressure of $H_2O(25°C)$ | 23.8mmHg |

(a) Calculate the number of moles of hydrogen gas collected
(b) Calculate the number of molecules of water vapour in the sample gas
(c) Calculate the ratio of average speed of the hydrogen molecules to the average speed of the water vapour molecules in the sample.
(d) Which of the two gases, $H_2$ or $H_2O$, deviate more from ideal behaviour? Explain your answer.

**Question 49**


Represented above are five identical balloons, each filled to the same volume at 25°C and 1 atmosphere pressure with the pure gases indicated.

(a) Which balloon contains the greatest mass of gas? Explain
(b) Compare the average kinetic energies of the gas molecules in the balloons? Explain
(c) Which balloon contains the gas that would be expected to deviate most from the behaviour of an ideal gas? Explain
(d) Twelve hours after being filled, all the balloons have decreased in size. Predict which balloon will be the smallest. Explain your reasoning.

**Question 50**

(a) *"Ideal gas law has crucial applications in various fields including in engineering."* Name at least three objects made by engineers to support this claim.
(b) The atomic radius of sodium is $1.86 \times 10^{-8}$cm, and the molar volume of sodium is 23.68 $cm^3$. If 68.52% of this volume is the actual volume occupied by sodium atoms, calculate the Avogadro's constant. (Volume of one sodium atom $\frac{4}{3}\pi r^3$).

## Question 51

(a) Why basketball shrinks when left in cold surface overnight?
(b) When carbon dioxide gas is put in a sealed container at 701K and pressure of 10 atm and is heated to 1401K, some of the $CO_2$ decomposes to carbon monoxide and oxygen gas and the pressure rises to 22.5 atm. Calculate the mole percent of $CO_2$ that decomposes.

**Question 52**

Traditionally, high-flying aircraft and Formula 1 racing cars have had their tyres inflated with nitrogen gas instead of air. Recently, this practice has been extended to some other cars.
A car tyre is filled with nitrogen gas to a volume of $8.98dm^3$ and a pressure of 207kPa at 20°C.

(i) Using the ideal gas equation, calculate the mass of nitrogen gas, in grams, present in the car tyre under these conditions. Show your work clearly.
(ii) During a car journey, the tyres become warm. Use the ideal gas equation to deduce the effect of that this has on the pressure in the tyres.
(iii) One reason for the use of nitrogen gas in car tyres is that less gas is lost from the tyres during use because nitrogen molecules are larger than oxygen molecules. A suggested explanation for this is that nitrogen atoms are larger than oxygen atoms. Explain why a nitrogen atom is larger than an oxygen atom.

**Question 53**

(a) Briefly explain the principle of Victor Meyer's method of determination of molecular mas of volatile substance.
(b) It takes 22 hours for neon-filled balloon to shrink to half its original volume at s.t.p. If the same balloon is filled with helium, then how long it has taken for the balloon to shrink to one third of its original volume at s.t.p?

# ANSWERS TO DIGGING DEEPER EXERCISES

## EXERCISE 1

**1.** Disagree

**Explanation**

Amount of pressure exerted by a gas does not directly depend on the mass of the gas; it depends on the number of gas molecules (particles). With equal mass of hydrogen and oxygen, hydrogen having smaller molar mass will possess greater number of gas molecules $\left(n = \frac{m}{M_r}\right)$ and hence greater pressure of hydrogen than that of oxygen despite the fact that the two have equal mass.

**2.** Incorrect

**Explanation**

For the volume of the gas to double in accordance to Charles's law the temperature in Kelvin (absolute temperature) must double too. Although the given temperature seems in to double in Celsius scale but converting them to Kelvin gives 283K and 393K respectively which is clear that the latter is not twice of the former.

**3.** Oppose

**Explanation**

To be valid, Gay-Lussac's needs the temperature to be in Kelvin (absolute temperature). So in Kelvin scale the increase in temperature is from 300K to 600K from which it is clear that the latter is the twice of the former and hence the pressure should in accordance to Gay-Lussac's law as suggested by John.

**4.** No, the ideal gas law equation (PV = nRT) is not applicable to liquids because they are not compressible and thus they have a constant volume.

**5. (i)** From Boyle's law: $V \propto \frac{1}{P}$; constants: n and T

From Charles's law: $V \propto T$; constants: n and P

Avogadro's law: $V \propto n$; constants: P and T

Combining the three laws: $V \propto \frac{nT}{P}$ or $V = \frac{nRT}{P}$ (All four variables of the gaseous state are changing).

Where R is the proportionality constant; and the which is known as universal molar gas constant

Hence $PV = nRT$ (ideal gas equation).

(ii) Because it shows relationship between all variables (pressure, volume, number of molecules and temperature) of gaseous state.

**6**. (i) Pressure of the gas decreases as the volume increases (or pressure of the gas increases as the volume decreases).

(ii) Temperature, number of gas molecules.

**7.** (i) The number of molecules in the gas increases as the volume increases.

(ii) Temperature, pressure

**8.** Gases whose molar masses are larger than that of oxygen gas will diffuse more slowly than oxygen. These are: $F_2$, $N_2O$, $Cl_2$ and $H_2S$

**9.** False

**Reason**

The amount of the gas which directly determine amount of pressure is the number of gas molecules and not mass. With smaller molecular mass, 2g of hydrogen possess greater number of molecules (1mol) than 4g of oxygen (0.125mol). So although the mass of oxygen is twice the mass of hydrogen the pressure exerted by hydrogen will be 8 times (greater by far) the pressure of oxygen.

**10**.(a) (i) The amount of pressure exerted by the gas increases as the amount of collision frequency increases.

(ii) The amount of pressure exerted by the gas increases as the amount of collision intensity increases.

(b) **Collision frequency** can be changed by one of the following ways:

- By changing temperature whereby increasing the temperature, increases the collision frequency.
- By changing pressure whereby increasing pressure by compression decreases volume of the gas and therefore increasing the collision frequency.
- By changing the volume of the container whereby using the container of smaller volume increases the collision frequency.
- By changing amount of the gas whereby adding the amount of the gas, increases the collision frequency.

**Collision intensity** can only be changed by changing pressure whereby increasing the temperature, increases the collision intensity.

**11.** The merger of Boyle's law and Charles's law is the combined gas law which can be represented as follows;

$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$, where n is constant.

When volume is constant, $V_1 = V_2 = V$

Then $\frac{P_1V}{T_1} = \frac{P_2V}{T_2}$ or $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ which is equivalent to Gay-Lussac's pressure law.

Hence the Gay-Lussac's law is contained in Gay-Lussac's law as shown above.

**12.** (i) Yes, the total pressure changes.

**Explanation**

Increasing the amount of gases, increases collision frequency between gas particles and walls of the flask and therefore increasing pressure. So adding the neon will increase pressure in the flask.

(ii) No effect.

**Explanation**

Neon is incapable of reacting with any gas present in the flask, so adding it in the flask will do both increase the total pressure in the flask and decrease the mole fraction of the gases by the same proportion and hence the partial pressures will remain the same.

**13.** According to Charles's law; hot air inside the balloon has larger volume and hence lower density than cold air outside; consequently, the balloon floats.

**14. Extreme high temperature** will cause high increase in pressure in accordance to Gay-Lussac's law and therefore the tank will burst leading to the explosion while **extreme low temperature** causes large decrease in pressure of the gas in accordance to the same law.

**15.** During driving, temperature of air inside car tyre increases while its volume remains constant which in turn means that the pressure in the tyre will increase in accordance to Gay-Lussac's pressure-temperature law.

**16.** Good flavour of chips is maintained by high pressure in the bag which ensures freshness of preservative chemicals added during the manufacture of the chips. Placing the bag in the freezer causes a reduction in pressure in accordance to Gay-Lussac's law, and hence good flavour is lost.

**17.** Bicycle tyre absorb heat energy from the sun raising its temperature which in turn will raise its pressure in accordance to Gay-Lussac's law. If the pressure in the tyre rises beyond its limit, the tyre will burst.

**18.** In the summer, the temperature is higher and therefore the pressure inside the tyre tend to increase in accordance to Gay-Lussac's law. So to prevent the bursting of the tyres, they are inflated to a slightly lower pressure.

**19**. (i) Avogadro's law.

(ii) Identical balloons have the same volume and therefore they both contain the same number of particles (molecules) in accordance with Avogadro's law. Since one atom of helium has smaller mass than one molecule of oxygen, with equal number of particles for each, the helium balloon will be lighter.

**20.** In making bakery product like bread, yeast is mixed with the dough where it releases carbon dioxide through fermentation of sugar present in the dough. Once the bread has baked, the heat causes the temperature to raise which in turn cause the carbon dioxide in the dough to increase its volume in accordance with Charles's law and hence the bread becomes fluffy.

**21.** In the summer, the temperature increases and therefore the pressure of the gas $(CO_2)$ inside the bottles tend to increase in accordance to Gay-Lussac's law. So to decrease the temperature and hence to avoid the explosion of the bottles, they are kept under water.

**22.** A flat tyre has smaller amount of air and therefore smaller volume while inflated tyre has larger amount of air and hence greater volume in accordance with Avogadro's law.

**23.** Inside a pressure cooker, the food is kept in water. As the temperature of the liquid water is increased, water vapour (gaseous water) is produced. This gaseous water cannot escape the pressure cooker and therefore keeping the volume constant. Consequently, according to Amontons's law, the pressure of the gaseous water keeps rising until the temperature of the liquid water and the gaseous vapour exceed the normal boiling point of water (100 °C). At this higher temperature (caused by the raise in pressure; i.e. higher pressure means higher boiling point), food can be cooked much faster.

**24.** Lower temperature in the outdoors, decreases the volume of gases inside the ball in accordance with Charles's law and hence the football shrinks.

**25.** High temperature inside of the fire increases the pressure of the gases inside the can in accordance to Gay-Lussac's law, and eventually if the pressure exceeds the pressure limit, the can will explode.

**26**. Boyles's law is applicable when amount of air is constant. During the inflation of the tyre, the amount of air is progressively increased in the tyre and therefore Boyle's law is inapplicable. At the initial stages of inflation, volume of the tyre will increase and pressure will remain almost constant in accordance with Avogadro's law. At later stage of the inflation, volume of the tyre remains almost constant but since amount of the gas in the tyre is still increasing, collision frequency between air molecules and the tyre's walls will increase making the pressure to increase too ($P \propto n$ a constant V and T); eventually the tyre will burst if the amount of air added is so large that the pressure exerted exceed pressure limit of the tyre.

**27.** (a) $P_{He} = 474\text{torr}$, $P_{Ar} = 26\text{torr}$ (b) $P_{total} = 500\text{torr}$

**28.** (a) 706.896mmHg (b) 0.0418g

**29.** Helium: 3.16 times as fast

**30.** 5050g/mol

**31.** 31.79g/mol

**32.** 0.400m

**33.** 2.56 mol/min

**34.** 0.43atm

**35.** 4atm

**Hint:** $O_2$ is in excess (only 1atm of it will react with 2atm of $H_2$) so after reaction there are 2atm of unreacted oxygen and 2atm of produced **gaseous** water making a total of 4atm.

**36.** (a) 0.25atm (Hint: $P_{total}$ stp is 1atm) (b) 0.3348mol (Hint: $n_{total} = 1$mol for 22.4L at stp) (c) Pressure is still 0.25atm

**37**. (a) 13.39g b) 0.6049atm c) 0.6522 (d) At s.t.p water would be frozen (and become ice). It could not behave like an ideal gas and hence the overall pressure has been overestimated.

**38.** (a) 1.4atm b) 0.2atm c) 0.857 **39.** 0.4atm **40.** 1.8atm

**41**. (a) 14atm (b) 0.7 (c)5g/L (d) $X_{H_2} = 0.5$ $X_{Ar} = 0.167, X_{H_2O} = 0.333$

**Note**: $H_2O$ is included in the answer because in the given question it is given as a gas

**42.** (i) 739torr (ii) 3.94g

**43.** 0.3g

**44.** 787.2mmHg

**45.** 2.93x seconds

**46.** Not correct.

**Reason:** CO and $O_2$ reacts, so direct application of Dalton's law of partial pressure is not allowed.

**Calculation of correct value**

At 30℃, CO reacts with $O_2$ According to the following equation:

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$

From which 3atm of CO reacts with 1.5atm $\left(^1/_2 \times 3\text{atm}\right)$ of $O_2$ to give 3atm (For gases pressure ratio is equal to mole ration).

So after the reaction there are:

0atm of CO (all of it reacted)
0.5atm (2atm − 1.5atm) of unreacted $O_2$
3atm of produced $CO_2$
Then by Dalton's law of partial pressure; the total pressure in the container is given by;

$P_T = P_{O_2} + P_{CO_2} = (3 + 0.5)\text{atm} = 3.5\text{atm}$

**Hence the correct total pressure is 3.5atm.**

**47**. 25% CO and 75%$CO_2$

**48.** $1.17\text{g/dm}^3$

**49.** 0.25atm

**50.** 84.5℃.

# EXERCISE 2

**1.** The kinetic molecular theory of gases explains how gases behave by assuming that they are made up of very fast randomly moving particles (atoms or molecules).

**2.** The three main components are:

(i) The molecules of the gas have linear motion (unless they collide with something).
(ii) No gain or loss in kinetic energy during a collision.
(iii) The individual gas particles have negligible mass and occupy negligible space (volume) in a container.

**3.** The concept of pressure directly follows from the theory because each collision imparts forces on the wall it hits, and so when very large number of collisions each second hit a unit area of a container's wall, the collective force per area is just the sum of force of all the individual collisions. Since $P = \frac{\text{Force}}{\text{Area}}$, the collective force per area associated with the collisions is the pressure of the gas.

**4.** Kinetic gas equation is an equation for the pressure of the gas which was derived by using the postulates of kinetic molecular theory. It can be written as; $PV = \frac{Nmc^2}{3}$; where:

P is the pressure of the gas
V is the volume of the gas
N is the number of gas particles
M is the mass of one gas particle
c is the root mean square speed of the gas

**5.** The molecular speed is high if the molecular mass is small and hence the correct order will be as follows:

$$\frac{Cl_2 < F_2 < O_2 < N_2}{\text{Increase in molecular speed}}$$

**6.** 70.7g/mol

**7.**

(i) Reducing the temperature of a gas reduces the average kinetic energy (or speed) of the gas molecules. This would reduce the frequency of collisions of gas molecules with the walls of the balloon and also would make those collisions less energetic. In order to maintain constant pressure against the external pressure, the volume must decrease (shrink).
(ii) The molecules of the gas do have volume, when they are cooled sufficiently, the intermolecular forces of attraction that exist between them cause them to liquefy or solidify.

**8.** The molecules of gas are in constant motion, so the HCl and $NH_3$ diffuse along the tube. Where they meet, the solid $NH_4Cl$ is formed. Since HCl has greater molar mass, its speed is lower, therefore, it does not diffuse as fast as the $NH_3$.

**9.** The wind is moving molecules of air that are going mostly in one direction. Upon encountering a flag, they transfer some of their kinetic energy to it and cause it to move.

**10. $H_2O$**. Cooling slows the velocities of the He atoms, causing them to behave as though they were heavier.

**11.** According to the kinetic molecular theory, low temperature in the cold room implies low kinetic energy to the gas. This in turn implies low speed to the perfume gaseous ingredients leading to slow diffusion rate and hence it becomes difficult to smell.

**12.** 4495℃

**13.** 197.74℃

**14. Boyle's law:** $P \propto \frac{1}{V}$ At constant T and n

**Justification:**

A decrease in V leads to an increased gas molecules concentration and thus an increase in the number of collisions per second with the walls of the container. More frequent collisions lead to greater pressure exerted by the gases in the container.

**Charles's law:** $V \propto T$ at constant P and n

**Justification:**

Initially an increase in T leads to an increase in kinetic energy, making the speed greater and thus frequency of collision is increased and the collisions become more energetic (both collision force and frequency become high). The only way to keep P from increasing under such conditions (so as to balance with the external pressure) it to increase V, which will decrease collision frequency despite the increased speed

**Avogadro's law:** $V \propto n$ at costant P and T

Initially, an increase in n leads to an increased gas molecules concentration and thus an increase in number of collisions per second with the walls, and thus pressure

The only way to keep P from increasing (so as to balance with the external pressure) under these conditions is to increase the volume proportionately, which will keep the concentration constant.

**15.** From the first postulate of kinetic molecular theory, the gas consists of very small molecules in a random motion of which there is a collision between gas molecules themselves and the collision between gas molecules and the walls of the container. This makes the direction of the motion of the gas to be completely random whereby the gas will continue to spread out until it is evenly distributed throughout the volume of the container.

**16. Yes.** At any given instant, there are a range of values of molecular speeds in a sample of gas. Any single molecule can speed up or slow down as it collides with other molecules. The kind of speed which is constant at constant temperature is the average velocity of all the molecules and not the molecular speed.

**17.** Kinetic energy (K.E) of n moles of a gas with total mass, m, moving with velocity, c, in a container of volume, V, at temperature, T, and pressure, P, is given by one of the following equations:

$K.E = \frac{1}{2}mc^2$-------------- (i)

$K.E = \frac{3}{2}PV$--------------- (ii)

$K.E = \frac{3}{2}nRT$------------- (iii)

(i) The decrease in volume and the increase in pressure occurs at the same proportion making the product PV (in (ii)) unchanged. Adding the fact that the temperature, T (in (iii)) was kept constant; no change in kinetic energy will occur and hence **the kinetic energy will remain the same**.

(ii) Increasing T (in (iii)) clearly increases the kinetic energy. Analogously increasing P while V is kept constant, increases the value of the product PV (in (ii)) which in turn increases kinetic energy. Hence **the kinetic energy is increased** in this case.

(iii) From (i) it is clearly understood that the increase of velocity (c) by factor of two, **increases the kinetic energy by factor of 4.**

# EXERCISE 3

**1.**

- Real gas molecules exhibit finite volume, thus excluding some volume from compression.
- Real gas molecules exhibit intermolecular forces of attraction, thus leading to fewer and less energetic collisions with the walls of the container and hence lower pressure.

**2.** Kinetic theory does not recognise that; at low temperature and high pressure:

- Intermolecular forces of attraction cannot be neglected.
- Volume of gas molecules cannot be neglected compared to the volume of whole gas (container).
- Collisions between gas particles and walls of the container are not perfectly elastic.

**3.** $SO_2$ shows greatest deviation.

**Reasons**:

- A molecule of $SO_2$ has largest size (or volume)

- $SO_2$ molecule exhibit strongest intermolecular forces of attraction (With largest molecular weight, $SO_2$ has strongest Van-der-Waals dispersion forces. Also $SO_2$ has dipole-dipole forces in additional to the strongest dispersion forces while other gases have dispersion forces only).

**4. High temperature** results in high kinetic energy which overcomes intermolecular forces of attraction.

**Low pressure** increases distance between molecules leading to greater volume occupied and therefore molecules comprise a small part of the volume and (due to greater distance apart between molecules) the intermolecular forces of attraction become very small.

**5.** To be ideal the gas must obey ideal gas equation in all conditions of temperature and pressure. This requires the intermolecular forces between gas molecules and molecular size (volume) of gases to be neglected which is not possible especially at low temperature and high pressure and hence no gas is ideal; making the whole concept just imaginary.

**6**. (i) Smaller value.

**Explanation**

The smaller value means less pressure deviation and therefore the real pressure will become closer to the ideal pressure.

(ii) Not possible.

**Explanation**

The given constants depend on the nature of the gas. While 'a' depends on the strength of intermolecular forces 'b' depends on the molecular size all of which depend on chemical nature of the gas and hence they cannot be altered.

**7.** At low temperature, kinetic energy is not enough to break intermolecular forces and therefore making the molecular attraction high.

**8.** That statement assumes that there are no intermolecular forces between gas particles. But in reality the intermolecular forces between gas particles they do exist and thus decreasing the speed of the particles and hence the collision becomes inelastic.

**9.** Ammonia having intermolecular hydrogen bonding which is stronger than the Van-der-Waals dispersion forces present in the nitrogen, has stronger intermolecular forces and hence larger value of 'a' for ammonia. But larger molecular mass of nitrogen implies that nitrogen molecule has larger molecular volume and hence larger value of 'b' for nitrogen.

**10.**

(i) $N_2$(Has a weakest intermolecular force of attraction. Among the non-polar, $N_2$ has smallest molecular weight and therefore smallest Van der Waals dispersion forces. $NH_3$ has a stronger intermolecular force than $N_2$ despite the fact that has smallest molecular weight because it is polar covalent molecule with hydrogen bond.

(ii) $CCl_4$(It has much greater molecular weight and therefore greatest size making its molecule to occupy greatest volume).

**11.** (i) 696K (ii) 731K

**12.** Liquefaction of a gas involves strengthening intermolecular forces potentially present in the gas. Ammonia having intermolecular hydrogen bonding in additional to Van-der-Waals dispersion forces has stronger intermolecular forces than fluorine which has Van-der-Waals dispersion forces only.

**13.** Presence of intermolecular forces as one of reasons of deviation of real gas from ideal behaviour makes liquefaction of gas possible. Since it is easier to store and transport liquid than gas, gases are usually liquefied before their storage or transportation.

**14.** Very low molecular mass of helium suggests that helium has very weak Van der Waals dispersion forces. The weak intermolecular forces make its liquefaction process difficult. As the result, the liquefaction of helium requires both cooling and compression equipment unlike other heavier gases like carbon dioxide which requires compression only for their liquefaction.

**15.** It helps to understand liquefaction process which is important in the transportation and storage of the gas.

**Explanation**

Gases with positive value of compressibility factor $(Z > 0)$ like hydrogen and helium show positive deviation from ideal gas behaviour and thus they have very weak intermolecular forces and they are **permanent gases**. Consequently, these gases need both cooling and compression for their liquefaction.

On another hand, gases with negative value of compressibility factor $(Z < 0)$ like ammonia and carbon dioxide show negative deviation and thus they have very strong intermolecular forces. This makes their liquefaction easier and they need only compression for the process.

**16.** The following are the two steps involved in the liquefaction of natural gas:

**1. Compression**

Here the pressure is increased, therefore pushing the gas molecules closer together.

**2. Cooling**

Here the temperature is dropped, which causes the intermolecular forces of attraction to increase.

**17.** The experimental molecular weight would be greater than the true value.

**Explanation**

Molecular weight of the vapourised liquid is calculated from the following formula:

$$M_r = \frac{mRT}{PV}$$

Significant intermolecular forces of attraction exist at temperature not far above boiling point. Therefore, the compressibility of the gas is greater and the value of PV is smaller than predicted. This would lead to a higher value of the molecular weight than the true value.

**18**. (a)

**'a'** indicates the intermolecular forces of attraction between molecules of real gases (Greater intermolecular forces, greater value of **'a'**).

**'b'** indicates actual volume of a molecule of real gas (Greater size or molecular weight of the molecule, greater value of **'b'**).

(b) $H_2S$ has higher value of **'a'**

**Reason:**

$H_2S$ molecules exhibit stronger intermolecular forces of attraction since it has stronger Van der Waals dispersion forces ($H_2S$ has greater molecular weight than $H_2$) and also has dipole-dipole forces in additional to the dispersion forces while $H_2$ has the dispersion forces only.

$H_2S$ has higher value of **'b'**

**Reason:**

Having greater molecular weight, $H_2S$ molecule has greater size and therefore greater volume than $H_2$.

(c) **'a'** is correlated to boiling point. The greater value of 'a' means stronger intermolecular forces of attraction and whence higher boiling point

**19.** (i) $57.1\text{atm}; \text{deviation} = 14.2\%$ (ii) $49.6\text{atm}; \text{deviation} = 0.8\%$

**20.** Agree

**Explanation**

Greater number of gas molecules means greater of both pressure deviation and volume deviation from their corresponding ideal results. This is because, with greater number of gas molecules the intermolecular forces will be higher with more gas molecules pulling the gas molecules backward before hitting the container's wall and hence more decrease in real pressure. Also greater number of gas molecules means greater volume occupied by gas molecules which in turn means less empty space is left compared to the volume of the container.

**21.** Doubling the pressure as result of doubling is the ideal behaviour which neglects presence of intermolecular forces. In real gas, doubling number of moles means more intermolecular forces which results into more pressure deviation making the increase in pressure to be less than one could expect if the gas would be ideal.

**22**. Kinetic energy of gas decreases as the temperature decreases toward its boiling point. At boiling point kinetic energy is so small that it unable to break intermolecular forces to the extent that the liquefaction of the gas starts to take place.

**23. At boiling point** the kinetic energy is too small to break intermolecular forces and therefore the deviation of real pressure from ideal pressure is maximum. Also the small kinetic energy implies that gas molecules are moving with small speed in close range and therefore occupying small volume which in turn makes inappropriate to neglect the volume of individual gas molecules compared to the volume of the whole gas and thus making the volume deviation to be maximum too. Consequently, the deviation of real gas from ideal behaviour is maximum at boiling point to the extent that the liquefaction of the gas starts to take place.

**At critical point** the kinetic energy is high enough to break almost all intermolecular forces and therefore the pressure deviation is negligible. Also high kinetic energy implies that gas molecules are moving with very high speed with very large separation distance making them to occupy very large volume and therefore making possible to neglect the volume of individual gas molecules compared to the volume of the whole gas leading to almost zero volume deviation. Consequently, the deviation of real gas from ideal behaviour is minimum at boiling point to the extent that the gas is almost ideal such that the liquefaction of the gas is extremely difficult.

**24.** Smaller molecular mass of helium means that helium has smaller molecular volume and weaker Van-der-Waals intermolecular forces and therefore comparing to ideal behaviour of gases, helium has smaller volume deviation and smaller pressure deviation respectively and hence it is closer to ideal gas than chlorine.

**25. The postulate related to the constant 'a':**

Intermolecular forces of attraction are negligible in the motion of gas molecules.

**Relationship:** Weaker intermolecular forces means smaller value of the constant and whence the postulate becomes valid while stronger intermolecular forces leads to larger value of the constant and thus the postulate becomes invalid.

**The postulate related to the constant 'b':**

Volume of a gas molecule (particle) is negligible compared to the volume of the whole gas or the volume of the container.

**Relationship:** Smaller molecular size (volume) means smaller value of the constant and whence the postulate becomes valid while larger molecular size leads to larger value of the constant and thus the postulate becomes invalid.

**26**. (i) Both constants 'a' and 'b'.

**Explanation**

During gas liquefaction both strengthening of intermolecular forces between gas molecules and decreasing of volume of empty space (occupied by gas molecules) to zero are done simultaneously. Since the intermolecular forces is related to 'a' and the volume of empty space is related to 'b', both constants are related to the liquefaction.

(ii) Both constants 'a' and 'b'.

**Explanation**

Large value of 'a' means stronger intermolecular forces while large value of 'b' implies large molecular volume which means less of the empty space is left and hence easier liquefaction for gases with large value of constants, 'a' and 'b'.

**27.** (i) $\frac{n^2a}{v^2}$ is the pressure deviation of real pressure from ideal pressure and therefore it corrects the real pressure (P) to be ideal pressure $(P + \frac{n^2a}{v^2})$.

nb is the volume deviation of real gas from ideal gas and therefore it corrects the real volume (V) to be ideal volume $(V - nb)$.

(ii) Compressibility factor, $z = \frac{PV}{nRT}$

From which; $V = \frac{ZnRT}{P} = \frac{0.5 \times 1mol \times 0.082atmdm^3mol^{-1}K^{-1} \times 273K}{100atm} = 0.11193\ dm^3$

But the volume of gas molecules is negligible, $b = 0$ and the given Van der Waals equation becomes:

$\left(P + \frac{n^2a}{v^2}\right)V = nRT$

Then substituting;

$$\left(100atm + \frac{1mol^2 \times a}{0.11193^2dm^6}\right) \times 0.11193dm^3 = 1mol \times 0.082atmdm^3mol^{-1}K^{-1} \times 273K$$

From which $a = 1.252\ dm^6atmmol^{-2}$

Hence Van der Waals constants are;

$a = 1.252\ dm^6atmmol^{-2}$ and $b = 0$

# EXERCISE 4

**1.** (a) Combined gas law enables conversion of the volume of the gas (formed after vapourisation of the substance) to the corresponding volume at STP by using the relation; $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ or $V_2 = \frac{P_1V_1T_2}{P_2T_1}$

Avogadro's law enables calculation of molecular mass from the STP volume of the gas by using the following relation; $\frac{V}{22.4dm^3/mol} = \frac{m}{M_r}$ or $M_r = \frac{m \times 22.4dm^3/mol}{V}$

(b) The alternative is ideal gas law by using the relation $PV = \frac{m}{M_r}RT$ or $M_r = \frac{mRT}{PV}$

(c) The most preferred alternative is ideal gas law.

**Reason:** No need to convert the gas volume to STP volume and therefore it is shorter alternative.

**2.** Abnormal results on experimentally determined molar mass are obtained when the substance undergoes dissociation or association. Dissociation splits one molecule into smaller molecules and therefore making experimental molar mass smaller than that suggested by the molecular formula while association join smaller molecules into one molecule and therefore making experimental molar mass larger than that suggested by the molecular formula.

**3. Advantages:**

1) The method is very simple to carry out.
2) The sample required for the experiment is very small.

**Disadvantages:**

1) This method is not applicable to non-volatile substances (with boiling point greater than $100°C$).
2) The method cannot be used for the substance which undergoes thermal decomposition.
3) Due to manual handling, there is the possibility of personal error.
4) It is not applicable to volatile substances which are water soluble.

**4.** The main assumptions are:

1) The vapour of the substance behaves exactly as ideal gas.
2) The volume of bulb remains constant throughout the experiment (no volume expansion on heating).

**5.** 120.43g/mol

**6.** 89.3g/mol

**7.** Victor Meyer's method is compatible with volatile substances whose boiling points are below $100°C$ so that they can be vapourised by steam. Table salt being non-volatile substance cannot be vapourised by Victor's Meyer apparatus and hence its molar mass cannot be determined by this method.

**8.** This is because methanol is highly soluble in water.

**9.** Molecular masses obtained from the given apparatuses can be used in:

1) Identification of unknown substances.
2) Determination of molecular formula.

**10. Yes, was correct.**

**Explanation**

It is not necessary to weigh the amount of liquid initially put into the flask because a large amount of the liquid is excess. We are concerned only with the vapour that fills the flask after the excess liquid has evaporated and exited the flask. At the end of the experiment, we allowed the remaining vapour to cool and condense into a liquid. It was necessary to weigh the cooled vapour (liquid) to determine the weight of the vapor that filled the flask.

**11. Finding the forgotten data:**

From; $PV = \frac{m}{M_r}RT; P = \frac{mRT}{VM_r}$

Substituting $P = \frac{0.292 \times 0.082 \times 295}{0.061 \times 116.56} atm = 0.9934 atm = 754.98 mmHg \cong 755 mmHg$

Thus the forgotten data was the pressure amounted to $755 mmHg$

**Calculating the correct molar mass (correction):**

$\text{Volume of air displaced} = \text{volume of the sample} = 61 cm^3 = 0.061 dm^3$

Mass of the sample $= 0.292g$

Pressure e exerted by the vapour of the sample $= \text{Total pressure} - \text{Vapour pressure of water}$

$= (755 - 22) mmHg = 733 mmHg$

From the ideal gas equation, it can be shown that; $M_r = \frac{mRT}{PV}$.

With: $m = 0.292g, T = 295K, P = 733 mmHg, V = 0.061 dm^3$;

$$M_r = \frac{0.292 \times 0.082 \times 295}{\frac{733}{760} \times 0.061} \text{ or } 120.1 g/mol$$

The correct molar mass was 120.1g/mol.

**12.** The Boyle's cannot be applied when the number of gas particles has been changed; that is reason of reaching the false conclusion which is "dissociation of the gas decreases amount of the pressure".

**13.** (a) 58.265 (b) 116.53

**14.** 16.8%

**15.** (a) 70.72g/mol (b) 173.6 mL.

**16.** (a) $0.64 atm$ b) $P_{PCl_5} = 0.28 \text{ atm}, P_{PCl_3} = 0.36 atm$

**17.** 53.33%

# SOLUTIONS TO EXAMINATION QUESTIONS

## PART ONE

**Questions 1**

(a) Above critical temperature, gas (vapour) particles are very fast moving with very high kinetic energy which breaks any attempt of forming intermolecular forces through application of high external pressure. Consequently, liquefaction of the substance becomes impossible and hence its liquid state cannot exist.

(b) Given that:

$v = 140cm^3 = \frac{140}{1000}dm^3;\ T = 150℃ = 423K$

$P = 755mmHg = \frac{755}{760}atm,\ \ m = 0.071g$

From $PV = \frac{M}{Mr}\ RT$

$Mr = \frac{mRT}{PV} = \frac{0.071 \times 0.082 \times 423 \times 760 \times 1000}{755 \times 140} = 17.7g/mol$

Thus the measured molar mass of water is approximately $18g/mol$

But the molecular formula $H_2O$ suggests molecular mass of water to be 18g/mol

Hence the given figures are in accordance with the formula $H_2O$ for steam

**Question 2**

(a) Enclosing the gas in the larger container at the same temperature (room was the same) means that each individual gas particle has to move greater distance before hitting the container's wall leading to smaller collision frequency and consequently the pressure will decrease after changing the container.

(b) If the oxidation number of Beryllium (Be) in the compound is x, then the molecular formula of its chloride will be $BeCl_x$

Where $x\ =\ \text{oxidation number of Be}\ =\ \text{number of moles of chlorine atoms in the compound}$

But percentage of Be in the Compound is 11.3%

So the percentage of chlorine atoms in the compound is $(100 - 11.3)\ \%\ =\ 88.7\%$

And molar mass of the compound ($BeCl_x$) $=\ \text{Relative vapour density}\ \times\ 2\ =\ 40\ \times\ 2\ =\ 80$

Thus mass of chlorine atoms in the compound $\frac{88.7}{100} \times 80 = 70.96g$

Therefore number of moles of chlorine atoms in the compound$= \frac{70.96}{35.5}mol = 2mol$

**So oxidation number of Be in the compound is 2**

The molecular formula of the compound is then become $BeCl_2$

It follows that $y\ +\ 71\ =\ 80$; where y is atomic mass of Be

From which $y\ =\ \ 9$

**Hence the relative atomic mass of Be is 9**

**It should be noted that:**

In the question it was asked to find the relative atomic mass of Be from the result of its oxidation number and not otherwise.

**Question 3**

(a) Pressure-volume gas law is Boyle's law which can be stated as follows: Volume of fixed mass of a gas varies inversely proportional to its pressure at constant temperature.

(b) From Graham's of diffusion

$\frac{t_x}{to_2} = \sqrt{\frac{M_x}{M_o}}$ or $M_x =\ Mo_2\left(\frac{t_x}{t_{O_2}}\right)^2$

Where $Mo_2 = 32g/mol$

$to_2 = 240$ seconds, $t_x = 3\frac{3}{4}$minutes $= 225$ seconds

Then $M_x = 32\ \times\left(\frac{225}{240}\right)^2 = 28g/mol$

Hence the relative molecular mass of X is 28

**Question 4**

(a) Temperature of negative Kelvin would imply that the gas has negative volume and it is impossible to have negative volume.

(b) Ozone always exists in a mixture with oxygen as result of its dissociation according to the following equation:

$2O_3(g)\ \rightleftharpoons\ 3O_2(g)$

So if the percentage of $O_3$ is 10%

Then the percentage of $O_2$ will be $(100\ - 10)\ \%\ =\ 90\%$

So average molecular mass of gases

$= \frac{10}{100} M_{O_3} + \frac{90}{100} M_{O_2}$

$= \left(\frac{10}{100} \times 48\right) + \left(\frac{90}{100} \times 32\right) = 33.6 \text{ g/mol}$

If $M_m$ and $t_m$ is the average molecular mass of the mixture and time taken by mixture to diffuse respectively;

Then by Graham's law of diffusion: $\frac{t_m}{t_{H_2}} = \sqrt{\frac{M_m}{M_{H_2}}}$ or $t_m = t_{H_2}\sqrt{\frac{M_m}{M_{H_2}}}$

So, $tm = 1\sqrt{\frac{33.6}{2}} = 4.1 \text{minutes} = 246 \text{ seconds}$

Hence the time required for ozonide oxygen is 246 seconds

**Questions 5**

(a) They are similar in a manner that they both involve movement of gas particles from region of higher gas concentration to that of lower concentration.
They are different in a manner that, while in effusion gas particles pass through aperture, in diffusion gas particles move through an open space.

(b) Since $NO_2$ and $N_2O_4$ are at equilibrium according to the following equation:

$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

If follows that:

Observed molar mass of $N_2O_4$ = observed molar mass of $NO_2$

But $M_r = 2 \text{ g/mol} \times \text{Relative vapour density} = 2 \times 24 = 48 \text{ g/mol}$

Using $i = \frac{\text{Expected molar mass}}{\text{Observed molar mass}}$

Then Vant'hoff factor for $N_2O_4 = \frac{92}{48} = 1.92$

Using $\alpha = \frac{i-1}{N-1}$ where $N = 2$

Then $\alpha = \frac{1.92-1}{2-1}$ =0.92 or 92%

Hence degree of dissociation of the gas is 92%

**Question 6**

(a) Nitrogen liquefies first.
**Reason:** Intermolecular forces are higher for gases with higher critical temperature, making easier to perform liquefaction process.

(b) $PCl_5$ (Phosphorous pentachloride) dissociates according to the following equation:

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$N = 2$

Using $\alpha = \frac{i-1}{N-1}$

Where $\alpha = 20\% = 0.2$

So $0.2 = \frac{i-1}{2-1}$ or $i = 1.2$

But $i = \frac{\text{Expected molar mass}}{\text{Observed molar mass}}$

From which Observed molar mass $= \frac{\text{Expected molar mass}}{i} = \frac{208.5}{1.2} = 173.75\text{g}$

But relative vapour density $= \frac{\text{Molar mass}}{2\text{g/mol}} = \frac{173.75}{2} = 86.875$

Hence the relative vapour density for dissociated mixture is 86.875.

**Questions 7**

(a)

(i) Is the temperature at and above which a gas cannot be liquefied, no matter how much pressure is applied.

(ii) Is the volume occupied by one mole of a gas at critical temperature and pressure.

(iii) Is the pressure required to liquefy a gas at its critical temperature

(b) Iodine dissociates according to the following equation: $I_2 \rightleftharpoons 2I$; $N = 2$

$M_r = 2\text{g/mol} \times \text{relative vapour density}$

So the observed molar mass of iodine $= 2 \times 87 = 174\text{g/mol}$

$i = \frac{\text{Expected molar mass}}{\text{Observed molar mass}} = \frac{254}{174} = 1.46$

$\alpha = \frac{i-1}{N-1} = \frac{1.46-1}{2-1} = 0.46$ or 46%

Hence the percentage dissociation of $I_2$ is 46%

**Questions 8**

(a)

(i) **'a'** indicates the intermolecular forces of attraction between molecules of real gases (Greater intermolecular forces, greater value of **'a'**).

**'b'** indicates actual volume of a molecule of real gas (Greater size or molecular weight of the molecule, greater value of **'b'**).

$H_2S$ has higher value of **'a'**

**Reason:**

(ii) $H_2S$ molecules exhibit stronger intermolecular forces of attraction since it has stronger Van der Waals dispersion forces ($H_2S$ has greater molecular weight than $H_2$) and also has dipole-dipole forces in additional to the dispersion forces while $H_2$ has the dispersion forces only.

$H_2S$ has higher value of **'b'**

**Reason:**

Having greater molecular weight, $H_2S$ molecule has greater size and therefore greater volume than $H_2$.

(iii) **'a'** is correlated to boiling point. The greater value of 'a' means stronger intermolecular forces of attraction and whence higher boiling point**.**

(b) Hydrogen iodide (HI) dissociate according to the following equation: $2HI \rightleftharpoons H_2 + I_2$

The liberated iodine reacts with sodium thiosulphate according to the following equation:

$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$

Where mole ratio of $I_2$ to $Na_2S_2O_3$ is $1:2$

But number of moles of $Na_2S_2O_3$ in $15cm^3$ of its solution

$= \frac{15}{1000} \times 0.1 \text{ moles} = 1.5 \times 10^{-3} \text{ moles}$ ( using $n = MV$)

So number of moles of liberated $I_2 = \frac{1.5\times10^{-3}}{2}$ moles $= 7.5 \times 10^{-4}$ moles

HI contain $1/128$ moles $= 7.8125 \times 10^{-3}$ moles

Thus $7.8125 \times 10^{-3}$ moles of HI dissociates to give $7.5 \times 10^{-4}$ moles of $I_2$

| | $2HI$ | $\rightleftharpoons$ | $H_2$ + | $I_2$ |
|---|---|---|---|---|
| After dissociation | $7.8125 \times 10^{-3} - 2x$ | | x | x |

Where $x = 7.5 \times 10^{-4}$ moles

Degree of dissociation $= \frac{\text{Number of moles dissociated}}{\text{Original number of moles before dissociation}} = \frac{2x}{7.8125\times10^{-3}}$

$$= \frac{2 \times 7.5 \times 10^{-4}}{7.8125 \times 10^{-3}} = 0.192 \text{ or } 19.2\%$$

**Since $n = \frac{m}{M_r}$ and for given element, $M_r$ is constant and hence percentage by mass of HI = percentage by moles**

So percentage by mass of HI which remain undissociated is

(100 – 19.2) % = 80.8%

**Question 9**

(a)

(i) $N_2$(Has a weakest intermolecular force of attraction. Among the non-polar, $N_2$ has smallest molecular weight and therefore smallest Van der Waals dispersion forces. $NH_3$ has a stronger intermolecular force than $N_2$ despite the fact that has smallest molecular weight because it is polar covalent molecule with hydrogen bond.

(ii) $CCl_4$(It has much greater molecular weight and therefore greatest size making its molecule to occupy greatest volume).

(b) From $PV = nRT, n = \frac{PV}{RT}$

Thus $n_{CO_2}$ evolved $= \frac{200 \times 850}{760 \times 1000 \times 0.082 \times 1073}$ moles $= 2.54227 \times 10^{-3}$moles

$CaCO_3$ Decompose according to the following equation:

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

From which mole ratio of $CO_2$ to $CaCO_3$ is 1:1

Thus number of moles of $CaCO_3$ decomposed is also $2.54227 \times 10^{-3}$ moles

And mass of $CaCO_3$ decomposed is $2.54227 \times 10^{-3} \times 100g = 0.254227g$ (Using $m = nM_r$)

Hence the percentage of $CaCO_3$ decomposed $= \frac{0.254227}{2.5} \times 100\% = 10.17\%$

Hence 10.17% of $CaCO_3$ decomposed

**Question 10**

(a) From the kinetic equation: $PV = \frac{Nmc^2}{3}$

But the kinetic energy of N molecules $= \frac{1}{2}Nmc^2$

Where m is the mass of one molecule and Nm is the total mass of N molecules.

So from $K.E = \frac{1}{2}Nmc^2$, $Nmc^2 = 2K.E$

Then substituting $Nmc^2 = 2K.E$ to the above kinetic equation gives: $PV = \frac{2}{3}K.E$

Thus $K.E = \frac{3}{2}PV$

But from ideal gas equation: $PV = nRT$

So $K.E = \frac{3}{2}nRT$ for n moles of gas

If n = 1 (for one mole of the gas): $\mathbf{K.E = \frac{3}{2}RT}$

Since **R** is constant, $\frac{\mathbf{3}}{\mathbf{2}}\mathbf{R}$ is also constant and therefore $K.E = \text{constant} \times T$ or $K.E \propto T$.

Hence the result of kinetic energy the kinetic energy of gas molecules varies directly proportional to the absolute temperature.

(b) Mass of water original present = $1cm^3 \times 1g/cm^3 = 1g$ (m=ρV)

At 2500℃, 3.98% of water dissociated;

That is mass of water dissociated = $\frac{3.98}{100} \times 1g = 0.0398g$

Number of moles of water dissociated = $\frac{0.0398}{18gmol^{-1}} = 2.2111 \times 10^{-3}$mole

Water vapour dissociated according to the following equation

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

From which mole ratio of $H_2O$ to $H_2$ is 1:1

Thus number of moles of hydrogen produced was also 2.2111$\times 10^{-3}$ moles

And also mole ratio of $H_2O$ to $O_2$ is 2:1

Thus number of moles of $O_2$ produced is $\frac{2.2111\times10^{-3}}{2}$ moles = 1.10555$\times 10^{-3}$moles

Percentage by mass of water which remain undecomposed = $(100\% - 3.98)$ % or 96.02%

Thus mass of water vapour (gas) which remain undecomposed

$= \frac{96.02}{100} \times 1g = 0.9602g$

Number of moles of the vapour = $\frac{0.9602}{18} = 0.0533$ moles

Total number of moles of gases

= Number of moles of water vapour + number of moles of $H_2(g)$ + number of moles of $O_2(g)$

= 2.2111$\times 10^{-3} + 1.10555 \times 10^{-3} + 0.0533$ = 0.0566moles

Using $PV = nRT$

From which V = $\frac{nRT}{P} = \frac{0.0566\times0.082\times2773\times760}{760}$ = 12.87dm$^3$

Hence the gases should occupy 12.87dm$^3$

**Question 11**

(a)

(i) The law that govern the breathing process is **Boyle's law** which state that: *The volume of fixed mass of a gas varies inversely proportional to its pressure at constant temperature.*

(ii) Boyle's law is obeyed by the gases at **high temperature** and **low pressure**.

(b) Mass of HI dissociated = $\frac{16}{100} \times 3g = 0.48g$

Number of moles of HI dissociated = $\frac{0.48}{128}$ moles = 3.75$\times 10^{-3}$moles

HI dissociated according to the following equation: $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

From which mole ratio of HI to $I_2$ is 2:1

Thus number of mole of $I_2$ produced = $^1/_2 \times 3.75 \times 10^{-3}$ moles = 1.875$\times 10^{-3}$moles

Iodine reacts with $Na_2S_2O_3$according to the following equation:

$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$

From which mole ratio of $I_2$ to $Na_2S_2O_3$ 1:2

Thus number of moles of $Na_2S_2O_3$ required was $2\times 1.875 \times 10^{-3}$ moles or $3.75\times 10^{-3}$moles

But $[Na_2S_2O_3] = 0.165M$

And $V = \frac{n}{[\ ]}$

Thus volume of $Na_2S_2O_3 = \frac{3.75\times10^{-3}}{0.165} = 0.0227dm^3$ or $22.7cm^3$

**Hence volume of sodium thiosuphate required is 22.7 $cm^3$**

Since mole ratio of $H_2$ to $I_2$ is 1:1; number of moles of $H_2$ produced was also $1.875\times 10^{-3}$moles

Using $m = nMr$

So mass of hydrogen gas $(H_2)$ which would remain uncombined

= $1.875 \times 10^{-3} \times 2g = 3.75 \times 10^{-3}g$

**Hence mass of uncombined hydrogen gas is $3.75 \times 10^{-3}g$**

**Question 12**

(a) The temperature, at which volume or pressure of any gas reduces to zero, is referred to as absolute zero temperature. Its value is equal to at 0K or $-273$℃. The absolute zero temperature is just hypothetical temperature because practically all gases become liquefied before reaching $-273$℃.

(b) For gases, volume ratio = moles ratio (Avogadro's law)

Thus we can treat volume in similar way as mole in stoichiometric ratio

$N_2O_4$ (Nitrogen tetraoxide) decompose partially into $NO_2$ according to the following equation:

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

If initial volume of $N_2O_4$ (before its decomposition at 27℃) is $V_1$

Then after decomposition at 27℃

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$V_1 - \frac{20}{100}V_1 = 0.8V_1 \qquad \frac{2\times20V_1}{100} = 0.4V_1$

Total volume of gaseous mixture = $0.8V_1 + 0.4V_1 = 1.2V_1$

But it is given that, the volume of the gaseous mixture = $1dm^3$

Then $1.2V_1 = 1$ or $V_1 = {}^5/_6\,dm^3$

Thus the initial volume of undecomposed $N_2O_4$ at 27℃ was ${}^5/_6\,dm^3$

Since pressure is kept constant at 760mHg; Charles law is applicable.

That is from Charles law $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

From which $V_2 = \left(\frac{T_2}{T_1}\right)V_1$

Thus the volume of undecomposed $N_2O_4$ at **(a) 100**℃= $\frac{373}{300} \times \frac{5}{6}dm^3 = \frac{373}{360}dm^3$

So at 100℃ (373K)

| | $N_2O_4(g)$ | $\rightleftharpoons$ | $2NO_2(g)$ |
|---|---|---|---|
| After Decomposition | $\frac{373}{360} - x$ | | $2x$ |

Total volume of gaseous mixture = $\frac{373}{360} - x + 2x = \frac{373}{360} + x$

But x = $\frac{90}{100} \times \frac{373}{360}$ (At 100℃ $N_2O_4$ is 90% decomposed)

x = 0.9325

So total volume = $\frac{373}{360} + x = \frac{373}{360} + 0.9325 = 1.969dm^3$

Hence the gases will occupy $1.969dm^3$ at 100˚C

Also from $V_2 = \left(\frac{T_2}{T_1}\right)V_1$

The volume of undecomposed $N_2O_4$ at (ii) 600˚C = $\frac{873}{300} \times {}^5/_6\,dm^3 = 2.425dm^3$

But at 600˚C, $N_2O_4$ is completely dissociated into nitrogen oxide and oxygen, so the equation for the reaction becomes: $N_2O_4(g) \rightarrow 2NO(g) + O_2(g)$

From which mole ratio of $N_2O_4$ to NO is 1:2

And mole ratio of $N_2O_4$ to $O_2$ is 1:1

Thus:

Volume of NO produced = $2\times 2.425 = 4.85\text{dm}^3$

Volume of $O_2$ produced = $2.425\text{dm}^3$

So total volume of the gaseous mixture = $(2.425 + 4.85)\text{dm}^3 = 7.275\text{dm}^3$

Hence the gases will occupy $7.275\text{dm}^3$ at 600˚C

**Question 13**

(a) Both association and dissociation lead to abnormal result of experimental determination of molar mass of volatile substances as explained below:

**Dissociation**

Dissociation is splitting of a large molecule into two or more smaller molecules. It leads to increase in number of gas molecules and whence the increase in volume of the gas. So from the ideal gas equation which can be written as $PV = \frac{m}{M_r}RT$; it is clearly understood that the volume (V) of the gas varies inversely proportional to its molar mass ($M_r$). So the increase in volume of the gas as the result of dissociation leads to decrease in molar mass of the gas. Hence dissociation makes the measured molar mass of volatile substance to be smaller than that suggested by its normal molecular formula.

**Association**

Association is the combining of more than one small molecule to form one larger molecule. It leads to decrease in number of gas molecules and whence decrease in volume of the gas. So from the ideal gas equation; $PV = \frac{m}{M_r}RT$ where volume of the gas varies inversely proportional to its molar mass, the molar mass of the gas must increase as result of association. Hence association makes the measured molar mass of volatile substance to be greater than suggested by its normal molecular formula.

(b) By Graham's law of diffusion: $\frac{V_{O_2}}{V_{N_2O_4}} = \sqrt{\frac{M_{N_2O_4}}{M_{O_2}}}$

From which: $M_{N_2O_4} = M_{O_2}\left(\frac{V_{O_2}}{V_{N_2O_4}}\right)^2 = 32 \times \left(\frac{3}{2}\right)^2 = 72\text{g/mol}$

Thus the observed molar mass of $N_2O_4$ is 72g/mol.

But the expected molar mass of $N_2O_4$ is 92g/mol. (as calculated from its molecular formula).

And $N_2O_4$ dissociated according to the following equation

$$N_2O_4(g) \rightleftharpoons 2NO_2(g);\ N = 2$$

Using $i = \frac{\text{Expocted molar mass}}{\text{Observed molar mass}} = \frac{92}{72} = 1.28$

So from $\alpha = \frac{i-1}{N-1}$

Degree of dissociation of $N_2O_4 = \frac{1.28-1}{2-1} = 0.28$ or 28%

**Hence the degree of dissociation of $N_2O_4$ is 28%**

**Question 14**

(a) From the kinetic equation of gases: $PV = \frac{N}{3}mc^2$; but $K.E = \frac{1}{2}Nmc^2$ or $Nmc^2 = 2K.E$

Then $PV = \frac{2}{3}K.E$

From one of the assumption of kinetic theory of gases; $K.E \propto T$

Thus $K.E = kT$ where k is the constant for proportionality

Therefore; $PV = \frac{2}{3}kT$ …………………………………………………..(i)

**If T is constant:**

$\frac{2}{3}kT$ = Constant and therefore (i) becomes: PV = Constant or $V = \frac{\text{Constant}}{P}$

Hence $\mathbf{V} \propto \frac{\mathbf{1}}{\mathbf{P}}$ which is is Boyle's law.

**If P is constant:**

$\frac{2k}{3P}$ = Constant and therefore the equation (i)above becomes: $V = \text{Constant} \times T$

Hence $\mathbf{V \propto T}$ which is Charles's law.

Since both laws can be derived from the kinetic equation of gases as shown above, the two laws are contained in the equation.

(b) Let $xcm^3$ of methane is mixed with $ycm^3$ of ethane

Then x + y = 24…………………………………… (i)

Equation for combustion of methane: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

From which mole of ratio and hence volume ratio of $CH_4$ to $CO_2$ is 1:1

Thus the volume of $CO_2$ produced by combustion of $CH_4$ was x $cm^3$

Equation for combustion of ethane: $C_2H_6 + {}^7/_2\, O_2 \rightarrow 2CO_2 + 3H_2O$

From which mole ratio and hence volume ratio of $C_2H_6$ to $CO_2$ is 1:2

Thus the volume of $CO_2$ produced from combustion of $C_2H_6$ was $2ycm^3$

So total volume of $CO_2$ produced from combustion $= (x + 2y)\ cm^3$

When KOH is introduced into the gases, the strong alkaline solution absorb $CO_2(g)$ according to the following equation: $2KOH(aq) + CO_2(g) \rightarrow K_2CO_3 + H_2O$

So the decrease in volume after introduction of KOH; is the volume of $CO_2$ which was formed from combustion of the two gases.

That is $x + 2y = 32$…………………….……….(ii)

Solving (i) and (ii) simultaneously gives: $x = 16$ and $y = 8$

**Hence there are $16cm^3$ of methane and $8cm^3$ of ethane in the mixture.**

**Question 15**

(a) From kinetic equation of gases: $PV = \frac{N}{3}mc^2$

But Nm is the total mass for N molecules of the gas, $m_g$;

It follows that: $PV = \frac{m_g c^2}{3}$

From which $P = \frac{m_g c^2}{3V}$

But $\frac{m_g}{V}$ density of the gas, $\rho_g$

Thus $P = \frac{\rho_g c^2}{3}$ or $c^2 = \frac{3P}{\rho_g}$

Whence $c = \sqrt{\frac{3P}{\rho_g}}$

If pressure P, is constant, $\sqrt{3P} = \text{constant}$

Then it becomes; $c = \frac{\text{constant}}{\sqrt{\rho_g}}$ or $c \propto \frac{1}{\sqrt{\rho_g}}$

Since the speed of the gas is directly proportional to the rate of diffusion (or effusion) of the gas, it can be concluded that:

Rate of diffusion $\propto \frac{1}{\sqrt{\rho_g}}$ which is the mathematical form of Graham's law of diffusion.

Since the Graham's law can be derived from kinetic equation of gases, the validity of the kinetic equation confirms the validity of the Graham's law.

(b) Let volume of carbon monoxide, methane and hydrogen be $xcm^3$, $ycm^3$ and $zcm^3$ respectively

Then $x + y + z = 32$---------------------(i)

Equation for combustion of carbon monoxide

$$\begin{array}{lll} CO(g) + \frac{1}{2}O_2(g) & \rightarrow & CO_2(g) \\ xcm^3 \quad\ {}^x/_2\ cm^3 & & xcm^3 \end{array}$$

Equation for combustion of methane

$$\begin{array}{lllll} CH_4(g) & + 2O_2(g) & \rightarrow & CO_2(g) & + 2H_2O(l) \\ ycm^3 & 2ycm^3 & & ycm^3 & \end{array}$$

Equation for combustion of hydrogen

$$\begin{array}{llll} H_2(g) & + {}^1/_2\, O_2(g) & \rightarrow & H_2O(l) \\ zcm^3 & {}^z/_2\ cm^3 & & \end{array}$$

Volume of $CO_2$ reduced volume after introducing $KOH(aq) = 22cm^3$

Thus x + y = 22……………………………………… (ii)

Volume of oxygen reacted = $(50 – 16)cm^3 = 34cm^3$

Then $\frac{x}{2} + 2y + \frac{z}{2} = 34$

or x +4y + z = 68……………………………………… (iii)

Solving (i), (ii) and (iii) simultaneously gives: $x = 10, y = 12$ and $z = 10$

Hence the composition of the mixture was carbon monoxide, $10cm^3$, methane, $12cm^3$ and hydrogen, $10cm^3$ respectively

**Question 16**

(a) **Statement 1:** Correct.

**Statement 2:** Incorrect

**Reason:**

For one mole of the gas to occupy the volume of 22.4L, the room pressure (1atm) must be accompanied with temperature of 0℃ (and not the room temperature which is 25℃). At room temperature and pressure volume of one mole of the gas will be greater than 22.4L.

(b) Let volume of hydrogen, carbon monoxide and nitrogen be $xcm^3, ycm^3$ and $zcm^3$ respectively

Then $x + y + z = 65$ ……………………………………….. (i)

Equation for combustion of hydrogen

$$H_2(g) \quad + \quad {}^1/_2\, O_2(g) \rightarrow H_2O(l)$$
$$xcm^3 \qquad \frac{x}{2}cm^3$$

Equation for combustion of carbon monoxide

$$CO(g) \quad + \quad {}^1/_2\, O_2(g) \quad \rightarrow \quad CO_2(g)$$
$$ycm^3 \qquad {}^y/_2\, cm^3 \qquad\qquad ycm^3$$

Nitrogen does not combust easily in oxygen

Volume of $CO_2$ = Reduced volume after introducing KOH $= (55 - 25) = 30cm^3$

Then y = 30…………………………………..………………(ii)

The gases which remain after introducing KOH are nitrogen and unreacted oxygen

Thus volume of unreacted oxygen + volume of nitrogen = $25cm^3$

But volume of reacted oxygen = $\left(\frac{x}{2} + \frac{y}{2}\right) cm^3$

So the volume of unreacted oxygen = $50 - \left(\frac{x}{2} + \frac{y}{2}\right)$

And volume of nitrogen = $z\ cm^3$

If follows that: $50 - \left(\frac{x}{2} + \frac{y}{2}\right) + z = 25$

or $x + y - 2z = 50$………………………………………..(iii)

Solving (i), (ii) and (iii) simultaneously gives

$x = 30, y = 30$ and $z = 5$

$\%H_2 = \frac{30}{65} \times 100\% = 46.15\%$

$\%CO = \frac{30}{65} \times 100\% = 46.15\%$

$\%N_2 = \frac{5}{65} \times 100\% = 7.7\%$

**Hence the percentage by volume of each gas in the original mixture was:**

| | |
|---|---|
| Hydrogen gas | 46.15% |
| Carbon monoxide gas | 46.15% |
| Nitrogen gas | 7.7% |

**Question 17**

(a) From the kinetic equation of gases: $PV = {}^1/_3\, Nmc^2$

If $N = N_A = 6.02 \times 10^{23}$ molecules, $n = 1$ (n is the number of moles of the gas)

And $Nm = N_A m = M_r (M_r$ is the molar mass of the gas)

Then $PV = \frac{M_r c^2}{3}$ but for $n = 1, PV = RT$

Then $RT = \frac{M_r c^2}{3}$ or $c^2 = \frac{3RT}{M_r}$

Hence $c = \sqrt{\frac{3RT}{M_r}}$

Where c is the root mean square (r.m.s) speed of gas molecules.

The kinetic energy (K.E) can also be deduced from the above equation for the root mean square speed as follows:

From $c = \sqrt{\frac{3RT}{M_r}}$

But kinetic energy(K.E)of the gas $= \frac{1}{2}mc^2$ where m is the given mass of the gas.

But $c = \sqrt{\frac{3RT}{M_r}}$

Then $K.E = \frac{1}{2}m\left(\sqrt{\frac{3RT}{M_r}}\right)^2 = \frac{3mRT}{2M_r}$; But $\frac{m}{M_r} = n$;

Hence $K.E = \frac{3}{2}nRT$ for n moles of the gas

(b) Number of moles of iodine in $11.2cm^3$ of its solution = $\frac{11.2}{1000} \times 0.05 = 5.6 \times 10^{-4}$ moles

Iodine reacts with sulphorous acid according to the following equation:

$$I_2 + H_2SO_3 + H_2O \rightarrow H_2SO_4 + 2HI$$

From which mole ratio of $I_2$ to $H_2SO_3$ is 1:1

Thus number of $H_2SO_3$ in $100cm^3$ of its solution is also $5.6 \times 10^{-4}$ moles

$H_2SO_3$ is formed by mixing $SO_2$ and water according to the following equation

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$

Thus number of moles of $SO_2$ in $100cm^3$ of acid solution was also $5.6 \times 10^{-4}$ moles

Hence number of moles of $SO_2$ per $1dm^3$ ($1000cm^3$) of the acid solution

$= 5.6 \times 10^{-4} \times 10$ moles $= 5.6 \times 10^{-3}$moles

Volume of the gas (dissolved$SO_2$) can be found by using ideal gas equation as follows:

From $PV = nRT$; $V = \frac{nRT}{p} = \frac{5.6 \times 10^{-3} \times 0.082 \times 288 \times 760dm^3}{742} = 0.1355dm^3$ or $135.5cm^3$

**Hence the volume of dissolved sulphur dioxide per $dm^3$ of the acid was $135.5cm^3$**

**Question 18**

(a) Duma's method works with volatile substances only. Glucose being non-volatile substance cannot be vapourised by Duma's apparatus and hence the method is not suitable in determining its molar mass.

(b) Given that:

Volume of sample of air = $200dm^3$

Mass of $CO_2$ in the air sample = 0.157g (potassium hydroxide bulb adsorbs $CO_2$ component only from the air components so the increase in mass of the bulb must be the mass of $CO_2$ in the air sample).

Temperature, $T = 14°C = 287K$

$P_{air} = 753\ mmHg = \frac{753}{760}$ atm

From ideal gas equation: $PV = nRT$

So $n_{air} = \frac{P_{air}V}{RT} = \frac{753 \times 200}{760 \times 0.082 \times 287} = 8.42$ moles

Using $n = \frac{m}{M_r}$

Then $n_{CO_2} = \frac{m_{CO_2}}{M_{CO_2}} = \frac{0.157g}{44gmol^{-1}} = 3.5682 \times 10^{-3}$ moles

But $\frac{n_{CO_2}}{n_{air}} = \frac{V_{CO_2}}{V_{air}}$ (From Avogadro's law)

So percentage by volume of $CO_2$ in the air = $\frac{n_{CO_2}}{n_{air}} \times 100\% = \frac{3.5682 \times 10^{-3}}{8.42} \times 100\% = 0.0424\%$

**Hence the percentage of $CO_2$ in the air is 0.0424% by volume.**

**Question 19**

Mass of $H_2SO_4$ in 100kg of 98% $H_2SO_4$ = $\frac{98}{100} \times 100kg = 98kg = 98000g$

Using $n = {}^{m}/_{M_r}$

Number of moles of $H_2SO_4 = \frac{98000g}{98gmol^{-}} = 1000$moles

But 1 mole of $SO_2$ produce 1 mole of $H_2SO_4$

Thus 1000moles of $H_2SO_4$ are produced by 1000moles of $SO_2$

But from;

$$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

Mole ratio of $FeS_2$ to $SO_2$ is 4:8 or 1:2

Thus number of moles of $FeS_2$ required to produce 1000moles of $SO_2$ is $\frac{1000}{2}\text{moles} = 500\text{moles}$

Using $m = nMr$

Mass of iron pyrites, $FeS_2 = 500 \times 120g = 60000g$ or 60kg

(a) Hence 60kg of iron pyrites would be required

Form the given equation: Mole ratio of $FeS_2$ to $O_2$ is 4:11

So number of moles of $O_2$ required to complete combustion = $\frac{11}{4} \times 500\text{moles} = 1375$ moles

If $n_{air}$ is the number of moles of air containing 1375 moles of $O_2$

Then $\frac{21}{100} n_{air}$ = 1375 moles (For gases, percentage by volume is equal to the percentage by moles)

So $n_{air} = \frac{1375 \times 100}{21}$ moles = $\frac{137500}{21}$ moles

From $PV = nRT$

$V_{air} = \frac{n_{air}RT}{P_{air}} = \frac{137500 \times 0.082 \times 288 \times 760}{21 \times 750} dm^3 = 156690dm^3$ or $156.69m^3$

(a) Hence $156.69m^3$ of air would be required for complete combustion of the pyrites.

**Question 20**

(a) Real gases fails to obey Charles's and Boyle's law at:

- Low temperature
- High pressure

(b) By Graham's law of diffusion: $\frac{V_{O_2}}{V_{inert}} = \sqrt{\frac{M_{inert}}{M_{O_2}}}$

So $M_{inert} = M_{O_2}\left(\frac{V_{O_2}}{V_{inert}}\right)^2 = 32 \times \left(\frac{50}{141.4}\right)^2 = 4gmol^{-1}$

**Hence the relative atomic mass of an inert gas is 4**

**Question 21**

(a)

(i) Intermolecular forces of attraction between gas molecules in motion is negligible.

(ii) The volume of individual gas molecules is negligible compared to the volume of the whole gas.

(b)

| Composition by element | C | H | O |
|---|---|---|---|
| Percentage by mass of each | 37.21 | 7.8 | 55 |
| Mass of each in 100g of the compound | 37.21g | 7.8g | 55g |
| Number of moles of each using $n = \frac{m}{Mr}$ | $\frac{37.21g}{12gmol^{-}} = 3.1mol$ | $\frac{7.8g}{1gmol^{-1}} = 7.8mol$ | $\frac{55g}{16gmol^{-1}} =$ 3.4375 mol |
| Divide by the smallest to get simpler ratio | $\frac{3.1\ mol}{3.1\ mol} = 1$ | $\frac{7.8\ mol}{3.1\ mol} = 3$ | $\frac{3.4375\ mol}{3.1\ mol}$ = 1 |

**So empirical formula of the compound is $CH_3Cl$ if the molecular formula of the compound is $(CH_3Cl)_n$**

Then $12n + 3n + 35.5n = M_r$

or $50.5n = M_r$

But $M_r = \frac{mRT}{PV} = \frac{2.4 \times 0.082 \times 298 \times 760 \times 1000}{740 \times 934} = 64$

Then $50.5n = 64$ or $n = 1$

**Hence the molecular formula of the compound is $CH_3Cl$**

**Question 22**

(a) At high temperature and low pressure.

(b) From Van – der – Waals equation: $\left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$

Substituting given values: $\left(11 + a\left(\frac{2}{4}\right)^2\right)\ (4 - \ (2\ \times 0.05)) = 2 \times 0.082 \times 300$

a = $6.46 atmL^2 mol^{-2}$

**Hence the value of 'a' for the gas is $6.46 atmL^2 mol^{-2}$**

**Question 23**

(a)

- Temperature must be kept constant.
- If there is no chemical reaction between gases.

(b) By Dalton's law of partial pressure total pressure ($P_T$) in the vessel is given by:

$P_T = P_{N_2} + P_u = \frac{n_{N_2}RT}{V} + \frac{n_uRT}{V}$

$P_T = (n_{N_2} + n_u)\frac{RT}{V}$; From which $n_u = \frac{P_TV}{RT} - n_{N_2} = \frac{4.18 \times 3}{0.082 \times 300} - 0.4 = 0.1$ moles

From Graham's law of diffusion: $\frac{V_{N_2}}{V_u} = \sqrt{\frac{M_u}{M_{N_2}}}$

But from Avogadro's law it can be shown that: $\frac{V_{N_2}}{V_u} = \frac{n_{N_2}}{n_u}$

Thus $\frac{n_{N_2}}{V_u} = \sqrt{\frac{M_u}{M_{N_2}}}$

$M_u = M_{N_2}\left(\frac{n_{N_2}}{n_u}\right)^2 = \left(\frac{0.4}{0.1}\right)^2 \times 28$g/mol = 448g/mol

**Hence molar mass of unknown gas is 448g/mol**

**Question 24**

(a)

(i) Boyle's law describes relationship between pressure and volume of ideal gas when temperature and amount of the gas are kept constant.

(ii) Charles's law describes relationship between volume and temperature of ideal gas when pressure and amount of the gas are kept constant.

(iii) Gay-Lussac's law describes relationship between pressure and temperature of ideal gas when volume and amount of the gas are kept constant.

(iv) Avogadro's law describes relationship between amount of ideal gas and its volume when pressure and temperature are kept constant.

(b) When another flask is immersed in the hot oil bath, the pressure in the hot flask will be greater than the pressure in the cold flask. So gas (hydrogen) molecules will start to move from the hot flask to the cold flask until the pressure in the two flasks balance; i.e. until Pressure in the cold flask = Pressure in the hot flask.

Let number of molecules moved from the hot flask be y.

Then number of moles of hydrogen molecules in the hot flask $= 0.35 - y$

And number of moles of hydrogen molecules in the cold flask $= 0.35 + y$

So when the pressure at the two flask are at equilibrium (balance each other)

$$\frac{(0.35-y)RT_2}{V} = \frac{(0.35+y)RT_1}{V}$$

Where $T_1$ is the temperature of the cold flask $= 27°C = 300K$

$T_2$ is the temperature of the hot flask $= 127°C = 400K$

(It should be noted that: In this calculation; the expansion of volume of the flask due to rise in temperature has been neglected, that is why the volume of the two flasks, V remains the same).

Substituting the given values: $(0.35 - y)\ 400 = (0.35 + y)\ 300$

From which, y = 0.05 moles

Hence

- Number of hydrogen gas in the hot flask is (0.35 – y) moles = (0.35 – 0.05) moles = 0.3 moles.
- Number of moles of hydrogen gas in the cold flask is (0.35 +y) moles = (0.35 + 0.05) moles = 0.4 moles

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

Where $n = 0.35, R = 0.082, T = 300K\ (27°C), P = 0.5atm$

So volume of each flask = $\frac{0.35 \times 0.082 \times 300}{0.5}\text{dm}^3 = 17.22\text{dm}^3$

Then the final pressure in each flask can be found from either cold or cold flask and will give the same result by using;

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

So for cold flask: $P = \frac{0.4 \times 0.082 \times 300}{1.722}\text{atm} = 5.7\text{atm}$

**Hence the final pressure of the system is 5.7atm in each flask**

**Question 25**

(a) (i) It is completely **elastic.**

(ii) Pressure

(iii) Under presence of intermolecular forces, the collision will not be elastic. This is because, the intermolecular forces lower speed as well as kinetic energy making the collision inelastic as some kinetic energy are transformed into intermolecular energy**.**

Also the intermolecular forces, lowers the observed pressure. This is because as result of decrease in speed, both collision frequency and collision force (intensity) are decreased resulting to decrease in pressure of the gas.

(b)

| Composition by element | C | H | N |
|---|---|---|---|
| Percentage by mass of each | 75.92 | 6.37 | 17.71 |
| Mass of each in 100g of the compound | 75.92g | 6.37g | 17.71g |
| Number of moles of each using, $n = \frac{m}{M_r}$ | $\frac{75.92g}{12gmol^{-1}} =$ 6.33mol | $\frac{6.37g}{1gmol^{-1}} =$ 6.37 mol | $\frac{17.71g}{14gmol^{-1}} =$ 1.265mol |
| Divide by smallest to get simpler ratio | $\frac{6.33mol}{1.265\ mol} = 5$ | $\frac{6.37\ mol}{1.265\ mol} = 5$ | $\frac{1.265\ mol}{1.265\ mol} = 1$ |

The empirical formula of the compound is $C_5H_5N$

From $M_r = \frac{mRT}{PV}$

But $\frac{m}{V}$ = density, ρ

Then $M_r = \frac{\rho RT}{P} = \frac{2.12 \times 0.082 \times 383 \times 760}{630} = 80g/mol$

Let molecular formula of the compound be $(C_5H_5N)_n$

Then $60n + 5n + 14n = 80$ or $79n = 80$ or $n = 1$

Hence the molecular formula of the compound is $C_5H_5N$

**Question 26**

(a)

(i) This describes relationship between pressure and temperature of an ideal gas when volume and amount of the gas are kept constant. The law states that: Pressure of given mass of a gas varies directly proportional to its absolute temperature provided that the volume of the gas is constant.

**Mathematical equation:**

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

(ii) This describes the relationship between volume, pressure and temperature of an ideal gas when amount of the gas is kept constant. The law states that: Volume of fixed mass of a gas varies directly proportional to absolute temperature and inversely proportional to its pressure.

**Mathematical equation:**

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

(b)

| Composition by element | C | H |
|---|---|---|
| Percentage by mass of each | 46.1 | 53.9 |
| Mass of each in 100g of the compound | 46.1g | 53.9g |
| Number of moles of each, $n = \frac{m}{M_r}$ | $\frac{46.1g}{12gmol^{-1}} = 3.84mol$ | $\frac{53.9g}{1gmol^{-1}} = 53.9\ mol$ |
| Divide by smallest to get simpler ratio | $\frac{3.84}{3.84} = 1$ | $\frac{53.9}{3.84} = 14$ |

So the empirical formula of the compound is $CH_{14}$

By Graham's law of diffusion: $\frac{t_X}{t_{O_2}} = \sqrt{\frac{M_X}{M_{O_2}}}$

$$M_X = M_{O_2}\left(\frac{t_X}{t_{O_2}}\right)^2 = 32\left(\frac{20}{15.7}\right)^2 = 52\text{g/mol}$$

If the molecular formula of the compound is $(CH_{14})_n$

Then $12n + 14n = M_r = 52$

$26n = 52$ or $n = 2$

Hence molecular formula of the compound is $C_2H_{28}$

$$\frac{V_{CO_2}}{V_X} = \sqrt{\frac{M_X}{M_{CO_2}}} \text{ or } V_{CO_2} = V_X\sqrt{\frac{M_X}{M_{CO_2}}}$$

$$V_{CO_2} = 50\sqrt{\frac{52}{44}} = 54.4\text{cm}^3$$

Hence $54.4\text{cm}^3$ of $CO_2$ would diffuse in 20 seconds

**Question 27**

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

**Before opening the cock:**

Number of moles of $SO_2 = \frac{0.75\times2.125}{0.082\times353}\text{moles} = 0.055\text{moles}$

Number of moles of $O_2 = \frac{0.5\times1.5}{0.082\times353}\text{moles} = 0.02591\text{moles}$

**After opening the cock:**

The two gases mix together then:

- Total number of moles of gaseous mixture, $n_T$ = (0.055+ 0.02591)moles = 0.08091moles
- Total volume of the gaseous mixture = total volume of the two chambers = (2.125+1.5)L = 3.625L

$$X_{SO_2} = \frac{n_{SO_2}}{n_T} = \frac{0.055}{0.08091} = 0.68$$

Thus mole fraction of $SO_2$ was 0.68

$$P_T = \frac{n_TRT}{V} = \frac{0.08091\times0.082\times353}{3.625} = 0.646\text{atm}$$

The total pressure is 0.646atm

Partial pressure of $SO_2$, $P_{SO_2} = X_{SO_2}P_T = 0.68 \times 0.646\text{atm} = 0.43928\text{atm}$

**If the mixture is allowed to react after passing through catalyst:**

$SO_2$ reacts with $O_2$ according to the following equation (Assuming reaction reach to completion i.e. it is irreversible):

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

From which mole ratio of $SO_2$ to $O_2$ is 2:1

Thus 0.02591moles of $O_2$ reacts with $0.02591 \times 2 = 0.05182$moles of $SO_2$

So $SO_2$ present in excess and $(0.055 - 0.05182)\text{moles} = 0.00318\text{moles}$ of it remain unreacted at the end of the reaction

Also from the above reaction equation; mole ratio of $O_2$ **(limited reactant)** to $SO_3$ is 1:2

Thus number of moles of $SO_3$ produced was $0.02591 \times 2 = 0.05182\text{moles}$

So at the end of the reaction there are 0.00318moles and 0.05182moles of $SO_2$ and $SO_3$ respectively.

Therefore; the total number of moles of the final gaseous mixture = $(0.05182 + 0.00318)$ moles = $0.055$moles

Then $X_{SO_3} = \frac{n_{SO_3}}{n_T} = \frac{0.05182}{0.055} = 0.9422$

Thus mole fraction of $SO_3$ in the final mixture was 0.3813

$$P_T = \frac{n_TRT}{V} = \frac{0.055 \times 0.082 \times 353}{3.625}\text{atm} = 0.4392\text{atm}$$

The total pressure in the final mixture is 0.4392atm

**Question 28**

(a) The four (main) postulates are:

1. The gas particles are so small compared with the distances between them that the volume of the individual particles can be neglected.
2. The gas particles are in constant motion of which they collide the walls of the container, therefore exerting pressure.
3. There is no intermolecular forces (neither attraction nor repulsion) between gas particles.
4. The average kinetic energy of a collection of gas particles is directly proportional to the absolute temperature of the gas.

(b) By Graham's law of diffusion: $\frac{V_{NH_3}}{V_{HCl}} = \sqrt{\frac{M_{HCl}}{M_{NH_3}}}$

(Time taken for diffusion of each solution is constant because the two ends of the tube were immersed in the solutions at the same time)

But volume of solution diffused varies directly proportional to the distance travelled by the solution.

It follows that: $\frac{l_{NH_3}}{l_{HCl}} = \sqrt{\frac{36.5}{17}} = 1.465$

$l_{NH_3} : l_{HCl} = 1.465 : 1$

If total length of the tube is l, then the distance traveled by $NH_3$ before forming a white cloud of

$$NH_4Cl = \left(\frac{1.465}{1 + 1.465}\right) l = \frac{293}{493} l$$

Hence a white cloud of $NH_4Cl$ (s) forms at $\frac{293}{493}$ of the total length of the tube from the ammonia.

**Question 29**

(a)

(i) "Volume of fixed mass of a gas varies inversely proportional to its pressure at constant temperature."

(ii) "The volume of the gas varies directly proportional to its number of molecules or moles at constant temperature and pressure."

(iii) "The total pressure exerted in the container of the mixture of two or more gases is equal to the summation of their partial pressures provided that the gases do not react.''

**(Have you noticed the difference between 'say about' (question 26) and 'say' (in this question) in the approach of answering questions?)**

(b) From $PV = \frac{m}{Mr} RT$ then $P = \left(\frac{m}{V}\right) \frac{RT}{Mr}$ but $\frac{m}{V} = \rho$

$$P = \frac{\rho RT}{Mr} \quad \text{or } \rho = \frac{PM_r}{RT}$$

If $P_B$ and $P_T$ are density of air at the bottom and the top of the mountain respectively

Then $\rho_T = \frac{P_T M_r}{RT_T}$ and $\rho_B = \frac{P_B Mr}{RT_B}$ So $\frac{\rho_T}{\rho_B} = \frac{P_T T_B}{P_B T_T} = \frac{710 \times 303}{760 \times 273} = 1.0369$

Hence $\rho_T = 1.0369 \rho_B$

Where $\rho_T$ is the density of air at the top of the mountain and $\rho_B$ is the density of air at the bottom of the mountain

**Question 30**

(a) Volume of all gases varies directly proportional to their number of moles and absolute temperature and inversely proportional to their pressure.

(b) $P_{N_2} = \frac{n_{N_2} RT}{V} = \frac{m_{N_2} RT}{M_{N_2} V}$

Where $m_{N_2} = 5.65g, R = 0.082, T = 300k$

$M_{N_2} = 28g/mol, V = (15L + 6L) = 21L$

$$P_{N_2} = \frac{5.65 \times 0.082 \times 300}{28 \times 21} = 0.2364 \text{ atm}$$

Partial pressure of nitrogen gas is 0.2364atm

$$P_{O_2} = \frac{n_{O_2} RT}{V} = \frac{m_{O_2} RT}{M_{O_2} V}$$

Where $m_{O_2} = 5g$ and $M_{O_2} = 32g/mol$

$$P_{O_2} = \frac{5 \times 0.082 \times 300}{32 \times 21} = 0.183 \text{ atm}$$

Partial pressure of oxygen gas 0.183atm

By Dalton's law of partial pressure: $P_T = P_{O_2} + P_{N_2} = (0.2364 + 0.183)\text{atm} = 0.4194 \text{ atm}$

The total pressure is 0.4194atm

**Question 31**

(a) The law is Dalton's law of partial pressure.

It states that: The total pressure exerted in the container of the mixture of two or more gases is equal to the summation of their partial pressure provided that the gases do not react.

(b) By Graham's law of diffusion: $\frac{\text{Rate of diffusion of oxygen gas}}{\text{Rate of diffusion of uknown gas}} = \sqrt{\frac{M_U}{M_{O_2}}}$

But rate of diffusion varies directly proportional to the rate of pressure change then $\frac{\frac{\Delta P_{O_2}}{t_{O_2}}}{\frac{\Delta P_U}{t_U}} = \sqrt{\frac{M_U}{M_{O_2}}}$

$$\frac{\Delta P_{O_2} t_U}{\Delta P_U t_{O_2}} = \sqrt{\frac{M_U}{M_{O_2}}} \quad \text{or} \quad \frac{(2000 \times 1500)85}{(2000 \times 1500)55} = \sqrt{\frac{M_U}{32}} \quad \text{or } M_U = 76 \text{ g/mol}$$

Hence molar mass of unknown gas is 76g/mol

**Question 32**

(a) From the kinetic equation of gases; $PV = \frac{Nmc^2}{3}$

But $K.E = \frac{1}{2}mc^2$ (for one molecule of the gas)

Or $mc^2 = 2K.E$; Then $PV = \frac{2}{3}N \times K.E$

But from one of the assumptions of kinetic theory of gases: $K.E \propto T$

Then $K.E = kT$ where k is constant for proportionality and $PV = \frac{2}{3}NkT$

But $\frac{N}{N_A} = n$ or $N = nN_A$ where n is the number of moles of the gas

Substituting $N = nN_A$ to $PV = \frac{2}{3}NkT$ gives $PV = \frac{2}{3}nN_AkT$

Since $N_A$ is constant, $\frac{2}{3}N_Ak$ gives another constant, R

Hence $\mathbf{PV = nRT}$ this is ideal gas equation

(b) $K.E = {}^3/_2\, RT$ for one mole of a gas

$K.E = {}^3/_2 \times 8.314 \times 300 = 3741.3J$

Hence kinetic energy for one mole of the gas is $3.7413kJ$

**Question 33**

$$n_{He} = \frac{P_{He}V}{RT} = \frac{187.1 \times 0.25}{0.082 \times 300 \times 760} = 2.5 \times 10^{-3}\text{moles}$$

(i) There were $2.5 \times 10^{-3}$moles of Helium in the original vessel.

$$n_{CO_2} = \frac{P_{CO_2}V}{RT} = \frac{561.3 \times 0.25}{0.082 \times 300 \times 760} = 7.5 \times 10^{-3}\text{moles}$$

(ii) Thus $7.5 \times 10^{-3}$moles of carbon dioxide gas was produced

(iii) If $n_{ea}$ and $n_{ee}$ represent number of moles of ethane and ethene respectively (which are originally present in the vessel)

Then from given equation for combustion:

Number of moles of $CO_2$ produced by combustion of ethane = $2n_{ea}$

And number of moles of $CO_2$ produced by combustion of ethene = $2n_{ee}$

It follows that: $2n_{ea} + 2n_{ee} = 7.5 \times 10^{-3}$ moles

From which: $n_{ea} + n_{ee} = 3.75 \times 10^{-3}$ moles

So total number of moles of gases present in the original vessel is:

$n_{ea} + n_{ee} + n_{He} = (3.75 + 7.5) \times 10^{-3}$ moles $= 6.25 \times 10^{-3}$moles

But total pressure present in the original vessel, $P_T = 680mmHg$

And $P_{He} = P_{He} = \left(\frac{n_{He}}{n_T}\right) \times P_T = \frac{2.5 \times 10^{-3}}{6.25 \times 10^{-3}} \times 680mmHg = 272mmHg$

Hence the partial pressure of Helium in the original vessel was 272mmHg

(iv) Using $V = \frac{nRT}{P}$

Substituting the value of partial pressure of Helium obtained in (iii) above;

$$V = \frac{2.5 \times 10^{-3} \times 0.082 \times 300 \times 760}{272} = 0.11718\text{dm}^3 \text{ or } 171.8\text{cm}^3$$

Hence the volume of the original vessel was $0.11718\text{dm}^3$ or $171.8\text{cm}^3$

**Question 34**

(a) **a** is the coefficient of attraction reflecting the strength of intermolecular force of attraction between gas particles (molecules).
**b** is the effective volume reflecting the molecular size of the gas.

(b) From Van der Waals equation for real gases: $\left(P + a\left(\frac{n}{v}\right)^2\right)(v - nb) = nRT$

Substituting given values $\left(P + 1.34\left(\frac{0.02}{1.6}\right)^2\right)(1.6 - (0.02 \times 0.32)) = 0.02 \times 0.082 \times 293$

$P = 0.3\text{atm}$

Hence the pressure of real gas is 0.3atm

**Question 35**

Using $M_r = \frac{mRT}{PV}$

At 110℃ (383K)

$$M_r = \frac{0.11 \times 0.082 \times 383 \times 760 \times 1000}{454 \times 63.7} = 91\text{g/mol}$$

Molar mass of ethanoic acid at 100℃ is 91g/mol

At 156℃ (429K)

$$M_r = \frac{0.081 \times 0.082 \times 429 \times 760 \times 1000}{458 \times 66.4} = 71\text{g/mol}$$

Molar mass of ethanoic acid at 110℃ is 71g/mol

**Interpretation of the results:**

Measured molar mass of $CH_3COOH$ is greater than its expected molar mass of 60g/mol, because molecules of the acid are capable of undergoing association as result of strong hydrogen bonding formed between its molecules. Degree of association of the acid decrease with an increase in temperature as the high temperature weakens the strength of hydrogen bonding and hence molar mass of $CH_3COOH$ at 156℃ become smaller than that measured at 110℃.

**Question 36**

(a) HCl and $NH_3$

**Explanation**

HCl and $NH_3$ being polar, they are highly soluble in water; so they will dissolve in it to make a solution and hence they would not come out the other end.

(b) By Dalton's law of partial pressure: $P_T = (n_{O_2} + n_{H_2})\frac{RT}{V} = \left(\frac{m_{O_2}}{M_{O_2}} + \frac{m_{H_2}}{M_{H_2}}\right)\frac{RT}{V}$

$$P_T = \left(\frac{86.2}{32} + \frac{1.5}{2}\right)\frac{0.082 \times 361}{3.2 \times 10^3}\text{atm} = 0.032 \text{ atm}$$

Hence the total pressure in the vessel is 0.032atm

**Question 37**

(a) It is describing the relationship between the total pressure of a mixture of non-reacting ideal gases and the partial pressures of each individual component.

(b) $\frac{t_J}{t_A} = \sqrt{\frac{M_J}{M_A}}$ or $M_J = M_A\left(\frac{t_J}{t_A}\right)^2 = 120 \times \left(\frac{300}{580.8}\right)^2 \text{ g/mol} = 32\text{g/mol}$

Hence relative molecular mass of J is 32g/mol

**Question 38**

(a)

(i) From its definition, compressibility factor (Z) is given by;

$$Z = \frac{\text{Real volume}}{\text{Ideal volume}}$$

If V represents real volume, the formula becomes: $Z = \frac{V}{\text{Ideal volume}}$

But ideal volume can be calculated from ideal gas equation with measured (actual) P, T and n

That is $V = \frac{nRT}{P}$ (From PV = nRT)

Where V is the ideal volume.

Then the formula $Z = \frac{V}{\text{ideal volume}}$ becomes $Z = \frac{V}{\frac{nRT}{P}} = \frac{PV}{nRT}$

Thus the compressibility factor, $Z = \frac{PV}{nRT}$

Where:

P is the measured (real) pressure

V is the measured (real) volume

n is the measured number of moles

(ii) For ideal behaviour, $Z = 1$

For the positive deviation, $Z > 1$

For the negative deviation, $Z < 1$

(b) From $PV = \frac{m}{Mr}RT$ or $m = \frac{PVMr}{RT} = \frac{0.12\times3\times207}{0.082\times353} = 2.57g$

Hence mass of the vapour is 2.57g

**Question 39**

(a)

(i) Is the gas which obeys ideal gas equation (PV=nRT) in all conditions of temperature and pressure.

(ii) Ideal gas equation can be derived by combining Boyle's law, Charles's law and Avogadro's law as shown below:

From Boyle's law: $V \propto \frac{1}{P}$; constants: n and T

From Charles's law: $V \propto T$; constants: n and P

Avogadro's law: $V \propto n$; constants: P and T

Combining the three laws: $V \propto \frac{nT}{P}$ or $V = \frac{nRT}{P}$

Where R is the proportionality constant; and the constant is known as universal molar gas constant

Hence $PV = nRT$ and the result is known as ideal gas equation.

(b) At = s.t.p. $T = 273K, P = 103100Pa$

So taking: $T_1 = 18°C = 291K, V_1 = 267cm^3, P_1 = 100400Pa, T_2 = 273K,$

$P_2 = 101300Pa, V_2 = ?$

From general gas equation: $\frac{P_2V_2}{T_2} = \frac{P_1V_1}{T_1}$

$$V_2 = \left(\frac{T_2}{T_1}\right)\left(\frac{P_1}{P_2}\right)V_1 = \frac{273 \times 100400 \times 267}{291 \times 101300}cm^3 = 248cm^3$$

Thus volume of the gas at s.t.p = $248cm^3$

Normal density, $\rho = \frac{m}{v} = \frac{0.162}{248} = 6.532 \times 10^{-4}g/cm^3$

(i) Normal density of the gas is $6.532 \times 10^{-4}g/cm^3$ or $0.6532g/dm^3$

Using $Mr = \frac{mRT}{PV} = \frac{\rho RT}{P} = \frac{0.6532\times0.082\times273\times101300}{101300} = 14.6g/mol$

Relative density of the gas $= \frac{Mr}{2g/mol} = \frac{14.6}{2} = 7.3$

(ii) Relative density of the gas is 7.3

**Question 40**

(a)

(i) Separation of gases having different densities by diffusion.

Others:

1. In determination of densities and molar masses of unknown gases by comparing the rates of diffusion with known gases.
2. In separation of isotopes of some of the elements.

(ii) During the preparation of gases by downward displacement of water.

(iii) In determination of molecular formula of gases.

Others:

1. In determination of atomicity of gases.
2. In establishing the relationship between relative molecular mass and vapour density.

From Graham's law of diffusion: $\frac{t_u}{t_{O_2}} = \sqrt{\frac{M_u}{M_{O_2}}}$ or $M_u = \frac{32g}{mol} \times \left(\frac{177}{250}\right)^2 = 16g/mol$

The relative molecular mass of unknown gas is 16

**Question 41**

(a) Only two postulates are free from error which are:

1. A gas consists of very small particles (molecules) in a random motion of which there is a collision between gas particles themselves and the collision between gas particles and the walls of the container, thus exerting a pressure.
2. Kinetic energy of gas particles varies directly proportional to the absolute temperature.

(b) Number of moles of $H_2$ reacted after t seconds $= (1 - 0.8)\text{moles} = 0.2\text{moles}$

$H_2$ and $I_2$ React according to the following equation: $H_2 + I_2 \rightarrow 2HI$

From which mole ratio of $H_2$ to HI is 1:2

Hence number of moles of HI formed after t seconds was $2 \times 0.2\text{moles} = 0.4\text{moles}$

**Question 42**

(a) The four factors are:

1. **Density (or molar mass) of the gas:** High density (or molar mass) means small rate of diffusion.
2. **Pressure:** High pressure of the gas means small rate of diffusion.
3. **Temperature:** High temperature of the gas means high rate of diffusion.
4. **Concentration difference (concentration gradient):** Large concentration difference from one point to another, means high rate of diffusion

(b) From Graham's law of diffusion: $\frac{R_{H_2}}{R_{Ne}} = \sqrt{\frac{M_{Ne}}{M_{H_2}}} = \sqrt{\frac{20.18}{2.02}} = 3.16$

If $t_{H_2}$ represents the time for $^2/_3$ of $H_2$ to diffuse and $t_{Ne}$ represents the time for $^2/_3$ of Ne (the same amount as that of $H_2$) to diffuse: and because rate of diffusion varies inversely proportional to the time taken for the diffusion to take place, it follows that: $\frac{R_{H_2}}{R_{Ne}} = \frac{t_{Ne}}{t_{H_2}} = 3.16$

Substituting $\frac{t_{Ne}}{6\text{hr}} = 3.16$: $t_{Ne} = 3.16 \times 6\text{hr} = 18.96\text{ hr}$

Thus 18.96 hours is required for $^2/_3$ of Ne to diffuse

Then (by cross-multiplication) $\frac{^1/_2 \times 18.96}{^2/_3}$ hours or 14.22hours is required for $^1/_2$ of Ne to diffuse

Hence the time taken for half the neon to diffuse is 14.22 hours.

**Question 43**

(a)(i) Dissociation and association

(ii) **Dissociation** makes the observed relative density of the compound to be lower than the expected from its molecular formula.

**Examples:**

1) Dissociation of $N_2O_4$ (g) into $NO_2$(g).
2) Dissociation of $PCl_5$(g) into $PCl_3$(g) and $Cl_2$(g).

**Association** makes the measured (observed) relative density of the compound to be greater than the expected from its molecular formula

**Examples:**

1) Association of two molecules of $AlCl_3$ to form a dimer which corresponds to the molecular formula of $Al_2Cl_6$.
2) Association of two molecules of ethanoic acid to form a dimer which corresponds to the molecular formula of $C_4H_8O_4$.

(b) Substituting $n = \frac{m}{M_r}$ in $PV = nRT$ gives $PV = \frac{mRT}{M_r}$

From which $M_r = \frac{mRT}{PV}$

If $M_m$ is the average molar mass of the mixture and $m_m$ is the mass of the mixture.

It follows that: $M_m = \frac{m_m RT}{PV}$

But $\frac{m_m}{V} = \rho_m$ where $\rho_m$ is the density of the mixture

Then $M_m = \frac{\rho_m RT}{P} = \frac{3.45 \times 0.082 \times 298}{1.6}\text{g/mol} = 52.69\text{ g/mol}$

If:

$X_u$ is the mole fraction of unknown gas

$M_u$ is the molecular mass of unknown gas

$X_k$ is the mole fraction of known gas and

$M_k$ is the molecular mass of known gas.

It follows that: $M_m = X_u M_u + X_k M_k$

Where $X_u = 0.35$: $X_k = 1 - X_u = 1 - 0.35 = 0.65$ and $M_k = 64\text{g/mol}$

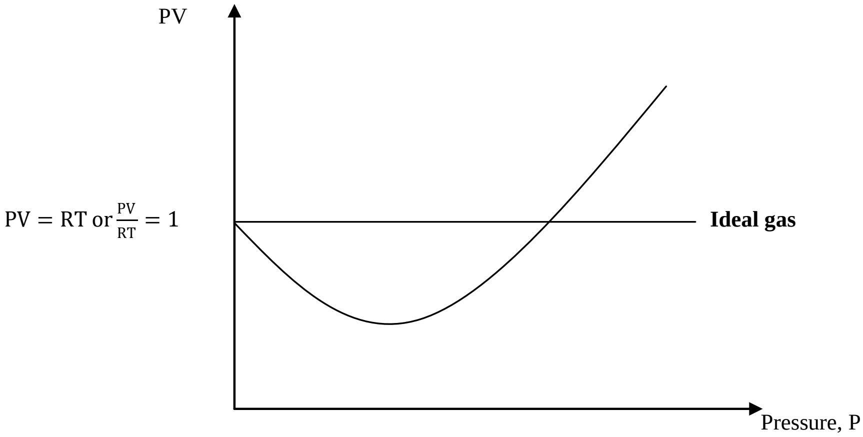
Substituting $52.69 = 0.35M_u + 0.65 \times 64$

From which $M_u = 31.69g/mol$

Hence molecular mass of the other component is $31.69g/mol$

**Question 44**

(a) Amagat's curve to show deviation of $CO_2$ from ideal has behaviour is shown below:




(b) From $\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$

If: $P_1 = P_2 = P$ and $V_2 = V$(P and V are constant)

$$\frac{PV}{n_1T_1} = \frac{PV}{n_2T_2} \text{ or } n_1T_1 = n_2T_2$$

Substituting $n_1 \times 300 = n_2 \times 360$

$$\frac{n_1}{n_2} = \frac{360}{300} = {}^6/_5$$

Thus $n_1 : n_2 = 6 : 5$ where $n_1$ is the number of moles of air before heating and $n_2$ is the number of moles of air after heating.

Then number of moles of air decreased (expelled)= $(6 - 5)mol = 1mol$

And percentage of air expelled= $\frac{\text{number of moles expelled}}{\text{original number of moles before heating}} = \frac{1}{6} \times 100\% = 16.67\%$

Hence the percentage of air expelled is $16.67\%$

**Question 45**

(a) An increase in temperature will increase the pressure inside the aerosol can in accordance with Gay-Lussac's law. So when the pressure inside the can goes beyond the pressure limit, will result into an explosion.

(b) Final volume, $V_{final} = V + 2V + V = 4V = V_2$

Since temperature is kept constant, Boyle's law is applicable

That is $P_1V_1 = P_2V_2$ or $P_2 = \frac{P_1V_1}{V_2}$

For container 1: $P_1 = P, V_1 = V$

Then $P_2 = \frac{P \times V}{4V} = \frac{1}{4}$ p atm

For container 2: $P_1 = 2$ p atm, $V_1 = 2V$

Then $P_2 = \frac{2P \times 2V}{4V} = 1$ P atm

For container 3: $P_1 = 3p$ atm, $V_1 = V$

Then $P_2 = \frac{3P \times V}{4V} = {}^3/_4$ P atm

By Dalton's law of partial pressure: $P_{final} = \left(\frac{P}{4} + P + \frac{3P}{4}\right)$ atm $= 2P$ atm

Hence the total final pressure is 2P atm

**Question 46**

(a) Boyles's law is applicable when amount of air is constant. When we fill air in the tyre, the amount of air is progressively increased in the tyre and therefore Boyle's law is inapplicable. At initial stages of filling air in the tyre, volume of the tyre increases and pressure remains almost constant in accordance with Avogadro's law and thereafter, volume of the tyre remains almost constant; but since amount of the gas in the tyre is still increasing, collision frequency between air molecules and the tyre's walls will increase making the pressure to increase too ($P \propto n$ a constant V and T). Eventually, both volume and pressure appear to increase.

(b) By Dalton's law of partial pressure: $P_T = P_{H_2O} + P_{CO}$

From which $P_{CO} = P_T - P_{H_2O} = (752 - 19.8)\text{mmHg} = 732.2\text{mmHg}$

From ideal gas equation $PV = nRT, n = \frac{PV}{RT}$

Thus $n_{CO} = \frac{732.2\times0.242}{760\times0.082\times295}\text{mol} = 0.00964\text{mol}$

But from the equation for the reaction, mole ratio of $CO$ to HCOONa is 1:1

Thus $n_{CO} = n_{HCOONa} = 0.00964\text{mol}$

Using $m = nMr; M_{HCOONa} = 0.00964\text{mol} \times 68\text{g/mol} = 0.65552\text{g}$

Then $\%HCOONa = \frac{M_{HCOONa}}{M_T} \times 100\% = \frac{0.65552}{0.964} \times 100\% = 68\%$

**Question 47**

(a) Equation for the reaction: $2H_2 + O_2 \longrightarrow H_2O$

From which mole ratio of $H_2$ to $O_2$ is 2:1; that is for each one mole of $O_2$ two moles of $H_2$ is required?

But it is given that $n_{H_2} = n_{O_2}$ and whence $O_2$ present in excess.

Thus the reactant remaining is **oxygen gas**

**Calculation of the amount remaining:**

By Dalton's law of partial pressure; total pressure exerted by gases before the sparking (reaction) is given by:

$P_T = P_{O_2} + P_{H_2} + P_{H_2O}$

Substituting $1146 = P_{O_2} + P_{H_2} + 24$ From which $P_{O_2} + P_{H_2} = 1122\text{mmHg}$

Because $n_{O_2} = n_{H_2};\ P_{O_2} = P_{H_2}$

Thus $P_{O_2} + P_{O_2} = 2P_{O_2} = 1122\text{mmHg}$ or $P_{O_2} = 561\text{mmHg}$

But from the equation of the reaction: number of moles of $O_2$ reacted$= \frac{1}{2}n_{H_2}$

Thus number of moles of $O_2$ remained $= n_{O_2} - \frac{1}{2}n_{H_2}$

But $n_{O_2} = n_{H_2}$

Then number of moles of $O_2$ remained$= n_{O_2} - \frac{1}{2}n_{O_2} = \frac{1}{2}n_{O_2}$

And because pressure varies directly proportional to the number of moles, pressure exerted by the remained oxygen gas $= \frac{P_{O_2}}{2} = \frac{561\text{mmHg}}{2} = 280.5\text{mmHg}$

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

Number of moles of $O_2$ gas remained $= \frac{280.5\times0.5}{760\times0.082\times298}\text{mol} = 0.00755\text{mol}$

Hence the number of reactant remaining is $0.00755\text{mol}$ of $O_2$

(b) From pressure law: $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ From which $P_2 = \left(\frac{T_2}{T_1}\right)P_1$

Partial of $O_2$ at $90°C = \frac{363}{298} \times 280.5$ or $341.68\text{mmHg}$

And by Dalton's law of partial pressure:

$P_T = P_{H_2O} + P_{O_2} = (526 + 341.68)\text{mmHg} = 867.68\text{mmHg}$

Hence the total pressure at $90°C$ is $867.68\text{mmHg}$

(c) $n_{H_2O} = \frac{P_{H_2O}V}{RT} = \frac{526\times0.5}{760\times0.082\times363}\text{mol} = 0.0116\text{mol}$

Hence number of moles of $H_2O$ at $90°C$ is $0.0116\text{mol}$

**Question 48**

(a) From Dalton's law of partial pressure: $P_T = P_{H_2} + P_{H_2O}$

From which $P_{H_2} = P_T - P_{H_2O} = (745 - 23.8)\text{mmHg} = 721.2\text{mmHg}$

Then $n_{H_2} = \frac{P_{H_2}V}{RT} = \frac{721\times0.09}{760\times0.082\times298}\text{mol} = 0.00349\text{mol}$

Hence number of moles of hydrogen gas collected is $0.00349\text{mol}$

(b) Using $n_{H_2O} = \frac{P_{H_2O}V}{RT} = \frac{23.8 \times 0.09}{760 \times 0.082 \times 298}\text{mol} = 0.00012\text{mol}$

Then number of molecules, $N = nN_A = 0.00012 \times 6.02 \times 10^{23}$ molecule $= 7.2 \times 10^{19}$ Molecule

Hence the number of molecules of water is $7.2 \times 10^{19}$ Molecule

(c) Using; $C = \sqrt{\frac{3RT}{M_r}}$

$C_{H_2} = \sqrt{\frac{3RT}{M_{H_2}}}$ ; $C_{H_2O} = \sqrt{\frac{3RT}{M_{H_2O}}}$

Then $\frac{C_{H_2}}{C_{H_2O}} = \sqrt{\frac{M_{H_2O}}{M_{H_2}}} = \sqrt{\frac{18}{2}} = 3$

Thus the ratio of speed of $H_2$ to $H_2O$ vapour is 3

(d) $H_2O$ deviate more from ideal behaviour

**Explanation**

$H_2O$ molecules exhibit stronger intermolecular forces of attraction due to its greater molecular weight and therefore stronger Van der Waals dispersion forces. It is also has hydrogen bonds which is very strong intermolecular forces of attraction.
$H_2O$ molecule has greater volume because it has greater size. Thus $H_2O$ molecule occupies greater space and its volume cannot be neglected compared to the whole volume of the water vapour (gas).

**Question 49**

(a) $CO_2$: according to Avogadro's law, they all contain the same number of particles, therefore, the heaviest molecule, $CO_2$ with molar mass of 44g/mol will have the greatest mass.
(b) All the same according to kinetic theory of gases: at the same temperature all gases have the same kinetic energy.
(c) $CO_2$: Since it $(CO_2)$ has greater molecular weight, it has strongest Van der Waals dispersion forces and therefore strongest intermolecular forces of attraction. Furthermore, having greatest molecular weight and therefore largest molecular size its molecules occupy greater space (volume).
(d) He: it has the smallest molar mass and therefore greatest rate of effusion

**Question 50**

(a)
1. Airbags
2. Refrigerator
3. Air conditioner
4. Airplanes

(b) Actual molar volume of sodium atoms $= \frac{68.52}{100} \times 23.68\text{cm}^3 = 16.2255\text{cm}^3/\text{mol}$

Volume of one sodium atom $= \frac{4}{3}\pi r^3 = \frac{4}{3} \times 3.14 \times (1.86 \times 10^{-8}\text{cm})^3 = 2.6941 \times 10^{-23}\ \text{cm}^3/\text{atom}$

Then actual molar volume $=$ Volume of one atom $\times$ Avogadro's constant, NA

From which;

$NA = \frac{\text{Actual molar volume}}{\text{Volume of onee atom}} = \frac{16.2255\text{cm}^3/\text{mol}}{2.6941 \times 10^{-23}\ \text{cm}^3/\text{atom}} = 6.02 \times 10^{23}\text{atom/mol}$

Hence the Avogadro's constant is $6.02 \times 10^{23}$.

**Question 51**

(a) At constant pressure, decrease in temperature (**cold** surface) leads to decrease in volume in accordance to Charles's law and hence the ball shrinks.
(b) Using Gay-Lussac's law to calculate the expected pressure of $CO_2$ at 1401K.

That is $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ or $P_2 = \left(\frac{T_2}{T_1}\right)P_1$

Where $P_1 = 10\ \text{atm}, T_1 = 701\text{K}, T_2 = 1401\text{K}$

Then $P_2 = \frac{1401 \times 10}{701}\text{atm} = 19.9857\ \text{atm}$

Using $i = \frac{\text{Observed pressure}}{\text{Expected pressure}} = \frac{22.5\ \text{atm}}{19.9857\ \text{atm}} = 1.1258$

$CO_2$ decompose according to the following equation:

$CO_2(g) \rightleftharpoons CO\ (g) + \frac{1}{2}O_2(g);\ \ N = 1.5$

Then using $\alpha = \frac{i-1}{N-1} = \frac{1.1258-1}{1.5-1} = 0.2516$ or $25.16\%$

Hence the percent of $CO_2$ that decomposes was $25.16\%$.

**Question 52**

(i) From ideal gas equation; $PV = nRT$; where $n = \frac{m}{M_r}$

$PV = \frac{m}{M_r}RT$; From which $m = \frac{PVM_r}{RT}$

$m = \frac{207000\,Nm^{-2} \times 8.98 \times 10^{-3}\,m^3 \times 28\,gmol^{-1}}{8.31\,Nmmol^{-1}K^{-1} \times 293K}$ $(1Pa = 1Nm^{-2}, 1J = 1Nm \text{ and } 1dm^3 = 10^{-3}m^3)$

$= 21.4g$

Mass of nitrogen gas is $21.4g$

(ii) From ideal gas equation; $PV = nRT$; $P = \frac{nRT}{V}$; $P \propto T$ (When V and n are constant)

Thus the increase in temperature will result in an increase in pressure of the tyres.

(iii) Nitrogen having fewer number of protons while shielding (screening) effect is the same for both; (both N and O have the same number of shells) experiences weaker effective nuclear attractive force.

**Question 53**

(a) A known mass of volatile substance is heated in Victor Meyer's tube. As a result, the liquid changes into vapour, the vapour, in turn, displaces an equal volume of air which is collected over water. The volume of air collected is measured at the pressure and temperature of the laboratory. This volume is converted to STP volume and using gram molar volume concept, molecular mass is calculated.

(b) From Grahm's law: $\frac{R_{Ne}}{R_{He}} = \sqrt{\frac{M_{He}}{M_{Ne}}}$

But $R_{Ne} = \frac{V_{Ne\,diffused}}{t_{Ne}} = \frac{\frac{1}{2}V_{Ne}}{t_{Ne}}$ (Volume of Ne diffused is half of its original volume)

And $R_{He} = \frac{V_{He\,diffused}}{t_{He}} = \frac{\frac{2}{3}V_{He}}{t_{He}}$ (Volume of He shrinked to $\frac{1}{3}$ of original volume meaning $\frac{2}{3}$ of the original volume effused).

Then $\frac{\frac{\frac{1}{2}V_{Ne}}{t_{Ne}}}{\frac{\frac{2}{3}V_{He}}{t_{He}}} = \sqrt{\frac{M_{He}}{M_{Ne}}}$

But $V_{Ne} = V_{He}$ (balloon was the same)

Substituting: $\frac{3 \times t_{He}}{4 \times 22hr} = \sqrt{\frac{4}{20}}$; $t_{He} = 13.12$ hours

Hence the time is 13.12 hours.