CHEMISTRY

FORM 3

1. GAS LAWS
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3. ORGANIC CHEMISTRY 1
4. NITOGEN AND ITS COMPOUNDS
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12.0.0 GAS LAWS

Kinetic Particle Theory

- Matter is made up of particles that are in constant motion
- The higher the temperature, the faster the particles move (more energy)
- Increase in temperature increase weakens interparticle forces, causing particles to spread apart and increase in volume/size (i.e. Expansion)
- Gases have greatest average energy while solids have smallest average energy

According to the kinetic theory, matter is made up of particles (atoms, molecules or ions) which are in constant motion because they have energy at all temperatures above zero Kelvin (absolute zero, 0K) or -273^{0}C. This energy is in the form of kinetic energy.

Consider heating a solid;

When a solid is heated, the particles vibrate more strongly as they gain kinetic energy and the particle attractive forces are weakened. Eventually, at the melting point, the attractive forces are too weak to hold the particles in the structure together in an ordered way and so the solid melts. The particles become free to move around and lose their ordered arrangement. Energy is needed to overcome the attractive forces and give the particles increased kinetic energy of vibration. On heating further, the particles gain more kinetic energy and move faster. In evaporation and boiling the particles with the highest kinetic energy can 'escape' from the attractive forces of the other liquid particles. The particles lose any order and become completely free to form a gas or vapour. Boiling is rapid evaporation anywhere in the bulk liquid and at a fixed temperature called the boiling point and requires continuous addition of heat.

DIFFUSION AND KINETIC ENERGY

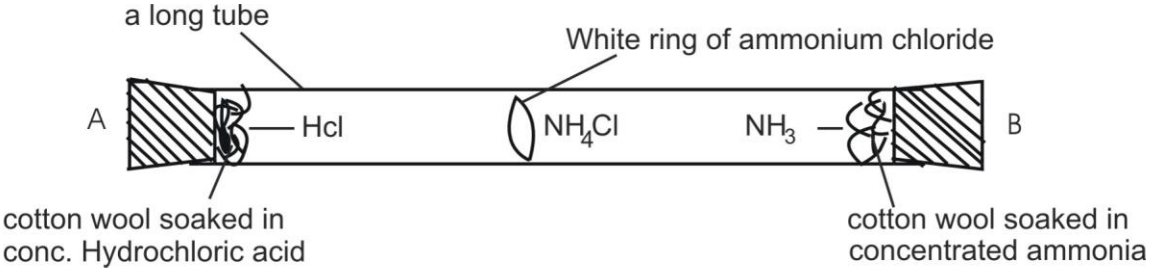
The natural rapid and random movement of the particles means that gases readily 'spread' or diffuse.

Diffusion is the movement of gas or solid particles from a region of high concentration to a region of low concentration.

Diffusion is fastest in gases where there is more space for them to move. The rate of diffusion increases with increase in temperature as the particles gain kinetic energy and move faster.

DIFFUSION OF AMMONIA AND HYDROGEN CHLORIDE

The following experiment is set up. One filter soaked in a solution of ammonia solution and the other soaked in a solution of concentrated hydrochloric acid are placed on the end of along glass tubing as shown.



When colourless NH_3 and HCl fumes meet, dense white smoke (fumes) of ammonium chloride are observed.

$$NH_{3\,(ag)} + \quad HCl_{\,(ag)} \longrightarrow NH_4\,Cl_{(s)}$$

Ammonia is diffused more rapidly than the hydrogen chloride because the gas traveled a longer distance in the same amount of time. Gases with greater R.M.M have higher densities than gases which have small molecules e.g. hydrogen chloride are heavier than ammonia molecules. If the concentration of hydrochloric acid and that of ammonia were increased in a separate experiment, the rate of diffusion would be faster.

Gas	**Mr.**
NH_3	17
HCl	35.5

Large heavy molecules move more slowly than small, light molecules. Therefore, dense gases diffuse more slowly than gases of low density. The rate of diffusion depends on the molecular mass/density of gas. Rate of diffusion is inversely proportional to mass of a gas.

RATE OF DIFFUSION;

- Increases with temperature
- Decreases with increasing R.M.M or R.A.M
- Increases with concentration

Graham's Law of Diffusion

Graham's law of diffusion relates the rate of diffusion of a gas to its density.

It states that the rate of diffusion of a gas at constant temperature and pressure is inversely proportional to the square root of its density.

$$\text{Rate of diffusion} \propto \frac{1}{\sqrt{\text{density}}}$$

If two gases A and B diffuse under the same conditions of temperature and pressure, then

$$\frac{\text{Rate of diffusion of A}}{\text{Rate of diffusion of B}} = \frac{\sqrt{\text{density of B}}}{\sqrt{\text{density of A}}}$$

The density of a gas is proportional to its molecular mass.

$$\text{Hence, rate of diffusion of a gas} \propto \frac{1}{\sqrt{\text{Molecular mass}}}$$

√

Or $\frac{\text{Rate of diffusion of A}}{\text{Rate of diffusion of B}} = \frac{\text{molecular mass of B}}{\text{molecular mass of A}}$

For equal volume of gas, rate of diffusion $\propto \frac{1}{\text{Time of diffusion}}$

$$\therefore \quad \frac{\text{Time of diffusion of A}}{\text{Time of diffusion B}} = \sqrt{\frac{\text{molecular mass of A}}{\text{molecular mass of B}}}$$

Example 1: Rates of diffusion of two gases A and B are in the ratio 2:1. If the molecular mass of gas of A is 16g, find the molecular mass of B.

$$\frac{\text{Rate of diffusion of A}}{\text{Rate of diffusion of B}} = \frac{\sqrt{\text{mol. Mass of B}}}{\sqrt{\text{mol. Mass of A}}}$$

$$\frac{2}{1} = \frac{\sqrt{M}}{\sqrt{16}}$$

$\sqrt{M} = 2 \times \sqrt{16} = 8$, hence $M = 8^2 = 64$
Molecular mass of B = 64 g.

Evaporation, boiling and kinetic theory

On heating particles gain kinetic energy and move faster. In evaporation and boiling the highest kinetic energy molecules can 'escape' from the attractive forces of the other liquid particles. The particles lose any order and become completely free to form a gas or vapour. Energy is needed to overcome the attractive forces in the liquid and is taken in from the surroundings. This means heat is taken in, so evaporation or boiling are endothermic (require energy input) processes. If the temperature is high enough boiling takes place. Boiling is rapid evaporation anywhere in the bulk liquid and at a fixed temperature called the boiling point and requires continuous addition of heat. The rate of boiling is limited by the rate of heat transfer into the liquid. Evaporation takes place more slowly at any temperature between the melting point and boiling point, and only from the surface, and results in the liquid becoming cooler due to loss of higher kinetic energy particles.

Differences between evaporation and boiling

Evaporation	Boiling
Takes place on the surface of the liquid	Takes place throughout the liquid
Causes cooling	Does not cause cooling
Occurs at any temperature although the rate increases with increasing temperature	Occurs only at the boiling point and no temperature change can occur during boiling
Only a few molecules have enough energy to escape	All molecules have the same energy and

Factors that affect the rate of evaporation

Evaporation occurs at all temperatures at the surface of the liquid. It happens more rapidly when:

i) The **temperature is higher**, since then more molecules in the liquid are moving fast enough to escape from the surface,

ii) The **surface area** of the liquid is large so giving more molecules a changes to escape because more are near the surface, and

iii) **Wind** or **draught** is blowing over the surface carrying vapour molecules away from the surface thus stopping them from returning to the liquid and making it easier for more liquid molecules to break free.

KINETIC THEORY AND GAS LAWS

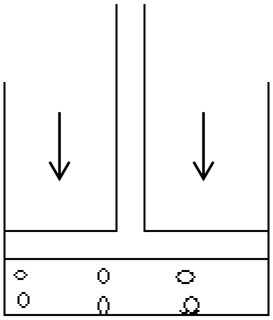
Due to the kinetic theory we begin to understand why gases exert pressure. The molecules of a gas are far apart and in continuous random motion, colliding with each other and with the walls of the vessel in which the gas is held. The molecules have mass, so they have energy hence they exert force on each collision and hence pressure.
If the temperature of the gas is increased at constant volume, the molecules gain more energy and move faster, hitting the walls with more force and exerting greater pressure.
If the volume of the gas is increased at constant temperature, the molecules have more space in which to move. The frequency of collisions decreases reducing the pressure.

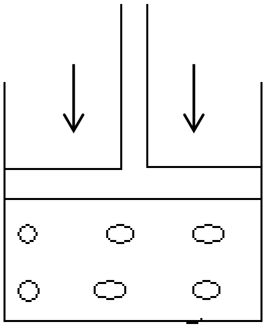
Boyle's law

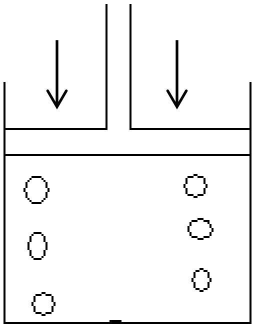
The pressure of a fixed mass of gas is inversely proportional to its volume if its temperature is kept constant.

Consider a gas trapped in a container as shown. The mass, hence number of moles are constant and do not change during the course of the investigation. The piston is frictionless and moves smoothly without allowing the gas to escape. When the pressure changes, the volume of the gas changes as shown.

P_1 = 1 atm P_2 = 2 atm P_3 = 4 atm







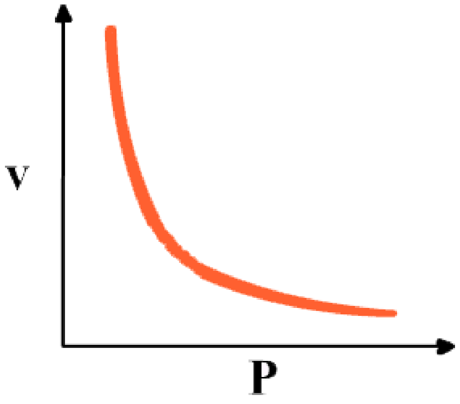
$V_1 = 12dm^3$	$V_2 = 6\ dm^3$	$V_3 = 3dm^3$
12 x 1= 12	6 x 2 = 12	3 x 4 = 12

$$P_1V_1 \quad = \quad P_2V_2 \quad = \quad P_3V_3$$

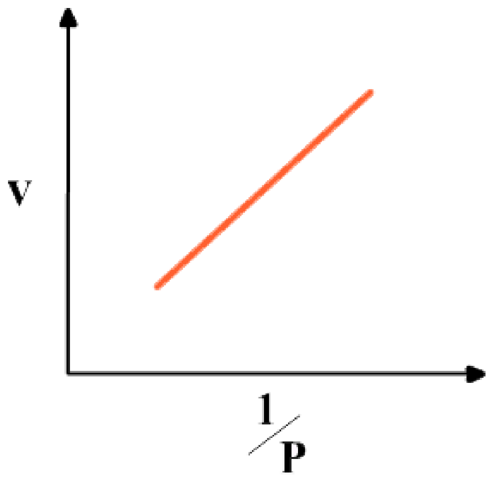
∴ PV = constant at constant temperature and mass.

<u>Graphical representation of Boyle's law</u>

Graph between P & V at constant temperature is a smooth curve known as "parabola"



Graph between 1/P & V at constant temperature is a straight line.



If pressure, p is doubled, the volume is halved. That is, p is inversely proportional to V. In symbols

$P \propto {}^{1}\!/_{v}$ or $p = \text{constant} \times {}^{1}\!/_{v}$

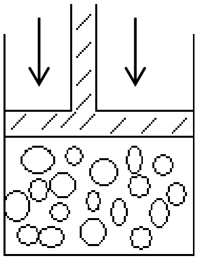
$PV = \text{constant}$

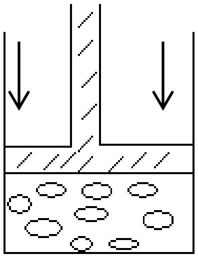
$p_1V_1 = p_2V_2 = \text{constant}$. This is **Boyle's law**

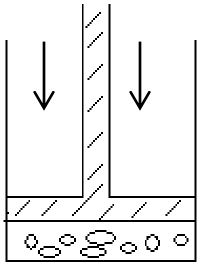
Charles' Law

The volume of a fixed mass of gas is directly proportional to its absolute temperature if the pressure is kept constant.

P = 1 atm P = 1 atm P = 1 atm







We can then say that the volume V is directly proportional to the absolute temperature T, i.e. doubling T doubles V, etc. Therefore

$$V \propto T \text{ or } \quad V = \text{constant} \times T$$

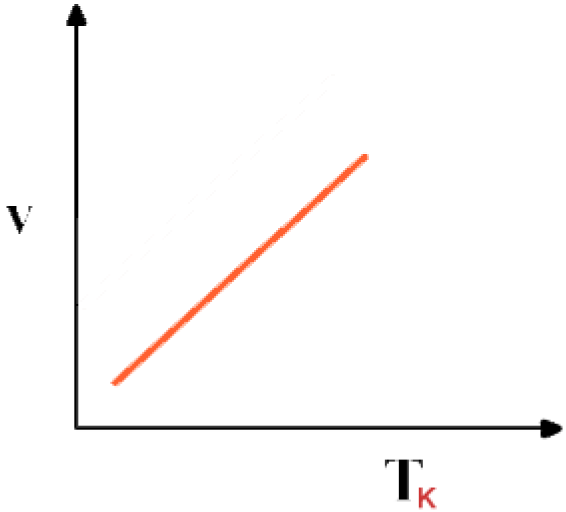
Or $V/T = \text{Constant}$

Volume	$V_1 = 1\text{dm}^3$	$V_2 = 2\text{dm}^3$	$V_3 = 3\text{dm}^3$
Temperature (^{O}C)	0 ^{o}C	273 ^{o}C	546 ^{o}C
Temp (K)	273 K	546K	819K
Volume/Temp	$^{1}/_{273}$	$^{2}/_{546}$	$^{3}/_{819}$
Equation		$\therefore \, ^{V1}/_{T1} = \, ^{V2}/_{T2} = \, ^{V3}/_{T3}$	

$\therefore V/T = \text{constant}$

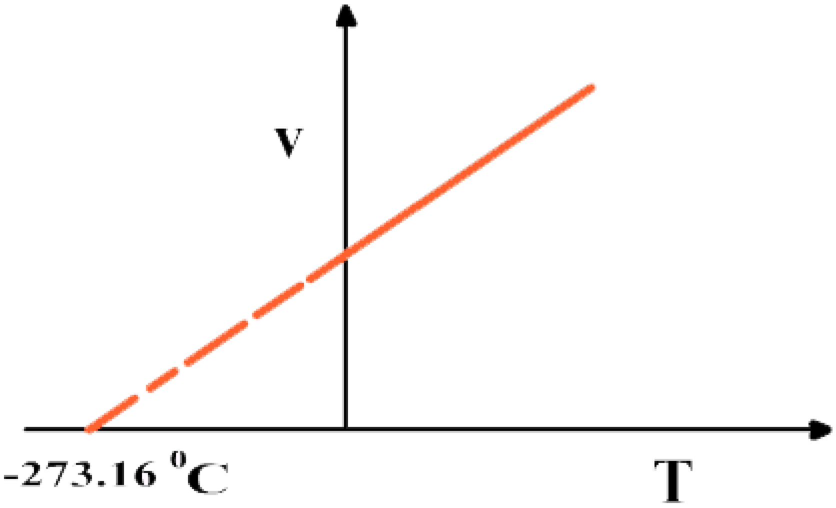
<u>Graphical representation</u>

Graph between Volume and absolute temperature of a gas at constant pressure is a "straight line"



Absolute scale of temperature or absolute zero

If the graph between V and T is extrapolated, it intersects T-axis at -273.16 0C .At -273.16 0C volume of any gas theoretically becomes zero as indicated by the graph.



But practically volume of a gas can never become zero. Actually no gas can achieve the lowest possible temperature and before -273.16 0C all gases are condensed to liquid. This temperature is referred to as absolute scale or absolute zero. At -273.16 ^{0}C all molecular motions are ceased. This temperature is called **Absolute Zero**.

Degrees on this scale are called Kelvin's and are denoted by K while θ stands for a Celsius scale temperature. They are exactly the same size as Celsius degrees. Since –273 ^{0}C = 0K, conversions from ^{0}C to K are made by adding 273. $T = 273 + \theta$

$$0\ ^0C = 273K$$

$$15\ ^0C = 273 + 15 = 288K$$

The letter T represents Kelvin or absolute temperatures and θ stands for a Celsius scale temperature.

Pressure law

The pressure of a fixed mass of gas is directly proportional to its absolute temperature if the volume is kept constant.

$$p \propto T \text{ or } \quad p = \text{constant X } T$$

$$\text{Or} \quad p/T = \text{Constant}$$

The three equations can be combined giving

$$\frac{\mathbf{Pv}}{\mathbf{T}} = \textbf{constant}$$

For cases in which p, V and T all change from say p_1, V_1 and T_1 to p_2, V_2 and T_2, then

$$\frac{P1V1}{T_1} = \frac{p_2V_2}{T_2}$$

Gases and the Kinetic Theory

The kinetic theory can explain the behaviour of gases

(a) Causes of gas pressure

All the molecules in a gas are in rapid motion, with a wide range of speeds, and repeatedly hit the walls of the container in huge numbers per second. The average force and hence the pressure they exert on the walls is constant since pressure is force on unit area.

(b) Boyle's law

If the volume of a fixed mass of gas is halved by halving the volume of the container, the number of molecules per cm^3 will be doubled. There will be twice as many collisions per second with the walls, i.e. the pressure is doubled. This is Boyle’s law.

(c) Temperature

When a gas is heated and its temperature rises, the average speed of its molecules increases. If the volume of the gas is to remain constant, its pressure increases due to more frequent and more violent collisions of the molecules with the walls. If the pressure of the gas is to remain constant, the volume must increase so that the frequency of collisions does not.

13.0.0 THE MOLE: FORMULAE AND CHEMICAL EQUATIONS

MOLE CONCEPT

What is a Mole?

A mole is a word which represents a number. Like the word "dozen" represents the number 12, so "mole" represents the number 6×10^{23}. This number is also called Avogadro's number. It is a very very big number (6 followed by 23 zeros). In the same way that you can have a dozen atoms, or cars, or apples, so you can also have a mole of atoms, or cars, or apples.

Needless to say, chemists are concerned with atoms, ions, molecules and compounds. A mole is defined as the number of atoms in exactly 12 grams of ^{12}C (carbon twelve). The number is called Avogadro's number. In the above definition, 12 is the mass number of carbon. So, one mole of carbon atoms has a mass of 12 grams. The relative atomic mass, which can be written as A_r or RAM, is the number just above the element in the periodic table

Relative atomic mass(r.a.m) and moles

Just as one mole of carbon atoms has a mass of 12 g,

so the mass of one mole of the atoms of any element
is its "relative atomic mass" in grams.

For example, look up the relative atomic mass of sodium (Na), (the larger number above it in the periodic table).

One mole of sodium has a mass of 23 g.

One mole of helium has a mass of 4 g,
One mole of neon has a mass of 20 g,
One mole of magnesium has a mass of 24 g,
One mole of calcium has a mass of 40 g.

This is easy for elements which exist as atoms.

As discussed ealier, the number of protons added to the number of neutrons is known as the relative atomic mass. This is the mass of 1 mol of an atom relative to the mass of 1 mol of C atoms that have 6 protons and 6 neutrons, which is taken to be 12.00 g. However there are complications due to isotopes and so very accurate atomic masses are not whole numbers. Isotopes are atoms of the same element with different masses due to different numbers of neutrons. The very accurate atomic mass scale is based on a specific isotope of carbon, carbon-12, $^{12}C = 12.0000$ units exactly, for most purposes C = 12 is used for simplicity.

The strict definition of relative atomic mass (A_r) is that it equals average mass of all the isotopic atoms present in the element compared to $^1/_{12}$th the mass of a carbon-12 atom.

Examples of relative atomic mass calculations

Example 1: chlorine consists of 75% chlorine-35 and 25% chlorine-37.

Think of the data based on 100 atoms, so 75 have a mass of 35 and 25 atoms have a mass of 37.

The average mass = [(75 x 35) + (25 x 37)] / 100 = 35.5

So the relative atomic mass of chlorine is 35.5 or **$A_r(Cl) = 35.5$**

What about elements which exist as molecules or compounds?

Relative formula mass of a compound (R.F.M):

To calculate the mass of one mole of a compound, the number of each type of atom in the compound is multiplied by that atoms relative atomic mass and all those numbers added together.

This value is called the **relative formula mass** (or **relative molecular mass** or **molar mass**) of a compound.

Notice that r.f.m, r.m.m, or **M_r** have no units because they are ratios. The molar mass is obtained from r.f.m, r.m.m, or **M_r** by simply adding g (grams)

If all the individual atomic masses of all the atoms in a formula are added together you have calculated the relative formula mass (for ionic compounds) or molecular mass (for covalent elements or compounds), M_r. can be used for any element or compound. Whereas relative atomic mass (above) only applies to a single atom, anything with at least two atoms requires the term relative formula/molecular mass.

The most common error is to use atomic/proton numbers instead of atomic masses, unfortunately, except for hydrogen, they are different!

Examples of formula/molecular mass calculations:

Example 1: The diatomic molecules of the elements hydrogen H_2 and chlorine Cl_2

relative atomic masses, Ar: H = 1, Cl = 35.5

Formula masses, M_r, are $H_2 = 2 \times 1 = 2$, $Cl_2 = 2 \times 35.5 = 71$ respectively.

Example 2: The compound calcium hydroxide $Ca(OH)_2$ (ionic)

Relative atomic masses are Ca=40, H=1 and O=16

$M_r = 40 + 2 \times (16+1) = 74$

(2) Mass from amount:

The key mathematical equation needed here is -

mass (g) = relative formula mass (g mol^{-1}) x amount (mol)

Using the triangular relationship from above if the mass section is covered over then the amount multiplied by the relative formula mass gives the mass.

Example -

(i) What is the mass of 0.25 mol of NaCl?

0.25 mol of NaCl $= 58.5\ \text{g mol}^{-1} \times 0.25\ \text{mol}$
$= 14.63\ \text{g}$

(ii) What is the mass of 3 mol of $Al_2(SO_4)_3$?

3 mol of $Al_2(SO_4)_3$ $= 342\ \text{g mol}^{-1} \times 3\ \text{mol}$
$= 1026\ \text{g}$ or $1.026\ \text{kg}$

(3) Amount from mass :

The key mathematical equation needed here is -

amount (mol) = mass (g) / relative formula mass (g mol^{-1})

Using the triangular relationship from above if the amount section is covered over then the mass divided by the relative formula mass gives the amount -

Exemplar calculations -

(i) What amount is 117 g of NaCl?

117 g of NaCl = 117 g / 58.5 g mol^{-1}
= 2 mol

(**ii**) What amount is 68.4 g of $Al_2(SO_4)_3$?

68.4 g of $Al_2(SO_4)_3$ = 68.4 g / 342 g mol^{-1}
= 0.2 mol

(4) Molar mass from mass and amount:

The key mathematical equation needed here is -

Relative formula mass (g mol^{-1}) = mass (g) / amount (mol)

Using the triangular relationship from above if the molar mass section is covered over then the mass divided by the amount gives the relative formula mass.

Exemplar calculation

What is the molar mass of a compound for which 0.2 mol of it has a mass of 42 g?

molar mass of compound = 42 g / 0.2 mol
= 210 g mol^{-1}

Every mole of any substance contains the same number of the defined species.

The actual particle number is known and is called the Avogadro Constant and is equal to 6.023×10^{23} 'defined species' per mole. This means there are that many atoms in 12g of carbon (C = 12) or that many molecules of water in 18g (H_2O = 1+1+16 = 18, H = 1; O = 16)

Note. Relative is just a number based on the carbon-12 relative atomic mass scale.

Molar mass is a term used to describe the mass of one mole i.e. the relative atomic/formula/molecular mass in grams (g).

Examples:

Example 1: 1 mole of ammonia, NH_3, Consists of 1 mole of nitrogen atoms combined with 3 moles of hydrogen atoms. Or you could say 2 moles of ammonia is formed from 1 mole of nitrogen molecules (N_2) and 3 moles of hydrogen molecules (H_2).

Example 2: 1 mole of aluminium oxide,

Al_2O_3, consists of 2 moles of aluminium atoms combined with 3 moles of oxygen atoms

(or 1.5 moles of O_2 molecules).

For calculation purposes **learn the following formula for 'Z'** and use a triangle if necessary.

(1) mole of Z = g of Z / atomic or formula mass of Z,

(2) or g of Z = mole of Z x atomic or formula mass of Z

(3) or atomic or formula mass of Z = g of Z / mole of Z

where Z represents atoms, molecules or formula of the particular element or compound defined in the question.

Example 1: How many moles of potassium ions and bromide ions in 0.25 moles of potassium bromide?

1 mole of KBr contains 1 mole of potassium ions (K^+) and 1 mole of bromide ions (Br^-).

So there will be 0.25 moles of each ion.

Example 2: How many moles of calcium ions and chloride ions in 2.5 moles of calcium chloride?

1 mole of $CaCl_2$ consists of 1 mole of calcium ions (Ca^{2+}) and 2 moles of chloride ion (Cl^-).

So there will be 2.5 x 1 = 2.5 moles of calcium ions and 2.5 x 2 = 5 moles chloride ions.

mass of NaCl formed = moles x formula mass = 0.

4 x 58.5 = **23.4g NaCl**

Using the Avogadro Constant, you can actually calculate the number of particles in known quantity of material.

Example 3: How many water molecules are there in 1g of water, H_2O?

Formula mass of water = (2 x 1) + 16 = 18

Every mole of a substance contains 6×10^{23} particles of 'it' (the Avogadro Constant).

Moles water = 1 / 18 = 0.0556

Molecules of water = $0.0556 \times 6 \times 10^{23} = 3.34 \times 10^{22}$

5.PERCENTAGE COMPOSITION IN A COMPOUND:

1. Calculating % Composition (from masses of each element)

Divide the mass of each element by the total mass of the compound and multiply by 100

2. Calculating % Composition (from formula)

Calculate formula mass

Divide the total atomic mass of each element by the formula mass and multiply by 100

Example 1. What is the percentage of oxygen in carbon dioxide gas?

mass of oxygen in one mole of carbon dioxide gas = 2×16 g
= 32 g
mass of one mole of carbon dioxide = 12 g + (2×16 g)
= 44 g
percentage of oxygen = (32 g/44 g) × 100
= 72.7 %

Example 2. What is the percentage of water of crystallization in hydrated copper (II) sulphate, $CuSO_4 \cdot 5H_2O$?

mass of water present in one mole of hydrated copper(II) sulphate =(5×18 g)
= 90 g

mass of one mole of hydrated copper(II) sulphate = 64 g + 32 g + (4×16 g) + (5×18 g)
= 250 g

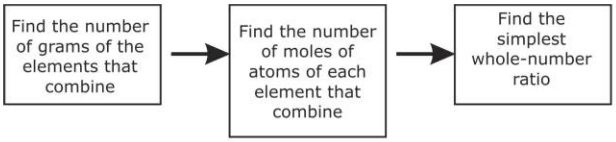
percentage of water of crystallization present = (90 g/250 g) × 100
= 36 %

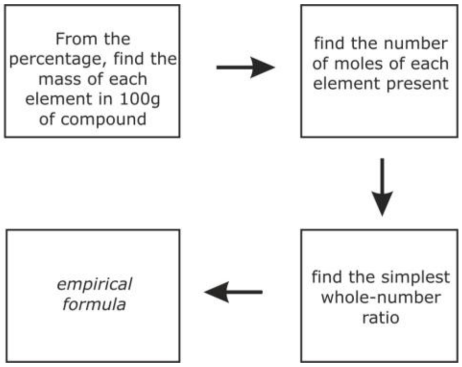
6. Empirical formula of a compound :

This technique covers essentially the reverse of the above process. A typical question here involves the calculation of the **lowest possible whole number ratio** of atoms in an organic molecule, given the percentage elemental composition for that molecule.

Calculating Empirical Formula (from % Composition)

- ✓ convert % of each element to grams based on 100 grams of the compound
- ✓ multiply grams of each element by 1/molar mass that element
- ✓ compare ratio of moles of each element and divide each by the smallest
- ✓ if result in step 3 gives a ratio with decimal equivalent to 1/4, 1/3, 1/2, 2.3, 3/4 instead of whole numbers, convert to the fraction and multiply all ratios by the denominator or the fraction





Calculating Empirical Formula (from experimentally determined masses)

- ✓ multiply the mass of each element (in grams) by 1/molar mass of that element
- ✓ Continue with steps 3 & 4 from IV above.

Example. An organic compound contains carbon and hydrogen only in the ratio of 85.7 % carbon to 14.3 % hydrogen. What is the empirical formula for that compound?

	C	H
% composition	85.7 %	14.3 %
mass of element in 100 g of compound	85.7 g	14.3 g
amount of element in 100 g of compound	$^{85.7\text{ g}}/_{12\text{ g mol}}$-1 = 7.14 mol	$^{14.3\text{ g}}/_{1\text{ g mol}}$-1 = 14.3 mol
lowest whole number ratio of element's amounts	$^{7.14\text{ mol}}/_{7.14\text{ mol}}$ = 1	$^{14.3\text{ mol}}/_{7.14\text{ mol}}$ = 2

The empirical formula for the compound is CH_2.

7. Molecular formula of a compound:

The molecular formula for a compound is simply the empirical formulae multiplied by some whole number (1, 2, 3, etc...).

Knowing the molar mass of the compound enables the molecular formula of it to be found.

Finding Molecular Formulas (when molar mass is known)

- ✓ calculate the empirical formula
- ✓ use the equation : (empirical formula mass)x n = molar mass
- ✓ find value for n: n = molar mass/empirical formula mass
- ✓ multiply each subscript in empirical formula by value for n

Example1. The actual molar mass of the compound in the previous example is 42 g mol^{-1}. What is the molecular formula for this compound?

The molar mass of CH_2 = $(12+(2\times1))\text{ g mol}^{-1} = 14\text{ g mol}^{-1}$

The molecular formula of this compound is $(CH_2)_n$, where n is a positive whole number.

The value of n = 42 g mol^{-1} / 14 g mol^{-1}
= 3

The molecular formula is $(CH_2)_3$ or more properly C_3H_6.

Examples of where the **empirical formula** is the **same** as the **molecular formula**

Water **H_2O**, methane **CH_4**, propane **C_3H_8** (these molecular formula cannot be 'simplified')

Examples of where the **molecular formula** is **different** from the **empirical formula**
Ethane **C_2H_6** (**CH_3**), phosphorus (V) oxide **P_4O_{10}** (**P_2O_5**), benzene **C_6H_6** (**CH**)

Three examples are set out below to illustrate all the situations. The relative atomic masses of the elements (A_r) are given in the tabular format method of solving the problem.

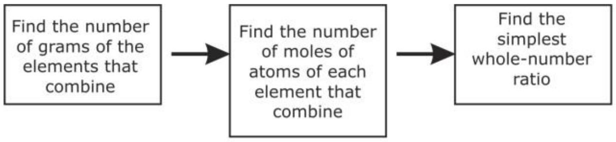
Example 2: 1.35g of aluminium was heated in oxygen until there was no further gain in weight. The white oxide ash formed weighed 2.55g. Deduce the empirical formula of aluminium oxide. Note: to get the mass of oxygen reacting, all you have to do is to subtract the mass of metal from the mass of the oxide formed.

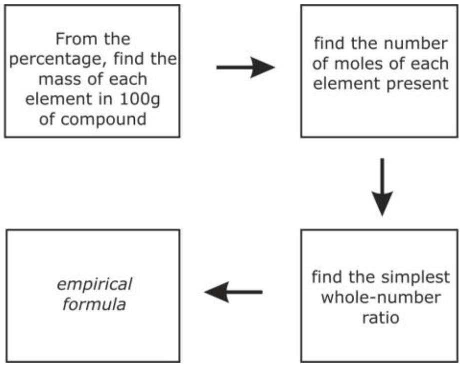
RATIOS ...	Aluminium Al (A_r = 27)	Oxygen O (A_r = 16)	Comments and tips
Reacting mass	1.35g	2.55 - 1.35 = 1.2g	not the real atom ratio
moles (mass in g / A_r)	1.35 / 27 = 0.05 mol	1.2 / 16 = 0.075 mol	can now divide by smallest ratio number or scale up by x factor to get simplest whole number ratio
simplest whole number ratio by trial and error	0.05 / 0.05 = 1 (then x 2 = 2) or 0.05 x 40 = 2	0.075 / 0.05 = 1.5 (then x 2 = 3) or 0.075 x 40 = 3	
therefore the simplest ratio = empirical therefore the formula for aluminium oxide = **Al_2O_3**			

Example 3: A chlorinated hydrocarbon compound when analysed, consisted of 24.24% carbon, 4.04% hydrogen, 71.72% chlorine. The molecular mass was found to be 99 from another experiment. Deduce the empirical and molecular formula. (you can 'treat' the %'s as if they were grams, and it all works out like examples 1 and 2)

RATIOS ...	Carbon (A_r = 12)	Hydrogen (A_r = 1)	Chlorine (Ar = 35.5)	Comments and tips

Reacting mass or % mass	24.24	4.04	71.72	just think of it as based on 100g
molar ratio (mass in g / A_r)	24.24 / 12 = 2.02 mol	4.04 / 1 = 4.04 mol	71.72 / 35.5 = 2.02 mol	can now divide by smallest ratio number
simplest whole number ratio	2.02 / 2.02 = 1	4.04 / 2.02 = 2	2.02 / 2.02 = 1	
therefore the simplest ratio = empirical formula for the chlorinated hydrocarbon = **CH_2Cl** BUT the molecular mass is 99, and the **empirical formula mass is 49.5** (12+2+35.5) AND 99 / 49.5 = 2, and so the **molecular formula** must be 2 x CH_2Cl = **$C_2H_4Cl_2$**				





8. REACTING MASS CALCULATIONS

You can use the ideas of relative atomic, molecular or formula mass and the law of conservation of mass to do quantitative calculations in chemistry. Underneath an equation you can add the appropriate atomic or formula masses. This enables you to see what mass of what, reacts with what mass of other reactants. It also allows you to predict what mass of products are formed (or to predict what is needed to make so much of a particular product). You must take into account the balancing numbers in the equation (e.g. 2Mg), as well of course, the numbers in the formula (e.g. O_2).

NOTE: The symbol equation must be correctly balanced to get the right answer!

Example 1:

(a) In a copper smelter, how many tonne of carbon (charcoal, coke) is needed to make 16 tonne of copper? (b) How many tones of copper can be made from 640 tones of copper oxide ore?

(a) $2CuO_{(s)} + C_{(s)} \longrightarrow 2Cu_{(s)} + CO_{2(g)}$

(atomic masses Cu=64, O=16, C=12)

Formula Mass ratio is 2 x (64+16) + (12) ==> 2 x (64) + (12 + 2x16)

= Reacting mass ratio 160 + 12 ==> 128 + 44

(In the calculation, impurities are ignored)

12 of C makes 128 of Cu

Scaling down numerically: mass of carbon needed

= 12 x 16 / 128 = **1.5 tonne of C**

(b) 160 of CuO make 128 of Cu (or direct from formula 80 CuO $\longrightarrow$ 64 Cu)

Scaling up numerically: mass copper formed

= 128 x 640 / 160 = **512 tones Cu**

Example 2:

What mass of carbon is required to reduce 20 tonne of iron(II) oxide ore if carbon monoxide is formed in the process as well as iron?

(Atomic masses: Fe = 56, O = 16)

Reaction equation: $\mathbf{Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO}$

Formula mass Fe_2O_3 = (2x56) + (3x16) = 160

160 mass units of iron oxide reacts with 3 x 12 = 36 mass units of carbon

So the reacting mass ratio is 160: 36

So the ratio to solve is **20: x**, scaling down,

x = 36 x 20/160 = **4.5 tones carbon** needed.

Note: $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$ is the other most likely reaction that reduces the iron ore to iron.

9. MOLAR VOLUME OF GAS

Avogadro's Law states that equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules.

So the volumes have equal moles of separate particles in them. One mole of any gas (or the formula mass in g), at the same temperature and pressure occupies the same volume. This is 24dm^3 (24 litres) or 24000 cm^3, at room temperature and pressure (r.t.p.).

Avogadro's Law and Molar Volume

Equal volumes of all gases contain the same number of molecules. In this table, N =6.02 X 10^{23} molecules, while V= 24000 cm^3 at room temperature and pressure (r.t.p), or 22400 cm^3 at standard temperature and pressure (s.t.p).

r.t.p = 25^{0}C and 1atmosphere pressure
s.t.p = 0^{0}C and 1 atmosphere pressure

		RMM	**Molecules**	
SO_2	1 mole	64g	N	V dm^3
CO_2	1 mole	44g	N	V dm^3
NH_3	1 mole	17g	N	V dm^3
H_2	1 mole	2g	N	V dm^3

1 mole of any gas always contains the same number of molecules (6.02 X 10^{23}) and hence has the same volume (at the same temperature and pressure).

When gases combine, they do so in small volumes which bear a simple ratio to one another and to the volume of product if gaseous. All volumes must be measured at the same temperature and pressure.

Some handy relationships for substance Z below:

moles Z = mass of Z gas (g) / atomic or formula mass of gas Z (g/mol)

mass of **Z** in g = moles of **Z** x atomic or formula mass of **Z**

atomic or formula mass of **Z** = mass of **Z** / moles of **Z**

1 mole = formula mass of **Z** in g.

gas volume of Z = moles of Z x **molar volume**

moles of **Z** = gas volume of **Z** / molar volume

Example 1: **What is the volume of 3.5g of hydrogen?** [$A_r(H) = 1$]

Hydrogen exists as H_2 molecules, so $M_r(H_2) = 2$, so 1 mole or

Formula mass in g = 2g

So moles of hydrogen = 3.5/2 = 1.75 mol H_2

So **volume H_2** = mol H_2 x molar volume = 1.75 x 24 = **42 dm^3** (or

42000 cm^3)

Example 4: **Given the equation $MgCO_{3(s)} + H_2SO_{4(aq)} \Longrightarrow MgSO_{4(aq)} + H_2O_{(l)} + CO_{2(g)}$**

What mass of magnesium carbonate is needed to make 6 dm^3 of carbon dioxide at r.t.p? [A_r's: Mg = 24, C = 12, O = 16, H =1 and S = 32]

method (a):

Since 1 mole = 24 dm^3, 6 dm^3 is equal to 6/24 = 0.25 mol of gas

From the equation, 1 mole of $MgCO_3$ produces 1 mole of CO_2, which occupies a volume of 24 dm^3.

So 0.25 moles of $MgCO_3$ is need to make 0.25 mol of CO_2

Formula mass of $MgCO_3$ = 24 + 12 + 3x16 = 84,

So **required mass of $MgCO_3$** = mol x formula mass = 0.25 x 84 = **21g**

Method (b):

Converting the equation into the required reacting masses ..

Formula masses: $MgCO_3$ = 84 (from above), CO_2 = 12 + 2x16 = 44

$MgCO_3$: CO_2 equation ratio is 1 : 1

so 84g of $MgCO_3$ will form 44g of CO_2

44g of CO_2 will occupy $24dm^3$

so scaling down, 6 dm^3 of CO_2 will have a mass of 44 x 8/24 = 11g

if 84g $MgCO_3$ ==> 44g of CO_2, then ...

21g $MgCO_3$ ==> 11g of CO_2 by solving the ratio, scaling down by factor of 4

10. REACTING GASES

Avogadro's Law states that 'equal volumes of gases at the same temperature and pressure contain the same number of molecules' or moles of gas.

This means the **molecule ratio of the equation** automatically gives us the **gas volumes ratio of reactants and products**, if all the gas volumes are measured at the same temperature and pressure.

This calculation only applies to gaseous reactants or products AND if they are all at the same temperature and pressure.

Example 1: $HCl_{(g)} + NH_{3(g)} \longrightarrow NH_4Cl_{(s)}$

- 1 volume of hydrogen chloride will react with 1 volume of ammonia to form solid ammonium chloride
- e.g. $25cm^3 + 25cm^3$ ==> products or $400dm^3 + 400\ dm^3$ ==> products (no gas formed)

Example 2: $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$

- ✓ 1 volume of nitrogen reacts with 3 volumes of hydrogen to produce 2 volumes of ammonia
- ✓ e.g. 50 cm^3 nitrogen reacts with 150 cm^3 hydrogen (3 x 50) ==> 100 cm^3 of ammonia (2 x 50)

Example 3: $C_3H_{8(g)} + 5O_{2(g)} \longrightarrow CO_{2(g)} + 4H_2O_{(l)}$

(a) What volume of oxygen is required to burn $25cm^3$ of propane, C_3H_8.

- Theoretical reactant volume ratio is $C_3H_8 : O_2$ is 1 : 5 for burning the fuel propane.
- so actual ratio is 25 : 5x25, so $125cm^3$ oxygen is needed.

(b) What volume of carbon dioxide is formed if $5dm^3$ of propane is burned?

- Theoretical reactant-product volume ratio is

  $C_3H_8 : CO_2$ is 1 : 3

- so actual ratio is 5 : 3x5, so $15dm^3$ carbon dioxide is formed.

(c) What volume of air ($^1/_5$th oxygen) is required to burn propane at the rate of $2dm^3$ per minute in a gas fire?

- Theoretical reactant volume ratio is $C_3H_8 : O_2$ is 1 : 5
- so actual ratio is 2 : 5x2, so $10dm^3$ oxygen per minute is needed,
- Therefore, since air is only $^1/_5$th O_2, 5 x 10 = $50dm^3$ of air per minute is required.

STOICHIOMETRIC AND IONIC EQUATIONS

Chemical word equations

For any reaction, what you start with are called the reactants, and what you form are called the products. So any chemical equation shows in some way the overall chemical change of.

REACTANTS ⟶ PRODUCTS

This can be written in words or symbols/formulae.

The arrow ⟶ means the direction of change from reactants =to=> products

No symbols or numbers are used in word equations. Always try to fit all the words neatly lined up from left to right, especially if it is a long word equation. The word equation is presented to summarise the change of reactants to products.

STOICHIOMETRIC EQUATIONS

Consider the reaction between zinc sulphide and oxygen. The equation can be written as;

$$ZnS(s) + O_2(g) \longrightarrow ZnO(s) + SO_2(g)$$

This is an example of a stoichiometric, or normal chemical(or symbol) equation. From this equation, we can deduce;

- What substances react(zinc sulphide (solid) and oxygen(gas)
- What products are formed (zinc oxide(solid) and sulphur dioxide(gas)
- Relative number of atoms and molecules taking part in the chemical reaction
- The state symbols(s), (l) or (g) to tell us the state of each reactant and each product.

Rules on Balancing Symbol equations

1. You should know what the reactants and products are,
2. write a word equation with appropriate reactants on the left and products on the right.
3. Writing the correct symbol or formula for each equation component.Numbers in a formula are written as subscripts after the element concerned

    - e.g. H_2SO_4 means 2 H's, 1 S and 4 O's
    - or the subscript number can double, treble etc. a part of the formula
    - e.g. $Ca(OH)_2$ means 1 Ca and 2 OH's (or 2 O's and 2 H's in total)

    Numbers before a formula double or treble it etc.

    - e.g. 2NaCl means 2 Na's and 2 Cl's in total
    - or $2H_2SO_4$ means 2 x H_2SO_4 = 4 H's, 2 S's and 8 O's in total

    NOTE: If the number is 1 itself, by convention, no number is shown in a formula or before a formula.

4. Using numbers if necessary to balance the equation.

5. If all is correct, then the sum of atoms for each element should be the same on both side of the equation arrow.
   a. in other words: atoms of products = atoms of reactants

      This is a chemical conservation law of atoms and later it may be described as the 'law of conservation of mass.

   b. the equations are first presented in 'picture' style and then written out fully with state symbols
   c. The individual formulas involved and the word equations have already been presented above.

IONIC EQUATIONS

- In many reactions only certain ions change their 'chemical state' but other ions remain in exactly the same original physical and chemical state.
- The ions that do not change are called 'spectator ions'.
- The ionic equation represents the 'actual' chemical change and omits the spectator ions.

1. Acid-base reactions: Acids can be defined as proton donors. A base can be defined as a proton acceptor. Any acid-alkali neutralisation involves the hydroxide ion is (base) and this accepts a proton from an acid.

$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$ which can be re-written as

$$2H^+_{(aq)} + \cancel{Cl^-_{(aq)}} + \cancel{Na^+_{(aq)}} + OH^-_{(aq)} \longrightarrow \cancel{Na^+_{(aq)}} + \cancel{Cl^-_{(aq)}} + H_2O_{(l)}$$

The spectator ions are Cl^- and Na^+

The remaining ions are $H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$

The spectator ions are Cl^- and Na^+

2. Insoluble salt formation: An insoluble salt is made by mixing two solutions of soluble compounds to form the insoluble compound in a process called 'precipitation'. A precipitation reaction is generally defined as 'the formation of an insoluble solid on mixing two solutions or a gas bubbled into a solution'.

(a) Silver chloride is made by mixing solutions of solutions of silver nitrate and sodium chloride.

- silver nitrate + sodium chloride $\longrightarrow$ silver chloride + sodium nitrate

$$Ag^{+}_{(aq)} + \cancel{NO_3^{-}}_{(aq)} + \cancel{Na^{+}}_{(aq)} + Cl^{-}_{(aq)} \longrightarrow AgCl_{(s)} + \cancel{NO_3^{-}}_{(aq)} + \cancel{Na^{+}}_{(aq)}$$

The ionic equation is: $Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \longrightarrow AgCl_{(s)}$

The spectator ions are NO_3^{-} and Na^{+}

(b) Lead (II) iodide can be made by mixing lead (II) nitrate solution with potassium iodide solution.

- Lead (II) nitrate + potassium iodide $\longrightarrow$ lead (II) iodide + potassium nitrate

$$Pb^{2+}_{(aq)} + 2\,\cancel{NO_3^{-}}_{(aq)} + 2\cancel{K^{+}}_{(aq)} + 2I^{-}_{(aq)} \longrightarrow 2\cancel{K^{+}}_{(aq)} + 2\,\cancel{NO_3^{-}}_{(aq)} + PbI_{2(s)}$$

- $Pb(NO_3)_{2(aq)} + 2KI_{(aq)} \longrightarrow PbI_{2(s)} + 2KNO_{3(aq)}$
- The ionic equation is: $Pbg^{2+}_{(aq)} + 2I^{-}_{(aq)} \longrightarrow PbI_{2(s)}$
- The spectator ions are NO_3^{-} and K^{+}

(c) Calcium carbonate forms on e.g. mixing calcium chloride and sodium carbonate solutions

- Calcium chloride + sodium carbonate $\longrightarrow$ calcium carbonate + sodium chloride

$$CaCl_{2(aq)} + Na_2CO_{3\,(aq)} \longrightarrow CaCO_{3(s)} + 2NaCl_{(aq)}$$

$$Ca^{2+}_{(aq)} + 2\cancel{Cl^{-}}_{(aq)} + 2\cancel{Na^{+}}_{(aq)} + C0_3^{2-}{}_{(aq)} \longrightarrow CaCO_{3(s)} + 2\cancel{Na^{+}}_{(aq)} + 2\cancel{Cl^{-}}_{(aq)}$$

- Ionically : $Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \longrightarrow CaCO_{3(s)}$
- The spectator ions are Cl^{-} and Na^{+}

- **(3) Redox reaction analysis:**

(a) Magnesium + iron (II) sulphate ⟶ magnesium sulphate + iron

- $Mg_{(s)} + FeSO_{4(aq)} \longrightarrow MgSO_{4(aq)} + Fe_{(s)}$
- This is the 'ordinary molecular' equation for a typical metal displacement reaction, but this does not really show what happens in terms of atoms, ions and electrons, so we use ionic equations like the one shown below.
- The sulphate ion $SO_4^{2-}{}_{(aq)}$ is called a spectator ion, because it doesn't change in the reaction and can be omitted from the ionic equation. No electrons show up in the full equations because electrons lost by x = electrons gained by y!!

$$Mg_{(s)} + Fe^{2+}{}_{(aq)} + \cancel{SO_4^{2-}}{}_{(aq)} \longrightarrow Mg^{2+}{}_{(aq)} + Fe_{(s)} + \cancel{SO_4^{2-}{}_{(aq)}}$$

- $Mg_{(s)} + Fe^{2+}{}_{(aq)} \longrightarrow Mg^{2+}{}_{(aq)} + Fe_{(s)}$

Mg oxidised by electron loss, Fe^{2+} reduced by electron gain.

(b) Zinc + hydrochloric acid ⟶ zinc chloride + hydrogen

- $Zn_{(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_{2(g)}$

$$\mathbf{Zn_{(s)} + 2H^+{}_{(aq)} + 2\ \cancel{Cl^-{}_{(aq)}} \longrightarrow Zn^{2+}{}_{(aq)} + 2\ Cl^-{}_{(aq)} + \cancel{H_{2(g)}}}$$

- The chloride ion Cl^- is the spectator ion
- $Zn_{(s)} + 2H^+{}_{(aq)} \longrightarrow Zn^{2+}{}_{(aq)} + H_{2(g)}$

Zn oxidised by electron loss, H^+ reduced by electron gain.

11. MOLARITY

It is very useful to be known exactly how much of a dissolved substance is present in a solution of particular concentration or volume of a solution. So we need a standard way of comparing the concentrations of solutions.

The concentration of an aqueous solution is usually expressed in terms of moles of dissolved substance per cubic decimetre, **mol dm^{-3}**, this is called **molarity**, sometimes denoted in shorthand as M.

> Note: **1dm^3 = 1 litre = 1000ml = 1000 cm^3**, so dividing **cm^3/1000 gives dm^3**, which is handy to know since most volumetric laboratory apparatus is calibrated in cm^3 (or ml), **but solution concentrations are usually quoted in molarity, that is mol/dm^3** (mol/litre).

Equal volumes of solution of the same molar concentration contain the same number of moles of solute i.e. the same number of particles as given by the chemical formula.

You need to be able to calculate:

- The number of moles or mass of substance in an aqueous solution of given volume and concentration
- The concentration of an aqueous solution given the amount of substance and volume of water.

You should recall and be able to use each of the following relationships.

(1) molarity of Z = moles of Z / volume in dm^3

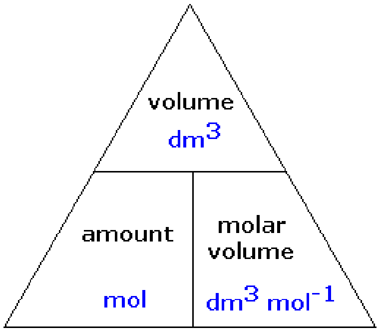
(2) molarity x formula mass of solute = solute concentration in g/dm^3,

dividing this by 1000 gives the concentration in g/cm^3

(3) (concentration in g/dm^3) / formula mass = molarity in mol/dm^3,

(4) moles Z = mass Z / formula mass of Z

(5) 1 mole = formula mass in grams



Example 1

What mass of sodium hydroxide (NaOH) is needed to make up 500 cm^3 (0.5 dm^3) of a 0.5M solution? [A_r's: Na = 23, O = 16, H = 1]

1 mole of NaOH = 23 + 16 + 1 = 40g

for 1000 cm^3 (1 dm^3) of 0.5M you would need 0.5 moles NaOH

which is 0.5 x 40 = 20g

however only 500 cm^3 of solution is needed compared to 1000 cm^3

so scaling down: **mass NaOH required** = 20 x 500/1000 = **10g**

Example 2

How many moles of H_2SO_4 are there in 250cm^3 of a 0.8M sulphuric acid solution? What mass of acid is in this solution? [A_r's: H = 1, S = 32, O = 16]

formula mass of sulphuric acid = 2 + 32 + (4x16) = 98, so 1 mole = 98g

if there was 1000 cm^3 of the solution, there would be 0.8 moles H_2SO_4

but there is only 250cm3 of solution, so scaling down ...

moles H_2SO_4 = 0.8 x (250/1000) = **0.2 mol**

mass = moles x formula mass, which is 0.2 x 98 = **19.6g of H_2SO_4**

Example 3

5.95g of potassium bromide was dissolved in 400cm^3 of water. Calculate its molarity. [A_r's: K = 39, Br = 80] moles = mass / formula mass, (KBr = 39 + 80 = 119)

mol KBr = 5.95/119 = 0.05 mol

400 cm^3 = 400/1000 = 0.4 dm^3

molarity = moles of solute / volume of solution

molarity of KBr solution = 0.05/0.4 = **0.125M**

Example 4

What is the concentration of sodium chloride (NaCl) in g/dm^3 and g/cm^3 in a 1.50 molar solution?

At. Masses: Na = 23, Cl = 35.5, formula mass NaCl = 23 + 35.5 = 58.5

Therefore **concentration** = 1.5 x 58.5 **= 87.8 g/dm^3**, and

concentration = 87.75 / 1000 = **0.0878 g/cm^3**

Example 5

A solution of calcium sulphate (CaSO4) contained 0.5g dissolved in 2dm^3 of water. Calculate the concentration in (a) g/dm^3, (b) g/cm^3 and (c) mol/dm^3.

(a) concentration = 0.5/2 **= 0.25 g/dm^3**, then since 1dm^3 = 1000 cm^3

(b) concentration = 0.25/1000 **= 0.00025 g/cm^3**

(c) At. masses: Ca = 40, S = 32, O = 64, f. mass $CaSO_4$ = 40 + 32 + (4 x 16) = 136

moles $CaSO_4$ = 0.5 / 136 = 0.00368 mol

concentration $CaSO_4$ = 0.00368 / 2 = **0.00184 mol/dm^3**

12. TITRATION: ACID AND ALKALI

Titrations can be used to find the concentration of an acid or alkali from the relative volumes used and the concentration of one of the two reactants.

You should be able to carry out calculations involving neutralisation reactions in aqueous solution given the balanced equation or from your own practical results.

1. Note again: **1dm^3 = 1 litre = 1000ml = 1000 cm^3**, so dividing **cm^3/1000 gives dm^3**.

2. and other useful formulae or relationships are:

  - **moles = molarity** (mol/dm^3) **x volume** (dm^3=cm^3/1000),
  - **molarity** (mol/dm^3) **= mol / volume** (dm^3=cm^3/1000),
  - **1 mole = formula mass in grams**.

In most volumetric calculations of this type, you **first calculate the known moles of one reactant from a volume and molarity**. Then, f**rom the equation, you relate this to the number of moles of the other reactant**, and then with the **volume of the unknown concentration**, you work out its molarity.

Example 1:

25 cm^3 of a sodium hydroxide solution was pipetted into a conical flask and titrated with 0.2M hydrochloric acid. Using a suitable indicator it was found that 15 cm^3 of acid was required to neutralise the alkali. Calculate the molarity of the sodium hydroxide and concentration in g/dm^3.

equation $\mathbf{NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}}$

moles HCl = (15/1000) x 0.2 = 0.003 mol

moles HCl = moles NaOH (1 : 1 in equation)

so there is 0.003 mol NaOH in 25 cm^3

scaling up to 1000 cm^3 (1 dm^3), there are ...

0.003 x (1000/25) = 0.12 mol NaOH in 1 dm^3

molarity of NaOH is 0.12M or mol dm^{-3}

since **mass = moles x formula mass**, and M_r(NaOH) = 23 + 16 + 1 = 40

concentration in g/dm^3 is 0.12 x 40 = **4.41g/dm^3**

Example 2:

20 cm^3 of a sulphuric acid solution was titrated with 0.05M potassium hydroxide. If the acid required 36 cm^3 of the alkali KOH for neutralisation what was the concentration of the acid?

equation $\mathbf{2KOH_{(aq)} + H_2SO_{4(aq)} \longrightarrow K_2SO_4 + 2H_2O_{(l)}}$

mol KOH = 0.05 x (36/1000) = 0.0018 mol

mol H_2SO_4 = mol KOH / 2 (because of 1 : 2 ratio in equation above)

mol H_2SO_4 = 0.0018/2 = 0.0009 (in 20 cm^3)

scaling up to 1000 cm^3 of solution = 0.0009 x (1000/20) = 0.045 mol

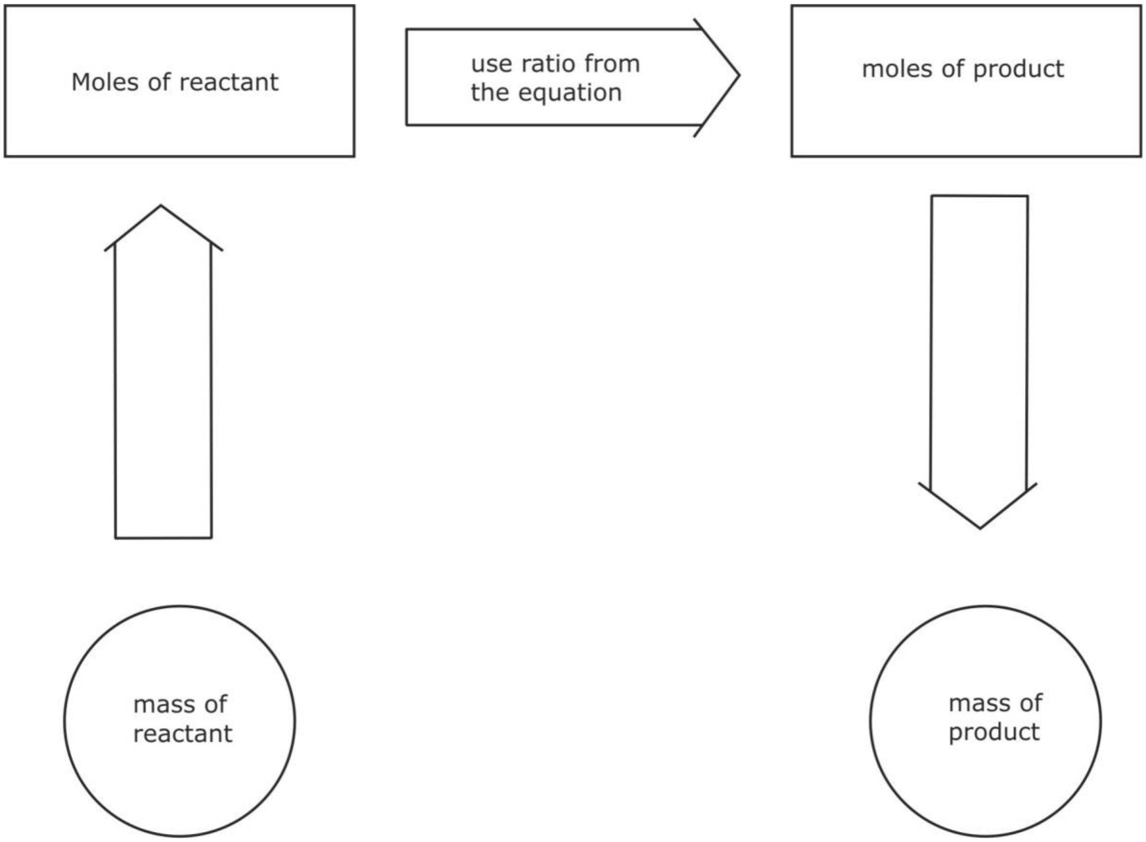
mol H_2SO_4 in 1 dm^3 = 0.045, so **molarity of H_2SO_4 = 0.045M or mol dm^{-3}**

since mass = moles x formula mass, and $M_r(H_2SO_4)$ = 2 + 32 + (4x16) = 98

Concentration in g/dm^3 is 0.045 x 98 = **4.41g/dm^3**

How to carry out a titration

The diagrams show the typical apparatus (1)-(6) used in manipulating liquids and on the left a brief three stage description of titrating an acid with an alkali:



Volumetric Analysis (Titrations)

A titration is a laboratory procedure where a measured volume of one solution is added to a known volume of another reagent until the reaction is complete. The operation is an example of volumetric (titrimetric) analysis. The equivalence point is usually shown by the colour change of an indicator and is known as the end-point.

Volumetric analysis is a powerful technique, which is used in a variety of ways by chemists in many different fields.

Practical Aspects

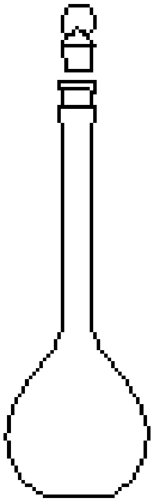
The practical aspects of titrations are required in the assessment of practical skills. Knowledge of the techniques of titrations is expected but it would be normal to assume that all apparatus would have been washed with distilled/deionised water. The description should include which reagent is placed in the burette, name of indicator (but no reason for choice of indicator), detection of **endpoint** and what should be observed, and repetition for accuracy.

When you have finished this section you should be able to:

- ✓ Perform titrations
- ✓ Record titration results in the form of a table

Use of a VOLUMETRIC FLASK

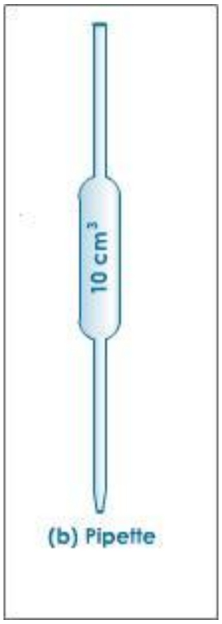
To prepare a solution of precisely known concentration (a **standard solution**), a definite amount of solute must be dissolved in a solvent to give a definite volume of solution.



The definite amount of material is measured by weighing, and the definite volume of solution prepared in a **volumetric flask**. A volumetric flask contains a definite volume when correctly filled to the calibration mark at the temperature stated on the flask. Tip the solid from a weighing bottle into a large (250 cm^3) beaker and add about 50 cm^3 of distilled water from a wash bottle. Stir well with a glass rod to dissolve. Take great care not to lose any of the solution and remember to wash the solution off the stirring rod back into the beaker. Rinse out the volumetric flask with distilled water and pour the cold solution into the flask through a clean filter funnel. Wash out the beaker several times and add all the washings to the flask. Now fill the flask to within about 1 cm of the calibration mark on the neck. Finally add water dropwise until the meniscus just rests on the calibration mark. Stopper the flask and invert a number of times to thoroughly mix the contents.

USE OF A PIPETTE

The pipette is designed to deliver a definite fixed volume of liquid when correctly filled to its calibration mark.



Before use, a pipette must be washed out with the solution it is to measure. To fill the pipette, use a safety filler to suck solution up a few centimetres above the calibration mark. Let the solution down until the bottom of the meniscus just touches the calibration mark. For a titration the contents of the pipette are run into a conical flask, which has been well washed with distilled water. Allow the pipette to drain for about 20 seconds, then touch the tip to the surface of the liquid in the conical flask. The volume of solution delivered by the pipette is known as the **aliquot**.

<u>Use of a BURETTE</u>

The burette is designed to deliver definite but variable volumes of liquid. First rinse out the burette with the solution it is to contain. Clamp the burette vertically in a stand.

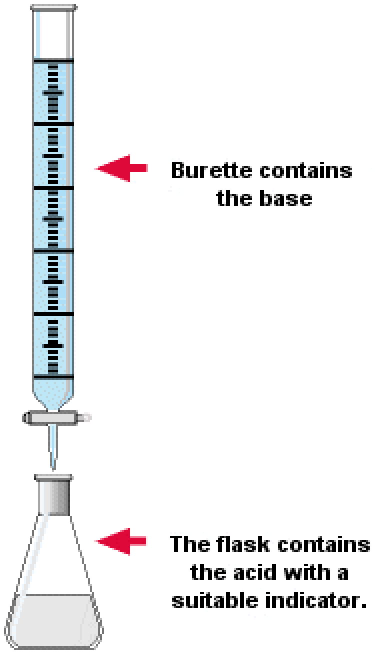
Fill the burette carefully using a beaker and a filter funnel. Open the tap briefly to fill the burette below the tap making sure there are no trapped air bubbles. Read the burette scale by observing the position of the bottom of the liquid meniscus, making sure your eyes are level with the graduation mark. To observe the meniscus more clearly, hold a white card behind the burette. Record the volume reading to the nearest 0.05 cm^3.

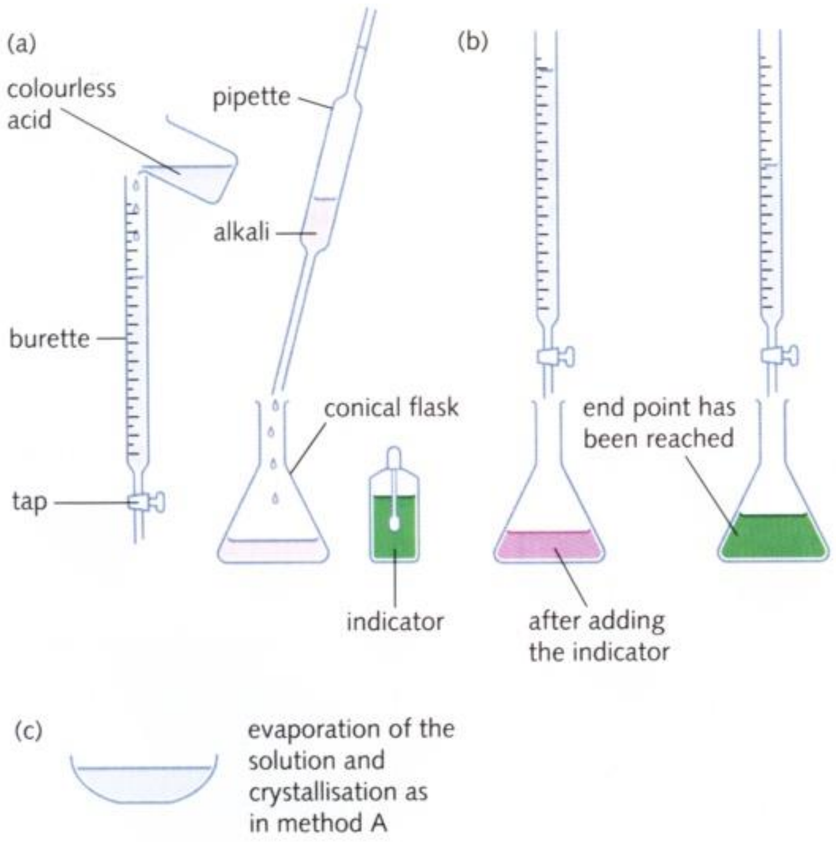
Some common indicators

Indicator	Colour in acid	Neutral colour	Colour in alkali
Litmus	Red	Purple	Blue
Phenolphthalein	Colourless	Colourless	Pink
Methyl orange	Red	Orange	Yellow
Universal indicator	Red	Green	Blue/violet
Bromothymol blue	Yellow	Green	Blue

TITRATION TECHNIQUE

When performing a titration, place the conical flask containing the aliquot on a white tile under the burette so that the tip of the burette is inside the mouth of the conical flask to avoid splashing.





Add a few drops of a suitable **indicator** to the solution in the conical flask. First perform a 'rough' titration by taking the burette reading and running in the solution in approximately 1 cm^3 portions, while swirling the flask vigorously. When the end-point is reached, as shown by the indicator changing colour, quickly close the tap. The new burette reading will give you a rough idea (to within about 1 cm^3) of the volume to be added. Now repeat the titration with a fresh aliquot. As the rough end-point volume is approached, add solution from the burette one drop at a time until the indicator changes colour. Record the volume. The volume run out from the burette to reach the end point is known as the **titre**.

Recording Titration Results

The results of a titration should be recorded;

- ✓ Immediately
- ✓ In ink
- ✓ In a table
- ✓ To the correct number of decimal places

Record the titration results in the form of a table.

Titration no.		Trial	1	2	3
Burette readings	Final				
	Initial				
Volume used (titre) /cm^3					
Mean titre /cm^3					

Accuracy

Record burette readings to the nearest 0.05 cm^3 (approximately 1 drop).

Consecutive titrations should agree to within 0.10 cm^3 and, strictly, you should repeat the titrations until this is achieved. However you may not have either the time or materials available to do this.

With practice, your technique should improve so that you should not need to do more than 4 titrations (1 trial + 3 accurate).

Calculate and use the mean (average) of the two (or preferably three) closest consecutive readings and quote this to the nearest 0.05 cm^3.

What do examiners look for in your answer sheet?

Abbreviation	What it stands for	Score
CT	Complete table → all titrations done	(1 mark)
D	Decimal use of decimals must be consistent if whole number used penalize fully if two decimals used, the 2nd decimal should be a 5 or a 0	(1 mark)
AC	Accuracy – titres must be within ± 0.2 cm of the teacher's value.	(1 mark)
PA	Principles of averaging	(1 mark)
	All the 3 values averaged must be within ± 0.2 otherwise penalize fully	
	If only 2 values from the table are within the range, only the 2 should be averaged.	
	If all the 3 are within the range and only 2 are averaged penalize fully	

FA	Final answer with unit	(1 mark)
Total		(5 marks)

CT	**1 mark**
D	**1 mark**
AC	**1 mark**
PA	**1 mark**
FA	**1 mark**
Total	**5 marks**

Specimen titration Table II

Titration no.		Trial	1	2	3
Burette readings	Final	33.10	32.70	32.70	42.80
	Initial	0.00	0.00	0.00	10.00
Volume used (titre) /cm^3		33.10	32.70	32.70	32.80
Mean titre /cm^3		32.73			

Average volume used of soln

$$\frac{32.70 + 32.70 + 32.80}{3}$$

$= 32.73\ cm^3$

Calculating the Concentration of a Solution from Titration Data

When you have finished this section you should be able to:

- ✓ Calculate the concentration of a solution from titration data and the balanced equation.
- ✓ Calculate the volume of solution required for titration from titration data and the balanced equation.

14.0.0 ORGANIC CHEMISTRY 1

Products from Oil

Coal, Oil and Natural Gas Formation - Fossil Fuels.

Just as coal has formed by the action of heat and pressure on the remains of trees and plants on land over millions of years, so oil and natural gas have formed by the action of heat and pressure on the remains of sea plants and animals over millions of years.

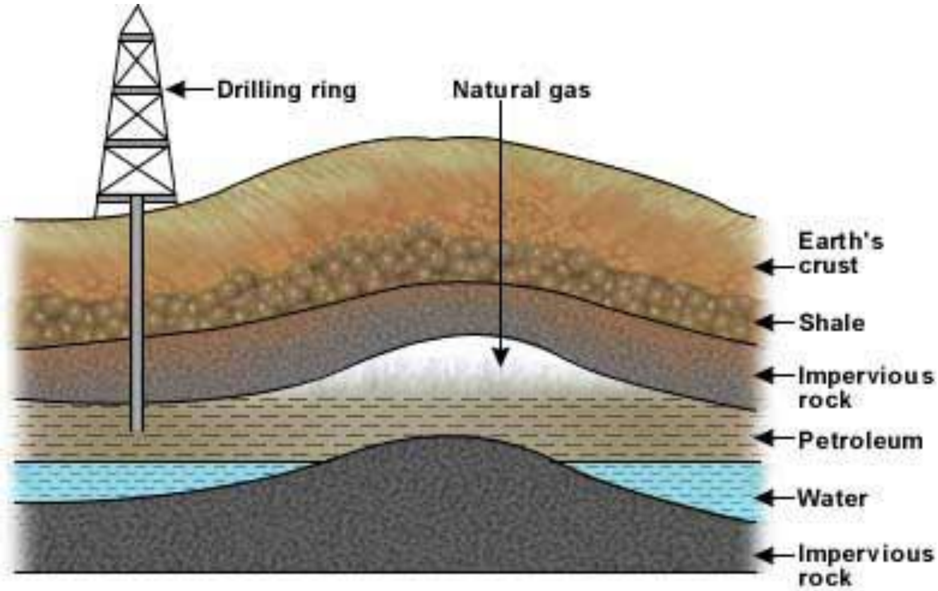


Diagram to show the occurrence of petroleum under the surface of earth.

The remains were buried in sediments which excluded the air (kept out oxygen) and stopped them decaying. More sediment buried the remains deeper and deeper until pressure and heat eventually turned them into coal, oil and natural gas. They are called fossil fuels because they are buried underground (from Latin fossilis - dug up).
Fossil fuels are a finite resource and non-renewable.

The oil deposits are formed in porous rock sediments. Porous rock has pores in it. Pores are small holes (see for example sandstone). The small holes allow the oil and natural gas to pass through the rock and rise until they are stopped by a layer of non-porous rock. Non-porous rock (for example shale) has no holes, and acts as a barrier to prevent the oil and natural gas rising. The oil and natural gas become trapped underground.

The oil is called crude oil (or petroleum, from Latin - rock oil), and has natural gas in it or in a pocket above it trapped by non-porous rock. Drilling through the rock allows the oil and gas to escape to the surface. Natural gas is mostly methane (CH_4). Crude oil is a mixture of substances (mostly hydrocarbons).

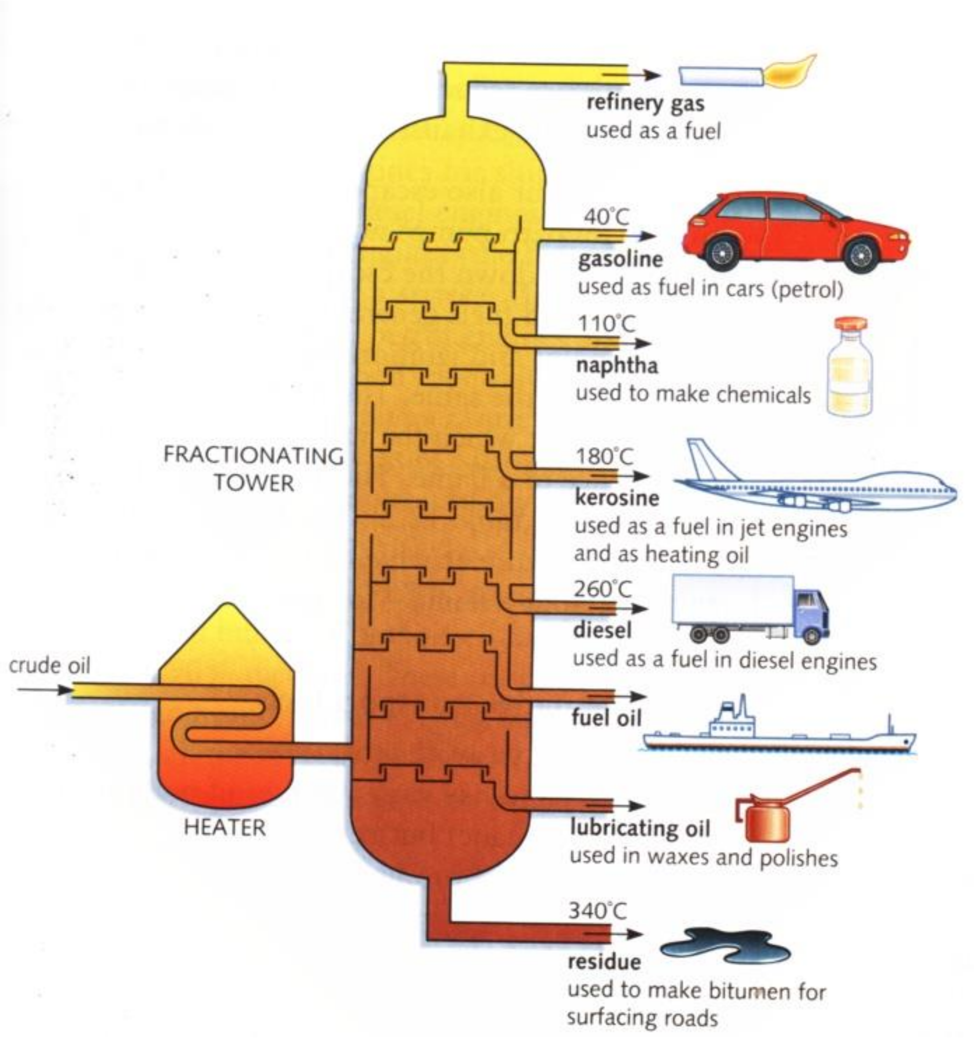
So what are Hydrocarbons?

Crude oil is a mixture of substances which are mostly hydrocarbons.

A hydrocarbon is a compound containing hydrogen and carbon only.

Since crude oil is a mixture of different hydrocarbon compounds, the different hydrocarbons will have different boiling points. A sample of crude oil will therefore have a range of boiling points, and the mixture can be separated by fractional distillation.

Fractional Distillation of Crude Oil.



Naming the fractions

The hydrocarbon fractions are mainly alkanes.

Name	Number of Carbon Atoms	Boiling Point (°C)	Uses

Refinery Gas	3 or 4	below 30	Bottled Gas (propane or butane).
Petrol	7 to 9	100 to 150	Fuel for car engines.
Naphtha	6 to 11	70 to 200	Solvents and used in petrol.
Kerosene (paraffin)	11 to 18	200 to 300	Fuel for aircraft and stoves.
Diesel Oil	11 to 18	200 to 300	Fuel for road vehicles and trains.
Lubricating Oil	18 to 25	300 to 400	Lubricant for engines and machines.
Fuel Oil	20 to 27	350 to 450	Fuel for ships and heating.
Greases and Wax	25 to 30	400 to 500	Lubricants and candles.
Bitumen	above 35	above 500	Road surface and roofing.

Crude oil is heated until it boils and then the hydrocarbon gases
are entered into the bottom of the fractionating column.
As the gases go up the column the temperature decreases.
The hydrocarbon gases condense back into liquids
and the fractions are removed from the sides of the column.

The smaller the hydrocarbon molecule,
the further it rises up the column before condensing.
The fractionating column operates continuously.
The temperatures shown are approximate.

A sample of crude oil may be separated in the laboratory
by fractional distillation. The collection vessel is changed
as the temperature rises to collect the different fractions.

Naming hydrocarbons.

Hydrocarbons are named
according to the number of carbon atoms in the molecule.

Number of Carbon Atoms	Name Prefix	Alkane	Alkene
1	meth	methane	-
2	eth	ethane	ethene
3	prop	propane	propene
4	but	butane	butene
5	pent	pentane	pentene
6	hex	hexane	hexene
7	hept	heptane	heptene
8	oct	octane	octene

Meth is pronounced meeth (like teeth),
Eth is pronounced eeth (like teeth),
Prop is pronounced prope (like rope),
But is pronounced bute (like beauty).
Pent is pronounced pent (like pentagon).
Hex is pronounced hex (like hexagon).
Hept is pronounced hept (like heptagon).
Oct is pronounced oct (like octagon).

The hydrocarbon fractions are mainly alkanes.

Properties of Different Fractions.

The different hydrocarbon fractions obtained from crude oil condense at different temperatures. The larger the hydrocarbon molecule (the more carbon atoms it has)

1) The higher the condensing temperature (the higher the boiling point).
2) The more viscous it is (it takes longer to flow - like syrup).
3) The less volatile it is (it evaporates less quickly).
4) The less flammable it is (it does not set fire so easily).

Gases from volatile hydrocarbons are denser than air and pose a fire hazard at ground level. This is why ignition sources (such as smoking) are not allowed at petrol stations.

Families of organic compounds

Homologous series

Organic compounds belong to different families, though all are based on **carbon C, hydrogen H,** and other elements such as **oxygen O and nitrogen N etc**. The compounds in each family have a similar chemical structure and a similar chemical formula. Each family of organic compounds forms what is called a **homologous series**. Different families arise because carbon atoms readily join together in chains (catenation) and strongly bond with other atoms such as hydrogen, oxygen and nitrogen. The result is a huge variety of '**organic compounds**'. The **name** comes from the fact that most of the original organic compounds studied by chemists came from plants or animals.

A **homologous series** is a family of compounds which have a **general formula** and have **similar chemical properties because they have the same functional group** of atoms (e.g. C=C alkene, C-OH alcohol or -COOH carboxylic acid).

Members of a homologous series have similar physical properties such as appearance, melting/boiling points, solubility etc. but show trends in them e.g. steady increase in melting/boiling point with increase in carbon number or molecular mass.

The **molecular formula** represents a summary of all the atoms in the molecule.

The structural or displayed formula shows the full structure of the molecule with all the individual bonds and atoms shown (though there are different 'sub-styles' of varying detail, see below).

What are alkanes?

These are obtained directly from crude oil by fractional distillation. They are saturated hydrocarbons and they form an homologous series called alkanes with a general formula C_nH_{2n+2} Saturated hydrocarbons have no C=C double bonds, only carbon-carbon single bonds, and so has combined with the maximum number of hydrogen atoms. i.e. no more atoms can add to it. Alkanes are the first homologous series. Examples of alkanes are:

The gases	Methane CH_4, ethane C_2H_6, propane C_3H_8, butane C_4H_{10}
Liquids	Pentane C_5H_{12}, hexane C_6H_{14} C_7H_{16}etc

The Names of all alkanes end in ...ane

Names.

Alkanes are the simplest homologous series of compounds and their names follow this pattern,

CH_4 - methane

C_2H_6 - ethane

C_3H_8 - propane

C_4H_{10} - butane

C_5H_{12} - pentane

I.e. they have a prefix (meth-, eth-, prop-, but-, etc.), which depends on the number of carbon atoms in the molecule and a common suffix (-ane).

The general chemical form la for an alkane is C_nH_{2n+2}

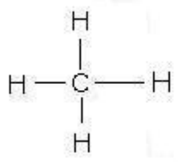
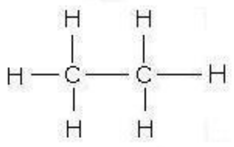
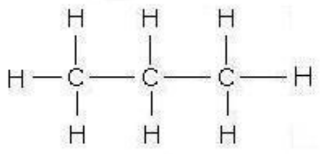
Structural formulae

As well as using a normal type of molecular formula to describe an organic molecule, they can be represented by drawing out their structure **i.e.** *by* showing how the atoms are connected, or bonded to each other.

In order to do this a few rules have to be followed;

(*i*) Carbon atoms must be bonded four times

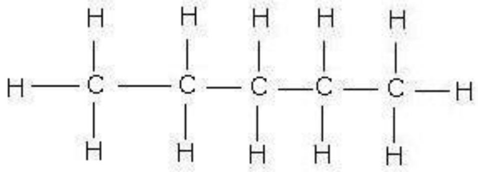
(***iii***) Hydrogen atoms must bond only once.

Name	Molecular formula	Structural formula
Methane	CH_4	
Ethane	C_2H_6	
Propane	C_3H_8	

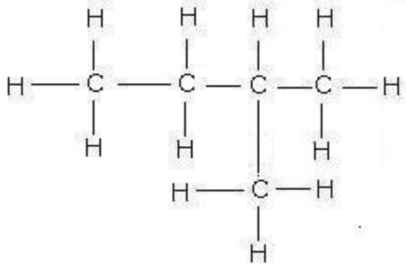
ISOMERISM

Isomerism occurs when two or more compounds have the same chemical formula but have different structures, e.g. for the molecular formula C_4H_{10} there are two possibilities - one 'linear' and one with carbon chain 'branching'. Butane is linear while its branched isomer is methyl propane.

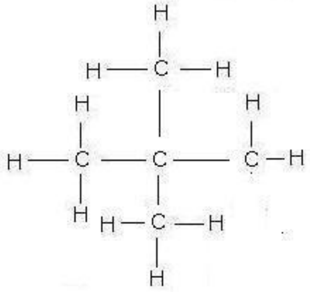
1. Butane



2. 2-Methylbutane



3. 2,2-Dimethylpropane



As the number of carbon atoms increases, the number of possible isomers increases rapidly. All families or homologous series exhibit isomerism.

Formula	Number of structural isomers
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
$C_{10}H_{22}$	75

Physical properties of alkanes	
Physical state	Lower molecular weight alkanes are gases. Methane, ethane, propane and butane are gases at ordinary room temperature. Higher alkanes up to those having 17 carbon atoms are liquids; higher alkanes are solids at room temperature.
Melting and boiling	Homologous alkanes show increase in melting and boiling

points	points. Similar to the behavior of elements in the same group in a periodic table.
Solubility	Alkanes, like all other organic chemicals are insoluble in water. They are however soluble in organic liquids. Alkanes are non-polar and are hence soluble in other non-polar liquids and not in water, as water is a polar molecule.

CHEMICAL REACTIONS OF ALKANES

1.Substitutional reactions of alkanes

Alkanes are most inert of all homologous series. They are not very reactive unless burned. But they will react with strong oxidising chemicals like chlorine when heated or subjected to u.v light. A substitution reaction occurs and a chloro-alkane is formed e.g. a hydrogen atom is swapped for a chlorine atom and the hydrogen combines with a chlorine atom forming hydrogen chloride. This process is called **halogenation**.

$$\underset{\text{Methane}}{CH_4} + \underset{\text{Chlorine}}{Cl_2} \xrightarrow{\text{Sunlight}} \underset{\text{Chloromethane or Methyl chloride}}{CH_3Cl} + \underset{\text{Hydrogen chloride}}{HCl}$$

The UV light causes the formation of **free radical** halogen atoms by providing enough energy for the bond between the two halogen atoms to break.

A halogen atom attacks the alkane, **substituting** itself for a hydrogen atom. This **substitution** may occur many times in an alkane before the reaction is finished.

2. Combustion

Alkanes, along with all other types of hydrocarbon, will burn in an excess of oxygen to give carbon dioxide and water only as the products,

e.g. $CH_{4\,(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$

in general,

$C_nH_{2n+2(g)} + (1.5n+0.5)O_{2(g)} \longrightarrow nCO_{2(g)} + (n+1)H_2O_{(g)}$

If there is not enough oxygen present then instead of carbon dioxide, carbon monoxide, CO, is produced. Carbon monoxide is particularly toxic and absorbed into blood, through respiration, very easily. For domestic heating systems it is particularly important that enough air can get to the flame to avoid carbon monoxide being generated in the home. Car engines also require a lot of air and there is a lot of research going on to make the internal combustion engine more efficient, and so put out less carbon monoxide.

3. Reactivity

Alkanes are **saturated** hydrocarbons. Molecules of saturated hydrocarbons contain only **single** bonds between all carbon atoms in the series. Hence their reactivity with other chemicals is relatively low.

What are alkenes?

Hydrocarbons, which contain two hydrogen atoms less than the corresponding alkanes, are called alkenes. They have one double bond and are unsaturated carbon compounds. Alkenes cannot be obtained directly from crude oil. They can only be obtained by cracking of alkanes.

Cracking

In industry the fractions obtained from the fractional distillation of crude oil are **heated at high pressure** in the presence of a **catalyst** to produce shorter chain alkanes and alkenes.

E.g. $\mathbf{C_{10}H_{22} \longrightarrow C_5H_{12} + C_5H_{10}}$

They are unsaturated hydrocarbons with a general formula C_nH_{2n}. **Unsaturated means the molecule has a C=C double bond to which atoms or groups can add after breaking the double bond**.

Alkenes all have a C=C double bond in their structure and their names follow this pattern. Their names end in ...ene

C_2H_4 - ethene

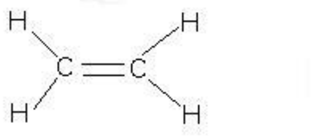
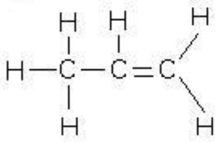
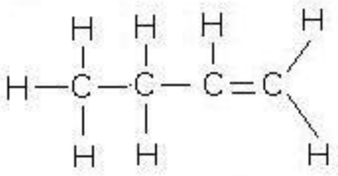
C_3H_6 - propene

C_4H_8 - butene

C_5H_{10} - pentene

The general chemical formula for an alkene is C_nH_{2n}

Name	Molecular formula	Structural formula

Ethene	C_2H_4	
Propene	C_3H_6	
Butene	C_4H_8	

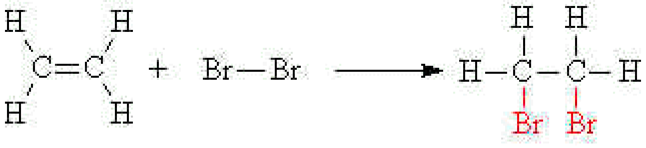
The general chemical formula for an alkene is C_nH_{2n}

(2) Addition reactions of alkenes :

(*i*) Bromination

The double bond of an alkene will undergo an ***addition reaction*** with aqueous bromine to give a dibromo compound. The **orange** bromine water is **decolourised** in the process.

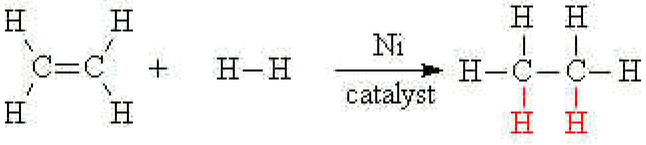
E.g. ethene reacts with bromine water to give 1,2-dibromoethane,



(*ii*) Hydrogenation

Alkenes may be turned into alkanes by reacting the alkene with hydrogen gas at a high temperature and high pressure. A nickel catalyst is also needed to accomplish this addition reaction.

E.g. ethene reacts with hydrogen to give ethane,

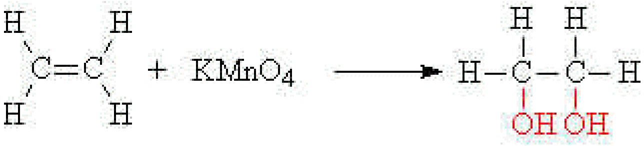


This reaction is also called **saturation** of the double bond. In ethene the carbon atoms are said to be **unsaturated**. In ethane the carbon atoms have the maximum number of hydrogen atoms bonded to them, and are said to be **saturated**.

(*iii*) Oxidation

The carbon-carbon double bond may also be oxidised ***i.e.*** have oxygen added to it. This is accomplished by using acidified potassium manganate (VII) solution at room temperature and pressure. The **purple** manganate (VII) solution is **decolourised** during the reaction.

E.g. ethene reacts with acidified potassium manganate $(VII)_{(aq)}$ to give ethan-1,2-diol,



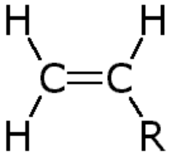
(3) Addition polymerisation :

All alkenes will react with free radical initiators to form ***polymers*** by a ***free radical addition*** reaction.

Some definitions -

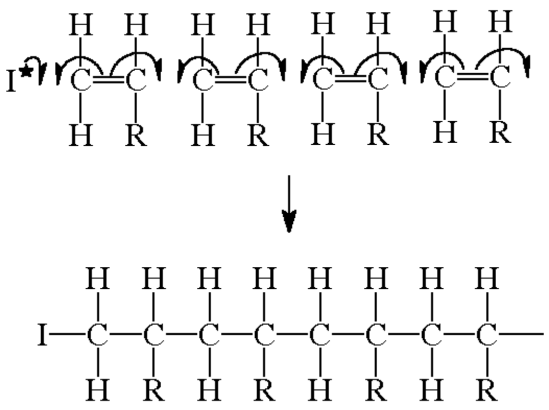
monomer - a single unit ***e.g.*** an alkene.

The alkene monomer has the general formula:



Where R is any group of atoms, ***e.g.*** R=CH_3 for propene.

The reaction progresses by the separate units joining up to form giant, long chains -



Polymer- a material produced from many separate single monomer units joined up together.

An addition polymer is simply named after the monomer alkene that it is prepared from.

Alkene	**Additional polymer**
Ethene	polyethene
Propene	poly propene
Phenylethene	phenylethene
Chloroethene	poly chloroethene

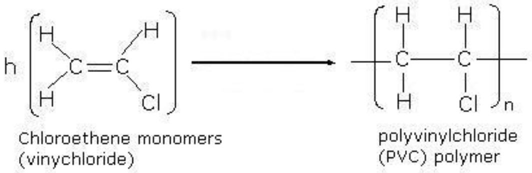
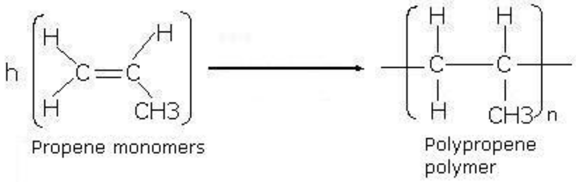
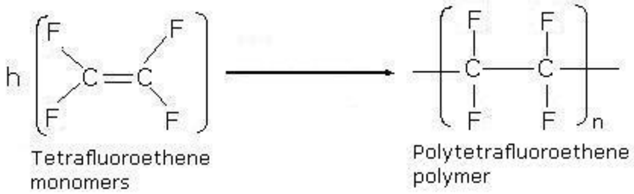
The structure above shows just 4 separate monomer units joined together. In a real polymer, however, there could be 1000's of units joined up to form the chains. This would be extremely difficult to draw out and so the structure is often shortened to a **repeat unit**.

There are 3 stages to think about when drawing a repeat unit for a polymer -

1) Draw the structure of the desired monomer.

2) Change the double bond into a single bond and draw bonds going left and right from the carbon atoms.

3) Place large brackets around the structure and a subscript **n** and there is the repeat unit.

Additional Polymers	Uses
	Plastic bags, bowls, packaging
	Insulation and pipes
	Crates, boxes, plastic ropes
	Non-stick frying pans

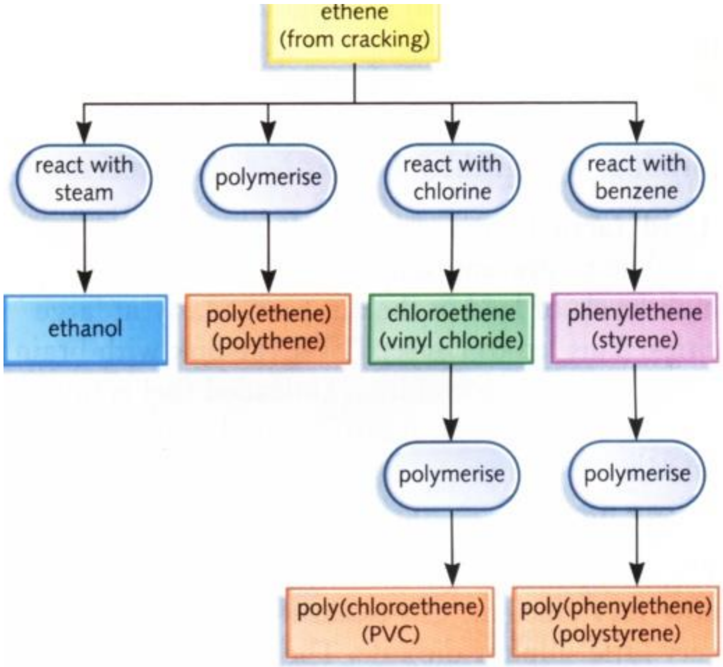
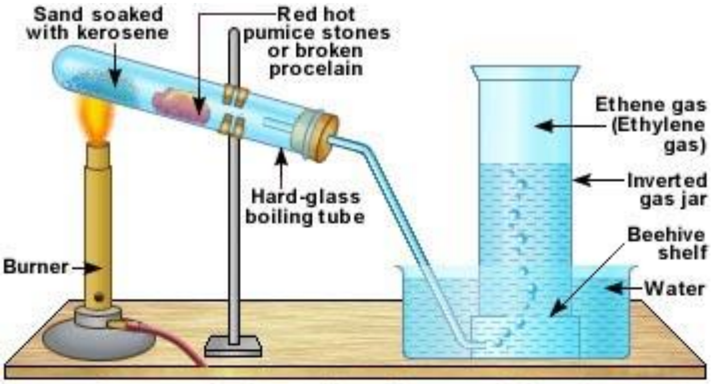


Figure 12.3 Important products can be made from the ethene

Laboratory preparation of ethene gas

In the lab ethene is prepared by cracking kerosene or candle wax.

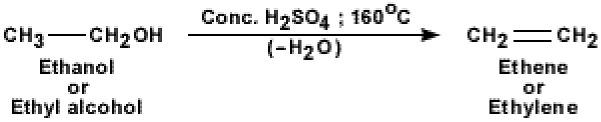


Apparatus for the cracking of kerosene hydrocarbon to prepare ethene gas.

Kerosene is poured over sand and this is kept at the bottom of a hard glass test tube. A few pieces of pumice stone or porcelain is kept a little distance away. The sand is slowly heated. After a while the porcelain portion of the test tube is heated. This is done alternately. The heated kerosene first vaporizes and then cracks. When the vapours pass over the hot porcelain, they crack again into smaller and smaller molecules. The gases are then passed over water. Ethene is collected by downward displacement of water. It can be understood that this method for collecting ethene gas does not give pure ethene gas. This is because from cracking, we get many types of molecules. All those, which are lighter than water and insoluble in water, will be collected.

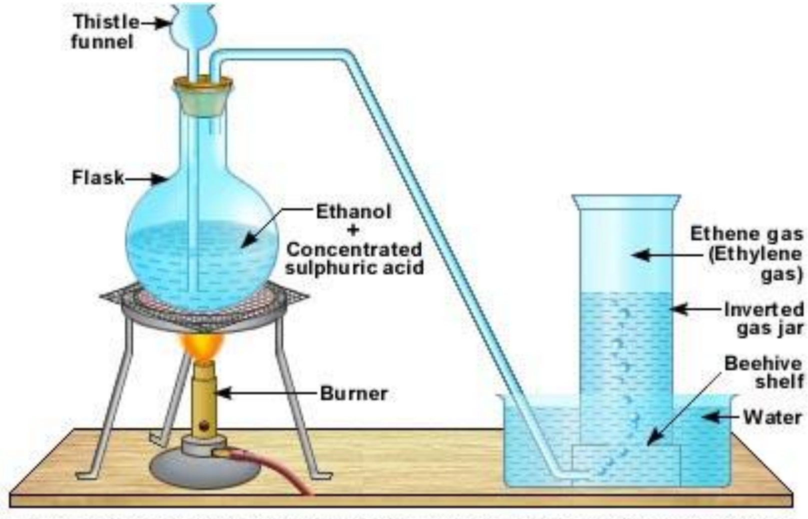
Ethene by dehydration of alcohols

To obtain pure ethene gas, another method is followed. This is from a chemical reaction with ethanol and concentrated sulphuric acid.



The temperature of the mixture of ethanol or ethyl alcohol and concentrated sulphuric acid is increased to 160°C. The acid acts as a dehydrating agent and picks up a water molecule from the ethanol molecule, leaving the reaction product as ethene gas.

The laboratory equipment to produce ethene gas is shown below. About 20 to 25 ml of ethanol is taken in a round bottomed flask.



Labelled diagram of the apparatus for the laboratory preparation of ethene gas.

Concentrated sulphuric acid is added to it from a thistle funnel slowly. Heat is supplied from a Bunsen burner and the temperature of the flask is raised to 160°C. Ethene gas starts evolving and it can be collected over water by downward displacement of water.

Uses of ethene

- Ethene is used for manufacturing organic compounds such as ethyl alcohol and ethylene glycol. Ethylene glycol is used for making artificial fibbers like polyesters.
- Ethene is used for manufacture of plastics. These plastics are made from polymerization of ethene into polythene. Polythenes are used for making bags, electrical insulation, etc.

Ethene is used artificial ripening of fruits such as mangoes, bananas, etc.

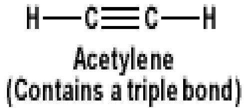
What are Alkynes?

Hydrocarbons that have two carbon atoms in a triple bond are called alkynes. They are unsaturated bonds. Their general formula is C_nH_{2n-2} and their names are derived from the alkanes by changing the ending "ane' of the alkane by "yne", for example, ethyne, propyne, butyne, etc. The simplest of alkynes has two carbon atoms in triple bond and is called ethyne. The table below gives names of the first three alkynes.

Alkyne	Known commonly as	Number of C-atoms	Number of H-atoms	Molecular formula
Ethyne	Acetylene	2	2	C_2H_2

Propyne	Methyl acetylene	3	4	C_3H_4
Butyne	Dimethyl acetylene	4	6	C_4H_6

The structural formula that is the actual arrangement of different atoms in space of the simplest alkyne namely ethyne ($CH \equiv CH$) is shown below.



Chemical properties of ethyne

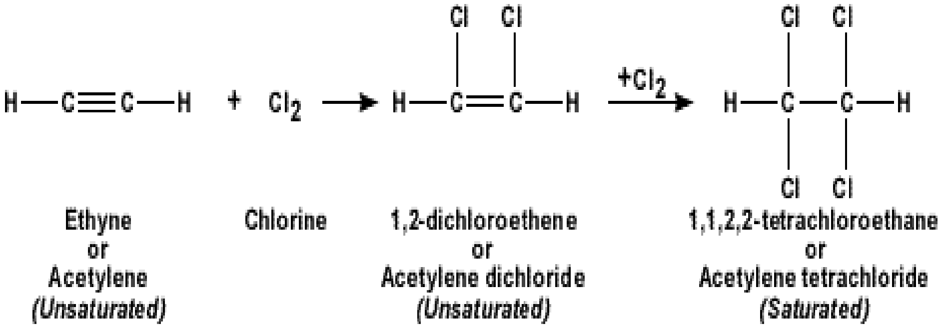
1. Combustion: Ethyne **burns** in air with a **sooty** flame. It forms carbon dioxide and water and gives out heat.

$$HC \equiv CH \quad + 5O_2 \longrightarrow 4CO_2 \quad + 2H_2O \quad + \text{heat}$$

The **sooty flame** is due to **higher amount of carbon** in ethyne than in methane. All the carbon atoms cannot get oxidized while burning this makes the flame sooty. But if ethyne is burnt with a proper control, for example, if the gas is made to pass through a small nozzle, then it gets ample air mixture to burn completely. This type of complete combustion is used for acetylene lamps in industries. Acetylene lamps produce very luminous non-sooty flame.

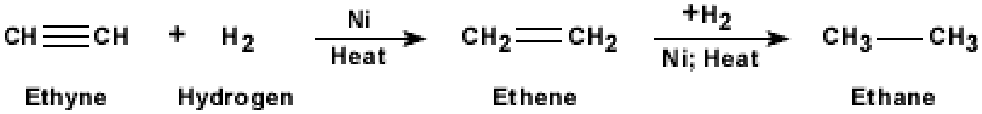
Ethyne combined well with oxygen can burn to give a flame whose temperature is 3000°C. This oxy-acetylene flame is used for welding metals, where very high temperatures are required.

2. Reactivity: Alkynes are more reactive than the alkanes or alkenes due to the presence of unsaturated bonds. Such a reaction is called addition reaction. In an addition reaction, the alkynes will become an alkane. For example if ethyne is reacted with chlorine, it becomes 1,1,2,2 tetra-chloro-ethane.



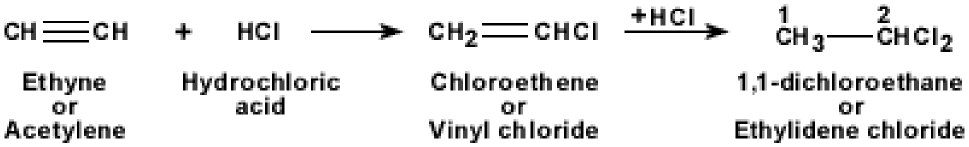
Similarly, addition reaction with bromine will give rise to 1,1,2,2, tetra-bromo-ethane. Bromine water decolorizes on reaction with ethyne. This is a prominent test for testing unsaturated nature of hydrocarbons.

When hydrogen is added to ethyne, and heated in the presence of nickel, it becomes ethene and then proceeds to become ethane. The bonds become saturated.



This is known as the process of **hydrogenation**. The addition of hydrogen to a double or triple bonded hydrocarbon leads to saturation of the bonds.

When hydrochloric acid is added to ethyne, it becomes first chloro-ethene and then 1,1- dichloro-ethane. The reaction is shown below.



Uses of ethyne

- Ethyne burns in oxygen to give a very luminous light. Hawkers use this as lamps.
- Ethyne is used for oxy-acetylene flame used for industrial welding.
- Ethyne is used for manufacture of synthetic plastics, synthetic rubbers, and synthetic fibers.
- Ethyne is also used making many industrially useful organic compounds like acetaldehyde, acetic acid, etc.

15.0.0 NITROGEN AND ITS COMPOUNDS

NITROGEN

Nitrogen is a colourless and odourless gas, N_2, which is insoluble in water. Although it does not support life, it is not poisonous.It reacts only with difficulty with other elements, requiring either high temperatures, a catalyst, or both, in order to form compounds. The most important of these are ammonia and ammonium salts, certain nitrogen oxides and nitric acid and its salts.

Composition of air

The atmosphere is the gaseous envelope which surrounds the earth. This gas, air, is a mixture consisting of about 78% nitrogen and 21 % oxygen. Water vapour is present in variable amounts (up to 5%), and so the composition of unpolluted air is normally based on the dry gas mixture. The figures below are percentages of the normal constituents by volume.

Gas	% by volume
nitrogen	78.1
oxygen	20.9
argon	0.93
carbon dioxide	0.035

Nitrogen comprises about 78.1% of the earth's atmosphere and it is the source of the commercial and industrial gas. Traces of other gases, notably He, Ne, Kr and Xe are also found, while near cities and industrial areas, all sorts of pollutants are also found. Air is liquefied, and the oxygen (about 20.9%) boiled off at -183 ^{o}C, leaving liquid nitrogen (which boils at -196 ^{o}C) behind. This process is known as fractional distillation.

Preparation of Nitrogen from Air

:

Industrial preparation

The chief source of free nitrogen is atmospheric air and nitrogen is usually prepared from it. Air free from dust, water vapour and carbon dioxide is compressed in a compression chamber for liquefaction. Firstly, the pressure on the air is increased to about 200 atmospheres. It is then released through a spiral into a low-pressure area, where intense cooling of the air takes place.

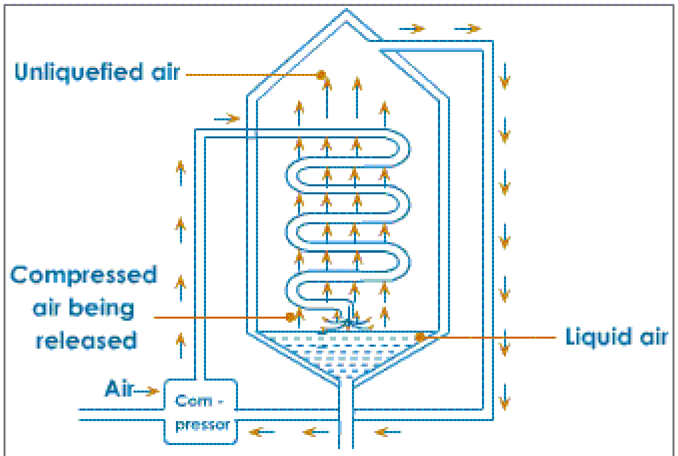
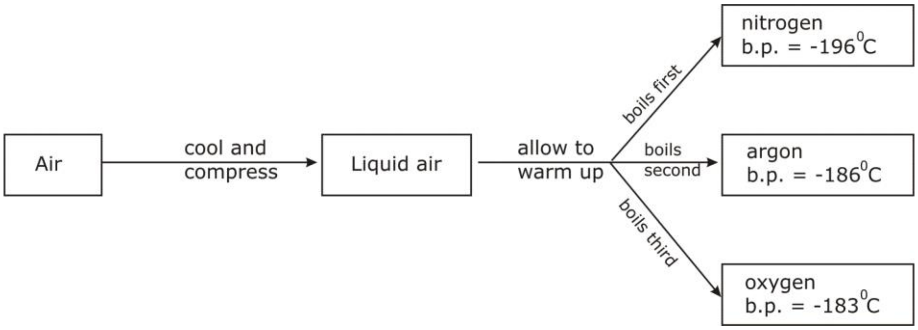


Fig. 12.1 Liquefaction of air

The cold air goes upwards and further cools the spiral that brings in a fresh batch of purified air. In this way the cold air in the spiral gets progressively cooled when released.

This procedure continues and the cooling becomes gradually more and more intense. Ultimately, the cooling becomes so great that the temperature drops to nearly -200^{o}C. At this temperature the air condenses to form liquid air (Nitrogen becomes liquid at -196^{o}C).

Liquid air is then led into a chamber, and allowed to warm up, by absorbing heat from the atmosphere. The boiling point of nitrogen is -196^{o}C; when this temperature is reached, nitrogen starts boiling and the vapours (gas) is collected and packed. The liquid left behind is mainly oxygen, which has a higher boiling point of 183^{o}C.



Preparарion from Ammonia and Ammonium Compounds

(i) By treating excess ammonia with chlorine, ammonium chloride and nitrogen are formed.

$$\underset{\text{Ammonia}}{8NH_3(g)} + \underset{\text{Chlorine}}{3Cl_2(g)} \longrightarrow \underset{\text{Ammonium chloride}}{6NH_4Cl(s)} + \underset{\text{Nitrogen}}{N_2(g)}$$

The products obtained are bubbled through water. The vapours of ammonium chloride dissolve in the water while nitrogen is collected separately.

(ii) By passing ammonia over heated metallic oxides like copper oxide and lead oxide.(Fig.12.3).

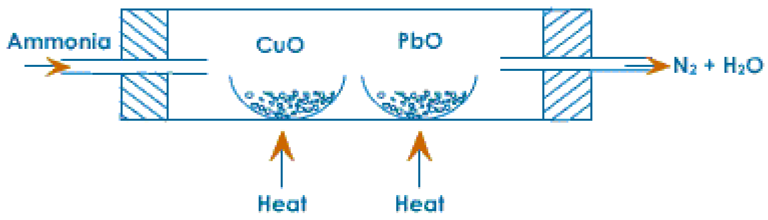


Fig. 12.3 Preparation of nitrogen from ammonia

$$\underset{\text{Copper(II) oxide}}{3CuO(s)} + \underset{\text{Ammonia}}{2NH_3(g)} \longrightarrow \underset{\text{Copper}}{3Cu(s)} + \underset{\text{Water}}{3H_2O(vap)} + \underset{\text{Nitrogen}}{N_2(g)}$$

$$\underset{\text{Lead oxide}}{3PbO(s)} + \underset{\text{Ammonia}}{2NH_3(g)} \longrightarrow \underset{\text{Lead}}{3Pb(s)} + \underset{\text{Water}}{3H_2O(vap)} + \underset{\text{Nitrogen}}{N_2(g)}$$

(iii) By burning ammonia in oxygen

Ammonia burns in oxygen to yield water vapour and nitrogen (Fig.12.4).

$$\underset{\text{Ammonia}}{4NH_3(g)} + \underset{\text{Oxygen}}{3O_2} \longrightarrow \underset{\text{Water vapour}}{6H_2O(l)} + \underset{\text{Nitrogen}}{2N_2(g)}$$

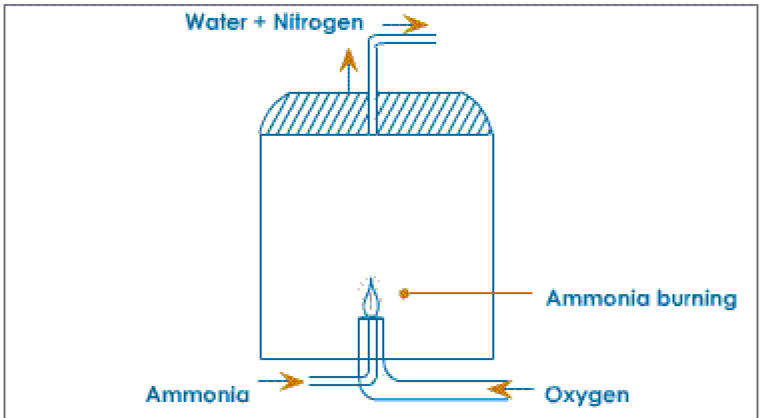


Fig. 12.4 Preparation of nitrogen by burning ammonia in oxygen

(iv) By heating a mixture of liquor ammonia with bleaching powder:

When bleaching powder is treated with liquor ammonia, calcium chloride, water vapour and nitrogen are formed.

$$\underset{\text{Bleaching powder}}{3Ca(OCl)Cl(s)} + \underset{\text{Ammonia}}{2NH_3(l)} \longrightarrow \underset{\text{Calcium chloride}}{3CaCl_2(aq)} + \underset{\text{Water}}{3H_2O(l)} + \underset{\text{Nitrogen}}{N_2(g)}$$

(v) By the action of heat on ammonium compounds: (ammonium dichromate)

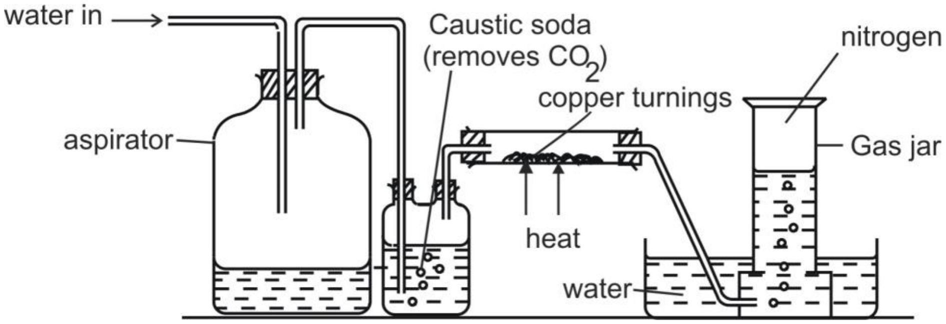
Ammonium dichromate is an orange coloured crystalline substance. When heated it starts decomposing, with the evolution of heat. Sparks can be seen inside the test tube and therefore further heating is not necessary. The products of decomposition are, a green coloured solid of chromic oxide, water vapour and nitrogen gas (Fig.12.5).

$$\underset{\text{Ammonium dichromate orange}}{(NH_4)_2Cr_2O_7(s)} \longrightarrow \underset{\text{Chromic oxide green}}{Cr_2O_3(s)} + \underset{\text{Water}}{4H_2O(vap)} + \underset{\text{Nitrogen}}{N_2(g)}$$

However, collecting nitrogen by this method is difficult. As the reaction is accompanied by heat and light, it is quite violent. Also the green coloured fluffy chromic oxide gets sprayed all over and thrown out of the test tube. It is therefore difficult to control this reaction.

Laboratory Preparation of Nitrogen

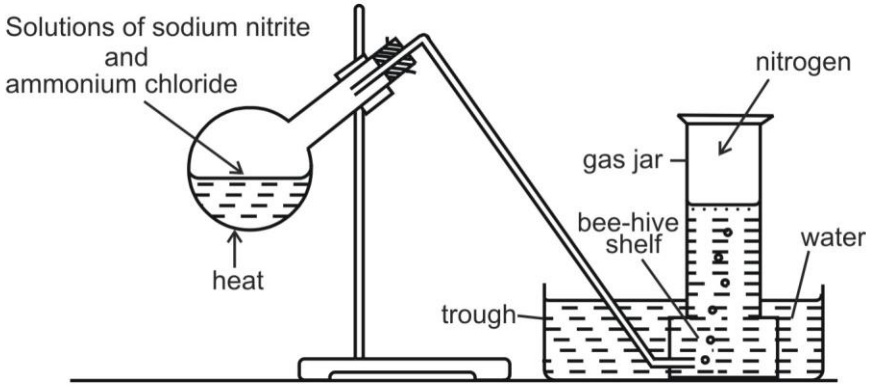
Method A


Preparation of nitrogen from air

Nitrogen can be prepared from the air as shown. Air flows into the respirator and onto caustic soda which dissolves carbon dioxide gas. It is then passed through a heated combustion tube containing heated copper turnings which remove oxygen. Nitrogen is then collected over water. Traces of noble gases present in air still remain in the final product.

Method B

Nitrogen can also be obtained by heating a mixture of sodium nitrite and ammonium chloride as shown. The gas collected by this method is purer than one in method A, even though it contains water vapour which could have been removed if the gas is passed through concentrated sulphuric acid before collection.



In the laboratory, nitrogen is prepared by heating a mixture of ammonium chloride and sodium nitrite and a small quantity of water. If ammonium nitrite is heated by itself it decomposes to produce nitrogen gas. However, this reaction is very fast and may prove to be explosive.

$$\underset{\text{Ammonium nitrite}}{NH_4NO_2(s)} \longrightarrow \underset{\text{Water}}{2H_2O(vap)} + \underset{\text{Nitrogen}}{N_2(g)}$$

For safety, a mixture of ammonium chloride and sodium nitrite approximately in the ratio of 4:5 by mass, is heated mildly with a small quantity of water. The presence of water prevents ammonium chloride form subliming when heated. Initially, the two substances undergo double decomposition to form sodium chloride and ammonium nitrite.

$$\underset{\text{Ammonium chloride}}{NH_4Cl(aq)} + \underset{\text{Sodium nitrate}}{NaNO_2(aq)} \longrightarrow \underset{\text{Sodium chloride}}{NaCl(aq)} + \underset{\text{Ammonium nitrite}}{NH_4NO_2(aq)}$$

The ammonium nitrite so formed then decomposes to form nitrogen gas and water vapor.

$$NH_4NO_2(aq) \longrightarrow 2H_2O(vap) + N_2(g)$$

Nitrogen gas is collected by downward displacement of water.

Uses of Nitrogen

(i) Nitrogen is used in high temperature thermometers where mercury cannot be used. This is because mercury boils at 356.7^{o}C and hence cannot be used in such thermometers. A volume of nitrogen is enclosed in a vessel and introduced into the region of high temperature. Depending upon the temperature, expansion of the nitrogen volume takes place. Then applying the gas equation, the temperature is calculated.

(ii) Nitrogen mixed with argon is used in electric bulbs to provide an inert atmosphere. It helps in prevention of oxidation and evaporation of the filament of the bulb, giving it a longer life.

(iii) It is used to produce a blanketing atmosphere during processing of food stuff, to avoid oxidation of the food. It is also used when food is being canned, so that microorganisms do not grow.

(iv) It is used in metal working operations to control furnace atmosphere and in metallurgy to prevent oxidation of red-hot metals.

(v) Nitrogen in the air helps as a diluting agent and makes combustion and respiration less rapid.

(vi) It is used by the chemical, petroleum, and paint industries to provide inactive atmosphere to prevent fires or explosions.

(vii) It is used in the industrial preparation of ammonia, which is converted into ammonium salts, nitric acid, urea, calcium cyanamide fertilizers etc.

(viii) Liquid nitrogen is used as a refrigerant for food, for storage of blood, cornea etc. in hospitals. Meat, fish etc., can be frozen in seconds by a blast of liquid nitrogen, which can provide temperatures below -196^{o}C.

(ix) Liquid nitrogen is used in scientific research especially in the field of superconductors.

(x) Nitrogen is essential for synthesis of proteins in plants. Proteins are essential for synthesis of protoplasm, without which life would not exist

(xi) Liquid nitrogen is used in oil fields, to extinguish oil fires.

Summary

Physical Properties

Colour	Colourless
Odour	Odourless
Density compared	Same as air

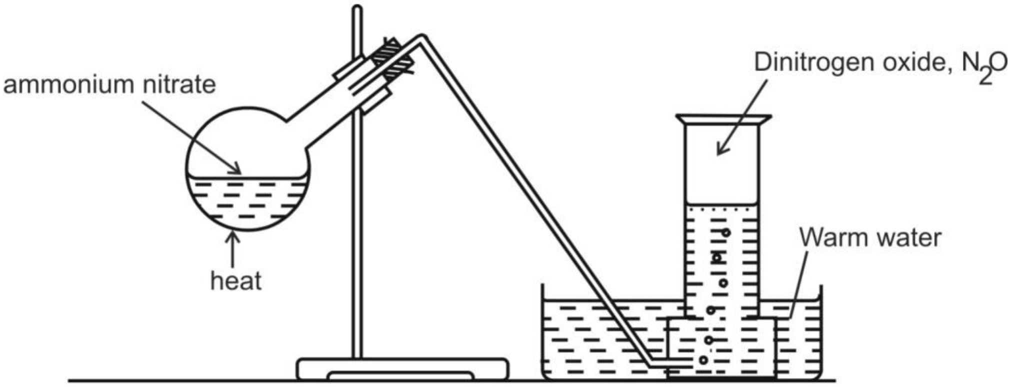
to air (heavier or lighter)	

Chemical Properties

Solubility in water	Slightly soluble
Burning	Does not support combustion
Moist pH paper	No reaction
Red rose petals	No reaction
Specific test	None

Nitrous oxide:

Nitrous oxide (dinitrogen oxide), N_2O, is prepared by gentle heating of ammonium nitrate:



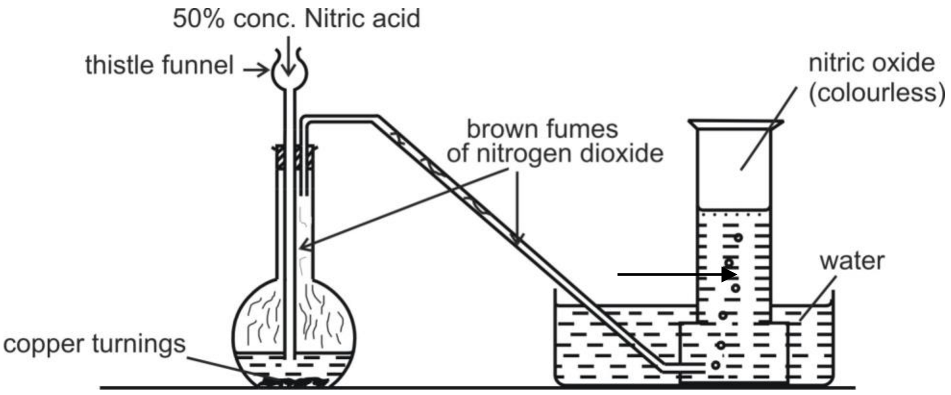
$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

Nitrous oxide is a linear molecule.

It has a boiling point of -88 °C, and a melting point of -102 °C. It is colourless and has a faintly sweet smell. It is used as an anaesthetic, popularly called **laughing gas**.

Nitric oxide:

Nitric oxide, NO, may be prepared by the action of dilute nitric acid on copper:



$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

It is a colourless gas, insoluble in water, which reacts with oxygen to form the brown gas nitrogen dioxide, NO_2:

$2NO + O_2 \longrightarrow 2NO_2$

Nitrogen dioxide:

Nitrogen dioxide, NO_2 is a planar molecule.

It is a deep red-brown gas, which may be prepared by the action of concentrated nitric acid on copper:

$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$

or by the decomposition of heavy-metal nitrates, such as lead nitrate:

$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$

At temperatures below 100 °C, it forms dinitrogen tetroxide, N_2O_4:

$2NO_2 \longrightarrow N_2O_4$ (REVERSIBLE ARROW)

Nitrogen dioxide will support combustion, as shown by the fact that a glowing splint of wood will ignite in this gas.

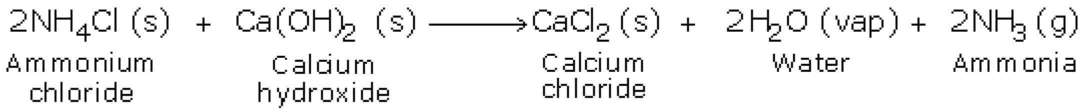
AMMONIA

Ammonia is a colorless gas. It has a characteristic pungent odor. It is bitter to taste. Its vapor density is 8.5. Hence it is lighter than air (vapor density of air = 14.4). When cooled under pressure ammonia condenses to a colorless liquid, which boils at -33.4°C. When further cooled, it freezes to a white crystalline snow-like solid, which melts at -77.7°C. Ammonia is one of the most soluble gases in water. At 0°C and 760 mm of Hg pressure one volume of water can dissolve nearly 1200 volumes of ammonia. This high solubility of ammonia can be demonstrated by the fountain experiment.

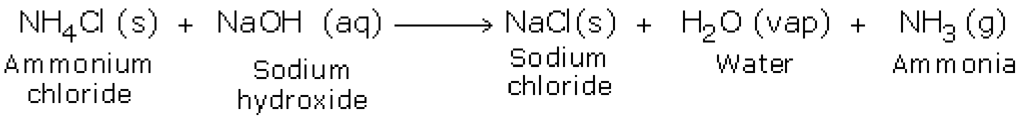
Preparation of Ammonia

By Heating any Ammonium Salt with an Alkali

$$\text{Ammonium salt} + \text{Alkali} \longrightarrow \text{Salt} + \text{Water} + \text{Ammonia}$$

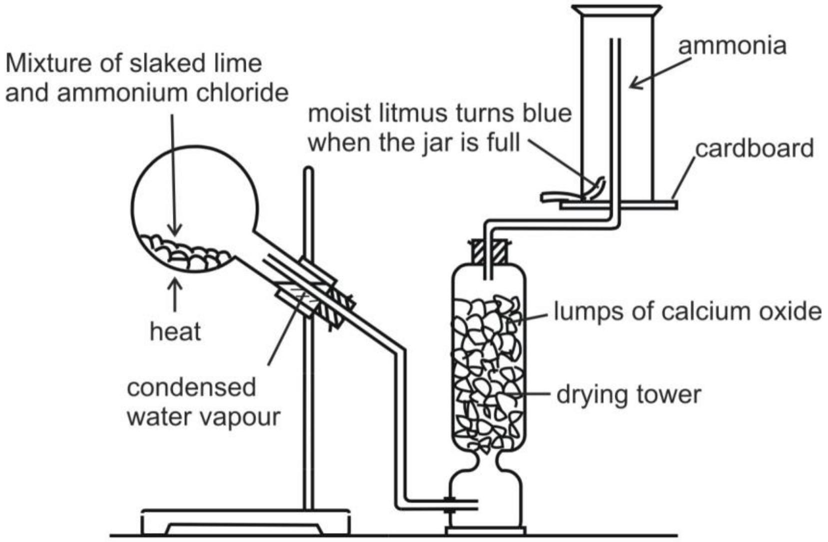


$$\underset{\text{Ammonium chloride}}{2NH_4Cl\ (s)} + \underset{\text{Calcium hydroxide}}{Ca(OH)_2\ (s)} \longrightarrow \underset{\text{Calcium chloride}}{CaCl_2\ (s)} + \underset{\text{Water}}{2H_2O\ (vap)} + \underset{\text{Ammonia}}{2NH_3\ (g)}$$



$$\underset{\text{Ammonium chloride}}{NH_4Cl\ (s)} + \underset{\text{Sodium hydroxide}}{NaOH\ \ (aq)} \longrightarrow \underset{\text{Sodium chloride}}{NaCl(s)} + \underset{\text{Water}}{H_2O\ (vap)} + \underset{\text{Ammonia}}{NH_3\ (g)}$$

In the laboratory, ammonia is usually prepared by heating a mixture of ammonium chloride and slaked lime in the ratio of 2 : 3 by mass. The arrangement of the apparatus is shown in the figure 6.2. As ammonia is lighter than air, it is collected by the downward displacement of air.



Drying of Ammonia

The drying agent used for ammonia is quick lime. Other drying agents such as concentrated sulphuric acid or phosphorus (V) oxide or fused calcium chloride cannot dry an alkaline gas like ammonia. Sulphuric acid and phosphorus (V) oxide are both acidic. They react with ammonia, forming their respective ammonium salt.

Industrial Preparation of Ammonia

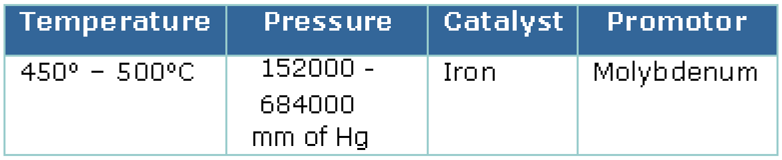
Haber's Process

Ammonia is manufactured by Haber's process using nitrogen and hydrogen (Fig.6.4).

Reactants: Nitrogen gas -1 volume and hydrogen gas -3 volumes

$$\text{Reaction : } N_2(g) + 3H_2(g) \underset{\substack{152000\text{ - }684000 \\ \text{mm of Hg}}}{\overset{450^{0}C\text{ -}500^{0}C}{\rightleftharpoons}} 2NH_3(g) + \text{Heat}$$

Conditions



Temperature	Pressure	Catalyst	Promotor
450° – 500°C	152000 - 684000 mm of Hg	Iron	Molybdenum

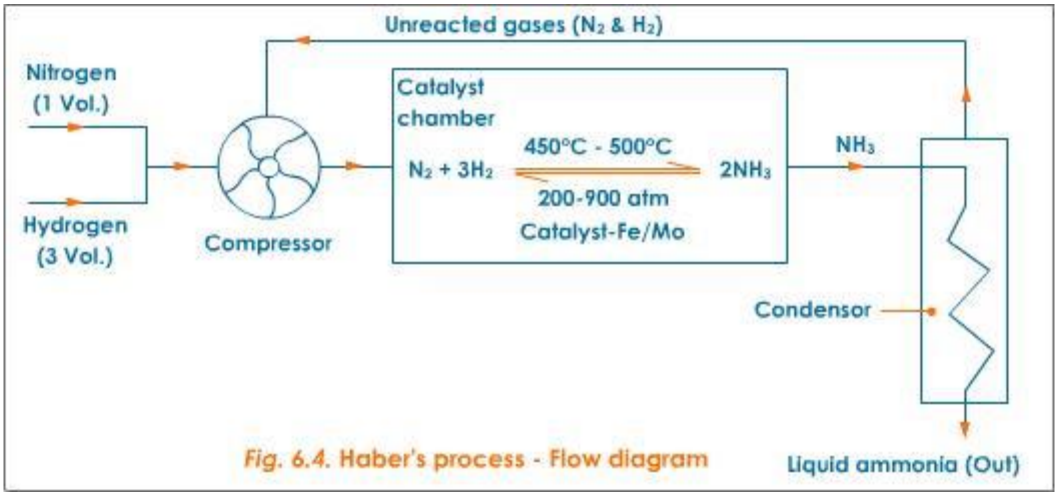
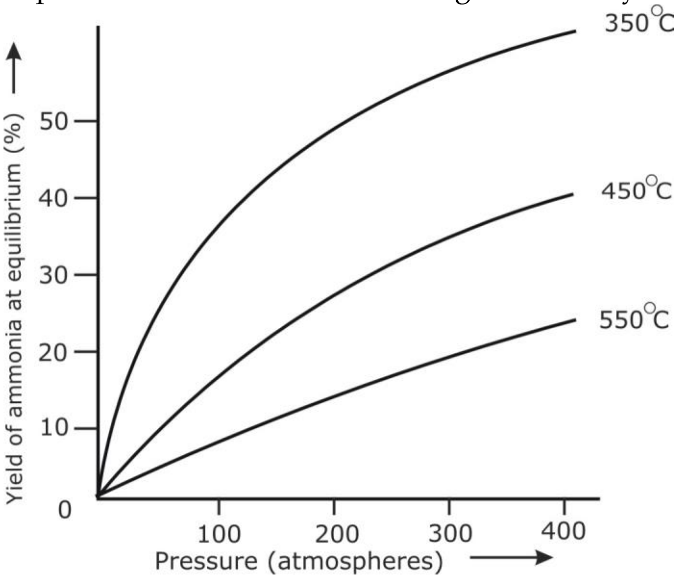
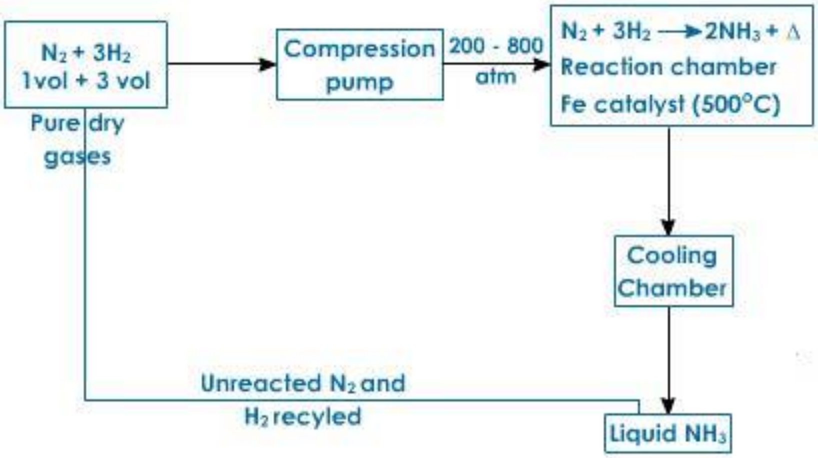


Fig. 6.4. Haber's process - Flow diagram

The reaction in Haber's process is exothermic and so external heating is not required once the reaction starts. Lowering the temperature to 450° - 500°C favours the reaction, but lowering the temperature below 450° - 500°C brings down the yield.





Nitrogen is obtained in large scale from air. Air free from dust and carbon dioxide is cooled under high pressure and low temperature to about 200°C and then allowed to warm. As nitrogen has lower boiling point (-169°C) as compared to oxygen (-183°C) it turns to gas leaving oxygen in liquid state.

Nitrogen can also be obtained by heating a ammonium nitrite (in small amounts)

$$\underset{\text{Ammonium nitrite}}{NH_4NO_2} \longrightarrow \underset{\text{Nitrogen}}{N_2} + \underset{\text{Water}}{2H_2O}$$

Chemical Properties of Ammonia

Combustibility

Ammonia is neither combustible in air nor does it support combustion. However it burns in oxygen with a greenish-yellowish flame producing water and nitrogen.

a) Burning of Ammonia in Oxygen

Activity

Set the apparatus as shown in figure 6.7.

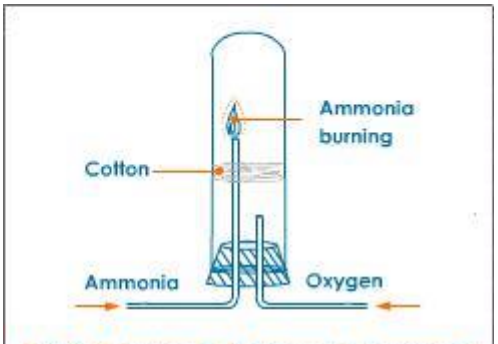


Fig. 6.7. Burning of ammonia in oxygen

Firstly, when ammonia is passed through the longer tube and is made to ignite, it does not catch fire. Then oxygen is sent through the shorter tube. Now when ammonia is ignited, it catches fire and the following reaction takes place:

$$\underset{\text{Ammonia}}{4NH_3(s)} + \underset{\text{Oxygen}}{3O_2(g)} \longrightarrow \underset{\text{Water}}{6H_2O(g)} + \underset{\text{Nitrogen}}{2N_2(g)}$$

Although the products formed in the above reaction are insignificant, it is an extremely important reaction from viewpoint of industry. This is because in the presence of platinum, catalytic oxidation of ammonia can take place to give various important products.

b) Catalytic Oxidation of Ammonia

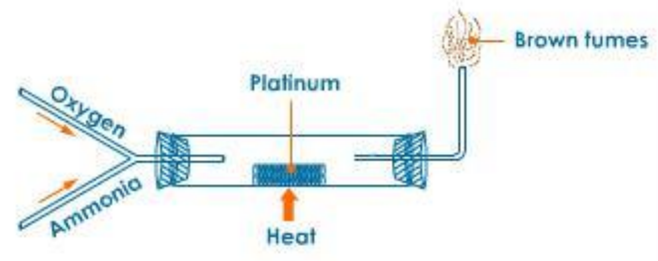


Fig. 6.8. Catalytic oxidation of ammonia

The platinum coil is heated at 800°C in a combustion tube till it becomes white hot. Then ammonia and oxygen are passed through the tube. Under these conditions and in the presence of the catalyst, ammonia combines with free oxygen or oxygen of the air, to form nitric oxide and water vapour.

$$4NH_3(g) + 5O_2\ (s) \longrightarrow \underset{\text{Nitric oxide}}{4NO(g)} \uparrow + 6H_2O(vap)$$

As colourless nitric oxide comes out into the air, it cools down and combines with the oxygen of the air to form reddish brown fumes of nitrogen dioxide.

$$2NO(g) + O_2\ (g) \longrightarrow \underset{\substack{\text{Nitrogen dioxide} \\ \text{(reddish brown)}}}{2NO_2\ (g)}$$

The formed nitrogen dioxide is converted into nitric acid in the presence of water and oxygen.

$$\underset{\text{Water}}{2H_2O\ (l)} + \underset{\text{Nirogen dioxide}}{4NO_2(g)} + \underset{\text{Oxygen}}{O_2\ (g)} \longrightarrow \underset{\text{Nitric acid}}{4HNO_3\ (aq)}$$

The importance of the above reactions lies in the production of nitric acid, which is a very important industrial product.

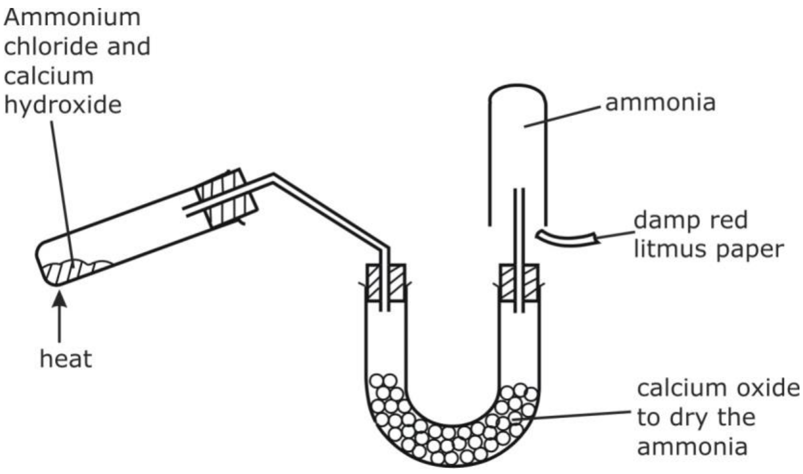
<u>Basic Nature</u>

Absolutely dry ammonia or pure liquefied ammonia is neutral. In the presence of water however, it forms ammonium hydroxide, which yields hydroxyl ions. As a result of this reaction, it exhibits basic nature. It is a weak base and is perhaps the only gas that is alkaline in nature.

$$\underset{\text{Ammonia}}{NH_3\ (g)} + \underset{\text{Water}}{H_2O\ (l)} \longrightarrow \underset{\substack{\text{Ammonium} \\ \text{hydroxide}}}{NH_4OH(aq)}$$

$$\underset{\substack{\text{Ammonium} \\ \text{hydroxide}}}{NH_4OH(aq)} \rightleftharpoons \underset{\text{Ammonium ion}}{NH_4^+\ (aq)} + \underset{\text{Hydroxyl ion}}{OH^-\ (aq)}$$

Ammonia is an alkaline gas. When damp red litmus paper is introduced into the gas, it turns blue due to the presence of hydroxide ions as shown in the equation above.



Colour changes with other indicators

Indicator	Initial Colour	Final colour
Litmus	Red	Blue
Methyl orange	Orange	Yellow
Phenolphthalein	Colourless	Deep pink

Test for ammonia gas

TEST METHOD	OBSERVATIONS	TEST CHEMISTRY
Strong pungent odour tested with damp red litmus	Litmus turns blue	Only common alkaline gas
conc. hydrochloric acid	White clouds with HCl fumes.	forms fine ammonium chloride crystals with HCl

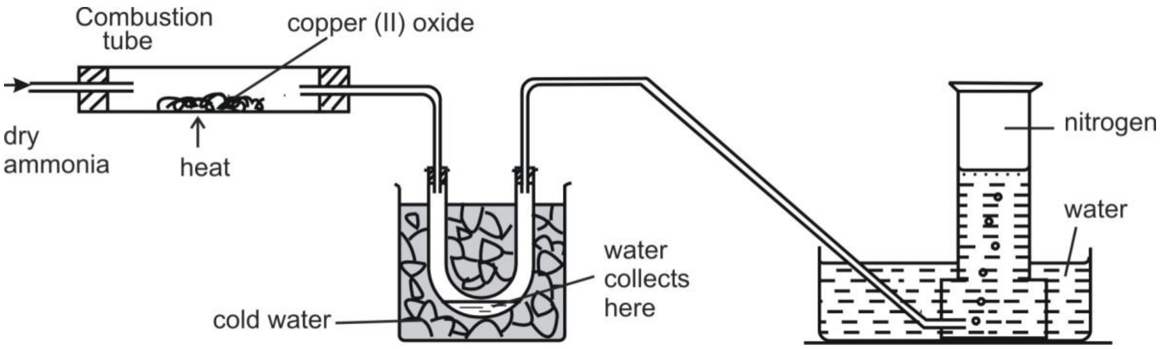
REACTIONS OF AQUEOUS AMMONIA (NH_4OH) with cations

TEST FOR	With aqueous sodium hydroxide	Test with aqueous ammonia	TEST CHEMISTRY
Magnesium(Mg2+)	White ppt. insoluble in excess	White ppt. insoluble in excess	$Mg^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Mg(OH)_{2(s)}$ white ppt. The pp t. is not soluble in excess of NH_3 or NaOH. You could

			distinguish Mg^{2+} from Ca^{2+} with a flame test
Calcium (Ca^{2+})	White ppt. insoluble in excess	No ppt. or very slight white ppt insoluble in excess	$Ca^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Ca(OH)_{2(s)}$ white ppt. The ppt. is not soluble in excess of NH_3 or NaOH.
Aluminium(Al^{3+})	White ppt. soluble in excess giving a colourless solution	White ppt. insoluble in excess	Aluminium ion:$Al^{3+} + 3OH^{-} \longrightarrow Al(OH)_3(s)$ in excess NaOH forms soluble ($Al(OH)_4^{-}$)
Zinc (Zn^{2+})	White ppt. soluble in excess giving a colourless solution	White ppt. soluble in excess giving a colourless solution	Zinc ion: $Zn^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Zn(OH)_{2(s)}$ white ppt. The ppt. dissolves in both excess sodium hydroxide and ammonia to give a clear colourless solution.
Lead (Pb^{2+})	White ppt. soluble in excess giving a colourless solution	White ppt. insoluble in excess	
Iron(II) (Fe^{2+})	Green ppt. insoluble in excess	Green ppt. insoluble in excess	iron(II) ion: $Fe^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Fe(OH)_{2(s)}$ dark green ppt. The ppt. is not soluble in excess of NH_3 or NaOH.
Iron (III) (Fe^{3+})	Red-brown ppt insoluble in excess	Red-brown ppt insoluble in excess	iron(III) ion: $Fe^{3+}_{(aq)} + 3OH^{-}_{(aq)} \longrightarrow Fe(OH)_{3(s)}$ brown ppt.* The ppt. is not soluble in excess of NH_3 or NaOH.
Copper (Cu^{2+})	Light blue ppt. insoluble in excess	Light blue ppt. soluble in excess giving a deep-blue solution	

Ammonia as a reducing agent

Heated dry ammonia gas can reduce copper (II) oxide to pure copper. This reaction can be used to prepare nitrogen.

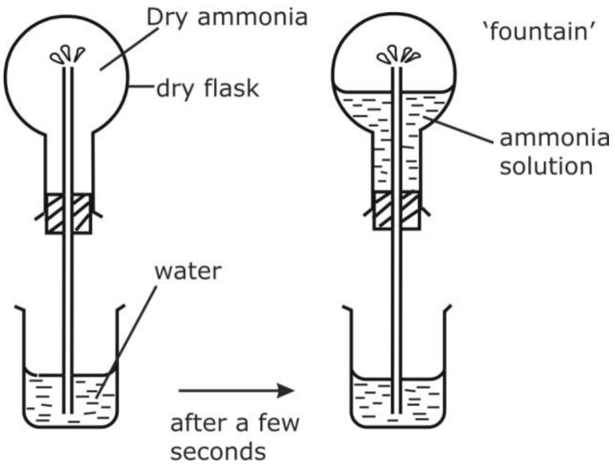


$NH_3\ (g) + CuO(s) \longrightarrow N_2\ (g) + H_2O\ (g)$

The gas passes through a U- tube surrounded by cold water which contains some melting ice. This helps to condense the vapour produced to liquid water. Nitrogen is finally collected by downward displacement of water.

Fountain experiment

Fill a clean dry round-bottomed flask with dry ammonia, close it by a one holed stopper, through which a long jet tube is introduced. The free end of the tube is dipped into a trough of water as shown.



Add two or three drops of an acid and a small quantity of phenolphthalein to the water in the trough. This water is colorless. Pour a small quantity of spirit or ether on a layer of cotton and place it over the inverted flask.

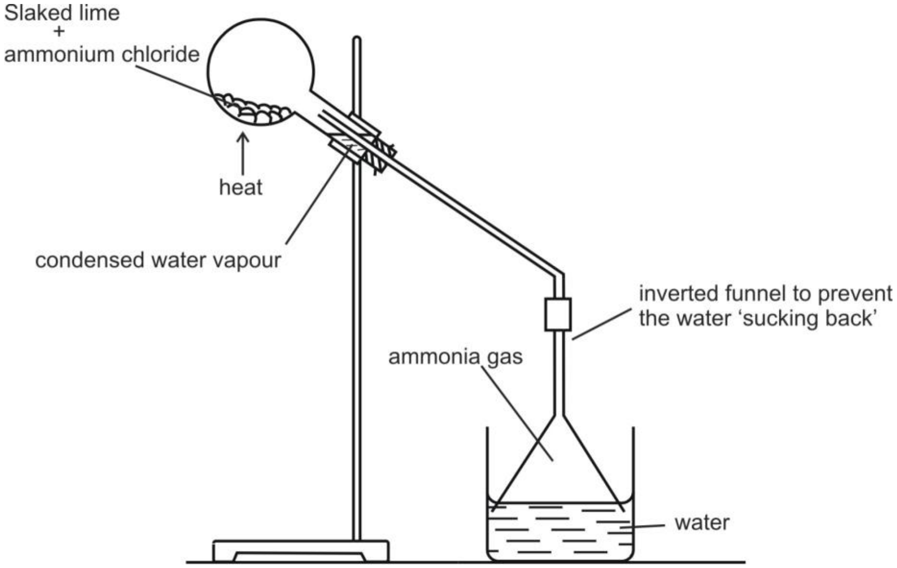
Due to the cooling effect produced by the process of evaporation of spirit or ether, the ammonia gas contracts a little and as a result, small quantity of the water gets sucked up. As soon as this water enters the flask, the ammonia dissolves in it, forming a partial vacuum. As a result of it, water rushes in and comes out of the tube as a jet of fountain. The color of the water turns deep pink.

The properties of ammonia

- Colourless gas
- Distinctive pungent smell
- Less dense than air
- Very soluble in water to give an alkaline solution

Dissolving Ammonia in Water

Due to its high solubility, ammonia cannot be passed through water like many other gases. Ammonia is dissolved in water, as shown below.



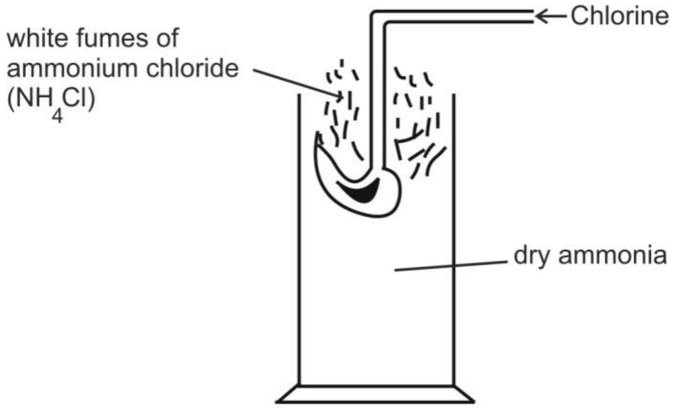
This arrangement is called funnel arrangement and its principle is the same as that discussed for HCl gas. The funnel arrangement prevents back suction of water, which can cause damage to the apparatus used. It provides larger surface area for dissolution of ammonia. A very strong solution of ammonia in water is called liquor ammonia. Ammonia can be obtained from it by boiling.

Action with Acids

Ammonia reacts with the acids to form their respective ammonium salts. The ammonium salts appear as white fumes

Ammonia gas + acid → ammonium salt

$$\underset{\text{Ammonia}}{NH_3\ (g)} + \underset{\text{Hydrochloric acid}}{HCl(aq)} \longrightarrow \underset{\text{Ammonium chloride}}{NH_4Cl\ (aq)}$$



$$\underset{\text{Ammonia}}{2NH_3\ (g)} + \underset{\text{Sulphuric acid}}{H_2SO_4\ (aq)} \longrightarrow \underset{\text{Ammonium sulphate}}{(NH_4)_2SO_4\ (aq)}$$

$$\underset{\text{Ammonia}}{NH_3\ (g)} + \underset{\text{Nitric acid}}{HNO_3\ (aq)} \longrightarrow \underset{\text{Ammonium nitrate}}{NH_4NO_3\ (aq)}$$

Uses of Ammonia

Following are the chief uses of ammonia:

1) Ammonia is used in the industrial preparation of nitric acid by Ostwald's process.

2) Fertilisers, such as ammonium sulphate, ammonium nitrate, ammonium phosphate, urea etc. are manufactured with the help of ammonia.

3) It is used in the manufacture of other ammonium salts, such as ammonium chloride, ammonium carbonate, ammonium nitrite etc.

4) It finds use in the manufacture of nitrogen compounds such as sodium cynamide, plastics, rayon, nylon, dyes etc.

5) It is used in the manufacture of sodium carbonate by Solvay's process. (Ammonia and carbon dioxide are treated with aqueous sodium chloride, crystals of sodium hydrogen carbonate are formed. They are heated to yield sodium carbonate)

6) Ammonia acts as refrigerant in ice plants. Evaporation of a liquid needs heat energy. About 17g of liquid ammonia absorb 5700 calories of heat from the surrounding water. This cools the water and ultimately freezes it to ice.

7) Ammonia is used to transport hydrogen. Hydrogen is dangerous to transport, as it is highly combustible. So it is converted to ammonia, liquefied, transported and then catalytically treated to obtain hydrogen.

8) Many ammonium salts are used in medicines. Inhaling the fumes produced by rubbing ammonium carbonate in the hands can revive people who have fainted.

9) It is used as a cleansing agent. Ammonia solution emulsifies fats, grease etc. so it can be used to clean oils, fats, body grease etc. from clothes. It is also used to clean glassware, porcelain, floors etc.

10) It is used as laboratory reagent.

Nitric acid:

Nitric acid is produced industrially from ammonia by the **Oswald process**. It is a strong acid, converting bases to salts called **nitrates:**

$$CuO + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$$

Copper(11) nitrate

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

Sodium nitrate

Nitric acid is also a strong oxidizing agent and may be reduced to nitric oxide or nitrogen dioxide:

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$$

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

Pure nitric acid slowly decomposes to form water, nitrogen dioxide and oxygen. This causes the nitric acid to become yellow. The process is accelerated on heating:

$$4HNO_3 \longrightarrow 2H_2O + 4NO_2 + O_2$$

OSWALD PROCESS

Nitric acid is prepared in large scale from ammonia and air (Fig.6.14).

Reactants

Pure dry ammonia (1 volume) and air (10 volumes)

Reactions

1) 1st step - Catalytic oxidation of ammonia to form nitric oxide

$$4NH_3 + 5O_2 \xrightarrow[700-800^oC]{Pt} 4NO + 6H_2O + 21.5\ k\,cal$$

2) 2nd step - Oxidation of nitric oxide to nitrogen dioxide.

$$2NO + O_2 \xrightarrow{50^oC} 2NO_2$$

3) 3rd step - Absorption of nitrogen dioxide in water to give nitric acid.

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

Catalyst

Platinum (for oxidation of NH_3)

Temperature

$700^o - 800^oC$

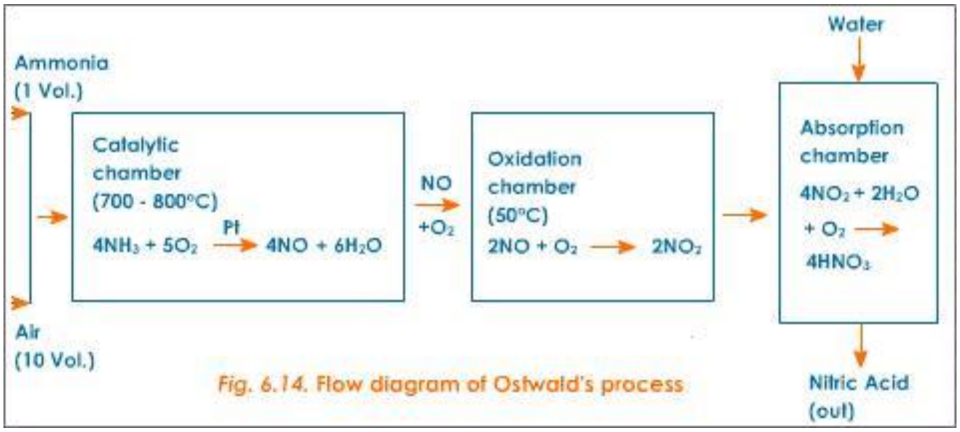


Fig. 6.14. Flow diagram of Ostwald's process

Reactions of Nitric Acid

Cuprous Oxide, Cu_2O reacts with dilute Nitric Acid, HNO_3, in the cold to form a solution of Cupric Nitrate, $Cu\ (NO_3)_2$, and Copper, Cu.

$$Cu_2O + 2\ HNO_3 \longrightarrow Cu\ (NO_3)_2 + Cu + H_2O$$

Cuprous Oxide, Cu_2O reacts with concentrated Nitric Acid, HNO_3, or with dilute Nitric Acid, HNO_3, on heating, when the Cuprous Oxide, Cu_2O dissolves with evolution of Nitric Oxide, NO.

$$3Cu_2O + 14HNO_3 \longrightarrow 6Cu\ (NO_3)_2 + 2NO + 7H_2O$$

Dinitrogen Pent oxide, N_2O_5, is best prepared by dehydrating concentrated Nitric Acid, HNO_3, by Phosphorus Pent oxide, P_2O_5.

$$2\ HNO_3 + P_2O_5 \longrightarrow N_2O_5 + 2\ HPO_3$$

Nitric Oxide, NO is prepared by the action of Copper, Cu, or Mercury, Hg, on dilute Nitric Acid, HNO3, and was called Nitrous Air.

$$3\ Cu + 8\ HNO_3 \longrightarrow 3\ Cu\ (NO_3)_2 + 2\ NO + 4\ H_2O$$

Nitrogen dioxide, NO_2, is a mixed acid anhydride and reacts with water to give a mixture of nitrous and nitric acids.

$$\mathbf{2\,NO_2 + H_2 \longrightarrow HNO_2 + HNO_3}$$

If the solution is heated the nitrous acid decomposes to give nitric acid and nitric oxide.

$$\mathbf{3\,HNO_2 \longrightarrow HNO_3 + 2\,NO + H_2O}$$

Sulphur Dioxide, SO_2, and Nitrogen Oxides, NO_x, are toxic acidic gases, which readily react with the Water, H_2O in the atmosphere to form a mixture of Sulphuric Acid, H_2SO_4, Nitric Acid, HNO_3, and Nitrous Acid, HNO_2, . The dilute solutions of these acids which result give rain water a far greater acidity than normal, and is known as Acid Rain.

Nitrates are the salts of nitric acid, and are strong oxidising agents.

The Oswald Process is the tree stage process by which Nitric Acid, HNO_3, is manufactured. Firstly, Ammonia, NH_3, is oxidised, at high temperature (900 ^{0}C.) over a platinum-rhodium catalyst, to form Nitrogen Monoxide, NO.

$$\mathbf{4\,NH_3\,(g) + 5O_2\,(g) \longrightarrow 4\,NO\,(g) + 6H_2O}$$

The Nitrogen Monoxide, NO, cools and reacts with oxygen, O_2, to produce Nitrogen Dioxide, NO_2.

$$\mathbf{2\,NO\,(g) + O_2 \longrightarrow 2\,NO_2\,(g)}$$

Finally, the Nitrogen Dioxide, NO_2 reacts with Water and Oxygen, O_2, oxygen to produce Nitric Acid, .

$$\mathbf{4\,NO_2\,(g) + 2\,H_2O\,(l) + O_2 \longrightarrow 4\,HNO_3\,(l)}$$

$$\mathbf{Cu_2O + 2\,HNO_3 \longrightarrow Cu\,(NO_3)_2 + Cu + H_2O}$$

Cuprous Oxide, Cu_2O reacts with concentrated Nitric Acid, HNO_3, or with dilute Nitric Acid, HNO_3, on heating, when the Cuprous Oxide, Cu_2O dissolves with evolution of Nitric Oxide, NO.

$$\mathbf{3\,Cu_2O + 14\,HNO_3 \longrightarrow 6\,Cu(NO_3)_2 + 2\,NO + 7\,H_2O}$$

Nitrates:

Salts of metals with nitric acid are called **nitrates**. Most nitrates are soluble in water.

The nitrates of alkali metals form nitrites when strongly heated:

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

The nitrate of other metals decompose on heating to form nitrogen dioxide and the metal oxide, or, in the case of some metals such as silver and gold, the pure metal, nitrogen dioxide, and oxygen:

$$2Pb(NO_3) \longrightarrow 2PbO + 4NO_2 + O_2$$

$$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$$

Summary of Action of Heat on Nitrates

Generally compounds of very reactive metals such as sodium and potassium are more stable to heat than the metals lower down in the reactivity series of metals.

Reactivity Series for Metal	Action of heat on nitrate of the metal.
K **Na**	Decompose to metal nitrite + oxygen
Ca **Mg** **Al** **Fe**	Decompose to metal oxide + oxygen + nitrogen dioxide

cu	
Hg **Ag** **Au**	Decompose to pure metal + Oxygen + nitrogen dioxide

Nitrogen pollution ??

16.0.0 SULPHUR AND ITS COMPOUNDS

SULPHUR

It takes the form of a yellow solid naturally and can be found in this state near volcanoes. Sulphur is also present in a number of metal ores, for example zinc blende (zinc sulphide, ZnS).

Sulphur has chemical symbol S. It has 16 protons and 16 neutrons. An atom of S is represented as $^{32}_{16}S$. Sulphur is a non-metal and exists in the earth's crust either as pure sulphur or as a metal-sulphide.

Since S has 16 protons, it also has 16 electrons; the electronic configuration of S is 2, 8, 6. S is placed in Group VI A of the periodic table, just after phosphorus, and below oxygen. The reaction of S is similar to oxygen.

Sulphur is found as a free element or in combined state in nature. Free sulphur is found in at a large depth below the earth's surface. Metal sulphides such as Zn, Fe, Ag, Ca, Pb, Cu are found in abundant quantities. Mineral ores containing S are:

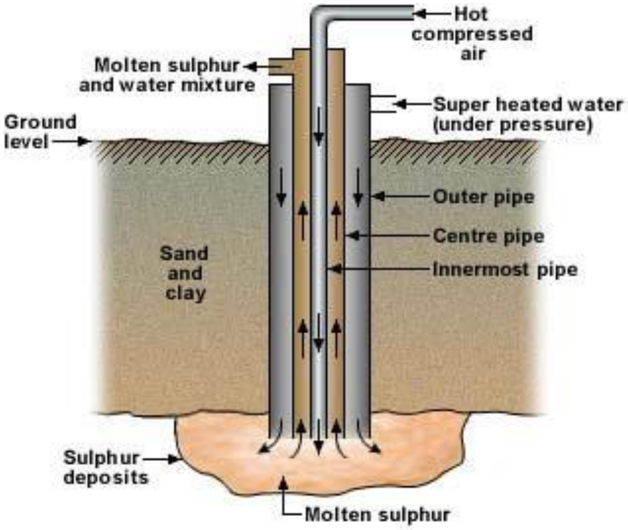
- Copper pyrites : $CuFeS_2$
- Galena : PbS
- Zinc blende : ZnS

- Iron pyrite : FeS_2

Sulphur is found as H_2S gas in petroleum gas, coal gas. H_2S is the familiar pungent smell of onions. It is present in hair, eggs, many proteins and wool.

Extraction of pure sulphur : Frasch process

Since sulphur in free state is found at depths of more than 150 to 300 meters below the earth's surface, the method of extraction of sulphur differs from other metal or non-metal extractions. Sulphur's relatively low melting point (115°C) is utilized in this process. This is known as the Frasch process. Here compressed super heated water (at 170°C) is pressed into a pipe which reaches up to the sulphur deposits. The sulphur here melts. Introducing hot compressed air through another pipe brings it up. The molten sulphur and water mixture is forced up and is collected in a settling tank. The sulphur is cooled and water is evaporated. The sulphur extracted in this way is more than 99% pure.

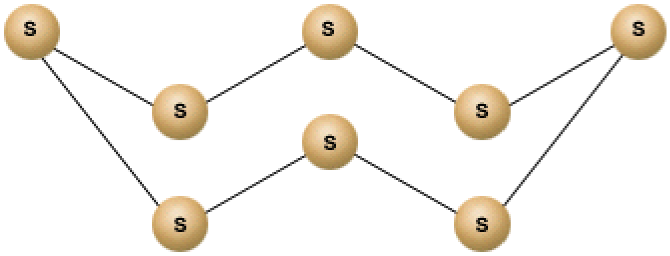


Frasch process for the extraction of sulphur (or mining of sulphur).

The sulphur obtained by Frasch process is a yellow and brittle solid or powder.

Physical properties of sulphur :

Since S has 6 electrons in its outermost shell, it needs 2 more electrons to complete its shell. But S combines with 7 other atoms to make a sulphur molecule that has a total of 8 sulphur atoms. Thus each S atom shares 2 electrons with its neighboring atom. The bonds are covalent in nature. A molecule of sulphur is represented as S_8. It is a ringed molecule. The structure is shown below.

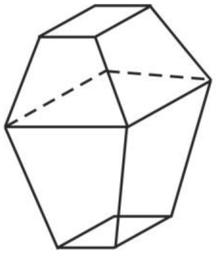


Structure of a sulphur molecule, S_8

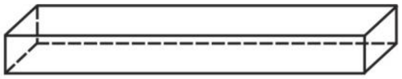
These large molecules each have many electrons , so the Van der Waals forces are quite strong and the melting point is quite high (119°C). There are two ways of packing the sulphur rings, so solid sulphur exists in two crystalline forms, called **rhombic** and **monoclinic**.

Allotropes of sulphur

Rhombic sulphur	**Monoclinic sulphur**
Yellow transparent crystals	Amber coloured needles
Melt pt. 113 °C	Melt pt. 119 °C
Obtained when sulphur crystallises from solution.	Obtained when sulphur solidifies above 95.6 °C.



Rhombic Sulphur Crystal



Monoclinic sulphur Crystal

Sulphur is a yellow crystalline solid. It is tasteless and odourless. The melting point of S is 115°C. Sulphur is an insulator and is a poor conductor of heat and electricity. S is insoluble in water but is soluble in CS_2. Sulphur forms covalent bonds and shows allotropic forms. The allotropes have different crystalline shapes such as rhombic and monoclinic. There is another allotrope which has no shape and is called plastic sulphur. Vapours of sulphur are pungent and although not poisonous, they can cause health problems to humans.

Chemical properties of sulphur :

1. Valence : Since S has 6 electrons in its outer shell. Hence S does not give off its electrons easily. It readily forms covalent bonds to complete its outer shell. It shows variable valence of 2 or 6. S is quite a reactive element and forms oxides, chlorides and sulphides readily.

2. Action of oxygen: Sulphur reacts with oxygen and burns with a blue flame. It forms sulphur dioxide which is a colourless gas having a pungent smell.

$$\underset{\text{Sulphur}}{S} + \underset{\substack{\text{Oxygen}\\ \text{(From air)}}}{O_2} \longrightarrow \underset{\text{Sulphur dioxide}}{SO_2}$$

Sulphur dioxide forms an acidic solution, sulphurous acid, when dissolved in water **i.e.** it turns damp blue litmus paper red.

It will also react with oxidising agents to produce sulphate ions **e.g.** **Orange** acidified dichromate (VI) ions are turned **green** and **purple** acidified manganese (VII) ions are turned colourless.

3. S reacts with other non-metals also. In all cases sulphur has to be heated or boiled for the reaction to take place.

$$\underset{\text{Hydrogen}}{H_2} + \underset{\substack{\text{Sulphur}\\ \text{(Boiling)}}}{S} \longrightarrow \underset{\substack{\text{Hydrogen sulphide}\\ \text{(Foul smell)}}}{H_2S}$$

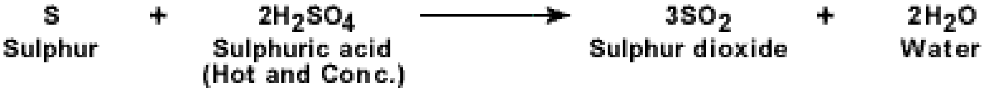
$$\underset{\text{Carbon}}{C} + \underset{\text{Sulphur}}{2S} \xrightarrow{\text{Heat}} \underset{\text{Carbon disulphide}}{CS_2}$$

4. Reaction with metals : Heated S reacts with metals like Fe, Cu, Zn, Sb directly to give metal-sulphide. A mixture of powdered zinc and sulphur, when heated up to a high temperature, will react together to produce an extremely exothermic change. A few reactions are shown below.

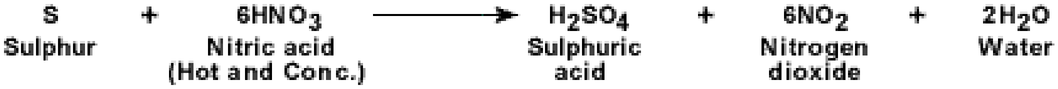
$$\underset{\text{Iron}}{Fe} + \underset{\text{Sulphur}}{S} \xrightarrow{\text{Heat}} \underset{\substack{\text{Iron (II) sulphide}\\ \text{or Ferrous sulphide}}}{FeS}$$

$$\underset{\text{Zinc}}{Zn} + \underset{\text{Sulphur}}{S} \xrightarrow{\text{Heat}} \underset{\text{Zinc sulphide}}{ZnS}$$

5. <u>Reaction with acids</u> : S is oxidized by strong concentrated oxidizing acids such as sulphuric acid and nitric acid.



$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$



$$S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

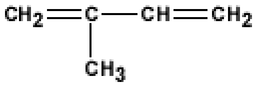
In both the reactions S acts as a reducing agent.

<u>Effect of heat on sulphur</u>:

A sulphur molecule consists of 8 atoms in a ring form. When heated, S melts at 115°C and a pale yellow liquid is formed. The S_8 ringed molecules are connected to other molecules in a long chain. On heating, the long chain breaks up. The individual molecules can slip over each other when melted. On further heating, the liquid becomes dark brown and viscous. When the temperature rises beyond 160°C, the intra-molecular bonds break. Sulphur boils at 444°C. At this temperature the large molecule breaks up into pieces of S_2 molecule. This molecule is pale yellowish-brown in colour. The vapours of S contains S_2 molecules.

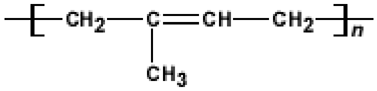
<u>Vulcanization of rubber</u> :

Natural rubber is a soft and sticky solid. Rubber is a long chain polymer made out of isoprene (2 – methyl butadiene) monomer. The long molecule forms a coil like structure.



$CH_2=C(CH_3)-CH=CH_2$

**Isoprene or 2-methyl butadiene
(Monomer of natural rubber)**



$-[-CH_2-C(CH_3)=CH-CH_2-]_n-$

**Natural rubber
(n = 11000 to 20000)**

The unique property of rubber is that it is elastic. When rubber is stretched, the molecular bonds can be extended out. When released, the molecules coil back to their original shape.

Natural rubber looses its rubber-like properties at temperatures above 60°C. Also its wear resistance and tensile strengths are low. The process of vulcanization can improve the quality of rubber. Raw rubber is heated with sulphur during vulcanization. This makes the rubber hard, more elastic and strong. During the process of vulcanization, the sulphur atoms attach themselves to extra loose bonds in the rubber molecule and also cross-link the molecules. The cross-linking locks the molecules in place and prevents slipping. Thus making the vulcanized rubber more strong. Vulcanized rubber is non-sticky and has higher elasticity. It does not loose its properties easily and can be used in a temperature range of – 40°C to 100°C.

Uses of sulphur :

- S is used to make H_2SO_4 acid, which is used in the manufacture of many compounds such as detergents, plastics, explosives, etc.
- S is used for making CS_2 molecule, gun powder, matches etc.
- S is used for manufacture of fire works.
- S is used in the rubber industry for vulcanization of rubber.
- S is used for making germicides, fungicides.
- S is used in many medicines.
- S is used in photographic development (sodium thiosulphate or hypo).
- S is used for making bleaching agents.
- S is used in making artificial hair colours or dyes.

The Properties Of Sulphur:

- Non-metallic yellow solid at room temperature
- Brittle
- Insoluble in water
- Soluble in organic solvents, for example methylbenzene
- Non-conductor of electricity whether solid, molten of dissolved.
- Relatively low melting point and boiling point.

Sulphur Dioxide

Moist sulphur dioxide (or sulphurous acid) is a reducing agent.
This fact is used as a test for the detection of sulphur dioxide

1. There is a colour change from purple (pink in dilute solution) to colourless on the addition of the gas to a solution of potassium manganate (VII) (permanganate)

   $2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$

2. There is a colour change from orange to blue on adding the gas to a solution of potassium dichromate (VI).

   $Cr_2O_7^{2-} + 3SO_2 + 2H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$

Sulphurous acid and Sulphites

Sulphur dioxide dissolves in water forming sulphuric (IV) acid (sulphurous acid).

$$SO_2\ (aq) + H2O\ (l) \longrightarrow H_2SO_3\ (aq)$$

This is a weak dibasic acid and ionises producing hydrogen ions and sulphite SO_3^{2-} ions.

$$H_2SO_3 \longrightarrow 2H^+ + SO_3^{2-}$$

1. Sulphites give sulphur dioxide on heating with dilute acids.

   $Na_2SO_3 + 2HCl \longrightarrow NaCl + SO_2 + H_2O$

2. With barium chloride they give a white precipitate of barium sulphite which is soluble in dilute hydrochloric acid.

   $Ba^{2+} (aq) + SO_3^{2-} (aq) \longrightarrow BaSO_3 (s)$

   (White precipitate)

   $BaSO_3 (s) + 2HCl \longrightarrow BaCl_2 + SO_2 (g) + H_2O$

   This reaction is used as a test for sulphite ions in solution.

SULPHUR DIOXIDE

Sulphur dioxide is a colourless gas, about 2.5 times as heavy as air, with a suffocating smell, faint sweetish odour.

Occurrence

Sulphur dioxide occurs in volcanic gases and thus traces of sulphur dioxide are present in the atmosphere. Other sources of sulphur dioxide are the combustion of the iron pyrites which are contained in coal. Sulphur dioxide also results from various metallurgical and chemical processes.

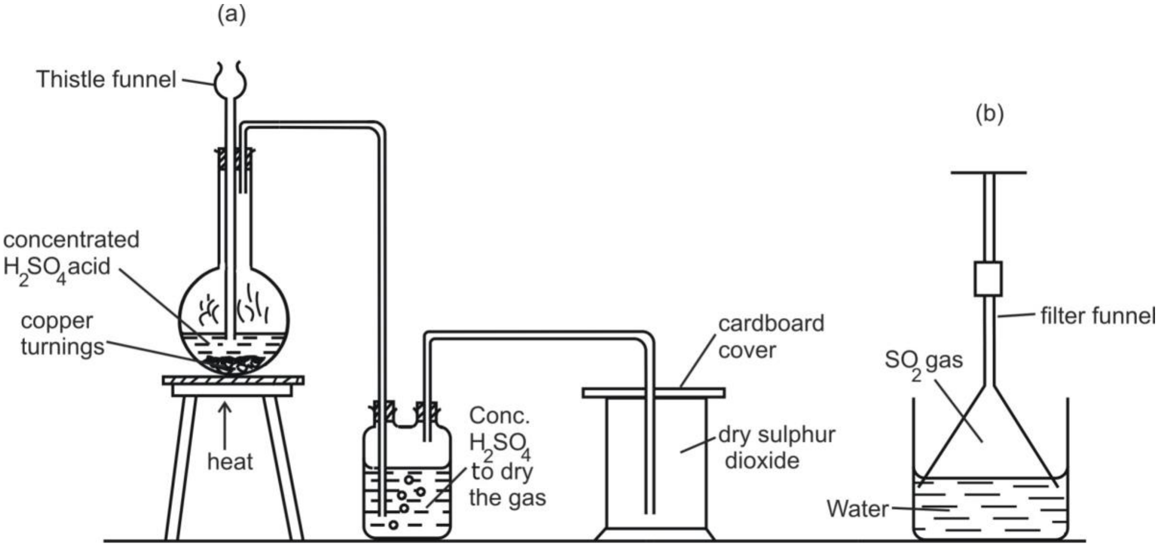
Preparation of Sulphur Dioxide

Sulphur dioxide is prepared by burning sulphur in oxygen or air.

$$S + O_2 \longrightarrow SO_2$$

Sulphur dioxide is usually made in the laboratory by heating concentrated sulphuric acid with copper turnings.

$$Cu + 2\,H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2\,H_2O$$



Sulphur dioxide is released by the action of acids on sulphites or acid sulphites (e.g. by dropping concentrated sulphuric acid into a concentrated solution of sodium hydrogen sulphite).

$$NaHSO_3 + H_2SO_4 \longrightarrow NaHSO_4 + SO_2 + H_2O$$

Properties of Sulphur Dioxide

Sulphur dioxide is a colourless liquid or pungent gas, which is the product of the combustion of sulphur on air. Its melting point is -72.7 ^{0}C, its boiling point is -10^{0}C and its relative density is 1.43.

Sulphur Dioxide is an acidic oxide which reacts with water to give sulphurous acid.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

Sulphur dioxide is a good reducing and oxidising agent.

Summary

Physical Properties

Colour	Colourless
Odour	Pungent odour
Density compared to air (heavier or lighter)	Heavier than air

Chemical Properties

Solubility in water	Soluble. It reacts with water to form a strong acid.
Burning	Does not support combustion
Moist pH paper	Acidic reaction
Red rose petals	Are bleached and lose their colour
Specific test	None

Uses of Sulphur Dioxide

a. Sulphur dioxide is a reducing agent and is used for bleaching and as a fumigant and food preservative.

b. Large quantities of sulphur dioxide are used in the contact process for the manufacture of sulphuric acid.
c. Sulphur dioxide is used in bleaching wool or straw, and as a disinfectant.
d. Liquid sulphur dioxide has been used in purifying petroleum products
e. It is used as a bleaching agent.

THE CONTACT PROCESS

This page describes the Contact Process for the manufacture of sulphuric acid, and then goes on to explain the reasons for the conditions used in the process. It looks at the effect of proportions, temperature, pressure and catalyst on the composition of the equilibrium mixture, the rate of the reaction and the economics of the process.

A brief summary of the Contact Process

The Contact Process:

- Makes sulphur dioxide;
- Converts the sulphur dioxide into sulphur trioxide (the reversible reaction at the heart of the process);
- Converts the sulphur trioxide into concentrated sulphuric acid.

Making the sulphur dioxide

This can either be made by burning sulphur in an excess of air:

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

or by heating sulphide ores like pyrite in an excess of air:

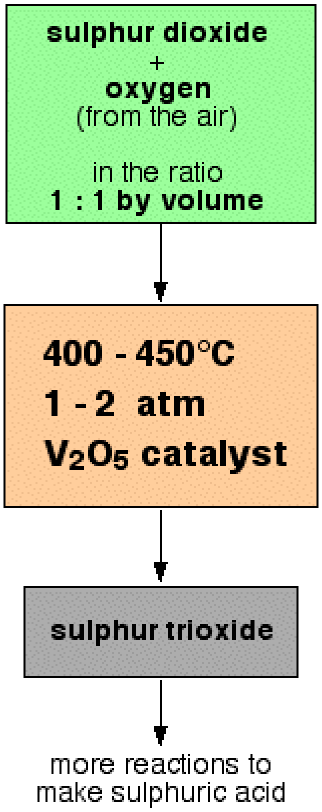
$$4FeS_{2(s)} + 11O_{2(g)} \longrightarrow 4Fe_2O_{3(s)} + 8SO_{2(g)}$$

In either case, an excess of air is used so that the sulphur dioxide produced is already mixed with oxygen for the next stage.

Converting the sulphur dioxide into sulphur trioxide

This is a reversible reaction, and the formation of the sulphur trioxide is exothermic.

A flow scheme for this part of the process looks like this:



Converting the sulphur trioxide into sulphuric acid

This can't be done by simply adding water to the sulphur trioxide - the reaction is so uncontrollable that it creates a fog of sulphuric acid. Instead, the sulphur trioxide is first dissolved in concentrated sulphuric acid:

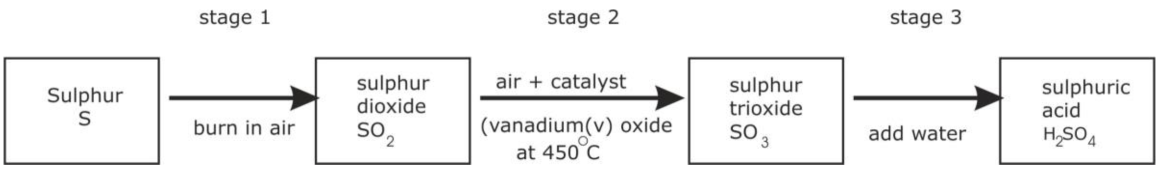
$$H_2SO_{4(l)} + SO_{3(g)} \longrightarrow H_2S_2O_{7(l)}$$

The product is known as **fuming sulphuric acid** or **oleum**.

This can then be reacted safely with water to produce concentrated sulphuric acid - twice as much as you originally used to make the fuming sulphuric acid.

$$H_2S_2O_{7(l)} + H_2O_{(l)} \longrightarrow 2H_2SO_{4(l)}$$

Summary



Explaining the conditions

The proportions of sulphur dioxide and oxygen

The mixture of sulphur dioxide and oxygen going into the reactor is in equal proportions by volume.

Avogadro's Law says that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. That means that the gases are going into the reactor in the ratio of 1 molecule of sulphur dioxide to 1 of oxygen.

That is an excess of oxygen relative to the proportions demanded by the equation.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H = -196\ kJ\ mol^{-1}$$

According to Le Chatelier's Principle, Increasing the concentration of oxygen in the mixture causes the position of equilibrium to shift towards the right. Since the oxygen comes from the air, this is a very cheap way of increasing the conversion of sulphur dioxide into sulphur trioxide.

Why not use an even higher proportion of oxygen? This is easy to see if you take an extreme case. Suppose you have a million molecules of oxygen to every molecule of sulphur dioxide.

The equilibrium is going to be tipped very strongly towards sulphur trioxide - virtually every molecule of sulphur dioxide will be converted into sulphur trioxide. Great! But you aren't going to produce much sulphur trioxide every day. The vast majority of what you are passing over the catalyst is oxygen which has nothing to react with.

By increasing the proportion of oxygen you can increase the percentage of the sulphur dioxide converted, but at the same time decrease the total amount of sulphur trioxide made each day. The 1: 1 mixture turns out to give you the best possible overall yield of sulphur trioxide.

The temperature

Equilibrium considerations

You need to shift the position of the equilibrium as far as possible to the right in order to produce the maximum possible amount of sulphur trioxide in the equilibrium mixture.

The forward reaction (the production of sulphur trioxide) is exothermic.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad \Delta H = -196\ kJ\ mol^{-1}$$

According to Le Chatelier's Principle, this will be favoured if you lower the temperature. The system will respond by moving the position of equilibrium to counteract this - in other words by producing more heat.

In order to get as much sulphur trioxide as possible in the equilibrium mixture, you need as low a temperature as possible. However, 400 - 450°C isn't a low temperature!

Rate considerations

The lower the temperature you use, the slower the reaction becomes. A manufacturer is trying to produce as much sulphur trioxide as possible per day. It makes no sense to try to achieve an equilibrium mixture which contains a very high proportion of sulphur trioxide if it takes several years for the reaction to reach that equilibrium.

You need the gases to reach equilibrium within the very short time that they will be in contact with the catalyst in the reactor.

The compromise

400 - 450°C is a compromise temperature producing a fairly high proportion of sulphur trioxide in the equilibrium mixture, but in a very short time.

The pressure

Equilibrium considerations

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad \Delta H = -196\ kJ\ mol^{-1}$$

Notice that there are 3 molecules on the left-hand side of the equation, but only 2 on the right.

According to Le Chatelier's Principle, if you increase the pressure the system will respond by favouring the reaction which produces fewer molecules. That will cause the pressure to fall again.

In order to get as much sulphur trioxide as possible in the equilibrium mixture, you need as high a pressure as possible. High pressures also increase the rate of the reaction. However, the reaction is done at pressures close to atmospheric pressure!

Economic considerations

Even at these relatively low pressures, there is a 99.5% conversion of sulphur dioxide into sulphur trioxide. The very small improvement that you could achieve by increasing the pressure isn't worth the expense of producing those high pressures.

The catalyst

Equilibrium considerations

The catalyst has no effect whatsoever on the position of the equilibrium. Adding a catalyst doesn't produce any greater percentage of sulphur trioxide in the equilibrium mixture. Its only function is to speed up the reaction.

Rate considerations

In the absence of a catalyst the reaction is so slow that virtually no reaction happens in any sensible time. The catalyst ensures that the reaction is fast enough for a dynamic equilibrium to be set up within the very short time that the gases are actually in the reactor.

Properties of Sulphuric Acid

Chemical Formula	H_2SO_4
Molar mass	98 g mol^{-1}
Melting point	$10^{o}C$
Boiling point	$340^{o}C$
Density	1.83g cm^{-3}

Sulphuric acid is a dense, oily liquid once known as oil of vitriol. Pure sulphuric acid is almost twice as dense as water (1.98 g cm^{-2}). As water is added the density drops. Car batteries contain concentrated sulfuric acid. As the battery is discharged, the concentration of the acid falls. By measuring the density of the acid the driver can check whether the battery is flat or not.

Action as an oxidising agent

It behaves as an oxidising agent only when hot and concentrated:

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + H_2O + SO_2$$

The sulphuric acid is reduced to sulphur dioxide.

Action as a dehydrating agent

Concentrated sulphuric acid has a great affinity for water. (It is important when diluting the concentrated acid to add the acid to water and NEVER water to acid.) The reaction is highly exothermic.

So great is its affinity for water that it can dehydrate compounds containing hydrogen and oxygen:

$C_{12}H_{22}O_{11} + nH_2SO_4 \longrightarrow 12C + (11H_2O + nH_2SO_4)$
sucrose + sulphuric acid → Carbon + (water + sulphuric acid)

$CH_3CH_2OH + nH_2SO_4 \longrightarrow CH_2 = CH_2 + (H_2O + nH_2SO_4)$
ethanol + sulphuric acid → ethene + (water + sulphuric acid)

It is used for drying gases, especially SO_2 and HCl, but cannot be used to dry a reducing gas such as H_2S or an alkaline gas such as NH_3.

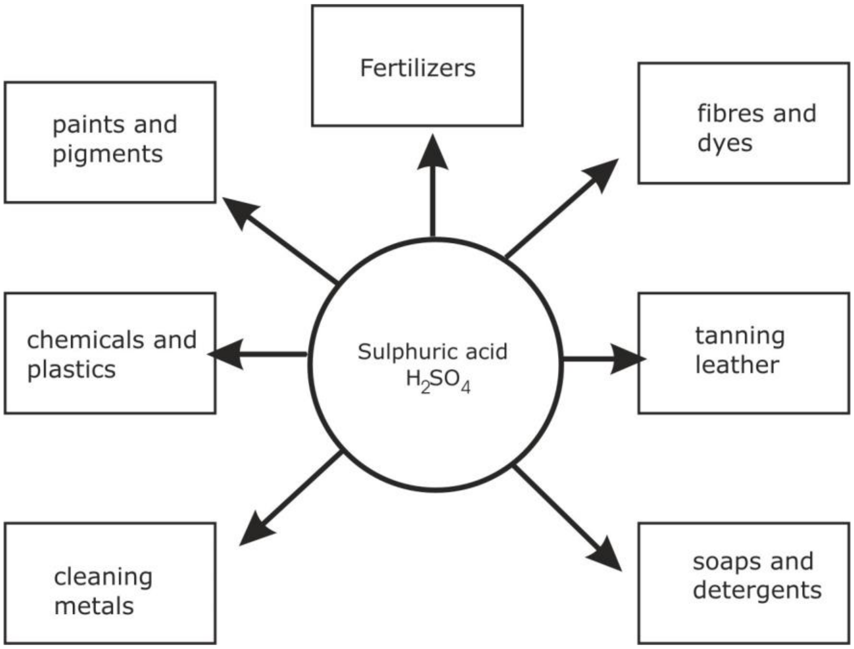
Action as a dehydrating agent

The properties of acids are due to the hydrogen ions in solution. Concentrated sulphuric acid contains molecules, rather than ions. Since it contains very few hydrogen ions it does not react significantly with metals and can safely be stored in steel containers. A piece of magnesium ribbon does not dissolve in concentrated sulphuric acid.

Diluted with water, sulphuric acid behaves as a typical acid:

- it reacts with metals to form sulphates plus hydrogen gas
- it reacts with metal carbonates to form metal sulphates plus carbon dioxide plus water
- It neutralises bases to form sulphates plus water.

Industrial uses



17.0.0 CHLORINE AND ITS COMPOUNDS

CHLORINE

Halogen is elements in group (vii) of the periodic table. Chlorine is a halogen as well as fluorine, bromine, iodine and astatine.
Chlorine has a symbol $^{35.5}$ Cl because it is made up of two isotopes ^{37} Cl and ^{35} Cl. It has an electronic arrangement of 2:8:7, hence justifying its position in group (vii).

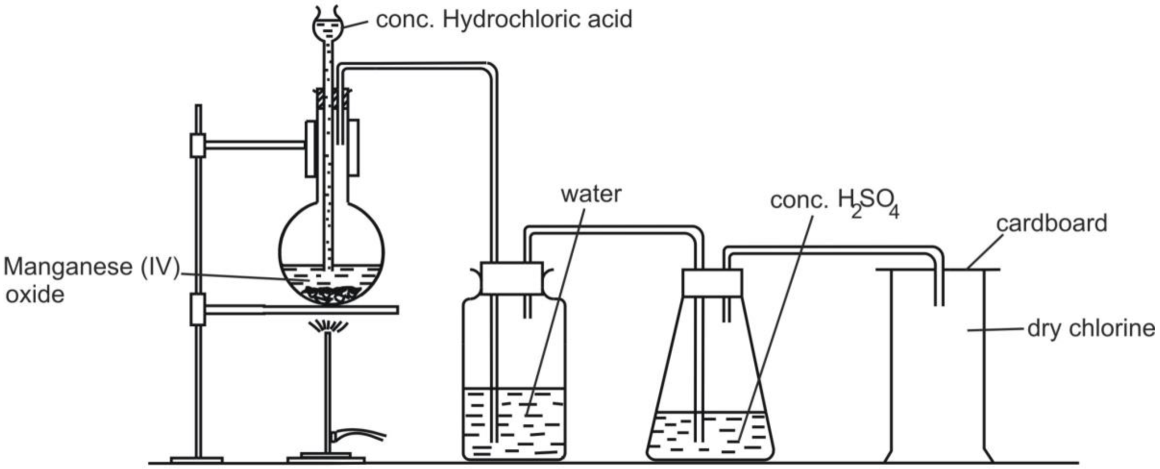
Laboratory preparation

In order to convert hydrogen chloride to chlorine, it is necessary to remove hydrogen. Removal of hydrogen is oxidation. A powerful oxidizing agent such as manganese (IV) oxide converts hydrogen chloride (HCl) to chloride (Cl_2)

The most common laboratory method for preparation of Chlorine is to heat of Manganese Dioxide with concentrated Hydrochloric Acid.

$$\text{Oxidising Agent} + \text{Conc. hydrochloric acid} \longrightarrow \text{Metal chloride} + \text{Water} + \text{Chlorine}$$

$$\underset{\text{Manganese (IV)oxide}}{MnO_2(s)} + \underset{\text{Hydrochloric acid}}{4HCl(l)} \xrightarrow{\Delta} \underset{\text{Manganese (II)chloride}}{MnCl_2(aq)} + \underset{\text{Water}}{2H_2O(l)} + \underset{\text{Chlorine}}{Cl_2(g)}$$



The gas is bubbled through water to remove any traces of hydrochloric gas that may be present and then it is dried by bubbling it through concentrated sulphuric acid. Chlorine may also be prepared by dropping cold concentrated Hydrochloric Acid on crystals of Potassium Permanganate.

$$2\ KMnO_4 + 16\ HCl \longrightarrow 2\ MnCl_2 + 2\ KCl + 8\ H_2O + 5\ Cl_2$$

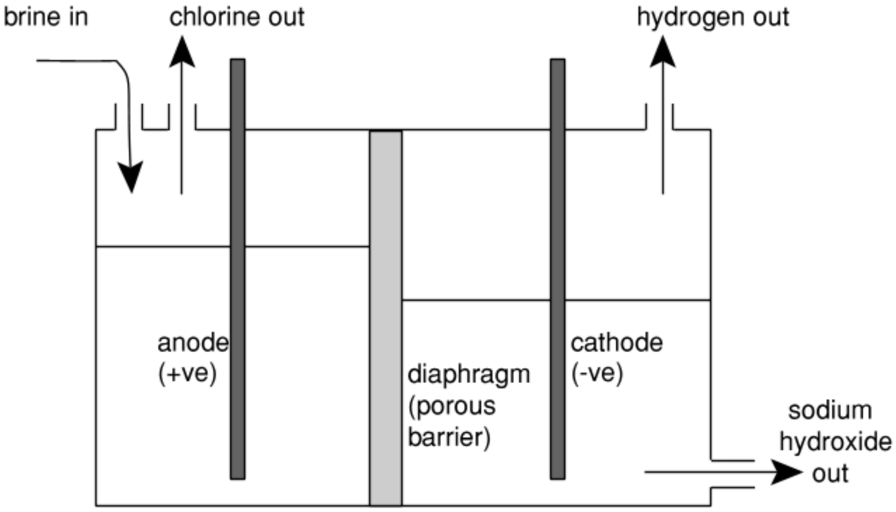
The gas is also bubbled through water to remove any traces of Hydrochloric Acid gas that may be present and then it is dried by bubbling it through concentrated Sulphuric Acid.

<u>Manufacture OF CHLORINE</u>

<u>Membrane cell</u>

Chlorine is manufactured industrially as a by-product in the manufacture of Caustic Soda by the electrolysis of brine.

$2\ NaCl + 2\ H_2O \longrightarrow Cl_2 + H_2 + 2\ NaOH$



The membrane cell has titanium anode and a nickel cathode. Titanium is chosen because it is not attacked by chlorine. The anode and the cathode compartments are separated by an ion exchange membrane. The membrane is selective; it allows Na^+ ions, H^+ and OH^- ions to flow but not Cl^- ions. These ions cannot flow backwards, so products are kept separate and cannot react with each other

At anode, the Cl^- ions are discharged more readily than OH^- ions because they are in higher concentration and are hence preferred.

$2\ Cl^- \longrightarrow Cl_2 + 2e^-$

A pale green gas is seen coming off at the anode

At cathode, it is the H^+ ions that accept electrons, as sodium is more reactive than hydrogen

$2\ H^+ + 2e^- \longrightarrow H_2$

Bubbles of hydrogen are seen at the cathode

The remaining ions of Na^+ and OH^- join up and come off as sodium hydroxide, NaOH.

<u>Products and uses</u>

Product	**Uses**
Chlorine	Poisonous greenish yellow gas Used for making; PVC, solvents for dry cleaning, paints and dye stuffs, bleaches, weed killers, pesticides, killing bacteria in swimming pools and in domestic water treatment.
Hydrogen	Colourless flammable gas

	Used for making: Margarine, nylon, hydrochloric acid
Sodium hydroxide	Alkaline and corrosive substance Used for making; Soap, detergents, textiles, textiles and paper.

Properties of chlorine

Test for Chlorine Gas, $Cl_{2(g)}$.

1) Will turn moist litmus or universal indicator paper red,
and then bleach it white.

(2) Is green-yellow in colour.

(3) Has a pungent choking smell and is poisonous. It is twice as dense as air.

(4) Will put out a lit splint.

Collecting Chlorine.

Chlorine is denser than air and can be collected by downward delivery or using a gas syringe.

Reactions

1.Chlorine is a highly reactive element, and undergoes reaction with a wide variety of other elements and compounds.

2.Chlorine is a good bleaching agent, due to its oxidising properties.

3.Chlorine is soluble in water (which solution is called Chlorine Water) and this loses its yellow colour on standing in sunlight, due to the formation of a mixture of Hypochlorous Acid and Hydrochloric Acid.

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

4.Chlorine gas supports the vigorous combustion of many elements to form their chlorides. For example, Sulphur and Phosphorus burn in the gas.

$$Cl_2 + S \longrightarrow SCl_2$$

$$Cl_2 + P \longrightarrow PCl_3 + PCl_5$$

Bleaching Action

If chlorine is passed through water, it forms two acids, hydrochloric acid.

$$Cl_2\,(g) + H_2O\,(l) \rightleftharpoons HCl\,(aq) + HOCl\,(aq)$$

Hypochlorous acid (the second acid) is the source of oxygen and is responsible for the bleaching of chlorine.

$$\underset{\text{(Coloured)}}{HClO\,(aq) + Dye} \longrightarrow \underset{\text{(Colourless)}}{HCl\,(aq) + \text{oxidized } Dye}$$

It is important to wash bleached clothes thoroughly to remove hydrochloric acid formed after the process.

Reaction of Chlorine with Hydrogen

A mixture of Chlorine and Hydrogen explodes when exposed to sunlight to give Hydrogen Chloride. In the dark, no reaction occurs, so activation of the reaction by light energy is required.

Hydrogen and chlorine gas also combine directly in presence of sunlight. A jar of hydrogen is inverted and placed on a jar containing chlorine in the sun. Soon hydrogen chloride is formed

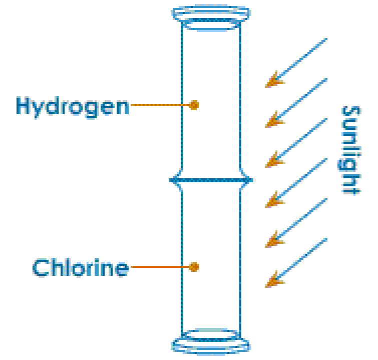


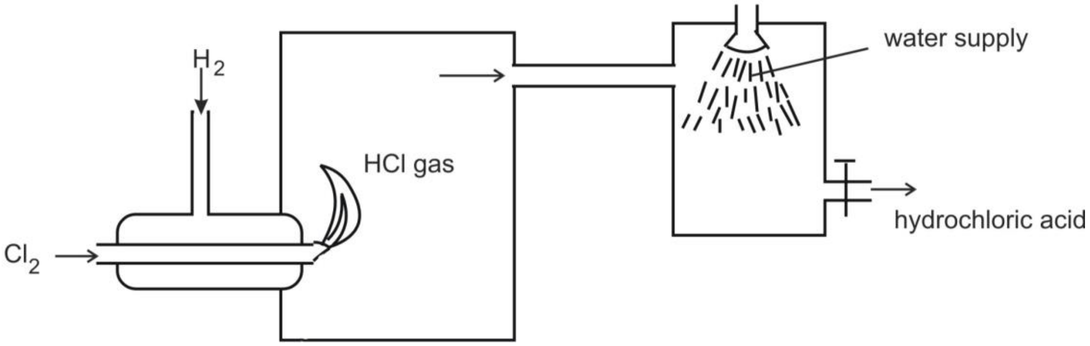
Fig. 14.7 Direct combustion of hydrogen and chlorine in direct sunlight

In diffused sunlight, the reaction slows down, and in the dark it is very slow.

$$Cl_2 + H_2 \longrightarrow 2\,HCl$$

Hydrogen chloride is highly soluble in water. It dissolves to form hydrochloric acid. This reaction can be used to produce hydrochloric when the hydrogen chloride gas produced is dissolved in water as shown.

Burning of Hydrogen in Chlorine



2. Reaction of Chlorine with Non-Metals

Chlorine combines directly with most non-metals (except with Nitrogen, Oxygen and Carbon, C).

3. Reaction of Chlorine with Metals

Thin foils of metals like sodium, copper, etc. when plunged into a jar of chlorine gas catch fire spontaneously to form their respective chlorides.

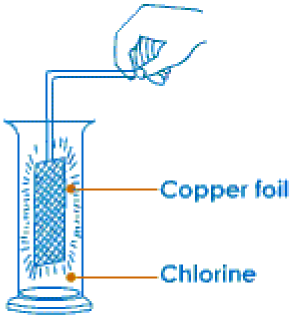


Fig. 14.10 Spontaneous combustion of copper in chlorine

$$\underset{\text{Sodium}}{2Na(s)} + \underset{\text{Chlorine}}{Cl_2(g)} \longrightarrow \underset{\text{Sodium chloride}}{2NaCl(s)}$$

$$\underset{\text{Copper}}{Cu(s)} + \underset{\text{Chlorine}}{Cl_2(g)} \longrightarrow \underset{\text{Copper(III)chloride}}{CuCl_2(s)}$$

<u>With yellow phosphorous</u>

Yellow phosphorus first melts and then catches fire spontaneously when introduced into a jar of chlorine gas. It forms thick white fumes of phosphorus (III) chloride and phosphorus (V) chloride

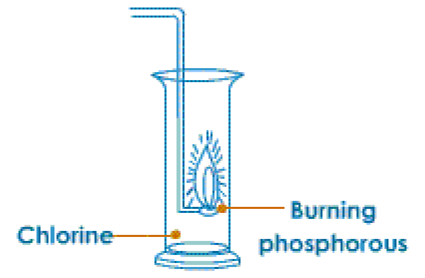


Fig. 14.9 Burning of phosphorous in chlorine

Reaction with hydrogen sulphide

On passing chlorine and hydrogen sulphide through separate vents in a upright combustion tube hydrogen sulphide gets oxidised to hydrogen chloride and sulphur . Hydrogen chloride comes out through the middle tube.

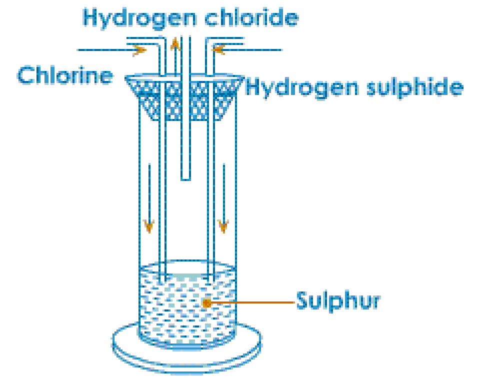


Fig. 14.12 Oxidation of hydrogen sulphide by chlorine

$$\underset{\text{Hydrogen sulphide}}{H_2S(g)} + \underset{\text{Chlorine}}{Cl_2(g)} \longrightarrow \underset{\text{Hydrogen chloride}}{2\,HCl(g)} + \underset{\text{Sulphur}}{S(s)}$$

If chlorine is passed through a solution of hydrogen sulphide in water the solution turns turbid due to the formation of free sulphur.

Reaction with aqueous sodium sulphite

When chlorine is passed through an aqueous solution of sodium sulphite it gets converted to sodium sulphate. Chlorine first reacts with the water to form nascent oxygen.

$$\underset{\text{Water}}{H_2O(l)} + \underset{\text{Chlorine}}{Cl_2(g)} \longrightarrow \underset{\substack{\text{Hydrochloric}\\\text{acid}}}{2\,HCl(aq)} + \underset{\substack{\text{Nascent}\\\text{oxygen}}}{[O](g)}$$

The nascent oxygen then gets added to the sodium sulphite to form sodium sulphate.

$$\underset{\substack{\text{Sodium}\\\text{sulphite}}}{Na_2SO_3(aq)} + \underset{\substack{\text{Nascent}\\\text{Oxygen}}}{[O]} \longrightarrow \underset{\substack{\text{Sodium}\\\text{sulphate}}}{Na_2SO_4(aq)}$$

The overall reaction can be written as:

$$\underset{\substack{\text{Sodium}\\\text{sulphite}}}{Na_2SO_3(aq)} + \underset{\text{Water}}{H_2O(l)} + \underset{\text{Chlorine}}{Cl_2(g)} \longrightarrow \underset{\substack{\text{Sodium}\\\text{sulphate}}}{Na_2SO_4} + \underset{\substack{\text{Hydrochloric}\\\text{acid}}}{2HCl(aq)}$$

Displacement of the Halogens by Chlorine

Halogens are the most electronegative elements. Fluorine is the most electronegative, followed by chlorine then bromine and then iodine.

The relative reactivity of the halogens, as described in group trends, can be shown by displacement reactions. These are similar to the metal displacement reactions.

For example, Bromine gas bubbled through a solution of potassium iodide in water will displace (take the place of) the less reactive iodine, forming iodine and potassium bromide.

Bromine + potassium iodide → potassium bromide + iodine.

$Br_{2(g)} + 2KI_{(aq)} \rightarrow 2KBr_{(aq)} + I_{2(s)}$

Similarly, chlorine will displace less reactive halogens.
Chlorine will displace both bromine and iodine from the appropriate salt. This can be used in the extraction of bromine from sea water.

Chlorine + potassium iodide → potassium chloride + iodine.

$Cl_{2(g)} + 2KI_{(aq)} \rightarrow 2KCl_{(aq)} + I_{2(s)}$

The equations can be written in terms of ions (called ionic equations).For example, the last equation can be written as

$$Cl_{2(g)} + 2I^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + I_{2(s)}$$

Potassium iodide, on the left, exists as potassium ions (K^+) and iodide ions (I^-) and potassium chloride, on the right, exists as potassium ions (K^+) and chloride ions (Cl^-).

Potassium ions (or other metal ions) can be left out of the ionic equation because they do not take part in the reaction.
They are called 'spectator ions', as though they just sit back and watch!

Fluorine being the most electronegative halogen can displace all the other elements of this group (chlorine, bromine and iodine) from the aqueous solution of their salts.

$$2KCl\ (aq) + F_2\ (g) \longrightarrow 2KF(aq) + Cl_2\ (g)$$

$$2\ KBr(aq) + F_2\ (g) \longrightarrow 2\ KF(aq) + Br_2\ (l)$$

$$2\ KI(aq) + F_2\ (g) \longrightarrow 2\ KF(aq) + I_2\ (s)$$

Chlorine can displace bromine and iodine from bromides and iodides respectively. However, it cannot displace fluorine from fluorides.

$$2\ KBr(aq) + Cl_2\ (g) \longrightarrow 2\ KCl(aq) + Br_2\ (l)$$

$$2\ KI\ (aq) + Cl_2\ (g) \longrightarrow 2\ KCl\ (aq) + I_2\ (s)$$

Bromine can displace iodine from iodides. But it cannot displace chlorine or fluorine from chlorides or fluorides respectively.

$$2\ KI\ (aq) + Br_2\ (l) \longrightarrow 2KBr(aq) + I_2\ (s)$$

Iodine being the least electronegative of the halogens cannot displace any other halogen from their respective halides.

SUMMARY OF DISPLACEMENT REACTIONS

Solution of halide \ Halide	F_2	Cl_2	Br_2	I_2
F^-	▨	×	×	×
Cl^-	✓	▨	×	×
Br^-	✓	✓	▨	×
I^-	✓	✓	✓	▨

Key

▨ halide in its solution. No reaction

× No reaction occurs

✓ Displacement reaction occurs

Bleaching Action of Chlorine

Chlorine bleaches (removes the color) organic colors by the process of oxidation in presence of moisture. The bleaching action takes place in few steps:

a) Chlorine first dissolves in water to give a mixture of hydrochloric acid and hypochlorous acid.

$$\underset{\text{Water}}{H_2O(l)} + \underset{\text{Chlorine}}{Cl_2(g)} \longrightarrow \underset{\substack{\text{Hydrochloric}\\ \text{acid}}}{HCl(aq)} + \underset{\substack{\text{Hypochlorous}\\ \text{acid}}}{HOCl(aq)}$$

b) As mentioned earlier hypochlorous acid is very unstable and decomposes to give hydrochloric acid and nascent oxygen.

$$\underset{\substack{\text{Hypochlorous}\\ \text{acid}}}{HOCl(aq)} \longrightarrow \underset{\substack{\text{Hydrochloric}\\ \text{acid}}}{HCl\ (aq)} + \underset{\substack{\text{Nascent}\\ \text{Oxygen}}}{[O]}$$

c) The nascent oxygen oxidises the coloring matter to colorless matter thereby bleaching them.

$$\underset{\text{matter}}{\text{Coloring}} + \underset{\text{Oxygen}}{\text{Nascent}} \longrightarrow \underset{\text{matter}}{\text{Colorless}}$$

Bleaching by chlorine is permanent. Chlorine bleaches cotton fabrics, wood pulp litmus etc. However, it is not used to bleach delicate articles such as silk, wool etc., as it is a strong bleaching and oxidizing agent. This dual action will damage the base material.

You must have noticed that in the very first stage, presence of water is essential to produce hypochlorous acid.

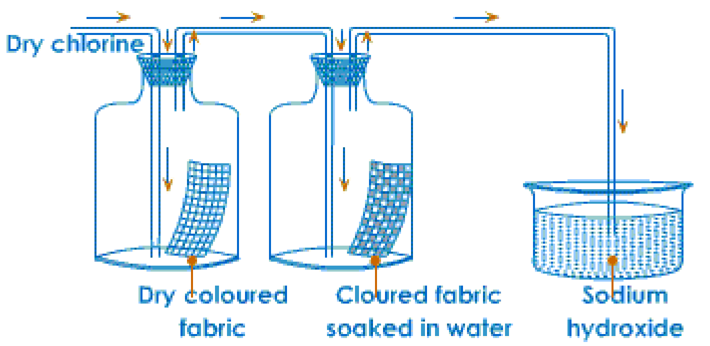


Fig. 14.16 Chlorine bleaches in presence of moisture

The dry coloured fabric does not bleach. The coloured fabric soaked in water is bleached. This shows that chlorine only bleaches in the presence of water. If water is absent no bleaching can take place. Dry chlorine therefore does not bleach.

Tests for Chlorine

1. Chlorine is a greenish yellow gas with a pungent and irritating odor.

2. It turns wet blue litmus paper red and then bleaches it.

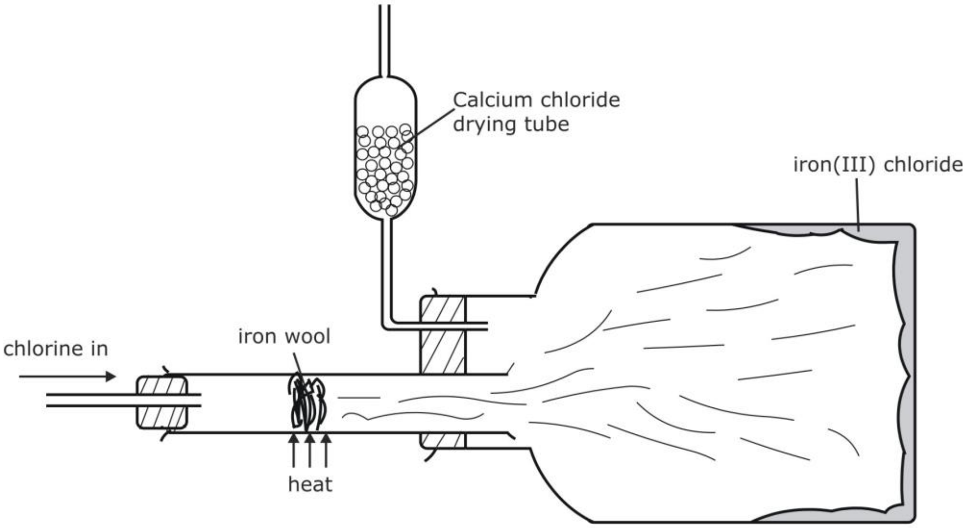
3. Colored petals and the leaves of plants can be bleached by it.

4. Chlorine turns wet starch potassium iodide paper blue by displacing the iodine from the potassium iodide, and causing iodine to turn the starch blue.

$$\underset{\text{Potassium iodide}}{2KI(aq)} + \underset{\text{Chlorine}}{Cl_2(g)} \longrightarrow \underset{\text{Potassium chloride}}{2KCl(aq)} + \underset{\text{Iodine}}{I_2(g)}$$

Oxidizing Reaction of Chlorine

Chlorine is a strong oxidising agent. Chlorine oxidises Iron (II) Chloride, $FeCl_2$, to the salt containing Iron in the higher oxidation state Iron (III) Chloride, $FeCl_3$. This is possible because Iron has a variable valency.



$2\,FeCl_2 + Cl_2 \longrightarrow 2\,FeCl_3$

Chlorine displaces the less electronegative Bromine and Iodine from their respective salts.

$Cl_2 + 2\,KBr \longrightarrow 2\,KCl + Br_2$ Chlorine removes Hydrogen from the hydrides of non-metals, forming Hydrogen Chloride, and leaving the non-metal element.

$Cl_2 + H_2S \longrightarrow 2\,HCl + S$

Affinity for Hydrogen

Chlorine combines with free hydrogen to form hydrogen chloride. It can also react with the hydrogen present in other compounds such as water, ammonia, hydrocarbon, hydrogen sulphide etc.

With water

Chlorine dissolves in water to form chlorine water. It slowly reacts with the water to form a mixture of hydrochloric acid and hypochlorous acid.

$$\underset{\text{Water}}{H_2O\ (l)} + \underset{\text{Chlorine}}{Cl_2\,(g)} \longrightarrow \underset{\substack{\text{Hydrochloric}\\ \text{acid}}}{HCl\ (aq)} + \underset{\substack{\text{Hypochlorous}\\ \text{acid}}}{HOCl(aq)}$$

Hypochlorous acid is very unstable and in presence of sunlight it decomposes to give hydrochloric acid and a nascent oxygen atom.

$$\underset{\text{Hypochlorous acid}}{HOCl(aq)} \longrightarrow \underset{\text{Hydrochloric acid}}{HCl(aq)} + \underset{\text{Nascent Oxygen}}{[O](g)}$$

Two such nascent oxygen atoms combine to form a molecule of oxygen.

$$[O] + [O] \longrightarrow O_2(g)$$

So if a solution of chlorine in water is exposed to sunlight as shown in figure 14.14, oxygen is formed.

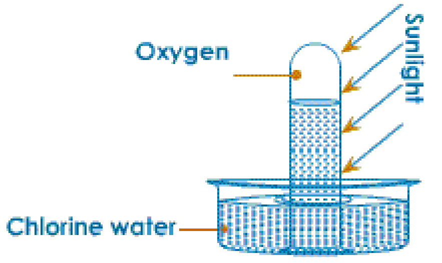


Fig. 14.14 Exposing chlorine water to sunlight

With ammonia

Depending on which of the two gases is in excess, chlorine reacts with ammonia in two ways.

(a) When ammonia is in excess the final products are ammonium chloride and nitrogen.

$$\underset{\text{Ammonia}}{2NH_3(g)} + \underset{\text{Chlorine}}{3Cl_2(g)} \longrightarrow \underset{\text{Nitrogen}}{N_2(g)} + \underset{\text{Hydrogen chloride}}{6HCl(g)}$$

Hydrogen chloride thus produced reacts with excess of ammonia to produce ammonium chloride.

$$\underset{\text{Ammonia}}{NH_3(g)} + \underset{\text{Hydrogen chloride}}{HCl(g)} \longrightarrow \underset{\text{Ammonium chloride}}{NH_4Cl(s)}$$

The overall reaction can be written as:

$$\underset{\text{Ammonia}}{8NH_3(g)} + \underset{\text{Chlorine}}{3Cl_2(g)} \longrightarrow \underset{\text{Ammonium chloride}}{6NH_4Cl(s)} + \underset{\text{Nitrogen}}{N_2(g)}$$

(b) When chlorine is in excess the final product is an oily explosive liquid called nitrogen trichloride.

$$\underset{\text{Ammonia}}{NH_3(g)} + \underset{\text{Chlorine}}{3Cl_2(g)} \longrightarrow \underset{\text{Nitrogen trichloride}}{NCl_3(l)} + \underset{\text{Hydrogen chloride}}{3HCl(g)}$$

<u>**With alkalis**</u>

Alkalis, at different temperatures and at different levels of concentration, behave differently with chlorine.

(i) With cold dilute alkalis

Chlorine reacts with cold dilute alkalis to form their respective chlorides, hypochlorites and water.

$$\underset{\text{Sodium hydroxide}}{2NaOH(aq)} + \underset{\text{Chlorine}}{Cl_2(g)} \longrightarrow \underset{\text{Sodium chloride}}{NaCl(aq)} + \underset{\text{Sodium hypochlorite}}{NaOCl(aq)} + \underset{\text{Water}}{H_2O(l)}$$

$$\underset{\text{Potassium hydroxide}}{2KOH(aq)} + \underset{\text{Chlorine}}{Cl_2(g)} \longrightarrow \underset{\text{Potassium chloride}}{KCl(aq)} + \underset{\text{Potassium hypochlorite}}{KOCl(aq)} + \underset{\text{Water}}{H_2O(l)}$$

(ii) With hot concentrated alkalis

Chlorine reacts with hot concentrated alkalis to form their respective chlorides, chlorates and water.

$$\underset{\text{Sodium hydroxide}}{6NaOH(aq)} + \underset{\text{Chlorine}}{3Cl_2(g)} \longrightarrow \underset{\text{Sodium chloride}}{5NaCl(aq)} + \underset{\text{Sodium chlorate}}{NaClO_3(aq)} + \underset{\text{Water}}{3H_2O(l)}$$

$$\underset{\text{Potassium hydroxide}}{6\,KOH(aq)} + \underset{\text{Chlorine}}{3Cl_2(g)} \longrightarrow \underset{\text{Potassium chloride}}{5\,KCl(aq)} + \underset{\text{Potassium chlorate}}{KClO_3(aq)} + \underset{\text{Water}}{3\,H_2O(l)}$$

Uses

Chlorine is used

- For the manufacture of bleaching powder and liquid bleaches,
- To bleach fabrics (e.g. linen and cotton), wood pulp and paper,
- For the direct manufacture of Hydrochloric Acid by the direct combination of its elements,

$H_2 + Cl_2 \longrightarrow 2\,HCl$

- In the manufacture Sodium Hypochlorite (i.e. domestic bleach), disinfectants, insecticides, plastics and Hydrochloric Acid,
- As a disinfectant used to kill bacteria in the preparation of drinking water.
- Chlorine is also important in the manufacture of paints, aerosol propellants and plastics.
- Also used to make some explosives, poison gases and pesticides.

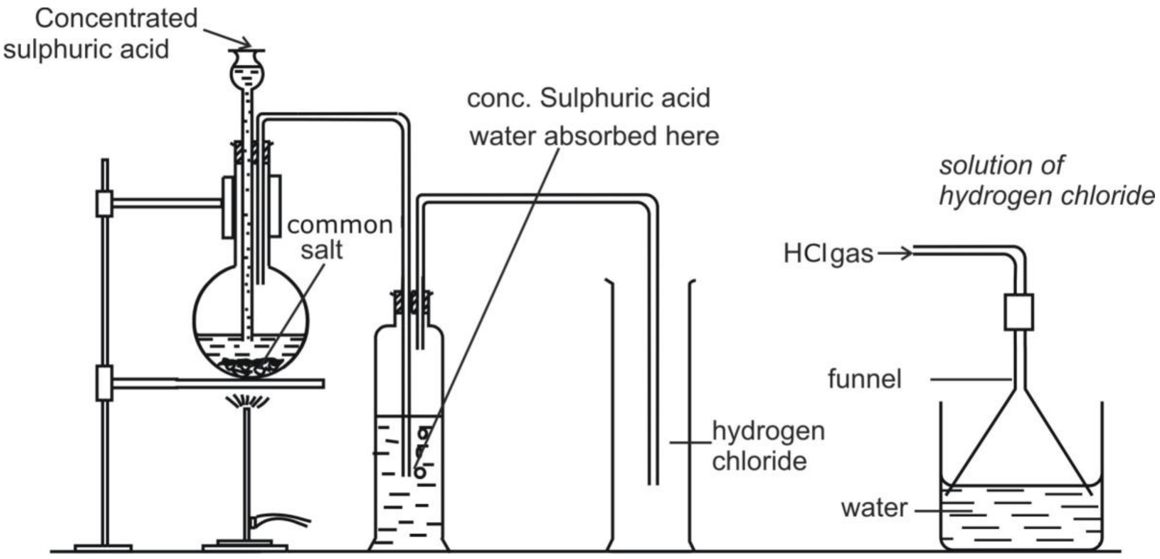
Hydrogen Chloride

Hydrogen chloride is an hydrogen compound of Chlorine. Chlorine is a highly reactive element and is mainly found in combined state. Its most important source is sodium chloride which is mainly found in large underground deposits, sea and lake such as lake Magadi. Sodium chloride is the main source of chlorine which is used to make hydrogen chloride.

Preparation of hydrogen chloride

Hydrogen Chloride may be prepared in the laboratory by heating Concentrated Sulphuric Acid, with Sodium Chloride.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$



Preparing and making a solution of hydrogen chloride

It is prepared industrially by the combustion of Hydrogen, H_2, in Chlorine, Cl_2.

$$H_2 + Cl_2 \longrightarrow 2HCl$$

Other way of producing chlorine

Chlorine, removes Hydrogen, from the hydrides of non-metals, forming Hydrogen Chloride, and leaving the non-metal element.

$$Cl_2 + H_2S \longrightarrow 2\,HCl + S$$

When Chlorine Water, (i.e. a solution of Chlorine gas, in Water) in a flask inverted in a basin of the same liquid is exposed to bright sunlight, the Chlorine is decomposed and a solution of Hypochlorous Acid remains.

$$H_2O + Cl_2 \longrightarrow HCl + HClO$$

The Hypochlorous Acid, is not very stable and the solution readily decomposes, especially when exposed to sunlight, yielding Oxygen,

$$2\,HClO \longrightarrow 2\,HCl + O_2$$

Chlorine is soluble in water (which solution is called Chlorine Water) and this loses its yellow colour on standing in sunlight, due to the formation of a mixture of Hypochlorous Acid, and Hydrochloric Acid.

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

PROPERTIES OF HYDROGEN CHLORIDE

Hydrogen chloride in solution

Hydrogen chloride is a colourless fuming gas. The polar covalent gas Hydrogen Chloride is very soluble in Water. In aqueous solution, the molecule exists in ionic form, as the positively charged Hydrogen Ion, H^+, and the negatively charged Chloride Ion, Cl^-.

$$HCl + aq \longrightarrow H(+) + Cl(-)$$

Hydrogen Hydrogen Chloride
Chloride Ion Ion

Its solution in water turns blue litmus paper red. Hydrogen chloride has no effect on dry litmus paper as no ions are present in dry gas.

The importance of water

The gas hydrogen chloride is made up of covalently bonded molecules. If the gas is dissolved in an organic solvent, such as methylbenzene, it does not show any of the properties of an acid.

Dissolving hydrogen chloride in water and methylbenzene

Test	**Observation with hydrogen chloride dissolved in water**	**Observation with hydrogen chloride dissolved in methylbenzene**
Temperature change when the solution is made	Marked temperature rise	Very slight temperatures change
Effect on dry litmus paper	Turns red	Little or no change
Reaction with magnesium ribbon	Hydrogen gas evolved rapidly	No reaction
Reaction with calcium carbonate	Carbon dioxide given off rapidly	No reaction
Electrical conductivity	Conducts electricity and hydrogen is evolved at the cathode	Non - conductor

For example, it does not conduct electricity or turn a piece of blue litmus paper red. However, when the gas is dissolved in water, a strongly acidic solution is produced. The acidic oxides of sulphur, phosphorus and carbon are the similar. They are covalent molecules when pure, but show acidic properties only when dissolved in water.

Reaction with Group 1 Alkali Metals

Alkali metals burn very exothermically and vigorously when heated in chlorine to form **colourless crystalline ionic salts** e.g. **NaCl** or Na^+Cl^-. This is a very expensive way to make salt! It's much cheaper to produce it by evaporating sea water!

E.g. **sodium + chlorine** → **sodium chloride**

$$2Na_{(s)} + Cl_{2(g)} \longrightarrow 2NaCl_{(s)}$$

The sodium chloride is soluble in water to give a neutral solution pH 7, universal indicator is green. The salt is a **typical ionic compound** i.e. a brittle solid with a high melting point. Similarly potassium and bromine form potassium bromide **KBr**, or lithium and iodine form lithium iodide **LiI**. Again note the **group formula** pattern.

Hydrochloric acid reacts with metals above hydrogen in the reactivity series. All of these metals react with hydrochloric acid liberating hydrogen which puts out a burning splint with a pop sound.

$$Zn(s) + 2HCl\ (aq) \longrightarrow ZnCl_2\ (aq) + H_2\ (g)$$

This is a common reaction for preparing hydrogen gas in the school laboratory. The hydrogen can then be collected over water. The salts produced can be obtained from the solution by filtration to obtain the filtrate which then transferred onto an evaporation dish for evaporation and crystallization. No hydrogen is liberated when the acid is reacted with lead, copper and mercury. Despite the fact that lead is above hydrogen in the reactivity series, the hydrogen chloride is not a strong enough oxidizing agent to liberate hydrogen.

Reaction with bases

Hydrochloric acid is a strong acid as it is well ionized in solution. It neutralizes bases and alkalis forming salts and water.

$$KOH\ (aq) + HCl\ (aq) \longrightarrow KCl\ (aq) + H_2O\ (l)$$

$$CuO(s) + HCl\ (aq) \longrightarrow CuCl_2\ (aq) + H_2O\ (l)$$

$$FeO(s) + 2\ HCl\ (aq) \longrightarrow FeCl_2\ (aq) + H_2O\ (l)$$

Reaction with carbonates

Hydrogen chloride reacts with carbonates and hydrogen carbonates producing carbon dioxide, salt and water. Carbon dioxide turns lime water milky.

$CaCO_3\ (aq) + 2HCl\ (aq) \longrightarrow CaCl_2\ (aq) + CO_2\ (g) + H_2O\ (l)$

Ionic equation

$CO_3^{2-}\ (aq) + 2H^+\ (aq) \longrightarrow CO_2 (g) + H_2O\ (l)$

$NaHCO_3\ (aq) + HCl\ (aq) \longrightarrow NaCl\ (aq) + CO_2\ (aq) + H_2O\ (l)$

Ionic equation

$HCO_3^-(aq) + H^+\ (aq) \longrightarrow CO_2(g) + H_2O(l)$

Reaction with hydrogen H_2

Halogens readily combine with hydrogen to form the **hydrogen halides** which are colourless **gaseous covalent molecules.**

E.g. hydrogen + chlorine ⟶ hydrogen chloride

$H_{2\ (g)} + Cl_{2\ (g)} \longrightarrow 2HCl\ (g)$

The **hydrogen halides dissolve in water** to form **very strong acids** with solutions of **pH1** e.g. hydrogen chloride forms **hydrochloric acid** in water **$HCl(aq)$** or **$H^+Cl^-(aq)$** because they are fully ionised in aqueous solution even though the original hydrogen halides were covalent! An acid is a substance that forms **H^+** ions in water.

Bromine forms hydrogen bromide gas **HBr** $_{(g)}$, which dissolved in water forms hydrobromic acid $HBr_{\ (aq)}$. Iodine forms hydrogen iodide gas **HI** $_{(g)}$, which dissolved in water forms hydriodic acid $HI_{\ (aq)}$. Note the **group formula** pattern.

Oxidation of hydrochloric acid

The most common laboratory method for preparation of Chlorine is to heat Manganese Dioxide, with concentrated Hydrochloric Acid.

$MnO_2 + 4\,HCl \longrightarrow MnCl_2 + 2\,H_2O + Cl_2$

The gas is bubbled through water to remove any traces of hydrochloric gas that may be present and then it is dried by bubbling it through concentrated sulphuric acid. Chlorine may also be prepared by dropping cold concentrated Hydrochloric Acid, on Potassium Permanganate.

$$2KMnO_4 + 16HCl \longrightarrow 2MnCl_2 + 2KCl + 8H2O + 5Cl2$$

Summary

Physical Properties

Colour	Colourless
Odour	Pungent odour Poisonous
Density compared to air (heavier or lighter)	Heavier than air.

Chemical Properties

Solubility in water	Very soluble in water. It reacts with water to form hydrochloric acid.
Burning	Does not support combustion
Moist pH paper	Acidic reaction
Red rose petals	No reaction
Specific test	It will fume in moist air

DEFINATION OF COMMON TERMS IN CHEMISTRY

Word	**Definition**
Acid	A corrosive substance which has a pH lower than 7. Acidity is caused by a high concentration of hydrogen ions.
Acid rain	Acid rain is caused when sulphur dioxide - released by the burning

	of coil and oil - dissolves in rainwater to form sulphuric acid.
Activation energy	The minimum energy required for a collision between particles, in order for a reaction to occur.
Addition polymer	Addition polymers are made when monomers (simple molecules) add together across a double bond.
Addition reaction	A reaction in which a small molecule adds on across a double bond.
Alkali	A base, which is soluble in water.
Alkali metals	The alkali metals are the elements in Group 1 of the periodic table. They have one electron in the outer shell.
Alkanes	Alkanes are saturated hydrocarbons. This means that each carbon atom has four bonds to other atoms.
Alkenes	Alkenes are unsaturated hydrocarbons with a double bond between the carbon atoms.
Allotropes	Allotropes are structurally different forms of an element. They differ in the way the atoms bond with each other and arrange themselves into a structure. Because of their different structures, allotropes have different physical and chemical properties
Alloy	An alloy is a mof two or more elements, at least one of which is a metal.
Anode	An anode is the electrode (electrical conductor) attached to the positive terminal of a battery.
Atom	All elements are made of atoms. An atom consists of a nucleus containing protons and neutrons, surrounded by electrons.
Atomic number	The atomic number (Z) of an element is the number of protons in the nucleus of the atom.
Bases	Substances with a pH higher than 7, and which have a high concentration of hydroxyl ions. Bases react with acids to form a salt and water (called neutralisation). Metal hydroxides, oxides and carbonates are all bases.
Biocatalyst	A biocatalyst is an enzyme or microorganism that activates or speeds up a biochemical reaction.
Boiling point	The temperature at which a liquid changes its state to gas.
Brittle	If something is brittle it is easily broken.
Catalyst	A catalyst changes the rate of a chemical reaction without being changed by the reaction itself.
Catalytic converter	A device in internal combustion engines which catalyses reactions converting harmful exhaust gases such as carbon monoxide into normal atmospheric gases.
Cathode	A cathode is the electrode (electrical conductor) attached to the negative terminal of a battery.

Chemical change	A chemical change involves new substances being formed and is very difficult to reverse.
Combustion	Combustion is the process of burning by fire.
Compound	A compound is a substance formed by the chemical union (involving bond formation) of two or more elements.
Condensation	Condensation is a change of state in which gas becomes liquid by cooling.
Conduct	To allow electricity, heat or other energy forms to pass through.
Conductor	An electrical conductor is a material which allows an electrical current to pass easily. It has a low resistance. A thermal conductor allows thermal energy to be transferred through it easily.
Corrode	To deteriorate (get weaker) due to the action of water, air, or an acid.
Covalent bond	A covalent bond between atoms forms when atoms share electrons to achieve a full outer shell of electrons.
Covalent compounds	A covalent compound is a compound of neutral atoms in which the atoms are held together by covalent bonds. Covalent bonds between atoms form when atoms share electrons to achieve a full outer shell of electrons.
Cracking	Cracking is the breaking down of large hydrocarbon molecules into smaller, more useful hydrocarbon molecules by vapourizing them and passing them over a hot catalyst.
Crude oil	Crude oil is formed from the remains of small animals and plants that died and fell to the bottom of the sea. Their remains were covered by mud. As the sediment was buried by more sediment, it started to change into rock as the temperature and pressure increased. The plant animal remains were "cooked" by this process and changed into crude oil.
Decomposition	A reaction in which substances are broken down, by heat, electrolysis or a catalyst.
Denatured	If a protein is denatured, its structure and function is altered. This can be caused by heat, altered pH or by chemical agents.
Displacement reactions	Displacement reactions happen when a more-reactive element replaces a less-reactive element in a compound.
Distillation	Distillation is when we make a liquid evaporate and then condense the vapour back to a purer liquid.
Double bond	A double bond is a covalent bond resulting from the sharing of four electrons (two pairs) between two atoms.
Ductile	If a material is ductile it is capable of being drawn into thin sheets or wires without breaking.
Electrode	Electrodes are conductors used to establish electrical contact with a

	circuit. The electrode attached to the negative terminal of a battery is called a negative electrode, or cathode. The electrode attached to the positive terminal of a battery is the positive electrode, or anode.
Electrolysis	Electrolysis is the decomposition (separation or break-down) of a compound using an electric current.
Electrolyte	An electrolyte is a substance which in solution will conduct an electric current.
Electron	An electron is a very small negatively charged particle found in an atom in the space surrounding the nucleus.
Electrostatic	An electrostatic force is generated by differences in electric charge (i.e. positive and negative) between two particles. It can also refer to electricity at rest.
Element	All atoms of an element have the same atomic number, the same number of protons and electrons and so the same chemical properties.
Endothermic	In an endothermic reaction, energy is taken in from the surroundings. The surroundings then have less energy than they started with, so the temperature falls.
Equilibrium	If the rate of the forward reaction and the rate of the back reaction in a reversible reaction are equal, the reaction is in equilibrium.
Eutrophication	Eutrophication is the enrichment of a water body with nutrients - such as nitrates - which results in excessive growth of algae and other aquatic plants, leading to depletion of oxygen.
Evaporation	Evaporation is a change in state in which a liquid becomes a gas (vapour); molecules near the surface of a liquid may leave the liquid to become a vapour.
Exothermic	Heat energy is released in an exothermic reaction. We know this because the surroundings get warm.
Filtrate	Filtrate is fluid that has passed through a filter.
Formula	A formula is a combination of symbols that indicates the chemical composition of a substance.
Fossil	Fossils are the remains of animals and plants from a past geological age, preserved in the Earth's crust.
Fossil fuels	Fossil fuels have been created over millions of years by the decay and compression of living things, particularly plants. Coal, gas and oil are fossil fuels.
Fractional distillation	In fractional distillation a mixture of several substances, such as crude oil, is distilled and the evaporated components are collected as they condense at different temperatures.
Groups	The groups of elements in the periodic table are the elements which have the same number of electrons in their outer shells and so have

	similar chemical properties. A group of elements all lie in same column in the periodic table.
Halogens	The halogens are the elements in Group VII of the periodic table. They have seven electrons in the outer shell.
Hydrocarbons	Hydrocarbons are a group of compounds, which contain the elements hydrogen and carbon.
Ion	An ion is a charged particle formed by loss or gain of electrons. When atoms lose an electron they become a positive ion. When they gain an electron they become a negative ion.
Ionic bond	An ionic bond forms between two atoms when an electron is transferred from one atom to the other, forming a positive-negative ion pair.
Ionic compound	An ionic compound occurs when a negative ion (an atom that has gained an electron) joins with a positive ion (an atom that has lost an electron). The ions swap electrons to achieve a full outer shell.
Isotopes	Atoms of the same element that have different numbers of neutrons are called isotopes.
Lattice	A lattice is a regular grid-like arrangement of atoms in a material.
Liquefy	To liquefy means to become liquid, for example through heating a solid or cooling a gas.
Lubricant	A substance used to reduce the friction between two solid surfaces.
Mass	Mass is a measure of the amount of material in an object. It is measured in grams (g).
Mass number	The mass number (A) of an element is the number of protons plus the number of neutrons in the nucleus of the *atom*.
Molecular compound	A molecular compound is made up of at least two different elements, which share electrons to form covalent bonds.
Molecule	A molecule is a collection of two or more atoms held together by chemical bonds. It is the smallest part of a substance that displays the properties of the substance.
Molten	Molten means reduced to liquid form by heating. It is mainly used to describe rock, glass or metal.
Monomer	A monomer is a simple molecule.
Natural gas	Natural gas is a fossil fuel formed from decaying plant and animal material.
Neutralisation	Neutralisation is the reaction between an acid and a base to form a salt plus water.
Neutron	A neutron is a particle that is found in the nucleus of an atom, has a mass approximately equal to that of a proton, and has no electric charge.

Noble gases	The noble gases are the elements in Group 0/Group VIII of the periodic table. They have a full outer shell of electrons and so are unreactive.
Nucleus	Found at the centre of an atom, the nucleus contains protons and neutrons.
Ore	An ore is a rock containing enough quantities of a mineral that it is profitable to extract it.
Oxidation	Oxidation is a reaction in which oxygen combines with a substance. Oxidation also means a loss of electrons.
Periods	The periods of elements in the periodic table are the elements in which the same outer shell is being filled up. A period of elements in the periodic table all lie in the same row.
Polymer	A polymer is a large molecule formed from many identical smaller molecules (monomers).
Polymerise	Polymerisation is the reaction in which many identical monomers are joined together to make a polymer.
Product	A product is a substance formed in a chemical reaction.
Protons	A proton is a small particle with a positive charge found in the nucleus of the atom.
Radioactive	A radioactive isotope gives off (or is capable of giving off) radiant energy in the form of particles or rays by the spontaneous disintegration of the nucleus.
Reactant	A reactant is a substance put together with another substance/substances to undergo a chemical reaction.

Reactant A reactant is a substance put together with another substance/substances to undergo a chemical reaction.

Re-crystallisation	When rocks are heated and put under pressure new crystals can form. These are often elongated in the direction of least pressure.
Redox reaction	Oxidation and reduction always take place together. The combined reaction is called a redox reaction.
Reduction	Reduction is a reaction in which oxygen is removed from a substance. Reduction also means a gain in electrons.
Relative atomic mass	The relative atomic mass is the number of times heavier an atom is compared to one twelfth of a carbon-12 atom.
Relative mass	The relative mass is the number of times heavier a particle is, compared to another.
Reversible reactions	Reversible reactions are chemical reactions, which can go both ways. The direction of the reaction depends on the condition of the reactants.
Salt	A compound formed by neutralisation of an acid by a base (e.g. a

	metal oxide) - the result of hydrogen atoms in the acid being replaced by metal atoms or positive ions. Sodium chloride - common salt - is one such compound.
Saturated	Filled to capacity. In a saturated hydrocarbon there are no more available bonds.
Slag	Slag is the non-metallic by-product resulting from the extraction of metals such as iron from their ores.
Solute	A solute is the material that dissolves in a solvent to form a solution.
Solution	A solution is the mixture formed when a solute dissolves in a solvent.
Solvent	A solvent is the liquid in which the solute dissolves to form a solution.
Stable	Atoms are stable if their outer shell contains its maximum number of electrons.
Sterilize	To sterilize means to make something free from microorganisms such as bacteria.
Thermal decomposition	A reaction in which substances are broken down by heat.
Unsaturated	An unsaturated compound contains at least one double or triple bond.
Vapour	Vapour is a cloud of liquid particles. Steam is water vapour.
Vapourized	Turned (generally through heating) into vapour. Vapour is a cloud of liquid particles. Steam is water vapour.