

CHAPTER ONE

MATTER

Matter is anything that occupies space and has weight.

Matter is made up of very tiny particles (building blocks) known as **atoms**, **molecules** or **ions**.

An atom is the smallest electrically neutral particle of an element that takes part in a chemical reaction.

A molecule is the smallest electrically neutral particle of a compound or an element that is formed by the combination of atoms in a whole number ratio and can exist on its own.

In a molecule of an element, the combining atoms are the same (for example; the oxygen molecule, O_2)

In a molecule of a compound, different atoms combine (for example the hydrogen chloride molecule, HCl)

A molecule retains the properties of that element or compound it contains.

An **ion** is an atom or a group of chemically combined atoms that has either lost one or more electrons, making it positively charged (a cation), or gained one or more electrons, making it negatively charged (an anion).

The structure of an atom

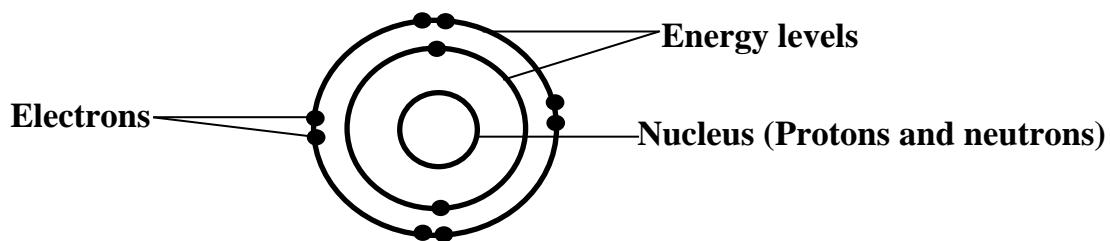
An atom is spherical in shape and has a small region in the center called the nucleus. The atom contains **protons** and **neutrons**, and **electrons** as fundamental particles.

The protons and neutrons are concentrated in a very small nucleus in the center of the atom while the electrons are all outside the nucleus in the energy levels and are constantly rotating around the nucleus.

The number of electrons in the energy levels (negative charges) is equal to the number of all protons in the nucleus (positive charge) hence an atom is neutral.

The energy level closest to the nucleus is called the first energy level or the K energy level. The second closest energy level to the nucleus is the second energy level or the L energy level. This is followed by the third energy level or the M energy level. So, the energy levels are named 1st, 2nd, 3rd, 4th, and so on or K, L, M, N and so on from the energy level closest to the nucleus outwards.

Diagrammatic illustration of an atom



The sub atomic particles

Electrons, protons and neutrons were the first small particles to be discovered and many of the properties of matter are explained in terms of them. For this reason, they are called the fundamental, basic or elementary particles of matter. More recent research has however shown that there are many other small particles that do exist.

A study of cosmic rays and the nature of nuclear changes have led to discovery of over 200 sub atomic particles which are classified according to the strength of the forces between them, their mass and their spin.

Some of the subatomic particles are shown below

<i>Leptons</i>		<i>Hadrons</i>			
		<i>baryons</i>		<i>mesons</i>	
electron	e^-	proton	p^+	pions	π^+
					π^0
muon	μ^-	neutron	n	kaons	K^+
					K^0
neutrino	ν	lambda	λ^0		

Most of the particles have an associated anti-particle with an equal but opposite charge. For example a positron is an anti- particle for an electron

Fundamental particles of an atom

The fundamental particles of an atom are the electron, proton and neutron.

1. Electrons

Electrons are negatively charged particles surrounding the nucleus.

The electrons are carried in circular paths known as energy levels that surround the nucleus

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An electron has a mass of $\frac{1}{1836}$ of a proton, therefore its mass is said to be

negligible; it carries a charge of negative one (-1).

The chemical reactions of an element are determined by the number of electrons (which is equal to the number of protons in the nucleus)

2. Protons

Protons are positively charged fundamental particles which are present in all atomic nuclei.

Protons have a unit mass of one (1) and each proton carries a charge of positive one (+1).

3. Neutrons

Neutrons are uncharged fundamental particles in the nuclei of atoms, with the exception of hydrogen.

Neutrons also have unit mass of one and carry no charge (they are neutral).

Particle	Charge	Mass
<i>Electron</i>	-	$\frac{1}{1836}$
<i>Proton</i>	+	1
<i>Neutron</i>	<i>No charge</i>	1

The Nucleus

The nucleus of an atom consists of protons (positively charged) and neutrons (which have no charge)

Protons and neutrons are collectively called **nucleons**.

The sum of the number of protons and neutrons in the nucleus of an atom is called **nucleon number or mass number (A)**.

The number of protons in the nucleus of an element is called the **Proton number or atomic number (Z)**.

The full symbol of an atom of an element X is given notation ${}^A_Z X$ where;

X is the symbol of the element

A is the nucleon number or mass number

Z is the proton number or atomic number

The atomic number provides some information about an element which may include;

- (i) The position of an element in the Periodic Table
- (ii) The number of protons present in the nucleus of an atom
- (iii) The total number of electrons present in the neutral atom

Isotopic notation

Isotopes are atoms of the same element with the same number of protons but different number of neutrons.

Isotopes therefore have different mass numbers.

Isotopy is the existence of atoms of the same element with the same number of protons but different number of neutrons.

Isotopes of the same element have very similar chemical properties because they have the same electronic configuration, but differ slightly in their physical properties. An unstable isotope is termed a radioactive isotope or radioisotope.

Element	Isotopic name	Isotopic formula	No. of protons	No. of electrons	No. of neutrons
Hydrogen	Protium	${}_1^1H$	1	1	0
	Deuterium	${}_1^2H$	1	1	1
	Tritium	${}_1^3H$	1	1	2
Carbon	Carbon-12	${}_6^{12}C$	6	6	6
	Carbon-14	${}_6^{14}C$	6	6	8
Oxygen	Oxygen-16	${}_8^{16}O$	8	8	8
	Oxygen-17	${}_8^{17}O$	8	8	9
	Oxygen-18	${}_8^{18}O$	8	8	10
Chlorine	Chlorine-35	${}_{17}^{35}Cl$	17	17	18
	Chlorine-37	${}_{17}^{37}Cl$	17	17	20
Uranium	Uranium-234	${}_{92}^{234}U$	92	92	142
	Uranium-235	${}_{92}^{235}U$	92	92	143
	Uranium-238	${}_{92}^{238}U$	92	92	146

Ionic formation

An ion is a charged particle formed from an atom or a group of chemically combined atoms by gaining or losing one or more electrons. Ions are either negatively charged (anions) or positively charged (cations).

a) Positive ions (cations)

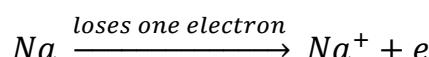
These are formed when atoms or group of chemically combined atoms lose one or more electrons. Atoms lose electrons so as to acquire a stable electronic configuration as the noble gases. The positive ions are formed by metal atoms, in ammonium ion and hydroxonium ion.

(i) Formation of sodium ion

The sodium atom has 11 electrons hence electronic configuration, 2: 8: 1.

The atom therefore has one electron more than the stable configuration of a noble gas, 2: 8.

To form the sodium ion, the sodium atom loses the one electron in the outer most energy level to form a noble gas configuration

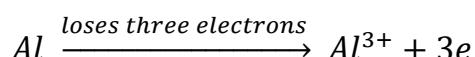


(ii) Formation of Aluminium ion

The aluminium atom has 13 electrons hence electronic configuration, 2: 8: 3.

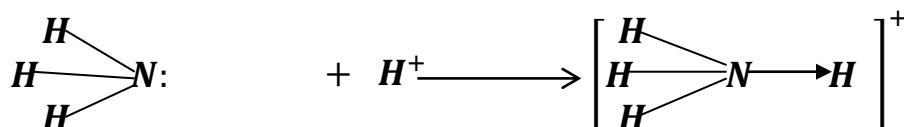
The atom therefore has three electrons more than the stable configuration of a noble gas, 2: 8.

To form the aluminium ion, the aluminium atom loses the three electrons in the outer most energy level to form a noble gas configuration



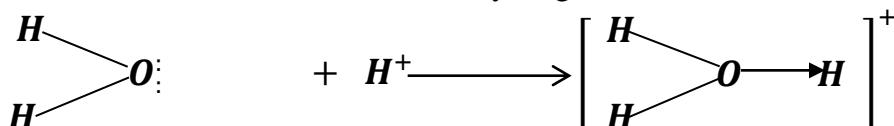
(iii) Formation of Ammonium ion

This is an ion formed by coordination of ammonia to a hydrogen ion. The formation of this ion is possible the nitrogen atom in the ammonia molecule has a lone pair of electrons which it donates to the electron deficient hydrogen ion to form a dative covalent bond. An arrow is often used to indicate which atom has donated the lone pair and also represents the co-ordinate bond/ dative bond.



(iv) Formation of the oxonium ion.

This is an ion formed by coordination of water to a hydrogen ion. The formation of this ion is possible the oxygen atom in the water molecule has lone pairs of electrons. It donates electrons to the electron deficient hydrogen ion to form a dative covalent bond.



b) Negative ions (anions)

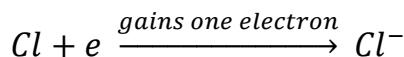
These are formed when atoms or group of chemically combined atoms gain one or more electrons. Atoms gain electrons so as to acquire a stable electronic configuration as the noble gases. The negative ions are formed by non-metallic atoms. Examples include the chloride ion, oxide ion, etc.

(i) **Formation of a chloride ion.**

The chlorine atom has 17 electrons hence electronic configuration, 2: 8: 7.

The atom therefore lacks an electron to gain the stable configuration of a noble gas, 2: 8: 8.

To form the chloride ion, the chlorine atom gains one electron in the outer most energy level to form a noble gas configuration

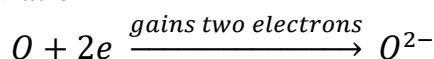


(ii) **Formation of an oxide ion**

The oxygen atom has 8 electrons hence electronic configuration, 2: 6.

The atom therefore lacks two electrons to gain the stable configuration of a noble gas, 2: 8.

To form the oxide ion, the oxygen atom gains two electrons in the outer most energy level to form a noble gas configuration



IUPAC nomenclature for cations, anions and salts

The International Union of Pure and applied Chemistry (IUPAC) recommends that every inorganic compound should have a name from which an unambiguous formula can be determined.

Naming monoatomic ions; cations and anions

The following rules are considered when naming monoatomic(single atom) ions

1. Monoatomic anions are named with a suffix ...ide

Consider the examples below

Mono atomic anion	IUPAC name
H^-	Hydride
N^{3-}	Nitride
B^{3-}	Boride
C^{4-}	Carbide
Si^{4-}	Silicide
O^{2-}	Oxide
Cl^-	Chloride
I^-	Iodide
Br^-	Bromide
F^-	Fluoride
S^{2-}	Sulphide
P^{3-}	Phosphide

2. Monoatomic cations are simply given the name of corresponding element followed by charge on the ion in parentheses and written in correct roman numerals. For elements that are monovalent like Al, Zn, Mg, Ca, Ba, etc., the charge may be ignored.

Monoatomic cation	Name
H^+	Hydrogen ion
Na^+	Sodium ion
Ag^+	Silver ion
Al^{3+}	Aluminium ion
Zn^{2+}	Zinc ion
Mg^{2+}	Magnesium ion
Ca^{2+}	Calcium ion
Ba^{2+}	Barium ion
Mn^{2+}	Manganese(II) ion
Sn^{2+}	Tin(II) ion
Sn^{4+}	Tin(IV) ion
Pb^{2+}	Lead(II) ion
Pb^{4+}	Lead(IV) ion
Fe^{2+}	Iron(II) ion
Fe^{3+}	Iron(III) ion
Cr^{3+}	Chromium(III) ion
Co^{2+}	Cobalt(II) ion
Ni^{2+}	Nickel(II) ion
Cu^+	Copper(I) ion
Cu^{2+}	Copper(II) ion

Naming polyatomic ions and compounds

There exist ions that contain more than one atom. These are called polyatomic ions. Most of the polyatomic ions contain oxygen atoms and these are called oxyanions.

Common polyatomic ions and their names

Formula	Name
NH_4^+	Ammonium ion
$\bar{O}H$	Hydroxide ion
$CH_3CO\bar{O}$	Ethanoate ion
$C_2O_4^{2-}$	Oxalate ion
NO_3^-	Nitrate ion
NO_2^-	Nitrite
HCO_3^-	Hydrogencarbonate ion
HSO_4^{2-}	Hydrogensulphate ion
O_2^{2-}	Peroxide ion
CO_3^{2-}	Carbonate
ClO_4^-	Chlorate(VII) ion
ClO_3^-	Chlorate(V) ion
PO_4^{3-}	Phosphate ion
CrO_4^{2-}	Chromate(VI) ion
$Cr_2O_7^{2-}$	Dichromate(VI) ion
MnO_4^{2-}	Manganate(VI) ion
MnO_4^-	Manganate(VII) ion
SO_4^{2-}	Sulphate ion
SO_3^{2-}	Sulphite ion
CN^-	Cyanide
I_3^-	Triiodide

Naming polyatomic compounds

1. The name should have the name of the cation followed by name of the anion.
2. The name of the cation is written first followed by the name of the anion
3. For cations that take on multiple charges, the charge is written using parentheses immediately following the element name.
4. When the formula contains two or more of the same polyatomic ion, that ion is written in parentheses with a subscript of the number of the polyatomic ions.

The Stock system

The Stock system of nomenclature was developed by the German Chemist Alfred Stock in 1919. In this system, the oxidation states of an element is indicated in parentheses and in Roman numerals.

It requires that there is usually no space between the end of the element name and the opening parentheses for example $CuCl$ has a correct name as copper(I) chloride and not copper (I) chloride.

Consider examples below

Formula of compound	Name
$SnCl_2$	Tin(II) chloride
$SnCl_4$	Tin(IV) chloride
$FeCl_2$	Iron(II) chloride
$FeCl_3$	Iron(III) chloride
CaO	Calcium oxide
Na_2O	Sodium oxide
$PbBr_2$	Lead(II) bromide
Cr_2O_3	Chromium(III) oxide
Al_2O_3	Aluminium oxide
Al_4C_3	Aluminium carbide

The stock system is widely used in modern chemistry to name compounds and complexes. It has been used to develop systemic names for various compounds.

Below is the procedure for naming binary ionic compounds.

1. The name should have the name of the cation followed by name of the anion.
2. For cations that take on multiple charges, the charge is written using parentheses immediately following the element name.

It is advisable that chemists use correct names of the compounds in their work. The other names (trivial names) are may however be acceptable in Applied Chemistry.

The names *Quick lime* and *calcium oxide* both indicate the same compound. *Calcium oxide* is called a systemic name(unambiguous name) and translates the structure of *Quick lime* clearly. It also provides an unambiguous reference to the compound.

Systemic/Correct/unambiguous name of some compounds

Formula	Systemic name	Common name
$CuCl$	Copper(I) chloride	Cuprous chloride
$CuCl_2$	Copper(II) chloride	Cupric chloride
$FeSO_4$	Iron(II) sulphate	Ferrous sulphate
$Fe_2(SO_4)_3$	Iron(III) sulphate	Ferric sulphate
$NaCl$	Sodium chloride	Brine
$NaOH$	Sodium hydroxide	Caustic soda
$NaCO_3 \cdot 10H_2O$	Sodium carbonate-10-water	Washing soda
CaO	Calcium oxide	Lime
$CaCO_3$	Calcium carbonate	Limestone
$K_4Fe(CN)_6$	Potassium hexacyanoferrate(II)	Potassium ferrocyanide
$K_3Fe(CN)_6$	Potassium hexacyanoferrate(III)	Potassium ferricyanide

The selection of correct Roman numeral

Roman numerals should be used correctly when writing names of compounds. For example the compound $Sn(SO_4)_2$ has only **tin(IV) sulphate** as the correct name. Students normally write wrong names such as;

Wrong name	Reason
Tin sulphate	<i>Tin has more than one oxidation states (+2 and +4). Therefore its exact oxidation state in the compound should be depicted</i>
Tin (IV) sulphate	<i>The oxidation state of +4 corresponds to tin and not the sulphate ion. It should be written immediately after tin and not in the middle of the compound</i>
Tin(IV)sulphate	<i>There should some little space between name of the cation with its charge, and name of the anion</i>
Tin(iv) sulphate	<i>Roman numerals do not have dots (.) above them.</i>
Tin(III) sulphate	<i>Roman numeral is wrong</i>

Writing the formula of a binary compound

At Ordinary level, the criss-cross method was used to write the formulae of compounds.

Another method may be used as follows;

Follow the steps below for formulae of Aluminium oxide and magnesium(II) chloride;

1. Write the symbol and charge of the cation first and the anion next	Al^{3+}	O^{2-}
	Mg^{2+}	Cl^{-}
2. Use a multiplier to make the total charge on the cations and anions equal and opposite to each other.	$Al^{(3+)}2$	$O^{(2-)}3$
	$Mg^{(2+)}1$	$Cl^{(-)}2$
3. The multipliers are then used as subscript for each ion.	Al_2O_3	
	Mg_1Cl_2	
4. The correct formula can then be written, but the charges are left out and all subscripts that are 1	Al_2O_3	
	$MgCl_2$	

MASS SPECTROMETRY

Mass spectrometry (mass spectroscopy) is a technique used to determine relative atomic masses and the relative abundance of isotopes, and for chemical analysis and the study of ion reactions.

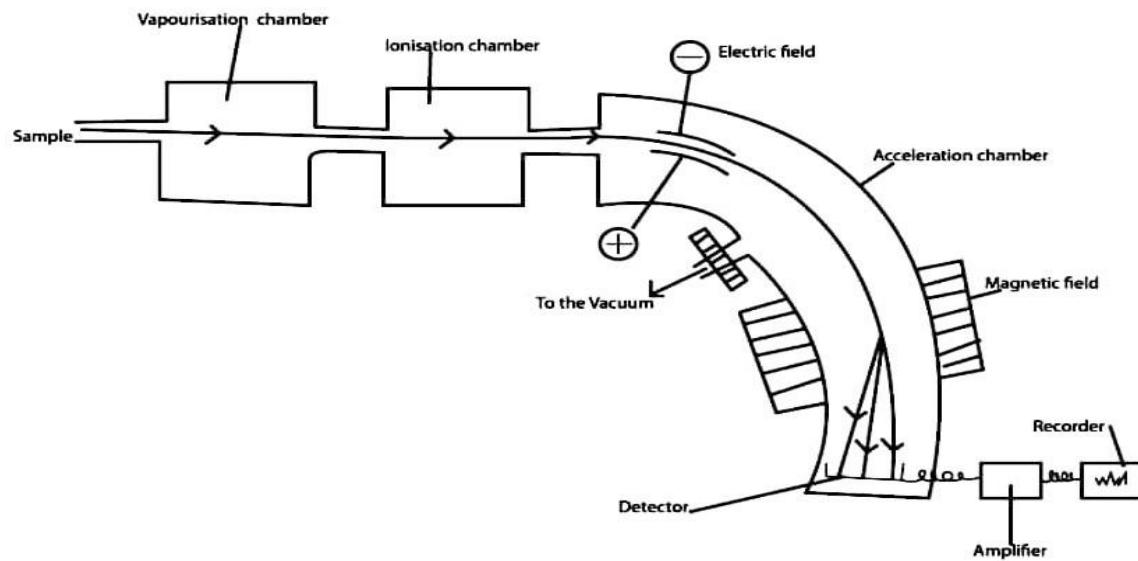
The earliest experiments of mass spectroscopy by J. J. Thomson used a stream of positive ions from a discharge tube, which were deflected by parallel electric and magnetic fields at right angles to the beam. Each type of ion formed a parabolic trace on a photographic plate (a mass spectrograph). In modern instruments, the ions are produced by ionizing the gas with electrons.

The essential parts and operation of a modern mass spectrometer

A mass spectrometer is usually used during mass spectroscopy. It is an instrument for producing ions in a gas and analyzing them according to their charge/mass ratio.

It mainly consists of the **vapourisation chamber**, **ionisation chamber**, **acceleration chamber**, **deflection chamber**, the **detector**, **amplifier** and **recorder**.

Diagram showing the essential parts of a modern mass spectrometer



Operation of a modern mass spectrometer

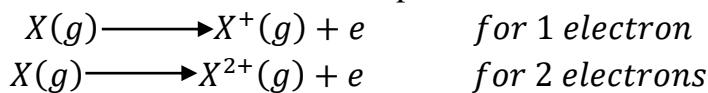
The whole apparatus is evacuated of air particles that may produce unnecessary ions.

1. Vapourisation chamber

The sample is heated by a tungsten filament to vapourise it. The vapourised sample is then introduced in the **ionisation chamber**.

2. The ionization chamber.

In this chamber, the vapourised sample is subjected to a beam of fast moving electrons emitted by a hot filament. These electrons bombard the atoms of the vapourised sample from which 1 or 2 electrons are removed to form positive ions.



3. The acceleration chamber.

The positive ions produced from the ionisation chamber are accelerated by a strong electric field of varying potentials such that only positive ions with the same velocity/kinetic energy but with different mass-charge ratio will pass through to the magnetic field.

4. The deflection chamber.

The magnetic field then deflects the ions according to their mass-charge ratio. The strength of the magnetic field is varied such that ions of the same mass-charge ratio are focused onto the detector.

5. The detector, amplifier and recorder

The ions are changed into sizeable electric currents which are sent to the amplifier for fine tuning and then to the recorder where they are recorded into peaks that show relative intensities of ions of a particular mass falling at the detector at that instant.

A mass spectrum is thus obtained consisting of a series of peaks of variable intensity to which mass/charge ratio (m/e) values can be assigned.

N.B

1. *If the sample introduced was that of an element, its relative atomic mass(R.A.M) can be obtained by the formula;*

$$R.A.M = \sum \text{Relative isotopic mass} \times \text{proportion of isotope}$$

2. *For organic molecules, the mass spectrum consists of a series of peaks, one corresponding to the parent ion and the others to fragment ions produced by the ionization process. Different molecules can be identified by their characteristic pattern of lines.*

Uses of a mass spectrometer

1. Mass spectrometers are used for accurate measurements of relative atomic mass.
2. Measuring relative molecular masses, particularly for carbon compounds.
3. For determining number of isotopes present in an element and analysis of isotopic abundance.
4. It can also be used to identify structures of organic compounds.
An organic compound bombarded with electrons forms a number of fragment ions. (Ethane (C_2H_6), for example, might form; $C_2H_6^+$, $C_2H_5^+$, CH_2^+ , C^+ , H^+ , etc). The relative proportions of different types of ions are used to find the structure of new compounds. The characteristic spectrum can also identify compounds by comparison with standard spectra.
5. Analysis of mixtures.
6. Detection of labeled atoms for example ^{18}O in radioactive tracing.
7. In forensic science. This is because it requires very small amount of the sample and usually the size of the sample received by forensic scientists at the scene of crime is very small. A sample of about $10^{-12} g$ can give a mass spectrum. Specimens left at the scene of crime can be compared by mass spectrometry with drugs or fibres found with a suspect.

Advantages of a mass spectrometer over other methods of determining atomic or molecular mass

1. It gives more accurate values
2. Uses a smaller quantity of the sample

The mass spectrum

A mass spectrum is a plot of percentage abundance or relative intensity against mass to charge ratio of the ions separated in a mass spectrometer.

The mass to charge ratio is however numerically equal to the mass of the ion since most of the ions formed in a mass spectrometer have a single charge.

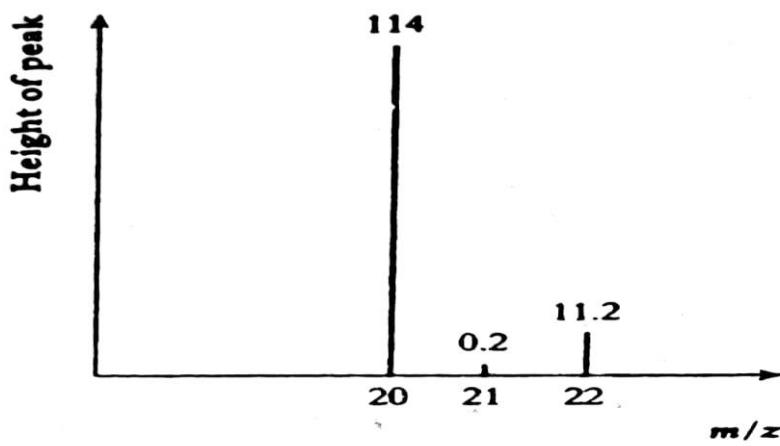
Interpreting a mass spectrum

The mass spectrum is usually has vertical lines and each vertical line represents an ion having a specific mass-to-charge ratio (m/z) and the length of the line indicates the relative abundance of the ion.

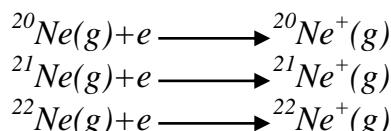
Relative abundance refers to the relative intensity of each isotope of an element represented as a ratio or percentage.

The tallest line is assigned an abundance of 100 and is referred to as the **base peak**. The intensities of the other ions are measured relative to this line.

Consider the mass spectrum for neon below;



According to this spectrum, there are three stable isotopes of neon. These include neon-20(^{20}Ne), neon-21(^{21}Ne) and neon-22 (^{22}Ne). The peaks at 20, 21 and 22 are due to the ions $^{20}\text{Ne}^+$, $^{21}\text{Ne}^+$ and $^{22}\text{Ne}^+$ respectively. These ions are formed by bombardment of the gaseous atoms by electrons as shown below;



The height of each peak is related to the relative abundance of each isotope of neon.

${}^{20}\text{Ne}^+$ has the highest peak so ${}^{20}\text{Ne}$ is the most abundant isotope.

${}^{21}\text{Ne}^+$ has the lowest peak so ${}^{21}\text{Ne}$ is the least abundant isotope.

The relative atomic mass of neon can be obtained using the mass spectrum.

The percentage abundances (proportion of isotope) should be obtained first

$$\text{Total height} = 114 + 0.2 + 11.2 = 125.4$$

$$\text{Percentage abundance of Neon - 20} = \left(\frac{114}{125.4} \times 100 \right) = 90.91$$

$$\text{Percentage abundance of Neon - 21} = \left(\frac{0.2}{125.4} \times 100 \right) = 0.16$$

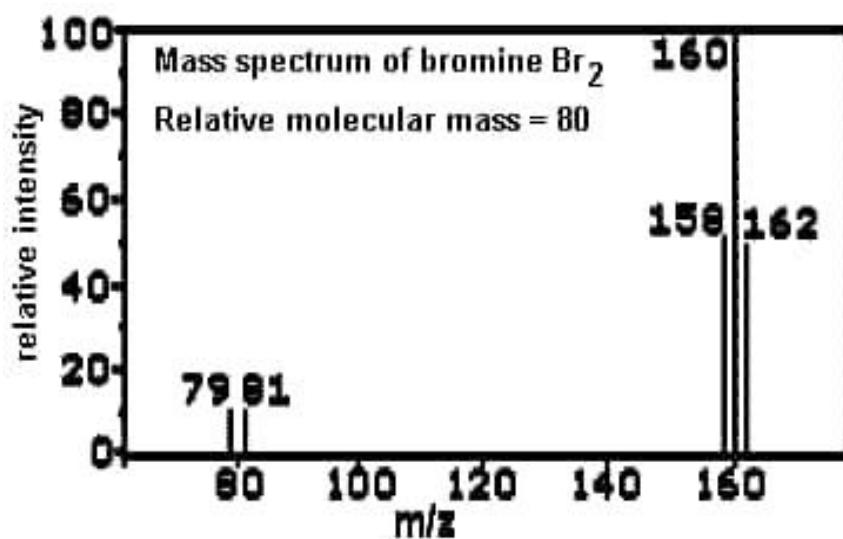
$$\text{Percentage abundance of Neon - 22} = \left(\frac{11.2}{125.4} \times 100 \right) = 8.93$$

$$R.A.M = \sum \text{Relative isotopic mass} \times \text{proportion of isotope}$$

$$R.A.M = (20 \times 90.91/100) + (21 \times 0.16/100) + (22 \times 8.93/100)$$

$$R.A.M = 20.18$$

Consider the mass spectrum for bromine below;



The spectrum has five peaks at mass-to-charge ratios 79, 81, 158, 160 and 162.

The first two peaks of almost equal height correspond to the ions $[{}^{79}\text{Br}]^+$ and $[{}^{81}\text{Br}]^+$ respectively. The two peaks are almost of equal height because bromine-79 and bromine-81 have almost the same abundance.

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The three more peaks are due to ionisation of molecular bromine and each peak corresponds to a specific diatomic ion as shown in the table below.

<i>Peak at m/z value of;</i>	<i>Formula of ion</i>
158	$[{}^{79}\text{Br} - {}^{79}\text{Br}]^+$
160	$[{}^{79}\text{Br} - {}^{81}\text{Br}]^+$
162	$[{}^{81}\text{Br} - {}^{81}\text{Br}]^+$

To determine the relative atomic mass of bromine, the monoatomic peaks are used as shown below.

Since the peaks are almost equal in length they are approximately in a ratio 1:1

$$\text{Total ratio} = 1 + 1 = 2$$

$$\text{Percentage abundance of Bromine - 79} = \left(\frac{1}{2} \times 100 \right) = 50$$

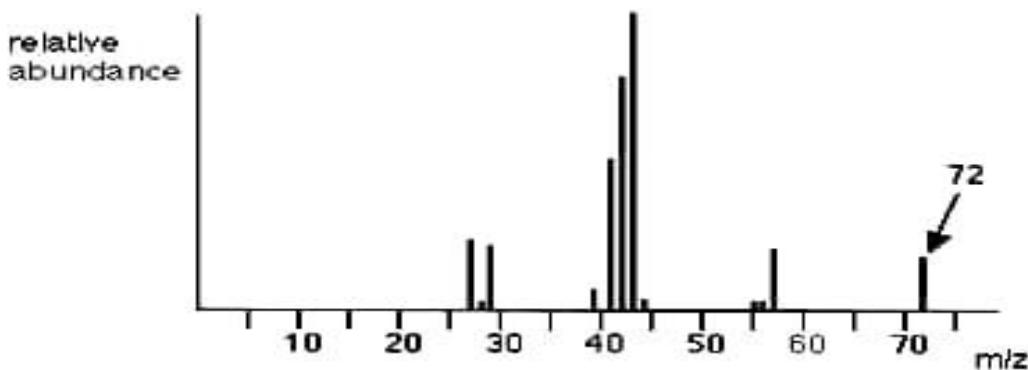
$$\text{Percentage abundance of Bromine - 81} = \left(\frac{1}{2} \times 100 \right) = 50$$

$$R.A.M = \sum \text{Relative isotopic mass} \times \text{proportion of isotope}$$

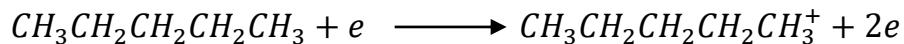
$$R.A.M = \left(\frac{(79 \times 50) + (81 \times 50)}{100} \right)$$

$$R.A.M = 80$$

Consider the mass spectrum below for pentane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$)



The largest mass-to-charge ratio value is 72. The line at this m/z represents the original molecular ion, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3^+$. It is formed by the reaction:



This largest value always gives the relative molecular mass of the compound. This represents the largest ion going through the mass spectrometer. The molecular mass of the compound is therefore 72.

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The longest line represents the most abundant ion formed by pentane which is at a m/z of 43. By simple calculation this ion must have 3 carbon atoms and not more. This gives a mass of 36. The remaining mass of 7 corresponds to the mass of 7 hydrogen atoms. Therefore this ion is $CH_3CH_2CH_2^+$. It is formed by cleavage of a carbon-carbon bond in the original molecular ion.

The use of a mass spectrum

1. It can be used to determine the number of isotopes of an element
2. To calculate the relative atomic mass of an element
3. To identify the relative abundance of particular isotopes
4. To elucidate the structure of an organic compound

Average atomic mass

This is the sum of the masses of the isotopes of an element, each multiplied by its natural abundance.

$$\text{Average atomic mass} = \frac{\sum fm}{\sum f}$$

where f is the natural abundance of the isotope

M is the mass number of the isotope

For example chlorine has two isotopes chlorine-35 and chlorine-37 of percentage abundances 75.77 and 24.23 respectively. Its average atomic mass can be obtained by the formula;

$$\begin{aligned}\text{Average atomic mass} &= \frac{\sum fm}{\sum f} \\ \text{Average atomic mass} &= \left(\frac{(75.77 \times 35) + (24.23 \times 37)}{100} \right) \\ \text{Average atomic mass} &= 35.48 \text{ amu}\end{aligned}$$

Relative atomic mass(Ar)

The relative atomic mass of an element is the ratio of the average mass of its naturally occurring atoms to $\frac{1}{12}$ th of the mass of an atom of the carbon-12 isotope.

or

The mass of an atom in grams on scale on which the mass of the carbon-12 isotope is 12 grams.

$$\text{Relative atomic mass}(A_r) = \frac{\text{average mass of atom}}{\frac{1}{12} \times \text{mass of } {}^{12}_6C}$$

Relative molecular mass(M_r)

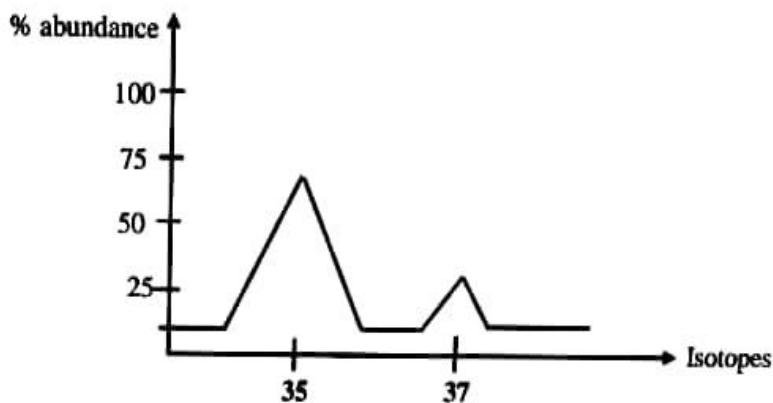
Relative is the average mass of one molecule of a compound to $\frac{1}{12}$ th of the mass of an atom of the carbon-12 isotope.

$$\text{Relative molecular mass} (M_r) = \frac{\text{mass of one molecule of a compound}}{\frac{1}{12} \times \text{mass of } {}^{12}_6\text{C}}$$

More calculations involving data from mass spectrometry

Examples

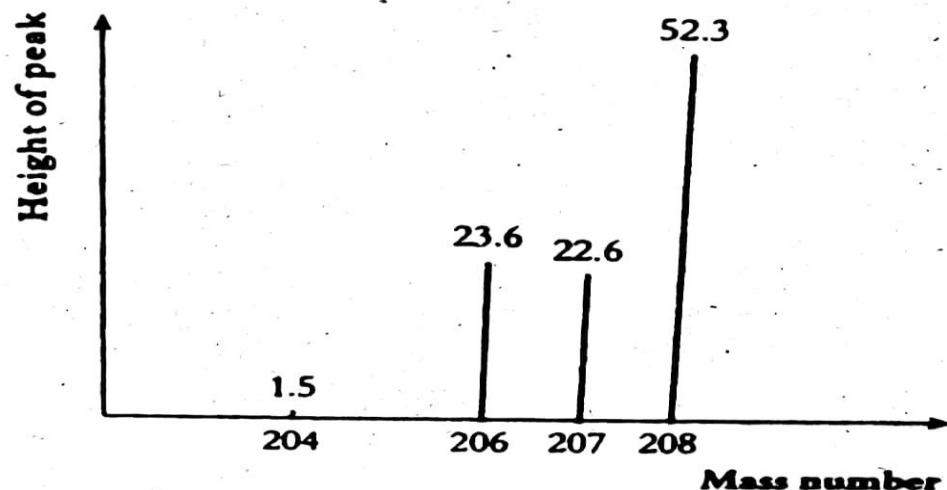
1. The figure below shows a mass spectrum for chlorine.



Determine the relative atomic mass of chlorine

$$\begin{aligned} R.A.M &= \sum \text{Relative isotopic mass} \times \text{proportion of isotope} \\ R.A.M &= (35 \times 75/100) + (37 \times 25/100) \\ R.A.M &= 35.5 \end{aligned}$$

2. The figure below shows the mass spectrum of lead. The heights of the peaks and the mass numbers of the isotopes are shown on the figure.
 - (a) Calculate the relative atomic mass of lead.
 - (b) Explain why the peaks have different heights.



$$(a) \text{Total height} = 1.5 + 23.6 + 22.6 + 52.3 = 100$$

$$\text{Percentage abundance of lead - 204} = \left(\frac{1.5}{100} \times 100 \right) = 1.5$$

$$\text{Percentage abundance of lead - 206} = \left(\frac{23.6}{100} \times 100 \right) = 23.6$$

$$\text{Percentage abundance of lead - 207} = \left(\frac{22.6}{100} \times 100 \right) = 22.6$$

$$\text{Percentage abundance of lead - 208} = \left(\frac{52.3}{100} \times 100 \right) = 52.3$$

$$R.A.M = \sum \text{Relative isotopic mass} \times \text{proportion of isotope}$$

$$R.A.M = (204 \times 1.5/100) + (206 \times 23.6/100) + (207 \times 22.6/100) + (208 \times 52.3/100)$$

$$R.A.M = 207.242$$

(b) *The peaks have different heights because the four isotopes have different percentage abundances. The abundances are in the order; lead - 208 > lead - 206 > lead - 207 > lead - 204*

3. The relative atomic mass of neon is 20.18. Naturally occurring neon has two isotopes; Neon-20 and Neon-22.

(a) Calculate the percentage abundance of the isotopes.

(b) Calculate the number of neon-22 atoms in a 13.2g sample of naturally occurring neon.

(a) let the percentage abundance of neon - 20 be y
 The percentage abundance of neon - 22 = $(100 - y)$

$$R.A.M = \sum \text{Relative isotopic mass} \times \text{proportion of isotope}$$

$$20.18 = (20 \times \frac{y}{100}) + \left(22 \times \frac{100-y}{100} \right)$$

$$20.18 = 2200 - 2y$$

$$y = 91$$

The percentage abundance of neon-20 is 91 and that of neon-22 is 9

$$(b) \text{ number of moles on neon in } 13.2 \text{ g} = \frac{13.2}{20.18} = 0.654$$

$$\begin{aligned} \text{number of neon atoms in } 0.654 \text{ mole} &= 0.654 \times 6.022 \times 10^{23} \\ &= 3.938 \times 10^{23} \text{ atoms} \end{aligned}$$

$$\begin{aligned} \text{number of neon - 22 atoms present} &= \frac{9}{100} \times 3.938 \times 10^{23} \\ &= 3.544 \times 10^{22} \text{ atoms.} \end{aligned}$$

4. The table below shows the information from a mass spectrum sample of lead.

Isotopic mass	Detector current(mA)
204	0.16
206	2.72
207	2.50
208	5.92

Calculate the relative atomic mass of lead.

$$\text{Total current} = 0.16 + 2.72 + 2.50 + 5.92 = 11.3 \text{ mA}$$

$$\text{Percentage abundance of lead - 204} = \left(\frac{0.16}{11.3} \times 100 \right) = 1.42$$

$$\text{Percentage abundance of lead - 206} = \left(\frac{2.72}{11.3} \times 100 \right) = 24.07$$

$$\text{Percentage abundance of lead - 207} = \left(\frac{2.50}{11.3} \times 100 \right) = 22.12$$

$$\text{Percentage abundance of lead - 208} = \left(\frac{5.92}{11.3} \times 100 \right) = 52.40$$

$$R.A.M = \sum \text{Relative isotopic mass} \times \text{proportion of isotope}$$

$$R.A.M = (204 \times \frac{1.42}{100}) + (206 \times \frac{24.07}{100}) + (207 \times \frac{22.12}{100}) + (208 \times \frac{52.4}{100})$$

$$\mathbf{R.A.M = 207.26}$$

5. The mass spectrum of dichloromethane (CH_2Cl_2) shows three peaks at mass-to-charge ratios of 84, 86 and 88.Explain why the three peaks arise as stated

Chlorine has two isotopes; chlorine-35 and chlorine-37.

The peak at 84 is due to $CH_2^{35}Cl^{35}Cl$.

The peak at 86 is due to $CH_2^{35}Cl^{37}Cl$.

The peak at 88 is due to $CH_2^{37}Cl^{37}Cl$.

Questions

1. (a) Describe how in a mass spectrometer the ions are;

- (i) formed
- (ii) accelerated
- (iii) separated
- (iv) detected

(b) Bromine has two isotopes ^{79}Br and ^{81}Br and the mass spectrum of bromine shows peaks at m/e of 158, 160 and 162. Write the formula(e) of the ion(s) corresponding to the peak(s)

<i>Peak at m/Z value of</i>	<i>Formula of ion</i>
158	
160	
162	

(c) By calculation, deduce which of the isotopes in (b) above is most abundant if the relative atomic mass of bromine is 79.9.

(d) Sketch a mass spectrum for bromine.

2. (a) With the aid of a labeled diagram, describe how a mass spectrometer can be used to determine;

(i) Molecular mass

(ii) Isotopic ratio

(c) When water was analyzed using a mass spectrometer, peaks occurred corresponding to the relative masses of 1, 3, 4, 17, 18, 19 and 20. Give one formula of an ion in each case responsible to the peaks shown.

PRIMARY AND SECONDARY STANDARDS

A primary standard is a substance that is analytically pure and chemically stable such that a known mass of it when weighed is the exact mass that dissolves in water to form a standard solution.

A standard solution is a solution whose concentration is accurately known i.e. one that contains a known amount of solute in a known volume of solution.

A primary standard can be used directly for the preparation of standard solutions without reference to some other concentration standard.

A primary standard has the following characteristics;

1. Readily soluble in water at room temperature such that all the weighed mass goes into solution.
2. It should have a fairly high molar mass such that weighing errors are minimized.
3. It should be obtainable in a pure state such that the quantity weighed indicates the actual mass present in the standard solution prepared.
4. It should not be deliquescent, efflorescent or hygroscopic such that the mass weighed is exactly that of the pure sample
5. It must be stable at ordinary temperatures (should not decompose easily) such that its chemical nature is not altered.
6. It should be able to undergo stoichiometric and instantaneous reactions such that titration errors are minimized.

Examples of common primary standards include;

Name of primary standard	Formula
Anhydrous sodium carbonate	Na_2CO_3
Sodium hydrogencarbonate	$NaHCO_3$
Ethane-1,2-dioic acid(Oxalic acid)	$H_2C_2O_4 \cdot 2H_2O$
Sodium oxalate	$Na_2C_2O_4$
Butane-1,4-dioic acid	$HOOCH_2CH_2COOH$
Disodium tetraborate decahydrate (Borax)	$Na_2B_4O_7 \cdot 10H_2O$
Potassium iodate	KIO_3
Sodium bromate	$NaBrO_3$

Most of the other substances make solutions of approximately known concentrations which must be standardized against a primary standard. These are called **secondary standards**.

A secondary standard is a substance that is not analytically pure and chemically unstable such that a known mass of it when weighed and dissolved in water makes solutions of approximate concentrations hence must be standardized by titration.

Examples of secondary standards include

Name of secondary standard	Formula	Suitable substance to standardise the secondary standard
Sodium hydroxide	$NaOH$	Oxalic acid
Sulphuric acid	H_2SO_4	Anhydrous sodium carbonate
Hydrochloric acid	HCl	Disodium tetraborate decahydrate (Borax) Anhydrous sodium carbonate
Nitric acid	HNO_3	Anhydrous sodium carbonate
Potassium manganate(VII)	$KMnO_4$	Sodium oxalate Oxalic acid
Sodium thiosulphate pentahydrate	$Na_2S_2O_3 \cdot 5H_2O$	Potassium iodate Potassium bromate

Sodium hydroxide which cannot be used to make a standard solution because;

- During weighing, it absorbs water vapour from the air.*
- It also reacts with carbon dioxide in the air to form sodium carbonate.*

Sulphuric acid and hydrochloric acid are not suitable for use as primary standards because the concentration of their concentrated solutions are not accurately known.

Nitric acid is not a suitable primary standard because it always contains a little nitrous acid which has a destructive action on so many acid-base indicators.

Potassium manganate(VII) is commonly used in volumetric analysis because;

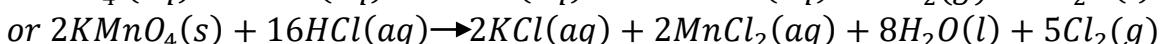
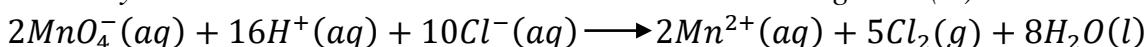
- It forms coloured solutions so it acts as own indicator*
- It oxidises a wide range of substances*
- It is not affected by the atmosphere while being weighed*
- It is fairly soluble in water*
- Has a high molecular mass hence minimising weighing errors*

However, it is not a good primary standard because;

- It is never obtained free from manganese(IV) oxide impurity*
- It is easily reduced by even weak reducing agents since it is a strong oxidising agents*

Potassium manganate(VII) can be acidified by sulphuric acid but neither acidified with hydrochloric acid nor nitric acid during titration because;

It oxidises hydrochloric acid to chlorine as it is reduced to manganese(II) ions.

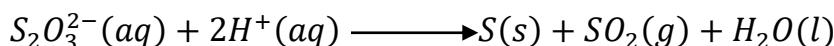


Nitric acid is itself an oxidising agent hence interferes with the oxidising ability of manganate(VII) ions.

Sodium thiosulphate cannot be used as a primary standard because;

1. *It is efflorescent*
2. *When its solution is left in air it forms a cloudy solution and a yellow solid deposit.*

This is because a solution of sodium thiosulphate absorbs carbon dioxide from the air which dissolves to form a weak carbonic acid. The acidic medium promotes disproportionation of thiosulphate ions into Sulphur dioxide and Sulphur.



Preparation of standard solutions by weighing and dissolving in water

Preparing a standard solution of anhydrous sodium carbonate (for example 250cm³ of 0.2M sodium carbonate solution)

- (i) **Calculate the mass of anhydrous sodium carbonate needed to make the standard solution.**

250cm³ of 0.2M sodium carbonate solution

$$\text{number of moles of } Na_2CO_3 = \left(\frac{250 \times 0.2}{1000} \right) = 0.05 \text{ moles}$$

$$\text{Molar mass of } Na_2CO_3 = (23 \times 2) + (12 \times 1) + (3 \times 16) = 106g$$

$$1 \text{ mole of } Na_2CO_3 \text{ weighs } 106g$$

$$0.05 \text{ moles weigh } \left(\frac{0.05 \times 106}{1} \right) g$$

$$= 5.3g \text{ of } Na_2CO_3$$

- (ii) Weigh a clean weighing bottle, and record its mass (to 1 or 2 decimal places). Use a clean spatula and add pure anhydrous sodium carbonate to the weighing bottle until the mass is the total mass of the weighing bottle and that of anhydrous sodium carbonate required.

Sample Results:

Mass of anhydrous sodium carbonate + weighing bottle 45.30 g

Mass of empty weighing bottle 40.00 g

Mass of anhydrous sodium carbonate used 5.30 g

- (iii) Transfer the weighed mass of anhydrous sodium carbonate carefully into a clean beaker. Using a wash bottle of distilled water, add a small volume of water so that

- all the washings run into the beaker. Add about 100 cm³ of and stir with a glass rod until all the solid has dissolved.
- (iv) Pour all the solution carefully through a filter funnel into a graduated flask (volumetric flask). Wash all the solution out of the beaker and off the glass rod to the volumetric flask.
 - (v) Add distilled water until the level of the solution is about 2 cm below the graduation mark (in this case 250cm³). Add the rest of the distilled water drop by drop from a dropping pipette until the bottom of the meniscus is level with the graduation mark when viewed at eye level.
 - (vi) Label the solution as required.

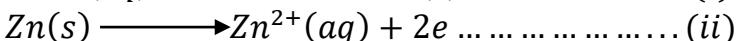
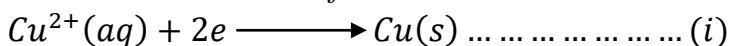
Questions:

- (a) Why is sodium hydrogencarbonate a suitable substance for preparing standard solutions?
- (b) Calculate the mass of sodium hydrogencarbonate required to prepare 500cm³ of a 0.01M solution.
- (c) Describe how you would prepare the solution in (b) above as accurately as possible.

REDOX REACTIONS (OXIDATION-REDUCTION REACTIONS)

Oxidation numbers are very important in deciding whether a reaction is reduction, oxidation and therefore a redox one.

Consider the half-cell reactions below



In the first half cell reaction, copper(II) ions are converted to copper. The subsequent change in oxidation number is therefore from +2 to 0. This is evident that the oxidation number has decreased. Electrons are also gained in the reaction. This is therefore a reduction reaction.

Reduction is therefore a reaction in which the oxidation number of an element is decreased

or

A reaction in which electrons are gained

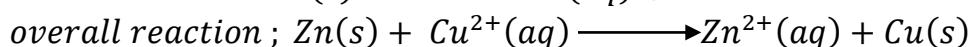
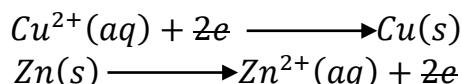
In the second half cell reaction, zinc is converted to zinc ions. The subsequent change in oxidation number is therefore from 0 to +2. This is evident that the oxidation number has increased. Electrons are also lost in the reaction. This is therefore an oxidation reaction.

Oxidation is a reaction in which the oxidation number of an element is increased

or

A reaction in which electrons are lost

When the combined cell of the two reactions (i) and (ii) is made, an overall reaction can be generated by crossing out the electrons.



This reaction involves Zn , oxidation number 0 , being converted to Zn^{2+} , oxidation number +2. Cu^{2+} , oxidation number +2 is converted to Cu , oxidation number, 0

Zinc has been oxidised and copper has been reduced. This is therefore a redox reaction.

A redox reaction is a reaction in which oxidation and reduction take place simultaneously.

The zinc metal loses (donates) the electrons that are gained (accepted) by copper(II) ions. Any substance that donates electrons is a reducing agent and any substance that accepts electrons is an oxidizing agent.

An oxidizing agent is an acceptor of electrons

A reducing agent is a donor of electrons

The mnemonics below can be used to remember the concepts well.

OIL RIG – Oxidation is loss of electrons, Reduction is gain of electrons

LEORA says GEROA- loss of electrons is oxidation (Reducing agent). Gain of electrons is reduction (Oxidising agent)

Common oxidizing species and their reduction products				
No.	Oxidizing agent	Colour	Reduction product	Colour
1	$\text{MnO}_4^-(aq)$	Purple solution	$\text{Mn}^{2+}(aq)$	Colourless
2	$\text{Cr}_2\text{O}_7^{2-}(aq)$	Orange solution	$\text{Cr}^{3+}(aq)$	Green
3	$\text{MnO}_2(s)$	Black solid	$\text{Mn}^{2+}(aq)$	Colourless
4	$\text{ClO}^-(aq)$	Yellow solution	$\text{Cl}^-(aq)$	
5	$\text{ClO}_3^-(aq)$	Yellow solution	$\text{Cl}^-(aq)$	
6	$\text{PbO}_2(s)$	Dark brown solid	$\text{Pb}^{2+}(aq)$	Colourless
7	$\text{IO}_3^-(aq)$	Colourless	$\text{I}_2(aq)$	Brown
8	$\text{H}_2\text{SO}_4(aq)$	Colourless	$\text{SO}_2(g)$	Colourless gas
9	$\text{HNO}_3(aq)$	Colourless	$\text{NO}_2(g)$	Brown fumes
10	$\text{H}_2\text{O}_2(aq)$	Colourless	$\text{H}_2\text{O}(l)$	Colourless
11	$\text{Fe}^{3+}(aq)$	Yellow or brown solution	$\text{Fe}^{2+}(aq)$	Green
12	$\text{Sn}^{4+}(aq)$	Colourless	$\text{Sn}^{2+}(aq)$	Colourless

13	$I_2(aq)$	Brown	$I^-(aq)$	
14	$Br_2(aq)$	Reddish brown	$Br^-(aq)$	
15	$Cl_2(g)$	Greenish yellow gas	$Cl^-(aq)$	

- The first ten species act as oxidizing agents in acidic medium and the species 11-15 gain electrons in the redox reactions in which they behave as oxidizing agents.
- The colours of some species in solutions have not been indicated because the colour of solutions in which they exist depend on the colour of cations present.
- Below are half-cell reactions for some of the species showing the electron gain.
- In each of the reactions, the electrons balance the total charge on the left hand side and on the right hand side.

Some of the half-cell reactions are shown below. Try to write out half-cell reactions for the other species on your own in the provided space below.

- $MnO_4^-(aq) + 8H^+(aq) + 5e \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
- $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
- $MnO_2(s) + 4H^+(aq) + 2e \rightarrow Mn^{2+}(aq) + 2H_2O(l)$
- $ClO_3^-(aq) + 6H^+(aq) + 6e \rightarrow Cl^-(aq) + 3H_2O(l)$
- 5.
- 6.
- 7.

Common reducing agents and their oxidation products

No.	Oxidizing agent	Colour	Reduction product	Colour
1	$SO_3^{2-}(aq)$		$SO_4^{2-}(aq)$	
2	$NO_2^-(aq)$		$NO_3^-(aq)$	
3	$Cr_2O_7^{2-}(aq)$	Orange solution	$CrO_5(aq)$	Blue solution
4	$CrO_4^{2-}(aq)$	Yellow solution	$CrO_5(aq)$	Blue solution
5	$Mn^{2+}(aq)$	Pale pink solution	$MnO_4^-(aq)$	Purple solution
6	$Cl^-(aq)$		$Cl_2(g)$	Greenish yellow gas
7	$Br^-(aq)$		$Br_2(aq)$	Reddish brown solution
8	$I^-(aq)$		$I_2(aq)$	Brown solution
9	$H_2S(g)$	Colourless gas with a rotten egg smell	$S(s)$	Yellow solid
10	$H_2O_2(aq)$	Colourless solution	$O_2(g)$	Colourless gas
11	NH_2NH_2	Colourless liquid	$N_2(g)$	Colourless gas
12	$Cu(s)$	Brown solid	$Cu^{2+}(aq)$	Blue solution
13	$Fe^{2+}(aq)$	Green solution	$Fe^{3+}(aq)$	Yellow or Brown solution
14	$S_2O_3^{2-}(aq)$	Colourless solution	$S_4O_6^{2-}(aq)$	Colourless solution
15	$Sn^{2+}(aq)$	Colourless solution	$Sn^{4+}(aq)$	Colourless solution

- The first five species act as reducing agents in solution (presence of water)
- The colour of some species in solutions have not been indicated because the colour of solutions in which they exist depend on the colour of cations present.
- Below are half-cell reactions for some of the species showing the electron loss.
- In each of the reactions, the electrons balance the total charge on the left hand side and on the right hand side.

Some of the half-cell reactions are shown below. Try to write out half-cell reactions for the other species on your own in the provided space below.

- $SO_3^-(aq) + H_2O(l) \longrightarrow SO_4^-(aq) + 2H^+(aq) + 2e$
- $NO_2^-(aq) + H_2O(l) \longrightarrow NO_3^-(aq) + 2H^+(aq) + 2e$
- $Cr_2O_7^{2-}(aq) + 3H_2O(l) \longrightarrow 2CrO_5(aq) + 6H^+(aq) + 8e$
- $CrO_4^{2-}(aq) + H_2O(l) \longrightarrow CrO_5(aq) + 2H^+(aq) + 4e$

Deriving equations for redox reactions

General steps taken

1. Identify the reducing and oxidizing species in the redox reaction. The oxidizing species is normally that one whose central atom is in the highest oxidation state such that it is reduced to a lower oxidation state. The reducing agent is that one whose central atom exists in the lowest oxidation state such that is oxidised to a higher oxidation state.
2. Write well balanced half-cell reactions for the oxidation reduction processes. Make sure the equation is balanced both in terms of atoms and charge.
The atoms are balanced the usual was of balancing any equation and the charge is balanced in terms of electrons.
You should note that in the reduction half equation, electrons are always on the left hand side and in the oxidation half equation they are on the right hand side.
3. Multiply each of the half equations by suitable factors so as to eliminate the electrons which should never appear in the overall equation. Once electrons still appear in this equation, then something is not correct.
4. Note that after step 3, the number of electrons in each of the equations is equal. It's now time to cross out everything that appears on the left hand side of one equation and on the right hand side of the other. Species to always consider for this step are electrons, H⁺ and

H₂O. The hydrogen ions or water species in one equation are normally more than those in the other. Subtraction is done and the remaining hydrogen ions or water molecules written on the side which originally had more of the species.

5. *The overall equation is now written with all the species on the left hand side maintained there as well as those on the right hand side.*
6. *Note that for examination purposes space is not enough to do all this hence side work is done and only overall equation written in the space provided. Writing other equations other than overall equation may lead to loss of marks.*

If the observation is as well required, then it is written first before the general equation.

Examples

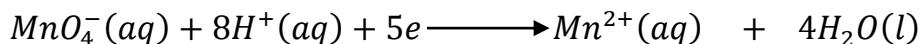
State what would be observed and explain your observation when;

1. Concentrated hydrochloric acid was added to potassium manganate(VII) solution

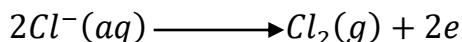
Step 1; Oxidizing species is MnO_4^- (aq) from potassium manganate(VII) and reducing species is Cl^- (aq) from hydrochloric acid.

Step 2;

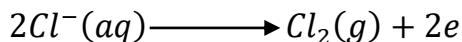
Reduction half equation;



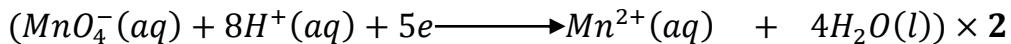
Oxidation half equation;



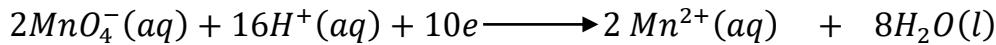
Step 3;



The first equation is multiplied by 2 and the second equation by 5. This is intended to make the number of electrons in each equation the same (10). Also note that these factors do not multiply only the electrons but also every other species in the equation.

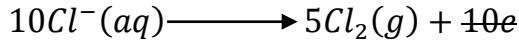
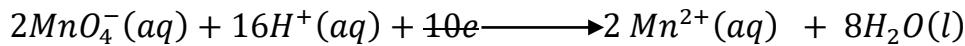


This now gives;



Step 4;

The electrons are equal and crossed out.

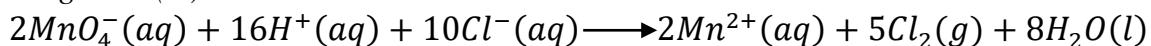


Step 5;

Observation; *The purple solution turns colourless and bubbles of a greenish yellow gas evolved.*

Explanation;

Potassium manganate(VII) oxidises hydrochloric acid to chlorine as it is reduced to manganese(II) ions.



2. Hydrogen sulphide gas was bubbled through acidified potassium dichromate(VI) solution.

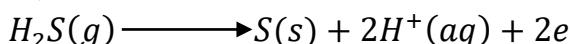
Step 1; Oxidizing species is $\text{Cr}_2\text{O}_7^{2-}(aq)$ from potassium dichromate and reducing species is H_2S

Step 2;

Reduction half equation;

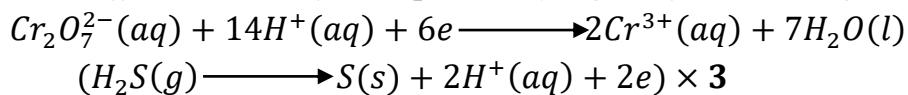


Oxidation half equation;

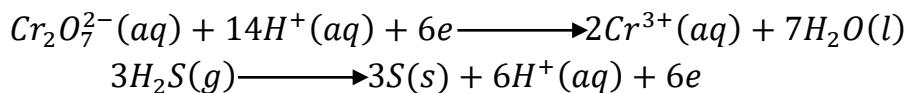


Step 3;

The first equation is left as it is but the second equation multiplied by 3. This is intended to make the number of electrons in each equation the same (6). If you choose to multiply the first equation by 2 and the second by 6. Then you will have to divide the stoichiometric coefficients in the final equation by a given factor through out.

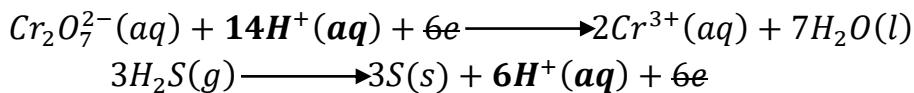


This now gives;



Step 4;

The electrons are equal and crossed out. The 6H^+ are subtracted from the 14H^+ to give 8H^+ on the left hand side.

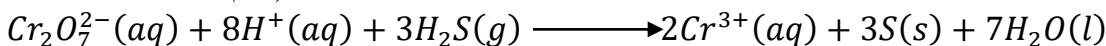


Step 5;

Observation; *The orange solution turns green and a yellow solid deposited.*

Explanation;

In acidic medium, dichromate ions oxidise hydrogen sulphide to Sulphur as they are reduced to chromium(III) ions.

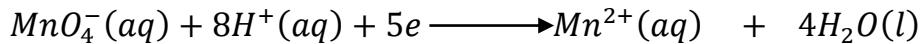


3. Hydrazine was added to acidified potassium manganate(VII) solution

Step 1; Oxidizing species is MnO_4^- (aq) from potassium manganate(VII) and reducing species is NH_2NH_2 (aq).

Step 2;

Reduction half equation;



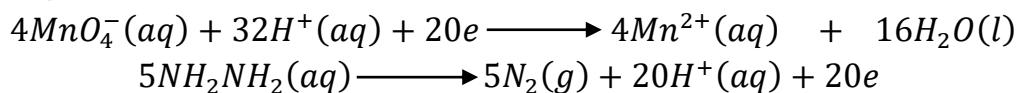
Oxidation half equation;



Step 3;

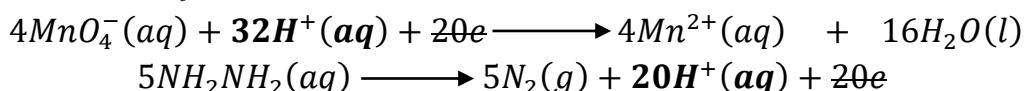
The first equation is multiplied by 4 and the second equation multiplied by 5. This is intended to make the number of electrons in each equation the same (20).

This now gives;



Step 4;

The electrons are equal and crossed out. The $20H^+$ are subtracted from the $32H^+$ to give $12H^+$ on the left hand side.

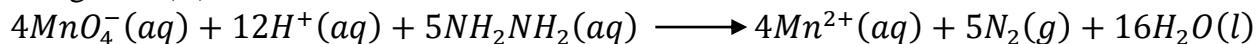


Step 5;

Observation; The purple solution turns colourless and bubbles of a colourless gas evolved.

Explanation;

Manganate(VII) ions oxidise hydrazine to nitrogen gas as they are reduced to manganese(II) ions.

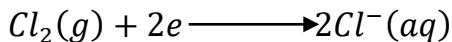


4. Chlorine was bubbled through potassium nitrite solution.

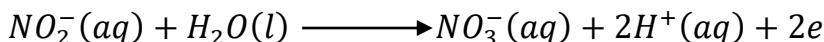
Step 1; Oxidizing species is $Cl_2(g)$ and reducing species is $NO_2^-(aq)$.

Step 2;

Reduction half equation;



Oxidation half equation;

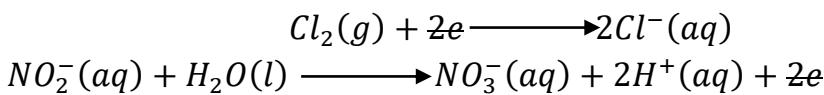


Step 3;

Since the number of electrons in both equations is the same, the overall equation can be written right away

Step 4;

The electrons are equal and crossed out.



Step 5;

Observation; Greenish yellow gas dissolved and a colourless solution is formed.

Explanation;

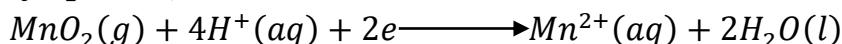
Chlorine oxidises nitrate ions to nitrite ions and itself reduced to chloride ions. $\text{Cl}_2(g) + \text{NO}_2^-(aq) + 3\text{H}_2\text{O}(l) \longrightarrow 2\text{Cl}^-(aq) + \text{NO}_3^-(aq) + 2\text{H}^+(aq)$

5. Manganese(IV) oxide was added to acidified solution of sodium oxalate and the mixture heated

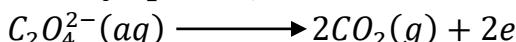
Step 1; Oxidizing species is $\text{MnO}_2(s)$ and reducing species is $\text{C}_2\text{O}_4^{2-}(aq)$.

Step 2;

Reduction half equation;



Oxidation half equation;

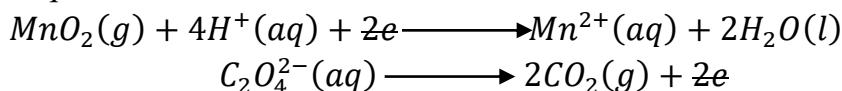


Step 3;

Since the number of electrons in both equations is the same, the overall equation can be written right away

Step 4;

The electrons are equal and crossed out.

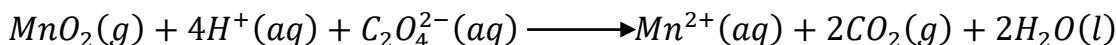


Step 5;

Observation; Black solid dissolved forming a colourless solution and bubbles of a colourless gas

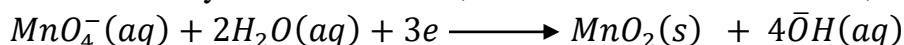
Explanation;

Manganese(IV) oxide oxidises oxalate ions to carbon dioxide and itself reduced to manganese(II) ions.



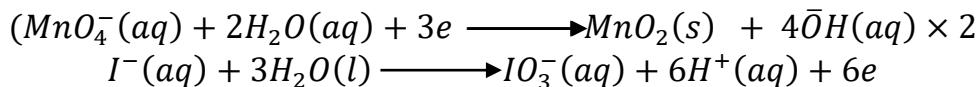
Balancing redox reactions in alkaline media

Although manganate(VII) ions are strongly oxidizing in acidic medium, they can also oxidise in neutral or weakly alkaline medium, in which the half reaction is;

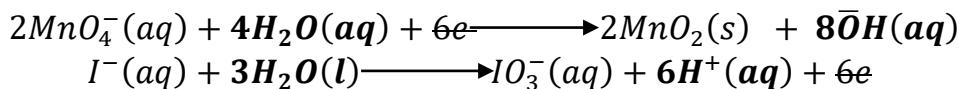


It oxidises potassium iodide to potassium iodate in the alkaline medium

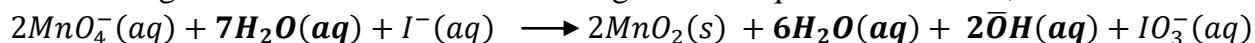
Qn. State what would be observed and write an equation for the reaction when potassium iodide was added to an alkaline solution of potassium manganate(VII)



Then;



On crossing out the electrons and combining the two equations we have;

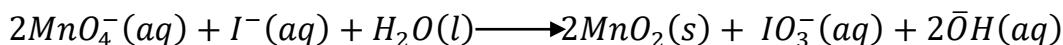


The **6H₂O(aq)** on the right hand side are as a result of complete neutralisation of the **6H⁺(aq)** by 6 of the **8OH(aq)** leaving a remainder of **2OH(aq)**. Subtraction leaves only one water molecule on the reactant side.

Observation;

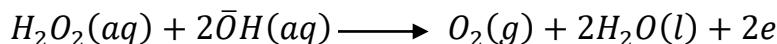
Purple solution forms a colourless solution and black solid deposited.

Equation

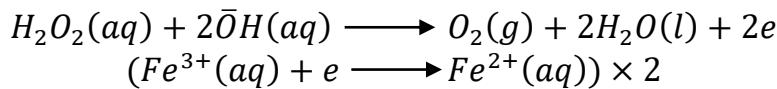


Although hydrogen peroxide is a strong oxidizing agent in acidic medium, it sometimes shows reducing properties depending on the conditions. Thus in alkaline conditions, hydrogen peroxide reduces iron(III) ions to iron(II) ions.

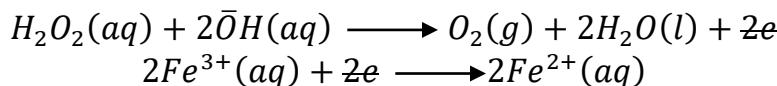
The half reaction is;



Qn. State what would be observed and write an equation for the reaction when Iron(III) chloride was added to an alkaline solution of hydrogen peroxide.

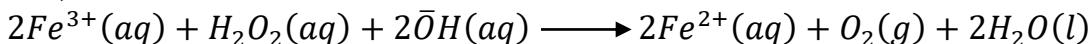


Then;



Observation; Brown solution turns green and bubbles of a colourless gas.

Equation;



Questions

State what would be observed and write equation for the reaction when;

You may try to do them as fast as possible without going through all the steps, this will give you good practice and masterly of the concepts.

1. Sodium bromide solution was added to tin(IV) chloride solution
2. Potassium iodide was added tin(IV) chloride solution
3. Concentrated hydrochloric acid was added to potassium manganate(VII) solution
4. Manganese(IV) oxide was added to hot concentrated hydrochloric acid
5. An acidified solution of hydrogen peroxide was added to manganese(IV) oxide.
6. Concentrated hydrochloric acid was added to lead(IV) oxide and the mixture heated
7. Tin(II) sulphate solution was added to acidified potassium permanganate solution
8. Chlorine was bubbled through iron(II) chloride solution.
9. Hydrogen sulphide gas was bubbled through acidified potassium dichromate(VI) solution.
10. Bromine water was added to iron(II) chloride solution.
11. Hydrazine was added to acidified potassium manganate(VII) solution
12. Tin(II) sulphate solution was added to iron(III) sulphate solution
13. Chlorine was bubbled through potassium nitrite solution.
14. Chlorine gas was bubbled through sodium sulphite.
15. Limited chlorine gas was bubbled through sodium thiosulphate solution.
16. Excess chlorine gas was bubbled through sodium thiosulphate solution.
17. Sulphur dioxide was bubbled through acidified potassium manganate(VII) solution.
18. Sodium sulphite was added to acidified potassium manganate(VII) solution.
19. Iodine solution was added to sodium thiosulphate solution.
20. Chlorine was bubbled through potassium bromide solution
21. Concentrated sulphuric acid was added to solid sodium iodide
22. Hydrogen sulphide gas was bubbled through acidified potassium permanganate solution.
23. Hydrogen peroxide was added to an acidified solution potassium dichromate(VI) solution.
24. Potassium bromide solution was added to concentrated sulphuric acid
25. Sodium iodide was added to acidified potassium chlorate(I) solution.
26. Potassium iodide solution was added to acidified hydrogen peroxide solution.
27. Tin(II) sulphate solution was added to acidified potassium dichromate(VI) solution
28. Potassium sulphite was added to acidified potassium dichromate(VI) solution.
29. Zinc powder was added to iron(III) sulphate solution.
30. Potassium nitrite solution was added to acidified potassium dichromate(VI) solution.
31. Iron(II) sulphate solution was added to acidified potassium dichromate(VI) solution

32. Manganese(IV) oxide was added to acidified solution of sodium oxalate and the mixture heated
33. Iron(II) sulphate solution was added to acidified potassium manganate(VII) solution
34. Acidified potassium peroxodisulphate solution was added to iron(II) sulphate solution
35. Lead(IV) oxide was added to manganese(II) sulphate solution followed by dilute nitric acid and the mixture heated
36. Hydrogen peroxide was added to an acidified solution of iron(II) sulphate.
37. Iron(III) chloride was added to an alkaline solution of hydrogen peroxide.
38. Potassium iodide solution was added to acidified potassium dichromate solution.
39. Potassium iodide was added to an alkaline solution of potassium manganate(VII)
Potassium nitrite was added to acidified potassium permanganate solution.

EMPIRICAL FORMULA, MOLECULAR FORMULA AND PERCENTAGE COMPOSITION BY MASS

The percentage composition by mass of an element or a molecule in a compound

From the formula of a compound and the relative atomic masses of the elements in it, the percentage of each element or molecule in the compound can be determined. This is called percentage composition by mass.

$$\text{Percentage by mass of an element} = \frac{n \times \text{molar mass of an element}}{\text{molar mass of compound}} \times 100\%$$

where n = number of atoms of an element

Examples

1. The Single Superphosphate(SSP) fertilizer is common phosphatic fertilizer chemically known as calcium dihydrogenphosphate. Calculate the percentage of phosphorus in the fertilizer.

$$\begin{aligned}\text{molar mass of } Ca(H_2PO_4)_2 &= (40 \times 1) + (1 \times 4) + (30 \times 2) + (16 \times 8) \\ &= 232g\end{aligned}$$

$$\text{Percentage by mass of } P = \frac{2 \times 30}{232} \times 100 = 25.86\%$$

- 2. State the element with the highest percentage by mass in one mole of copper(II) sulphate-5-water.**

$$\text{molar mass of } CuSO_4 \cdot 5H_2O = (63.5 \times 1) + (32 \times 1) + (16 \times 4) + (18 \times 5) = 249.5g$$

$$\text{Percentage by mass of } Cu = \frac{63.5 \times 1}{249.5} \times 100 = 25.45\%$$

$$\text{Percentage by mass of } S = \frac{32 \times 1}{249.5} \times 100 = 12.83\%$$

$$\text{Percentage by mass of } O = \frac{16 \times (4 + 5)}{249.5} \times 100 = 57.72\%$$

$$\text{Percentage by mass of } H = \frac{1 \times 10}{249.5} \times 100 = 4.00\%$$

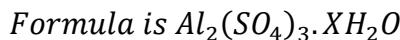
Therefore oxygen has the highest percentage by mass in copper(II) sulphate-5-water.

- 3. Calculate the percentage by mass of water of crystallization in diammonium iron(II) sulphate-6-water, $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$.**

$$\begin{aligned} \text{Molar mass of } (NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O \\ = 2(14 + 2) + (32 \times 1) + (16 \times 4) + (56 \times 1) + (32 \times 1) + (16 \times 4) + (6 \times 18) \\ = 392g \\ \text{Percentage by mass of } H_2O = \frac{6 \times 18}{392} \times 100 = 27.55\% \end{aligned}$$

- 4. A hydrated aluminium sulphate contains 8.1% by mass of aluminium. Calculate the percentage by mass of the water of crystallization in it.**

Let the number of moles of water of crystallisation be x



$$\begin{aligned} \text{molar mass of } Al_2(SO_4)_3 \cdot XH_2O &= (27 \times 2) + (32 \times 3) + (16 \times 12) + (18X) \\ &= 54 + 96 + 192 + 18X \end{aligned}$$

$$\text{molar mass} = (342 + 18X)g$$

$$\text{Percentage by mass of } Al = \frac{(27 \times 2)}{(342 + 18X)} \times 100$$

$$8.1 = \frac{(27 \times 2)}{(342 + 18X)} \times 100$$

$$\frac{8.1}{100} = \frac{(27 \times 2)}{(342 + 18X)}$$

$$2770.2 + 145.8X = 5400$$

$$145.8X = 2629.8$$

$$X = 18$$

$$\text{molar mass} = (342 + 18X) = (342 + 18 \times 18) = 666\text{g}$$

$$\text{Percentage by mass of } H_2O = \frac{18 \times 18}{666} \times 100 = 48.65\%$$

Exercise

1. Calculate the percentage by mass of the named element in each of the following compounds
 - (a) nitrogen in Sodium nitrate
 - (b) nitrogen in Ammonium sulphate
 - (c) magnesium in magnesium nitride
 - (d) bromine in calcium bromide
2. Calculate the percentage of water of crystallization in;
 - (a) sodium carbonate decahydrate
 - (b) Iron(II) sulphate heptahydrate
3. A metal sulphate, $Y_2(SO_4)_3$ contains 28% by mass of metal Y. Determine the relative atomic mass of Y and the relative molecular mass of $Y_2(SO_4)_3$
4. Hydrated iron(III) sulphate, $Fe_2(SO_4)_3 \cdot YH_2O$ contains 19.9% by mass of iron. Find the value of Y.

Empirical formulae and molecular formulae

The empirical formula is the simplest formula that expresses the simplest ratio of the atoms present in a given compound. It is the formula obtained by experimental analysis of a compound and it can be related to a molecular formula only if the molecular weight is known.

The molecular formula simply gives the types and numbers of atoms present. The formula of a compound showing the number and types of the atoms present in one molecule of the compound, but not the arrangement of the atoms. For example, C_2H_6O represents the molecular formula both of ethanol (C_2H_5OH) and methoxymethane (CH_3OCH_3). The molecular formula can be determined only if the molecular mass is known. The molecular mass can be obtained from the following known formulae;

$$(i) \quad \text{Molecular mass} = \text{vapour density} \times 2$$

$$(ii) \quad \text{The ideal gas equation; } PV = nRT \rightarrow PV = \frac{m}{M_r} RT$$

where P is pressure in Pa or Nm^{-2} ,

V is volume in m^3

R is molar gas constant = $8.31\text{JK}^{-1}\text{mol}^{-1}$

T is temperature in Kelvin

m is mass given and M_r is molecular mass

A simplified, well elaborated , illustrative approach to Physical Chemistry

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- (iii) *Graham's law(Rates of diffusion)*
- (iv) *Data from steam distillation*
- (v) *Data from colligative properties.*

The molecular formula can be got from the empirical formula using the relationship;

$$(Empirical\ formula)n = Molecular\ formula$$

where n is number to be determined

Molecular formula can be the same as empirical formula if $n = 1$

Name of compound	Empirical formula	Simplest ratio	Molecular formula	Value of n
Ethanoic acid	CH_2O	1:2:1	$C_2H_4O_2$	$n = 2$
Glucose	CH_2O	1:2:1	$C_6H_{12}O_6$	$n = 6$
Water	H_2O	2:1	H_2O	$n = 1$
Ethene	CH_2	1:2	C_2H_4	$n = 2$
Benzene	CH	1:1	C_6H_6	$n = 6$
Phosphorus(V) oxide	P_2O_5	2:5	P_4O_{10}	$n = 2$

The table above shows the empirical formula-molecular formula relationship for some compounds.

Note; during the process of obtaining the empirical formula, the simplest ratio is obtained as a decimal fraction. This ratio should have whole numbers only. Therefore figures of the type 1.1, 1.2, 2.7, 3.8 and 4.9, can be rounded off to 1,1,3,4 and 5 respectively.

However, values of the type; 1.333, 2.4, 1.5, and 3.666 should not be rounded off. Rounding them off creates a very big error. They must be multiplied by a factor to make them whole numbers as summarized below.

Sample calculated ratio	Factor	Correct ratio
1 : 1.333	3	3 : 4
1.5 : 2	2	3 : 4
2 : 2.499	2	4 : 5
1 : 3.666 : 3	3	3 : 11 : 9
3 : 2.4	2	6 : 5

Calculations on empirical formulae and molecular formulae

Examples

(a) From percentage composition

- 1.** An organic compound Y contains 66.7% carbon, 11.1% hydrogen and the rest being oxygen. If the vapour density of Y is 36, determine its molecular formula.

$$\text{percentage mass of } O = 100 - 66.7 - 11.1 = 22.2$$

Elements	C	H	O
% mass	66.7	11.1	22.2

moles	$\frac{66.7}{12}$	$\frac{11.1}{1}$	$\frac{22.2}{16}$
-------	-------------------	------------------	-------------------

simplest ratio	$\frac{5.5583}{1.3875} : \frac{11.1}{1.3875} : \frac{1.3875}{1.3875}$
	4 : 8 : 1

Empirical formula is C_4H_8O

$$(C_4H_8O)_n = 36 \times 2$$

$$(48 + 8 + 16)_n = 36 \times 2$$

$$72n = 72$$

$$n = 1$$

Molecular formula is C_4H_8O

- 2.** A compound Q contains 54.5% carbon, 9.09% hydrogen and the rest being oxygen.

(a) Calculate the empirical formula

(b) 0.542g of Q occupies 148cm³ at a temperature of 20°C and a 740mmHg pressure. Determine the molecular formula of Q.

(c) If Q which produces effervescence with magnesium powder, deduce its structural formula.

(a) percentage mass of O = 100 - 54.5 - 9.09 = 36.41

Elements	C	H	O
% mass	54.5	9.09	36.41

moles	$\frac{54.5}{12}$	$\frac{9.09}{1}$	$\frac{36.41}{16}$
-------	-------------------	------------------	--------------------

simplest ratio	$\frac{4.5417}{2.2756} : \frac{9.09}{2.2756} : \frac{2.2756}{2.2756}$
	2 : 4 : 1

Empirical formula is C_2H_4O

(b) $m = 0.542\text{g}$
 $V = 148 \times 10^{-6}\text{m}^3$
 $T = (20 + 273) = 293\text{K}$
 $P = \left(\frac{740}{760} \times 101325\right)\text{Pa}$
 $PV = nRT$
 $PV = \frac{m}{M_r}RT$
 $M_r = \frac{mRT}{PV}$
 $M_r = \frac{0.542 \times 8.31 \times 293}{\left(\frac{740}{760} \times 101325\right) \times 148 \times 10^{-6}}$

$$\begin{aligned} M_r &= 90.38 \\ \text{molar mass of } Q &\approx 90 \\ (C_2H_4O)_n &= 90 \\ (24 + 4 + 16)_n &= 90 \\ 44n &= 90 \\ n &= 2 \end{aligned}$$

Molecular formula is $C_4H_8O_2$

(c) Hint; its carboxylic acids that form hydrogen when reacted with magnesium.

Q is $CH_3CH_2CH_2COOH$

3. A compound J contains 62.1% carbon, 10.3% hydrogen and the rest being oxygen. If J has a density of $2.59 \times 10^{-3}\text{gcm}^{-3}$ at s.t.p;

(a) Determine the empirical formula of J

(b) Molecular formula of J

(a) percentage mass of O = $100 - 62.1 - 10.3 = 27.6$

Elements	C	H	O
% mass	62.1	10.3	27.6
moles	$\frac{62.1}{12}$	$\frac{10.3}{1}$	$\frac{27.6}{16}$

simplest ratio	$\frac{5.175}{1.725} : \frac{10.3}{1.725} : \frac{1.725}{1.725}$
	3 : 6 : 1

Empirical formula is C_3H_6O

(b) 1 cm^3 at stp contains $2.59 \times 10^{-3}\text{g of J}$

22400 cm^3 at stp will contain $\left(\frac{22400 \times 2.59 \times 10^{-3}}{1}\right)$ g of J

$$\begin{aligned} M_r &\approx 58 \\ \text{molar mass of } Q &= 58\text{g} \\ (C_3H_6O)_n &= 58 \end{aligned}$$

$$\begin{aligned} (36 + 6 + 16)_n &= 58 \\ 58n &= 58 \\ n &= 1 \end{aligned}$$

Molecular formula is C_3H_6O

(b) From combustion data

4. When a hydrocarbon L was burnt in excess air, 14.4g of water and 13.44dm³ of carbon dioxide were obtained at s.t.p.

(a) Determine the empirical formula of L.

(b) If the vapour density of L is 22. Determine the molecular formula of L.

(a) *From 14.4g of H₂O;*

$$\text{molar mass of H}_2\text{O} = 2 + 16 = 18\text{g}$$

$$\text{mass of H} = \frac{2}{18} \times 14.4 = 1.6\text{g}$$

From 13.44dm³ of CO₂;

22.4 dm³ of CO₂ at stp contain 1 mole

$$13.44 \text{ dm}^3 \text{ of CO}_2 \text{ at stp contain } \left(\frac{13.44 \times 1}{22.4} \right) \text{ mole}$$

$$= 0.6 \text{ moles}$$

$$\text{molar mass of CO}_2 = 12 + 32 = 44\text{g}$$

$$\text{mass of C} = \frac{12}{44} \times 26.4 = 7.2\text{g}$$

Elements mass(g)	C	H
	7.2	1.6

moles	$\frac{7.2}{12}$	$\frac{1.6}{1}$

$$\text{simplest ratio} \quad \frac{0.6}{0.6} : \frac{1.6}{0.6}$$

$$1 \times 3 : 2.6667 \times 3$$

$$3 : 8$$

Empirical formula is C₃H₈

(b) $(C_3H_8)_n = 22 \times 2$

$$(36 + 8)_n = 44$$

$$44n = 44$$

$$n = 1$$

Molecular formula is C₃H₈

5. When 0.236g of organic compound Q on combustion gave 0.528g of carbon dioxide and 0.324g of water. If the same mass of Q at s.t.p gave 44.8cm³ of

nitrogen gas, determine the molecular formula of Q if its relative molecular mass is 59.

From 0.528g of CO_2 ;

$$\text{molar mass of } \text{CO}_2 = 12 + 32 = 44\text{g}$$

$$\text{mass of C} = \frac{12}{44} \times 0.528 = 0.144\text{g}$$

From 0.324g of H_2O ;

$$\text{molar mass of } \text{H}_2\text{O} = 2 + 16 = 18\text{g}$$

$$\text{mass of H} = \frac{2}{18} \times 0.324 = 0.036\text{g}$$

molar mass of $\text{N}_2 = (2 \times 14) = 28\text{g}$

22400 cm^3 at stp contain 1 mole of N_2

22400 cm^3 at stp contain 28g of N_2

$$44.8 \text{ cm}^3 \text{ at stp contain } \left(\frac{44.8 \times 28}{22400} \right) \text{ g of } \text{N}_2 \\ = 0.056\text{g of } \text{N}_2$$

Elements mass(g)	C 0.144	H 0.036	N 0.056
moles	$\frac{0.144}{12}$	$\frac{0.036}{1}$	$\frac{0.056}{14}$
simplest ratio	$\frac{0.012}{0.004} : \frac{0.036}{0.004} : \frac{0.004}{0.004}$		$1 : 1 : 1$

Empirical formula is $\text{C}_3\text{H}_9\text{N}$

$$(\text{C}_3\text{H}_9\text{N})_n = 59$$

$$(36 + 9 + 14)_n = 59$$

$$59n = 59$$

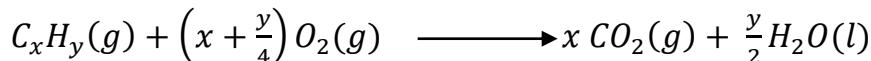
$$n = 1$$

Molecular formula is $\text{C}_3\text{H}_9\text{N}$

(c) From other experimental data

One analytical method for determination of molecular formula of a hydrocarbon is **Eudiometry** which uses **Avogadro's hypothesis**, “equal volumes of different gases at the same temperature and pressure contain the same number of molecules”. i.e. doubling the number of molecules present doubles the volume at constant pressure. In this process, an unknown volume of a gaseous hydrocarbon is exploded with excess oxygen. The hydrocarbon completely burns to form carbon dioxide and water as the only products. The vapour is then cooled and contraction in volume occurs due to condensation of water vapour. The resultant volume (residual gas) left is due to carbon dioxide formed and the unreacted oxygen. The volume of carbon dioxide is determined by adding aqueous sodium hydroxide or potassium hydroxide. All the carbon dioxide formed is absorbed and the diminution (reduction) in the volume of the gases is due to carbon dioxide. The

volume of gas that remains at this point is the unreacted oxygen. The volume of water formed is regarded as negligible.



Assume $J \text{ cm}^3$ of hydrocarbon was exploded in $Q \text{ cm}^3$ of excess oxygen to form $V \text{ cm}^3$ of gas. On addition of concentrated potassium hydroxide, the volume reduced to $W \text{ cm}^3$.

Volume of carbon dioxide formed is $(V - W) \text{ cm}^3$

Volume of oxygen that reacts is $(Q - W) \text{ cm}^3$

From the above equation, 1 volume of C_xH_y forms x volumes of CO_2 .

Relating the volumes; $J \text{ cm}^3$ of C_xH_y forms $(V - W) \text{ cm}^3$ of CO_2

$Jx = (V - W)$; from which x can be determined if J, V and W are known

Similarly; 1 volume of C_xH_y reacts with $\left(x + \frac{y}{4}\right)$ volumes of O_2 .

Relating the volumes; $J \text{ cm}^3$ of C_xH_y reacts with $(Q - W) \text{ cm}^3$ of O_2

$J\left(x + \frac{y}{4}\right) = (Q - W)$; from which y can be determined if J, Q and W and x are known

6. 20 cm³ of a hydrocarbon Z was exploded with 200 cm³ of oxygen. On cooling to room temperature, the residual gases occupied 160 cm³. When the residual gases were passed through sodium hydroxide solution, the volume reduced to 20 cm³.

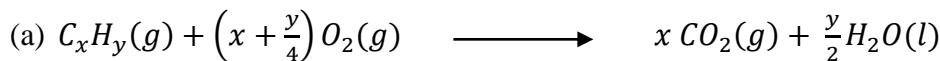
(a) Write equation for the reaction between Z and oxygen.

(b) Determine the molecular formula of Z.

(c) Compound Z burns with a sooty flame. When Z was treated with hot alkaline potassium manganate(VII) solution followed by dilute hydrochloric acid, compound T was formed. T reacts with magnesium ribbon liberating hydrogen gas.

(a) Identify Z and T

(b) Write equation to show how Z can be obtained from an alkyne.



(b) Volume of carbon dioxide formed is $(160 - 20) = 140 \text{ cm}^3$

Volume of oxygen that reacted = $(200 - 20) = 180 \text{ cm}^3$

From the above equation, 1 volume of C_xH_y forms x volumes of CO_2 .

20 cm^3 of C_xH_y forms 140 cm^3 of CO_2

$$20x = 140$$

$$x = 7$$

Similarly; 1 volume of C_xH_y reacts with $\left(x + \frac{y}{4}\right)$ volumes of O_2 .

20 cm^3 of C_xH_y reacts with 180 cm^3 of O_2

$$20\left(x + \frac{y}{4}\right) = 180$$

$$20\left(7 + \frac{y}{4}\right) = 180$$

$$140 + 5y = 180$$

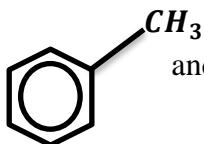
$$y = 8$$

Molecular formula of Z is C_7H_8

- (c) Hint; burning with a sooty flame indicates Z is aromatic. On reacting it with alkaline potassium manganate(VII) solution followed by dilute hydrochloric acid, the compound T formed is a carboxylic acid since it liberates hydrogen gas when reacted with magnesium.

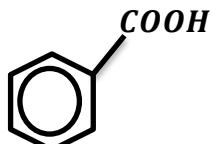
(i)

Z is



CH_3

and T is



$COOH$

(ii)

Try this on your own (convert ethyne to methylbenzene)

7. 15 dm³ of gaseous hydrocarbon X was exploded with 105dm³ of excess oxygen. The residual gas occupied 75dm³. On addition of concentrated potassium hydroxide, the volume reduced by 45dm³. Determine the molecular formula of X.



Volume of carbon dioxide formed = 45 dm³

Volume of unreacted oxygen = $(75 - 45) = 30$ dm³

Volume of oxygen that reacted = $(105 - 30) = 75$ dm³

From the above equation, 1 volume of C_xH_y forms x volumes of CO_2 .

15 dm³ of C_xH_y forms 45 dm³ of CO_2

$$15x = 45$$

$$x = 3$$

Similarly; 1 volume of C_xH_y reacts with $\left(x + \frac{y}{4}\right)$ volumes of O_2 .

15 dm³ of C_xH_y reacts with 75 dm³ of O_2

$$15\left(x + \frac{y}{4}\right) = 75$$

$$15\left(3 + \frac{y}{4}\right) = 75$$

$$y = \left(\frac{75}{15} - 3\right)4$$

$$y = 8$$

Molecular formula of X is C_3H_8

8. When 142cm³ of a hydrocarbon Y, of formula, C_aH_b and molecular mass 58g was exploded with excess oxygen and cooled to room temperature, the volume of

the residual gas was 694cm^3 . On treatment with concentrated potassium hydroxide solution, the volume decreased to 126cm^3 .

- Determine the molecular formula of Y.
- Write the structural formula and IUPAC name of all possible isomers of Y.



(i) Volume of carbon dioxide formed is $(694 - 126) = 568 \text{ cm}^3$

From the above equation, 1 volume of C_xH_y forms x volumes of CO_2 .

142 cm^3 of C_xH_y forms 568 cm^3 of CO_2

$$142x = 568$$

$$x = 4$$

$$C_xH_y = 58$$

$$C_4H_y = 58$$

$$(4 \times 12) + y = 58$$

$$y = 10$$

Molecular formula of Z is C_4H_{10}

(ii)

Structural formula of isomer	Name of isomer
$CH_3CH_2CH_2CH_3$	Butane
$CH_3\begin{matrix} \\ CHCH_3 \\ \\ CH_3 \end{matrix}$	2-methypropane

Questions

Note; some of the questions in this exercise will require you to apply knowledge from either other topics or branches of chemistry. Feel free to consult those topics or consult your teacher or wait for them to be covered and revisit the questions.

- Compound G, with molecular mass 237.9g, contains 24.8% cobalt, 29.8% chlorine, the rest being water of crystallisation.
 - Calculate the empirical formula
 - Determine the molecular formula of G.
- 0.464g of an organic compound Q when burnt gave 1.32g of carbon dioxide and 0.315g of water. When 0.2325g of Q was separately burnt, 7.08 cm^3 of nitrogen gas at s.t.p was produced. Determine the molecular formula and structural formula of Q if its relative density is 46.5.

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3. 1.363g of compound Y containing carbon, hydrogen and bromine on complete combustion gave 1.10g of carbon dioxide and 0.45g of water. When 0.35g of Y was vapourised, it occupied 39.5cm^3 at 20°C and 750mmHg . Calculate;
 - (i) the simplest formula of Y
 - (ii) the molecular formula of Y

(b) Y forms a compound Z when treated with a mixture of potassium hydroxide and an alcohol under reflux. Z reacts with ammoniacal silver nitrate to form a white precipitate Q. Identify Y, Z and Q.

(c) Write;

 - (i) equation for the reaction between Z and ammoniacal silver nitrate solution.
 - (ii) the mechanism for the reaction leading to formation of Z.
4. (a) A gaseous hydrocarbon Q contains 90% carbon. The density of Q is $1.785 \times 10^{-3}\text{gcm}^{-3}$ at stp. Determine;
 - (i) the empirical formula of Q
 - (ii) the molecular formula of Q.

(b) Q forms a white precipitate with ammoniacal silver nitrate solution. Identify Q.

(c) Using equations only, show how Q can be synthesized from propanoic acid.
5. (a) When 2.3g of a compound P, containing carbon, oxygen and hydrogen was burnt in excess oxygen, 2.2g of carbon dioxide and 0.9g of water was produced. Calculate the empirical formula of P
- (b) The density of P is 2.0536g l^{-1} at s.t.p. Determine the molecular formula of P.
- (c) P dissolves in sodium hydrogencarbonate solution with effervescence. Write the structural formula of P.
- (d) State what would be observed and write equation for the reaction that would take place when a solution of P is treated with:
 - (i) acidified potassium manganate(VII) solution
 - (ii) Fehling's solution.
6. 20cm^3 of a gaseous hydrocarbon W were exploded with 120cm^3 of Oxygen. After the explosion, the volume of gases remaining was 90cm^3 and this decreased to 50cm^3 on treatment with aqueous potassium hydroxide. Determine the molecular formula of the hydrocarbon.
7. 30cm^3 of a gaseous hydrocarbon Z was mixed with 140cm^3 of oxygen and exploded. After cooling to room temperature and pressure, the residual gas occupied 95cm^3 . On absorption with concentrated potassium hydroxide solution there was a fall in volume by 60cm^3 . Determine the molecular formula of Z.
8. 15 cm^3 of a gaseous hydrocarbon were exploded with 105 cm^3 of oxygen in a sealed vessel after cooling, the residual volume occupies 75cm^3 . On addition of caustic

potash, there was a diminution of volume to 30cm^3 . Determine the molecular mass of a hydrocarbon.

9. 30cm^3 of a gaseous hydrocarbon Z was exploded with 200cm^3 of oxygen, which was in excess. The residual gas volume was found to be 155cm^3 on cooling to room temperature. The volume of the residual gas reduced to 35cm^3 on treatment with concentrated potassium hydroxide solution.

(a) (i) Write the general equation for the reaction between Z and oxygen

(ii) Calculate the molecular formula of Z.

(b) When Z was treated with ammoniacal copper(I) chloride solution, a red precipitate was formed.

(i) Identify Z

(ii) Write equation for the formation of the red precipitate.

(c) Z was reacted with water in the presence of dilute sulphuric acid and mercury(II) sulphate at 60°C . Write equation for the reaction and the accepted mechanism.

(d) Write equations to show how Z can be synthesized from but-1-ene.

10. When 20cm^3 of a gaseous alkyne P, C_nH_{2n-2} , was exploded with 135cm^3 of excess oxygen and on cooling to room temperature, the residual gas occupied a volume of 105cm^3 . When the residual gas was passed through concentrated sodium hydroxide solution, the volume decreased by 80cm^3 .

(a) (i) Write the equation for combustion of P.

(ii) Determine the molecular formula of P.

(b) Write the structural formulae and names of possible isomers of P.

(c) P reacts with sodium metal in presence of liquid ammonia to form compound Q.

Identify;

(i) P

(ii) Q.

(d) P was bubbled through ammoniacal silver nitrate solution.

(i) State what was observed

(ii) Write equation for the reaction

(e) Write equation and suggest a mechanism for the reaction between;

(i) P and bromine water

(ii) Q and 1-bromopropane

(f) With the aid of an equation, describe how P reacts with water.

11. A compound Z, whose molecular mass is 142, contains 16.9% magnesium, 33.8% carbon, 45.1% oxygen, and the rest being hydrogen.

(a) (i) Determine the empirical formula of Z.

(ii) Work out the molecular formula of Z.

- (b) On heating, Z decomposes to form a white residue, X and a gas Y that forms a yellow precipitate with 2,4-dinitrophenylhydrazine in acidic medium.
- Deduce the chemical formula of Z.
 - Identify X and Y.
- (c) Write equation for the reaction that;
- takes place when Z is heated.
 - leads to formation of the yellow precipitate.
- (d) (i) State what will be observed when dilute sulphuric acid is added to X.
(ii) Write equation for the reaction between dilute sulphuric acid and X.
- (e) Write;
- the mechanism for the reaction in (c)(i)
 - equation(s) for conversion of Y to ethene.

12. A solid inorganic sulphate contains 9.76% of magnesium 13.00% of sulphur and 51.22% of water.

- Determine the empirical formula of the compound.
- Hence determine the molecular formula of the compound (the molecular mass of compound is 245)
- Name the reagent(s) that can be used to confirm the ions present in the compound.
In each case state what is observed.

13. An organic compound T consists of 48.6% carbon, 8.1% hydrogen and the rest being oxygen.

- Determine the empirical formula of Y.
- 0.453g of a vapourised sample of Y occupied 200cm^3 at 100°C and 95.0kPa pressure.
 - Calculate the molecular mass of Y.
 - Determine the molecular formula of Y.
- Y reacts with magnesium metal with evolution of a gas. Write;
 - the structural formula of Y
 - the equation for the reaction between Y and magnesium.

14. (a) An organic compound, Z, contains carbon 80%, hydrogen 6.7%, the rest being oxygen. Calculate the empirical formula of Z.

- (b) 0.25g of Z when vapourised at 150°C and 760mmHg occupies 72.30cm^3 . Determine the:
- molecular mass of Z
 - molecular formula of Z

- (c) Z burns with a yellow sooty flame and forms a yellow-orange solid with Brady's reagent. Z also reacts with a solution of iodine in sodium hydroxide to form a yellow solid.
- Identify Z
 - Write the mechanism for the reaction between Z and Brady's reagent.
15. (a) A compound Y contains 22.6% by mass of oxygen, 8.57% by mass hydrogen and the rest being carbon.
- Calculate the empirical formula of Y.
 - When 0.3g of Y was vapourised at 80°C and 700mmHg , it occupied a volume of 134.77cm^3 . Determine the molecular formula of Y.
- (b) Y forms a yellow precipitate with 2,4-dinitrophenylhydrazine and does not react with Tollen's reagent.
- (c) Write equation for the formation of the yellow precipitate in (b).
16. (a) A compound P contains carbon, hydrogen and oxygen. 0.0291g of P on combustion gave 0.0581g of carbon dioxide and 0.0239g of water.
- Calculate the empirical formula of P.
 - When 0.14g of P was vapourised at 20°C and 740mmHg pressure, it occupied a volume of 39.5cm^3 . Determine the molecular formula of P.
- (b) When P was treated with sodium bicarbonate, effervescence of a colourless gas occurred. Identify P.
- (c) P was treated with iron(III) chloride solution. State what was observed and write equation for the reaction that takes place.
17. A compound Q contains 63.7% lead, 14.8% carbon, 1.8% hydrogen and the rest being oxygen. When vapourised, 0.225g of Q occupy 15.5 cm^3 at standard temperature and pressure.
- (a) (i) Calculate the empirical formula of Q.
- (ii) Deduce the molecular formula of Q.
- (b) Compound Q decomposed on heating to form a yellow residue on cooling and a colourless vapour that turned limewater milky and formed a yellow precipitate with 2,4-dinitrophenyl hydrazine in presence of sulphuric acid.
- Write the name and formula of Q.
 - Write equation leading to formation of the yellow precipitate.
18. A compound P contains 52.2% carbon, 13.0% hydrogen and the rest being oxygen.
- Determine the empirical formula of P
 - When vapourised, 0.1g of P occupied 78.8 cm^3 at 157°C and a pressure of 740mmHg.

- (i) Calculate the formula mass of P
(ii) Determine the molecular formula of P.
(c) Write the structural formulae of all possible isomers of P
(c) P does not react with sodium metal. Identify P.
(d) Write an equation to show how P can be prepared from methanol.
19. (a) An organic compound A contains carbon, hydrogen and oxygen only. On combustion, 0.463g of A gave 1.1g carbon dioxide and 0.563g of water. Determine the empirical formula of A
(b) When vapourised, 0.1g of A occupies 54.5cm^3 at 208°C and 98.3kPa . Determine the molecular formula of A.
(c) A reacts with sodium metal with evolution of a gas. Write the structural formula of all possible isomers of A.
(d) A reacts with anhydrous zinc chloride and concentrated hydrochloric acid to give a cloudy solution in about 5 minutes.
(i) Identify A
(ii) Show how A could be synthesised from but-2-ene
20. A solid inorganic nitrate contains 9.37% by mass of magnesium, 10.93% nitrogen and 42.18% of water. Determine the molecular formula of the nitrate if its molecular mass is 256.
21. When 0.203g of hydrated magnesium chloride, $\text{MgCl}_x \cdot n\text{H}_2\text{O}$, was dissolved in water and titrated with 0.1M silver nitrate solution, 20.0cm^3 of the silver nitrate solution was required for complete reaction. A sample of the hydrated chloride lost 53.2% of its mass when heated in a stream of hydrogen chloride gas. Calculate the value of x and n .
22. A compound Z contained 19.1% nitrogen, 43.6% oxygen and the rest being manganese.
- (i) Calculate the empirical formula of Z
(ii) 10g of Z in 1000g of water lowered the freezing point of water by 0.127°C . Calculate the molecular formula of Z (k_f for water is $1.86^\circ\text{C}\text{mol}^{-1}\text{kg}^{-1}$)
(b) When Z was strongly heated, brown fumes were given off. Z dissolved in water to form a pink solution which decolourises acidified potassium manganate(VII) solution. Identify Z.
(c) State what would be observed and write equation(s) for the reaction(s) that took place when to the solution in (b) was;
(i) added concentrated nitric acid and lead(IV) oxide and the mixture boiled.
(ii) sodium carbonate solution was added

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23. (a) When 0.1g of aluminium was vapourised at 350 °C and a pressure of 1 atmosphere, 19.2 cm³ of vapour was formed.

- (i) Calculate the relative molecular mass of aluminium chloride.
- (ii) Write the structural formula and molecular formula of aluminium chloride in the gaseous state at 350 °C.

(b) Aluminium chloride is normally contaminated with traces of iron(III) chloride.

(i) Name one reagent that can be used to detect the presence of iron(III) ion in a contaminated solution of aluminium chloride.

(ii) State what would be observed if the contaminated aluminium chloride solution was treated with the reagent you have named in (b)(i)

(iii) Write equation for the reaction leading to the observation you have stated in (b)(ii)

(c) Water was added drop wise to aluminium chloride.

(i) State what was observed.

(ii) Write equation for the reaction that took place.

(d) State one use of aluminium chloride in organic synthesis.

24. When 0.13g of a chloride of iron was vapourised at 600K and 1 atmosphere, 20 cm³ of a vapour was formed.

(a) Calculate the relative molecular mass of the chloride of iron.

(b) Determine the;

- (i) Molecular formula of the chloride of iron,
- (ii) Structural formula of the chloride of iron in vapour phase.

25. An organic compound, Q contains 58.8% carbon, 9.8% hydrogen and the rest oxygen.

(a) Calculate the empirical formula of Q.

(b) Determine the molecular formula of Q (*RFM of Q = 102*)

(c) (i) Q reacts with aqueous sodium hydroxide under reflux to produce propan-1-ol as one of the products. Identify Q.

(ii) Write an equation to show how R can be synthesized from propan-1-ol and indicate a mechanism for the reaction.

26. A compound Q contains 60.0% carbon, 13.3 % hydrogen and the rest being oxygen.

(a) Calculate the simplest formula of Q.

(b) When 0.698g of Q was dissolved in 100g of a solvent, there was 0.19 °C depression in freezing point of the solution. (*K_f of the solvent = 1.63°C*)

Calculate;

(i) The empirical formula of Q

(ii) The molecular formula of Q

(c) Write the names and structural formulae of all possible isomers of **Q**. (d)

When **Q** was reacted with iodine in aqueous sodium hydroxide, a yellow precipitate was formed.

(i) Identify **Q**

(ii) Write equation for the reaction between **Q** and iodine in aqueous sodium hydroxide.

(iii) State what would be observed when **Q** is reacted with acidified potassium dichromate(VI) solution and name the major organic product.

(d) When **Q** was heated with excess concentrated sulphuric acid, a gas **W** which turned the purple solution of acidified manganate(VII) to colourless was evolved. Write equation for the reaction between:

(i) **Q** and sulphuric acid and suggest a mechanism for the reaction.

(ii) **W** and acidified manganate(VII) ions and name the product.

(e) Suggest a plausible mechanism for the reaction between **Q** and hot concentrated sulphuric acid.

27. A compound **Q** contains 76.32% carbon, 6.38% hydrogen and the rest being oxygen. A solution of **Q** in water is acidic but does not liberate carbon dioxide from carbonates. A solution of 1.50g of **Q** in 20.90g of benzene freezes at 1.3°C while pure benzene freezes at 5.50°C.

(a) Determine;

(i) the empirical formula of **Q**.

(ii) the molecular formula and write the structural formula of **Q**.
(*K_f* of benzene is 5.49°C per 1000g mol⁻¹)

(b) Explain why a solution of **Q** in water is acidic.

(c) Describe the reaction between **Q** and bromine water.

(d) Write equation and outline mechanism for the reaction between **Q** and;

(i) ethanoylchloride

(ii) chloromethane in presence of sodium hydroxide.

(e) Write equations to show how **Q** can be;

(i) Prepared from benzene and propene.

(ii) Converted to methylbenzene.

28. (a) An organic compound **Z** contains by mass 51.90% carbon, 4.86% hydrogen and the rest being bromine. Determine the empirical formula of **Z**.

(c) When 0.8g of **Z** was vapourised at 80°C and a pressure of 700mmHg, it occupied a volume of 136 cm³. Determine the molar mass of **Z**.

(d) Deduce the molecular formula of **Z**.

- (e) When Z was heated with excess sodium hydroxide solution, it formed a compound Y. On heating Y with acidified manganese(IV) oxide, a substance W was formed. W formed a yellow precipitate with 2,4-dinitrophenylhydrazine in presence of dilute sulphuric acid but gave no observable change with aqueous ammonia in the presence of silver nitrate solution.
- (i) Write the chemical equation leading to formation of substances Y and W indicating all reagents and conditions.
- (ii) Write the chemical equation for the reaction between substance W and semicarbazine in presence of dilute sulphuric acid. Outline the mechanism for the reaction.
- (iii) Write equation(s) to show how compound Y can be synthesized from benzene. Indicate the necessary conditions and reagents.
29. 8.15g of a saturated bromocompound X, with a general formula of $C_nH_{2n-1}Br$ contains 49.08% by mass of bromine.
- (a) (i) Determine the molecular formula of X.
(ii) Write the name and structures of possible isomers of X.
- (b) When X was heated with sodium hydroxide , a product Y was formed. When Y was heated with concentrated orthophosphoric acid, cyclohexene was formed.
- (i) Name X and Y.
(ii) Write equation for the reaction between X and sodium hydroxide and that for formation of cyclohexene.
- (c) Discuss the reactions between X and;
(i) Sodium hydroxide
(ii) Silver ethanoate
(iii) Phenol
(Your answer should include conditions and mechanisms for the reactions)
30. (a) A gaseous hydrocarbon X contains 11.11% by mass of hydrogen.
- (i) Calculate the empirical formula of X.
(ii) If the vapour density of X is 27, determine the molecular formula of X.
(iii) Write the structural formulae and IUPAC names of all possible isomers of X.
- (b) 1 mole of X reacts completely with 1 mole of hydrogen gas in the presence of nickel catalyst at 150°C. Identify X.
- (c) When X was warmed with a mixture of concentrated sulphuric acid and water, substance Y was formed. Y was readily oxidised to compound Z when treated with hot acidified potassium dichromate solution. Identify;

- (i) Y
(ii) Z
- (d) Write equation for the reaction and suggest a mechanism for the reaction when;
- (i) X was warmed with a mixture of concentrated sulphuric acid and water
(ii) Z was reacted with acidified solution of semicarbazide.
31. An organic compound ,T , on complete combustion yielded 13.2g of carbon dioxide and 2.7g of water. When 4.7g of T was vapourised at standard temperature and pressure, it occupied a volume of $2.7 \times 10^{-3} m^3$.
- (a) (i) Calculate the empirical formula of T
(ii) Determine the molecular formula of T.
- (b) T burns with a sooty flame. Identify T
- (c) Discuss the reactions of T with;
- (i) Bromine
(ii) Propene
(iii) Ethanoylchloride.
- (Your answer should include conditions for the reactions and mechanisms for the reactions where applicable)*
- (d) Write equation to show how T can be synthesized from benzaldehyde.
32. A compound Y contains by mass 61.02% carbon, 15.25% hydrogen and the rest being nitrogen.
- (a) Determine the empirical formula of Y
- (b) Compound Y has a density of $2.63 g dm^{-3}$ at s.t.p. Determine the molecular formula of Y.
- (c) Write the structural formula of possible isomers of Y.
- (d) Compound Y forms yellow oils when reacted with cold concentrated hydrochloric acid and sodium nitrite.
- (i) Identify Y
(ii) Write equation for the reaction that took place.
- (e) (i) Name the reagent that can be used to confirm the functional group in compound Y.
(ii) State the observation made
(iii) Write equation for the reaction for the reaction that takes place when the named reagent in (e)(i) is reacted with compound Y.

($H = 1; O = 16; C = 12; Mg = 24; N = 14; Al = 27; Si = 28.1; Cl = 35.5;$

$Fe = 56; Co = 58.9; Br = 79.9$)

Questions 15, 18 and 19 will be simpler after covering colligative properties in Phase equilibria and gaining more knowledge of organic chemistry.

THE PERIODIC TABLE

The historical development of the Periodic Table

Prout, an Englishman, made the earliest attempt to show a connection between atoms of different elements. This was in 1815, seven years after the publication of the atomic theory.

He found out that the many atomic weights determined by **Dalton**, **Berzelius** and others were approximately whole number multiples of the atomic weight of hydrogen. Prout therefore suggested that atoms of different elements were composed of hydrogen atoms in various numbers. This whole number rule as however abandoned soon.

In 1858, **Cannizzaro** introduced a method of finding relative atomic masses. Chemists soon observed a periodic relationship between the properties of elements and their relative atomic masses.

In 1864, **Newlands** showed that if elements were arranged in order of their atomic weights, elements with similar properties appeared in intervals. Part of his table is shown below.

H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr	Ti	Mn	Fe

Elements that were chemically similar such as lithium, sodium and potassium usually occurred in every eighth position. From his observation, Newland put forward the following periodic law; *the properties of elements are a periodic function of their atomic weights*.

Newlands' law however did not convince majority of the chemists. This is because some elements were placed in the table but assigned incorrect relative atomic masses. In addition, no allowance was given for the possibility of the undiscovered elements.

In 1869, the Russian chemist, **Demitri Mendeleeff**, used Newlands basic idea to devise a new kind of table. He arranged all the known elements in order of their relative atomic masses to show the relationships between the elements more clearly. He improved Newlands' table by;

1. Leaving gaps in the Periodic Table on a prediction the new elements would be discovered to fill the gaps. He predicted the properties of the undiscovered elements. When the elements were discovered and found to have relative atomic mass and the

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physical and chemical properties Mendeleeff predicted, chemists strongly believed in his Periodic Table.

2. Introducing long rows periods for the elements now called transition elements. This implied that the elements *Ti, Mn, Fe* were not placed under nonmetals *Si, P, S* as in Newlands' system.

Below is part of Mendeleef's Periodic Table;

								1	2	3	4	5	6	7	8
1	<i>H</i>														
2	<i>Li</i>	<i>Be</i>	<i>B</i>	<i>C</i>	<i>N</i>	<i>O</i>	<i>F</i>								
3	<i>Na</i>	<i>Mg</i>	<i>Al</i>	<i>Si</i>	<i>P</i>	<i>S</i>	<i>Cl</i>								
4	<i>K</i>	<i>Ca</i>	<i>Ti</i>	<i>V</i>	<i>Cr</i>	<i>Mn</i>	<i>Fe</i>	<i>Co</i>	<i>Ni</i>	
5	<i>Cu</i>	<i>Zn</i>	<i>As</i>	<i>Se</i>	<i>Br</i>								

More elements were soon discovered including the noble gases which now make the Modern Periodic Table.

Unique position of Hydrogen in the Periodic Table

The position of hydrogen in the Periodic Table is great source of argument. Whereas some authors place it above lithium in group I, others place it above fluorine in group VII. Others place isolate it to a central position to indicate that it is unique and has no genuine analogues.

From its electronic structure, $1s^1$, hydrogen resembles group I elements which have one electron in the outermost sub energy level. Hydrogen is also similar to group I elements in being electropositive because it is liberated at the cathode when aqueous solutions of acids are electrolyzed.

Also just like group VII elements, the hydrogen atom is one electron short of a noble gas configuration. Therefore hydrogen resembles elements in both groups in being consistently monovalent when combining with other elements.

The properties of hydrogen relate it much more to the halogens than alkali metals. It has a much higher ionisation energy and electronegativity than alkali metal. This gives it a nonmetallic character. It also resembles halogens by existing as diatomic molecules. Just like salts of halogens, when fused metallic hydrides liberate hydrogen at the anode on electrolysis.

The Modern Periodic Table

The structure of the Modern Periodic Table

In the modern Periodic Table, elements are arranged in **order of increasing atomic numbers** instead of atomic mass. Atomic numbers increase from left to right and from top to bottom in the table. The modern Periodic Table has more elements than Mendeleef's table because many elements have been discovered since his time. The elements can be classified in three classes; **metals, metalloids and non-metals**.

In the modern Periodic Table, each element is represented by its chemical symbol, atomic mass and mass number. The rows in the table are called Periods and the columns are the groups. The table has a total of **18 groups** and **7 periods**.

The first period has only 2 elements. The second and third periods have 8 elements each. The fourth and fifth have 18 elements each. The sixth has 32 elements. The seventh period has 32 elements including **Nihonium-113, Moscovium-115, Tennesine-117** and **Oganesson-118**. These new elements were approved in 2015 by IUPAC and added to the table to complete the seventh period to 32 elements.

There is a separate group of elements at the bottom of the table. It consists of 14 elements of the sixth period called the **lanthanides** and 14 elements of the seventh period called the **actinides**.

Elements in the same group have similar chemical properties and the same outermost configuration.

GROUPS

	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII		IB	IIB	IIIB	IVB	VB	VIB	VIIB	O	
1	^{1.0} ₁ H															^{1.0} ₁ H	^{4.0} ₂ He	
2	^{6.9} ₃ Li	^{9.0} ₄ Be						^{10.8} ₅ B	^{12.0} ₆ C	^{14.0} ₇ N	^{16.0} ₈ O	^{19.0} ₉ F	^{20.2} ₁₀ Ne					
3	²³ ₁₁ Na	^{24.3} ₁₂ Mg						^{27.0} ₁₃ Al	^{28.1} ₁₄ Si	^{31.0} ₁₅ P	^{32.1} ₁₆ S	^{35.4} ₁₇ Cl	^{40.0} ₁₈ Ar					
4	^{39.1} ₁₉ K	^{40.1} ₂₀ Ca	⁴⁵ ₂₁ Sc	^{47.9} ₂₂ Ti	^{50.9} ₂₃ V	⁵² ₂₄ Cr	^{54.9} ₂₅ Mn	^{55.8} ₂₆ Fe	^{58.9} ₂₇ Co	^{58.7} ₂₈ Ni	^{63.5} ₂₉ Cu	^{65.7} ₃₀ Zn	^{69.7} ₃₁ Ga	^{72.6} ₃₂ Ge	^{74.9} ₃₃ As	^{79.9} ₃₄ Se	^{79.9} ₃₅ Br	^{83.8} ₃₆ Kr
5	^{85.5} ₃₇ Rb	^{87.6} ₃₈ Sr	^{88.9} ₃₉ Y	^{91.2} ₄₀ Zr	^{92.9} ₄₁ Nb	^{95.9} ₄₂ Mo	^{98.9} ₄₃ Tc	¹⁰¹ ₄₄ Ru	¹⁰³ ₄₅ Rh	¹⁰⁶ ₄₆ Pd	¹⁰⁸ ₄₇ Ag	¹¹² ₄₈ Cd	¹¹⁵ ₄₉ In	¹¹⁹ ₅₀ Sn	¹²² ₅₁ Sb	¹²⁸ ₅₂ Te	¹²⁷ ₅₃ I	¹³¹ ₅₄ Xe
6	¹³³ ₅₅ Cs	¹³⁷ ₅₆ Ba	¹³⁹ ₅₇ La	¹⁷⁸ ₇₂ Hf	¹⁸¹ ₇₃ Ta	¹⁸⁴ ₇₄ W	¹⁸⁶ ₇₅ Re	¹⁹⁰ ₇₆ Os	¹⁹² ₇₇ Ir	¹⁹⁵ ₇₈ Pt	¹⁹⁷ ₇₉ Au	²⁰¹ ₈₀ Hg	²⁰⁴ ₈₁ Tl	²⁰⁷ ₈₂ Pb	²⁰⁹ ₈₃ Bi	²¹⁰ ₈₄ Po	²¹⁰ ₈₅ At	²²² ₈₆ Rn
7	²²³ ₈₇ Fr	²²⁶ ₈₈ Ra	²²⁷ ₈₉ Ac	²⁶¹ ₁₀₄ Rf	²⁶² ₁₀₅ Db	²⁶⁶ ₁₀₆ Sg	²⁶⁴ ₁₀₇ Bh	²⁷⁷ ₁₀₈ Hs	²⁷⁸ ₁₀₉ Mt	²⁸¹ ₁₁₀ Ds	²⁸⁰ ₁₁₁ Rg	²⁸⁵ ₁₁₂ Cn	²⁸⁶ ₁₁₃ Nh	²⁸⁹ ₁₁₄ Fl	²⁸⁹ ₁₁₅ Mc	²⁹³ ₁₁₆ Lv	²⁹⁴ ₁₁₇ Ts	²⁹⁴ ₁₁₈ Og

Lanthanum series	¹⁴⁰ ₅₈ Ce	¹⁴¹ ₅₉ Pr	¹⁴⁴ ₆₀ Nd	¹⁴⁷ ₆₁ Pm	¹⁵⁰ ₆₂ Sm	¹⁵² ₆₃ Eu	¹⁵⁷ ₆₄ Gd	¹⁵⁹ ₆₅ Tb	¹⁶² ₆₆ Dy	¹⁶⁵ ₆₇ Ho	¹⁶⁷ ₆₈ Er	¹⁶⁹ ₆₉ Tm	¹⁷³ ₇₀ Yb	¹⁷⁵ ₇₁ Lu
Actinium series	²³² ₉₀ Th	²³¹ ₉₁ Pa	²³⁸ ₉₂ U	²³⁷ ₉₃ Np	²⁴² ₉₄ Pu	²⁴³ ₉₅ Am	²⁴⁷ ₉₆ Cm	²⁴⁵ ₉₇ Bk	²⁵¹ ₉₈ Cf	²⁵⁴ ₉₉ Es	²⁵³ ₁₀₀ Fm	²⁵⁶ ₁₀₁ Md	²⁵⁴ ₁₀₂ No	²⁵⁷ ₁₀₃ Lu

Classification of elements based on the electronic configuration as s, p, d and f blocks.

A simplified, well elaborated , illustrative approach to Physical Chemistry

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The Periodic Table is divided into **four** main blocks; these blocks are *s-block*, *p-block*, *d-block* and *f-block*

s-block elements

They are placed in the left hand block of the table. The s-block contains the elements whose outermost electrons occupy the s sub-energy level. The s-block consists of two groups of elements;

IA whose electronic configuration ends with ns^1 ,

IIA whose electronic configuration ends with ns^2 .

p-block elements

These occupy the right hand block of table. The p-block contains the elements whose outermost electrons occupy the p sub-energy level except helium.

All elements placed in groups IIIB, IVB, VB, VIB, VIIB and O are p-block elements.

d-block elements

They occupy the middle block of the table. The d-block contains the elements with the outermost electrons in the d sub-energy level after the s sub-energy level is filled. The d-block elements are classified according to the outer energy sub-energy level and the period number into three series which are:

1. *The first transition series:*

It includes the elements in which the 3d sub-energy level is filled successively. It lies in the fourth period and includes the elements from scandium ($_{21}Sc$) to zinc ($_{30}Zn$).

2. *The second transition series:*

It includes the elements in which the 4d sub-energy level is filled successively. It lies in the fifth period and includes the elements from yttrium ($_{39}Y$) to cadmium ($_{48}Cd$).

3. *The third transition series:*

It includes the elements in which the 5d sub-energy level is filled successively. It lies in the sixth period and includes the elements from lanthanum ($_{57}La$) to mercury ($_{80}Hg$), excluding the lanthanides.

f-block elements

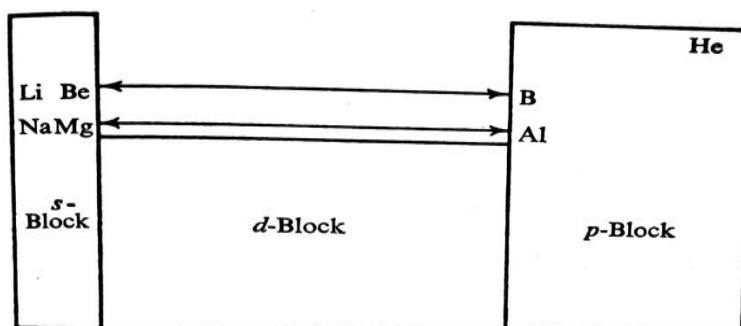
They are separated down the Periodic table , to avoid being a very wide table , In which the f sub-energy level is filled successively , The f-block is divided into 2 series, each with 14 elements. These are:

1. *The lanthanides*

These are in the sixth period, in which the 4f sub-energy level is filled successively. The elements of this series are quite similar in behaviour and very difficult to be separated as the outermost energy level for all of them $6s^2$.

2. *The actinides*

These are placed in seventh period, in which the 5f sub-energy level is filled successively. All the elements of this series are radioactive and their nuclei are unstable.



The table below shows the common elements. Use their electronic configurations to classify them into groups, periods and the the s, p, d and f blocks

<i>Element</i>	<i>Atomic number</i>	<i>Electronic configuration</i>	<i>Group</i>	<i>Period</i>	<i>Periodic Block</i>
<i>H</i>	1				
<i>He</i>	2				
<i>Li</i>	3				
<i>Be</i>	4				
<i>B</i>	5				
<i>C</i>	6				
<i>N</i>	7				
<i>O</i>	8				
<i>F</i>	9				
<i>Ne</i>	10				
<i>Na</i>	11				
<i>Mg</i>	12				
<i>Al</i>	13				
<i>Si</i>	14				
<i>P</i>	15				
<i>S</i>	16				
<i>Cl</i>	17				
<i>Ar</i>	18				

K	19					
Ca	20					
Sc	21					
Ti	22					
V	23					
Cr	24					
Mn	25					
Fe	26					
Co	27					
Ni	28					
Cu	29					
Zn	30					
Ge	32					
Sr	38					
Sn	50					
I	53					
Ba	56					
Pb	82					

Classification into metals, metalloids and non-metals

^{1.0} ₁ H													^{1.0} ₁ H	^{4.0} ₂ He				
^{6.9} ₃ Li	^{9.0} ₄ Be																	
²³ ₁₁ Na	^{24.3} ₁₂ Mg																	
^{39.1} ₁₉ K	^{40.1} ₂₀ Ca	⁴⁵ ₂₁ Sc	^{47.9} ₂₂ Ti	^{50.9} ₂₃ V	⁵² ₂₄ Cr	^{54.9} ₂₅ Mn	^{55.8} ₂₆ Fe	^{58.9} ₂₇ Co	^{58.7} ₂₈ Ni	^{63.5} ₂₉ Cu	^{65.7} ₃₀ Zn	^{69.7} ₃₁ Ga	^{10.8} ₅ B	^{12.0} ₆ C	^{14.0} ₇ N	^{16.0} ₈ O	^{19.0} ₉ F	^{20.2} ₁₀ Ne
^{85.5} ₃₇ Rb	^{87.6} ₃₈ Sr	^{88.9} ₃₉ Y	^{91.2} ₄₀ Zr	^{92.9} ₄₁ Nb	^{95.9} ₄₂ Mo	^{98.9} ₄₃ Tc	¹⁰¹ ₄₄ Ru	¹⁰³ ₄₅ Rh	¹⁰⁶ ₄₆ Pd	¹⁰⁸ ₄₇ Ag	¹¹² ₄₈ Cd	¹¹⁵ ₄₉ In	^{27.0} ₁₃ Al	^{28.1} ₁₄ Si	^{31.0} ₁₅ P	^{32.1} ₁₆ S	^{35.4} ₁₇ Cl	^{40.0} ₁₈ Ar
¹³³ ₅₅ Cs	¹³⁷ ₅₆ Ba	¹³⁹ ₅₇ La	¹⁷⁸ ₇₂ Hf	¹⁸¹ ₇₃ Ta	¹⁸⁴ ₇₄ W	¹⁸⁶ ₇₅ Re	¹⁹⁰ ₇₆ Os	¹⁹² ₇₇ Ir	¹⁹⁵ ₇₈ Pt	¹⁹⁷ ₇₉ Au	²⁰¹ ₈₀ Hg	²⁰⁴ ₈₁ Tl	²⁰⁷ ₈₂ Pb	²⁰⁹ ₈₃ Bi	²¹⁰ ₈₄ Po	²¹⁰ ₈₅ At	²²² ₈₆ Rn	
²²³ ₈₇ Fr	²²⁶ ₈₈ Ra	²²⁷ ₈₉ Ac	²⁶¹ ₁₀₄ Rf	²⁶² ₁₀₅ Db	²⁶⁶ ₁₀₆ Sg	²⁶⁴ ₁₀₇ Bh	²⁷⁷ ₁₀₈ Hs	²⁷⁸ ₁₀₉ Mt	²⁸¹ ₁₁₀ Ds	²⁸⁰ ₁₁₁ Rg	²⁸⁵ ₁₁₂ Cn	²⁸⁶ ₁₁₃ Nh	²⁸⁹ ₁₁₄ Fl	²⁸⁹ ₁₁₅ Mc	²⁹³ ₁₁₆ Lv	²⁹⁴ ₁₁₇ Ts	²⁹⁴ ₁₁₈ Og	

¹⁴⁰ ₅₈ Ce	¹⁴¹ ₅₉ Pr	¹⁴⁴ ₆₀ Nd	¹⁴⁷ ₆₁ Pm	¹⁵⁰ ₆₂ Sm	¹⁵² ₆₃ Eu	¹⁵⁷ ₆₄ Gd	¹⁵⁹ ₆₅ Tb	¹⁶² ₆₆ Dy	¹⁶⁵ ₆₇ Ho	¹⁶⁷ ₆₈ Er	¹⁶⁹ ₆₉ Tm	¹⁷³ ₇₀ Yb	¹⁷⁵ ₇₁ Lu
²³² ₉₀ Th	²³¹ ₉₁ Pa	²³⁸ ₉₂ U	²³⁷ ₉₃ Np	²⁴² ₉₄ Pu	²⁴³ ₉₅ Am	²⁴⁷ ₉₆ Cm	²⁴⁵ ₉₇ Bk	²⁵¹ ₉₈ Cf	²⁵⁴ ₉₉ Es	²⁵³ ₁₀₀ Fm	²⁵⁶ ₁₀₁ Md	²⁵⁴ ₁₀₂ No	²⁵⁷ ₁₀₃ Lr

	Metals
	Metalloids
	Non-metals

The elements in the Modern Periodic table can be classified as metals, metalloids or non-metals. Most of the elements in the table are metals. In the periodic table, there is a change from metallic to non-metallic properties across the table, and an increase in metallic properties down a group. Consequently there is a diagonal nearer the center of the table (*B, Si, As, Te*) in which there is a borderline between metals and non-metals, and the metalloids are the borderline cases.

The **metals** are good conductors of heat and electricity have a shiny lustre, malleable and ductile, usually have high melting points and high densities.

The **non-metals** are poor thermal conductors, good heat insulators, and are neither malleable nor ductile.

Metalloids are a class of chemical elements that are intermediate in properties between metals and non-metals. Elements such as arsenic, germanium, and tellurium are semiconductors and their conductivity increases as their temperature increases.

Periodicity of atomic properties in the Periodic Table

The common atomic properties include

- *Atomic radius*
- *Ionisation energy*
- *Electron affinity*
- *Electronegativity*
- *Electropositivity*
- *Metallic character*
- *Standard electrode potential*

The factors affecting atomic properties of elements include;

1. *Nuclear charge (Z)*
2. *Shielding effect/ screening effect(S)*
3. *Electronic configuration*
4. *Atomic radius.*

1. Nuclear charge (Z)

This is simply the total number of positive charges in the nucleus of an atom. It is an equivalent to the number of protons.

2. Shielding effect/ screening effect(S)

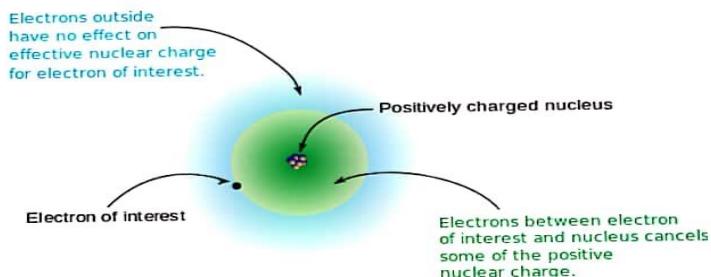
This is the repulsion of the outermost electrons by those in the innermost sub energy levels from nuclear attraction. Electrons in an atom shield each other from the pull of the nucleus. Shielding effect describes the decrease in attraction between an electron and the nucleus in any atom with more than one energy level. The greater the number of energy levels, the greater the shielding effect.

3. Effective nuclear charge(Z_{eff})

This is the net positive charge experience by an electron in an atom. Effective nuclear charge is given by the equation;

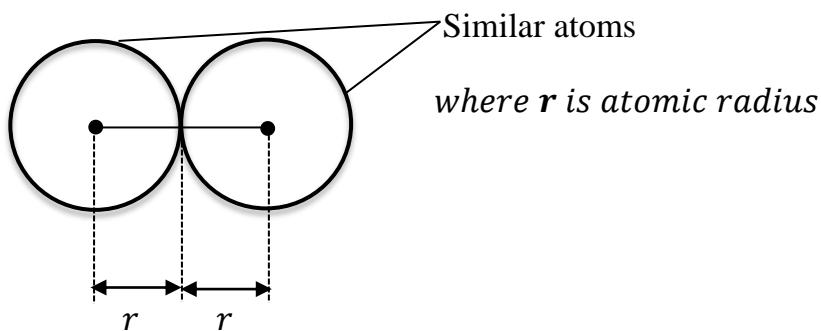
$$Z_{eff} = Z - S$$

Using the formula, it can be interpreted that if the nuclear charge is high and the screening effect is low, then effective nuclear charge increases. When the screening effect is high and nuclear charge is low, the effective nuclear charge reduces.



Atomic and Ionic radius

Atomic radius is half the internuclear distance between two atoms in a covalently bonded diatomic molecule with similar atoms or in a metallic bond.



The variation in atomic radius down a group or across a period is determined by the factors;

1. Nuclear charge

The higher the nuclear charge, the more strongly are the outermost electrons attracted closer to the nucleus, reducing the atomic radius. The lower the nuclear charge, the weaker the attraction of the outer most electrons to the nucleus hence the increasing the atomic radius.

2. Screening effect.

The greater the screening effect, the stronger the repulsion of the outermost electrons from the nuclear attraction. The electrons are thus far and weakly attracted to the nucleus, increasing the atomic radius. The lower the screening effect, the lower the repulsion of the outermost electrons from the nuclear attraction. The electrons are thus nearer and strongly attracted to the nucleus, reducing the atomic radius.

Variation in atomic radius and ionic radius in Periods and groups

1. The table below shows variation in atomic and ionic radii across Period 3

Element	Na	Mg	Al	Si	P	S	Cl
Atomic radius(nm)	0.156	0.136	0.125	0.117	0.110	0.104	0.099
Ionic radius(nm)	0.095	0.065	0.054		0.212	0.184	0.181

(a) State and explain the trend in atomic radius of the elements

Atomic radius decreases from sodium to chlorine.

This is because from sodium to chlorine, nuclear charge increases because a proton is added to nucleus from element to element. Screening effect almost remains constant, because electrons are added to the same energy level. Effective nuclear charge increases, and outer most electrons get closer and more strongly attracted than repelled by the nucleus.

(a) Explain why:

- (i) the ionic radii of Na^+ , Mg^{2+} and Al^{3+} are smaller than those of the corresponding atoms.

The ions are formed by losing electrons. When the electrons are lost, the number of protons becomes greater than the number of remaining electrons. Screening effect is reduced. Effective nuclear charge increases. The remaining electrons become strongly attracted by the nucleus than they are repelled.

- (ii) the ionic radii of P^{3-} , S^{2-} and Cl^- are larger than those of the corresponding atoms

The ions are formed by gaining electrons. When the electrons are gained, the number of electrons becomes greater than the number of existing protons. Screening effect increases. Effective nuclear charge reduces. The electrons become more strongly repelled by the nucleus than they are attracted.

(b) The ions Na^+ , Mg^{2+} and Al^{3+} have the same electronic configuration, yet they have different ionic radii. Suggest a reason for this.

The ions are formed by losing electrons, reducing the screening effect. The number of protons however remains unchanged. The effective nuclear charge therefore increases in the order $Na^+ < Mg^{2+} < Al^{3+}$ since proton number increases in the same order. The ionic radius therefore decreases in the order $Na^+ > Mg^{2+} > Al^{3+}$

2. The table below shows the atomic radii and ionic radii of the elements in Group II of the Periodic Table.

Element	Be	Mg	Ca	Sr	Ba
Atomic radius(nm)	0.089	0.136	0.174	0.191	0.198
Ionic radius(nm)	0.031	0.065	0.099	0.113	0.135

(a) State and explain the trend in atomic radius of the elements

Atomic radius increases from Beryllium to Barium.

This is because from Beryllium to Barium, nuclear charge increases; screening effect also increases, because an extra energy level completely filled with electrons is added. Increase in screening effect outweighs increase in nuclear charge. Effective nuclear charge decreases, and outer most electrons are far and weakly attracted by the nucleus.

(b) Explain why the ionic radius is smaller than the atomic radius of corresponding neutral atom for each element.

The cations are formed by gaining losing electrons. When the electrons are lost, the number of remaining electrons becomes lower than the number of existing protons. Screening effect decreases. Effective nuclear charge increases. The electrons become more strongly attracted by the nucleus than they are repelled reducing the ionic radius. In the neutral atom, the screening effect is counterbalanced by nuclear charge.

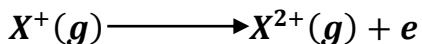
Ionisation energy

This is the minimum amount of energy required to remove an electron from a gaseous atom to form a charged gaseous ion.

Ionisation energy can be first, second or third,... ionisation energies depending on which electron is being removed from the atom



$\Delta H = \text{First ionisation energy}$



$\Delta H = \text{Second ionisation energy}$

First ionisation energy is the minimum amount of energy required to remove an electron from a gaseous atom to form a unipositively charged gaseous ion.

The variation in first ionisation energy down a group or across a period is determined by the factors;

1. Nuclear charge

The higher the nuclear charge, the higher the first ionisation energy because the outermost electron is strongly attracted by the nucleus, requiring a high amount of energy to be removed. The lower the nuclear charge, the lower the first ionisation energy because the outermost electron is weakly attracted by the nucleus, requiring a low amount of energy to be removed.

2. Screening effect

The higher the screening effect, the lower the first ionisation energy because the outermost electron is more strongly repelled than it is attracted by the nucleus, requiring a low amount of energy to be removed. The lower the screening effect, the higher the first ionisation energy because the outermost electron is more strongly attracted by the nucleus than it is repelled, requiring a high amount of energy to be removed.

3. Atomic radius

The larger the atomic radius, the lower the first ionisation energy because the outermost electron is far and weakly attracted by the nucleus, requiring a low amount of energy to be removed. The smaller the atomic radius, the higher the first ionisation energy because the outermost electron is nearer and strongly attracted by the nucleus requiring a higher amount of energy to be removed.

4. Electronic configuration/ electronic structure

Atoms with outermost sub energy levels half-filled or completely filled with electrons are thermodynamically stable and require abnormally higher amount of energy to remove an electron. Atoms whose outermost sub energy levels are neither half-filled nor completely filled with electrons are unstable and require a low amount of energy to remove an electron.

5. Penetrating power of valence electrons

If an electron is to be removed in a sub energy level which is more penetrating, the first ionisation energy is higher. If the electron is in a less penetrating sub energy level, the ionisation energy is lower. Penetrating power increases in the order; $f < d < p < s$.

Variation in ionisation energy in Periods and groups

- The table below shows the first ionization energies of the elements in Period 2 of the Periodic Table.

Element	<i>Li</i>	<i>Be</i>	<i>B</i>	<i>C</i>	<i>N</i>	<i>O</i>	<i>F</i>	<i>Ne</i>
First ionization energy (kJmol ⁻¹)	520	899	800	1086	1402	1314	1681	2080

(a) State and explain the general trend in first ionisation energy

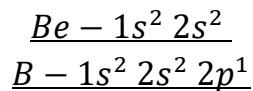
(b) Briefly explain why;

- (i) Beryllium has an abnormally higher value than boron
- (ii) Oxygen has an abnormally lower value than nitrogen
- (iii) the ionisation energy of neon is very high

(a) First ionization energy generally increases from lithium to neon.

This is because from lithium to neon, nuclear charge increases because a proton is added to nucleus from element to element. Screening effect almost remains constant, because electrons are added to the same energy level. Effective nuclear charge increases, atomic radius reduces and outer most electron is closer and more strongly attracted than repelled by the nucleus requiring a high amount of energy to be removed.

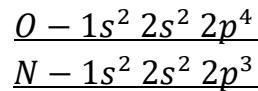
(b) (i)



For Beryllium, an electron is removed from a completely filled 2s-sub energy level which is thermodynamically stable. Higher amount of energy is required to remove the electron

For Boron, an electron is removed from a 2p-sub energy level which has only one electron hence thermodynamically unstable. Lower amount of energy is required to remove the electron.

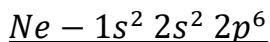
(ii)



For oxygen, the electron is removed from a 2p-sub energy level which has four electrons hence thermodynamically unstable. Lower amount of energy is required to remove the electron.

For nitrogen, an electron is removed from a half filled 2p-sub energy level which is thermodynamically stable. Higher amount of energy is required to remove the electron

(iii)



For neon, an electron is removed from a completely filled 2p-sub energy level which is thermodynamically stable. High amount of energy is required to remove the electron

2. The table below shows the first ionization energies of Group VII elements.

Element	F	Cl	Br	I
First ionisation energy (kJmol^{-1})	1681	1255	1142	1007

State and explain the trend in ionization energy of the elements

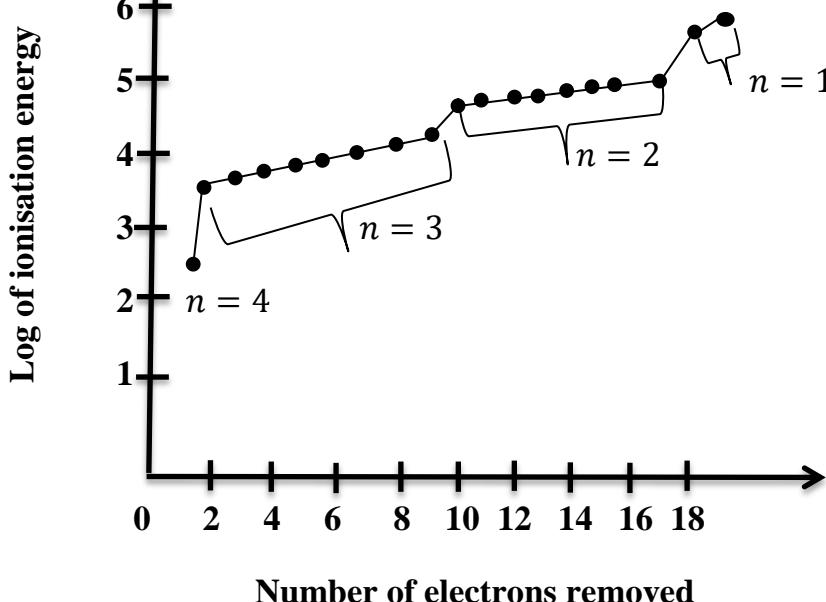
First ionization energy decreases from fluorine to iodine.

This is because from fluorine to iodine, nuclear charge increases, screening effect also increases, because an extra energy level completely filled with electrons is added from element to element. Increase in screening effect outweighs increase in nuclear charge. Effective nuclear charge decreases, atomic radius increases and outer most electron is far and weakly attracted by the nucleus requiring a low amount of energy to be removed.

Successive ionisation energies

The evidence for arrangement of electrons in energy levels of atoms is provided by values of successive ionisation energies for elements. A plot of successive ionisation energies against the order in which electrons can be made for any atom. A logarithmic plot of the ionisation energies is used to give a condensed graph.

1. Below is a plot of \log_{10} Ionisation energy against number of electrons removed for element Q



A lot of information can be obtained from the graph about element Q.

(i) **The atomic number**

From the graph, a *total of 19 electrons* are removed from the atom. Since *number of electrons is equal to proton number for a neutral atom*, **Q has atomic number 19**. The number of successive ionisation energies indicate the number of electrons removed from an atom.

(ii) **Group of an element in the Periodic Table.**

From the graph, the removal of the first electron requires the *lowest ionisation energy*. This electron is the *easiest to remove* because it is *strongly shielded from nuclear attraction and weakly attracted by the nucleus*. Q therefore is in **group I**

(iii) **Valeency**

Q has valence one since it has one electron in the outermost energy level, strongly shielded from the nucleus and easily lost.

(iv) **Electronic configuration and number of energy levels.**

From the graph, there is an abnormally large increase from first to second ionisation energies. This implies that the second electron is removed from an inner energy level, completely filled with electrons, thermodynamically stable and closer to the nucleus than the outermost energy level. The outermost energy level therefore has one electron. There is a gradual increase from second to ninth ionisation energies. This implies that the next

eight electrons occupy the same energy level, nearer to the nucleus than the outermost energy level. There is an abnormally large increase from the ninth to tenth ionisation energies. This implies that the tenth electron is removed from an inner energy level, completely filled with electrons, thermodynamically stable and closer to the nucleus. There is a gradual increase from tenth to seventeenth ionisation energies. This implies that the next eight electrons occupy the same energy level and nearer to the nucleus. There is an abnormally large increase from the seventeenth to eighteenth ionisation energies. This implies that the eighteenth electron is removed from an inner energy level, completely filled with electrons, thermodynamically stable and closer to the nucleus. The last two electrons occupy the innermost energy level, closest to the nucleus and require the highest amount of energy to be removed due to a very strong nuclear attraction.

Q therefore has **four energy levels** with electronic configuration as shown below.

Energy level	$n = 1$	$n = 2$	$n = 3$	$n = 4$
Number of electrons	2	8	8	1
Electronic configuration	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6$	$4s^1$

(v) **Period in the Periodic Table**

Q is in Period 4 since it has four energy levels

From all the information above, it can be concluded that element Q is potassium.

Successive ionisation energies can also be used to determine whether an element is metallic or non-metallic. Nonmetals have first ionisation energy values of magnitude 800kJmol^{-1} and above while metals have first ionisation energies normally below 800kJmol^{-1} .

Noble gases have the highest first ionisation energies because they have stable configurations and require very high energies to remove an electron.

2. The table below shows the first four successive ionisation energies of elements A, B, C, D and E.

Element	Ionisation energy(kJmol^{-1})			
	1 st	2 nd	3 rd	4 th
A	800	2400	3700	25000
B	900	1800	14800	21000
C	500	4600	6900	9500
D	1090	2400	4600	6200
E	1310	3400	5300	7500

(a) Explain the trend in the ;

- (i) Successive ionisation energies for the elements.
- (ii) Successive ionisation energies for element E.

(b) With reasons, state the group to which the elements A, B, C and D belong.

(a) (i) Successive ionisation energies increase from first to second to third to fourth because as **successive electrons** are removed, the number of protons becomes greater than the number of the remaining electrons, screening effect reduces, effective nuclear charge increases and the remaining electrons become strongly attracted by the nucleus thus requiring a high amount of energy to be removed.

(ii) For element E, successive ionisation energies increase from first to second to third to fourth because as **successive electrons** are removed, the number of protons becomes greater than the number of the remaining electrons, screening effect reduces, effective nuclear charge increases and the remaining electrons become strongly attracted by the nucleus thus requiring a high amount of energy to be removed. **However, there is a greater increase in ionisation energy from first to second compared to the second and third, third and fourth ionisation energies because the second electron is in an inner energy level, completely filled with electrons, thermodynamically stable and nearer the nucleus.**

(b) **A belongs to group III.** This is because the difference between the third and fourth ionisation energies is very big compared to the difference between first and second, second and third ionisation energies. This implies that the fourth electron is removed from an inner energy level, completely filled with electrons, thermodynamically stable and closer to the nucleus and *the first three electrons are in an outermost energy level.*

B belongs to group II. This is because the difference between second and third ionisation energies is very big compared to the difference between first and second, third and fourth ionisation energies. This implies that the third electron is removed from an inner energy level, completely filled with electrons, thermodynamically stable and closer to the nucleus and *the first two electrons are in an outermost energy level.*

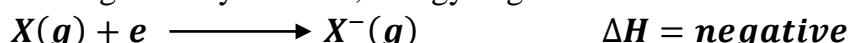
C belongs to group I. This is because the difference between first and second ionisation energies is very big compared to the difference between second and third , third and fourth ionisation energies. This implies that the second electron is removed

from an inner energy level, completely filled with electrons, thermodynamically stable and closer to the nucleus and *the first electron is in an outermost energy level.*

D belongs to group I. This is because the difference between first and second ionisation energies is very big compared to the difference between second and third , third and fourth ionisation energies. This implies that the second electron is removed from an inner energy level, completely filled with electrons, thermodynamically stable and closer to the nucleus and *the first electron is in an outermost energy level.*

Electron affinity

When an electron is gained by an atom, energy is given out.



This energy is called first electron affinity.

First electron affinity is the energy given out when **one mole** of electrons combines with **one mole** of gaseous atoms to form **one mole** of uninegatively charged gaseous ions or

The energy given out when **an electron** is added to a gaseous atom to form a uninegatively charged **gaseous ion**

First electron affinity is an **exothermic process** (energy is given out)

The uninegatively charged gaseous ion can gain one more electron to form a dinegatively charged ion. This is called second electron affinity and is an **endothermic process** (energy is absorbed)



- Explain why the first electron affinity of oxygen is -142 kJmol^{-1} and the second electron affinity of oxygen is $+702 \text{ kJmol}^{-1}$



First electron affinity of oxygen is negative because heat is given out when an electron is added to **neutral gaseous oxygen atom** to form uninegatively charged gaseous oxygen atom. This incoming electron experiences a greater attraction by the nucleus than it is repelled. There is however repulsion when an electron is being added to the **negatively charged gaseous ion**. Energy must be absorbed to add this electron such that the repulsion is overcome. This makes the second electron affinity positive.

The variation in first electron affinity down a group or across a period is determined by the factors;

1. Nuclear charge

The higher the nuclear charge, the higher the first electron affinity because the incoming electron is strongly attracted than it is repelled by the nucleus, giving off a high amount of energy. The lower the nuclear charge, the lower the first electron affinity because the incoming electron is weakly attracted by the nucleus, giving off a low amount of energy.

2. Screening effect

The higher the screening effect, the lower the first electron affinity because the incoming electron is strongly repelled than it is attracted by the nucleus, giving off a low amount of energy. The lower the screening effect, the higher the first electron affinity because the incoming electron is more strongly attracted by the nucleus than it is repelled, giving off a high amount of energy.

3. Atomic radius

The larger the atomic radius, the lower the first electron affinity because the incoming electron is far and more strongly repelled than it is attracted by the nucleus, giving off a low amount of energy. The smaller the atomic radius, the higher the first electron affinity because the incoming electron is nearer and more strongly attracted by the nucleus than it is repelled giving off a higher amount of energy.

4. Electronic configuration

Atoms with outermost sub energy levels half-filled or completely filled with electrons are thermodynamically stable and resist addition of an incoming electron. Energy must be absorbed to add this electron because it experiences greater repulsion than attraction. This results into a low amount of energy of first electron affinity. Atoms whose outermost sub energy levels are neither half-filled nor completely filled with electrons are unstable. The incoming electron experiences more attraction than repulsion, giving off a higher amount of energy.

2. The table below shows the variation in the first electron affinity of the elements in Period 3 of the Periodic Table.

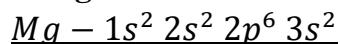
Element	Na	Mg	Al	Si	P	S	Cl	Ar
First electron affinity (kJmol^{-1})	-21	+67	-44	-135	-72	-200	-364	0

(a) Plot a graph of first electron affinity against atomic number

(b) State and explain the general trend in first electron affinity from sodium to argon

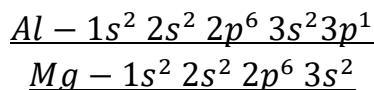
From sodium to argon, nuclear charge increases because a proton is added to nucleus from element to element. Screening effect almost remains constant, because electrons are added to the same energy level. Effective nuclear charge increases, atomic radius reduces. The attraction for the incoming electron increases thus increasing the electron affinity.

- (i) the first electron affinity of magnesium is lower than the rest.



For magnesium, the electron is added to a completely filled 3s-sub energy level which is thermodynamically stable. The incoming electron experiences greater repulsion by the existing electrons than nuclear attraction. Energy must therefore be absorbed to add the incoming electron. The first electron affinity is therefore endothermic.

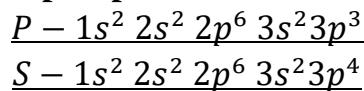
- (ii) the first electron affinity of aluminium is lower than that of magnesium



For aluminium, the electron is added to the 3p-sub energy level which has one electron and thermodynamically unstable. The incoming electron experiences more attraction by the nucleus than repulsion.

For magnesium, the electron is added to a completely filled 3s-sub energy level which is thermodynamically stable. The incoming electron experiences greater repulsion by the existing electrons than nuclear attraction.

- (iii) the first electron affinity of phosphorus is lower than that of Sulphur.



For phosphorus, the electron is added to a half filled 3p-sub energy level which is thermodynamically stable. The incoming electron experiences more repulsion than attraction by the nucleus.

For Sulphur, the incoming electron is added to a 3p-sub energy level which has four electrons, thermodynamically stable. The incoming electron experiences greater repulsion by the existing electrons than nuclear attraction.

3. The table below shows the first electron affinities and atomic numbers of the elements in Group VII

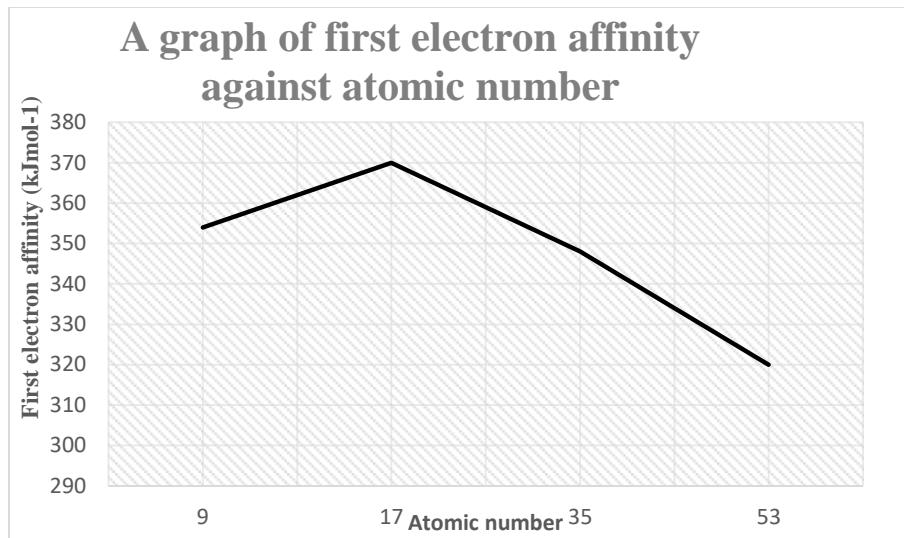
Element	<i>F</i>	<i>Cl</i>	<i>Br</i>	<i>I</i>
Atomic number	9	17	35	53
First electron affinity(kJmol ⁻¹)	-354	-370	-348	-320

(a) Explain what is meant by the term first electron affinity

(b) Plot a graph of first electron affinity against atomic number of the elements.

(To be done by student. When plotting the graph, the negative sign may be eliminated since it's on all values and it just indicates that the process is exothermic. The graph below is just a sketch and not on scale)

- (c) (i) Explain the general trend in variation of the first electron affinities
(ii) Explain why fluorine has an abnormal value



- (a) (i) Generally, first electron affinity decreases from fluorine to iodine.

This is because from fluorine to iodine, nuclear charge increases, screening effect also increases, because an extra energy level completely filled with electrons is added from element to element. Increase in screening effect outweighs increase in nuclear charge. Effective nuclear charge decreases, atomic radius increases and incoming electron is far and weakly attracted by the nucleus giving off a low amount of energy.

(ii) Fluorine has the smallest atomic radius, highest **electron density**, strongly repels the incoming electron and energy is consumed to add the electron to its atom.

Electronegativity

The tendency of an atom to attract bonding electrons towards itself in a covalent bond.

Electronegativity is very important factor in determining the degree of polarity of in any covalent bond. The greater the difference between the electronegativities of two atoms, the greater the ionic character. In hydrogen fluoride, the electron density of the bonding electrons lies more towards the fluorine atom than the hydrogen atom because fluorine is more electronegative than hydrogen. This makes fluorine gain a partial negative charge and hydrogen a partial positive charge, making the hydrogen fluorine bond polar.



Fluorine is the most electronegative element, followed by oxygen and nitrogen. The halogens follow after the three elements. Alkali metals have lowest values of electronegativity.

The table below shows some common elements and their electronegativity values

H	2.1	Be	1.5	B	2.0	C	2.5	N	3.0	O	3.5	F	4.0
Li	1.0	Mg	1.2	Al	1.5	Si	1.8	P	2.1	S	2.5	Cl	3.0
Na	0.9	Ca	1.0									Br	2.8
K	0.8	Sr	1.0									I	2.5

The variation in electronegativity down a group or across a period is determined by the factors;

1. Nuclear charge

The higher the nuclear charge, the higher the electronegativity because the bonding electrons are strongly attracted by the nucleus. The lower the nuclear charge, the lower the electronegativity because the bonding electrons are weakly attracted by the nucleus.

2. Screening effect

The higher the screening effect, the lower the electronegativity because the bonding electrons are strongly repelled. The lower the screening effect, the higher the electronegativity because the bonding electrons are less shielded from the nuclear attraction.

3. Atomic radius

The larger the atomic radius, the lower the electronegativity because the bonding electrons are far and weakly attracted by the nucleus. The smaller the atomic radius, the higher the electronegativity because the bonding electrons are nearer and strongly attracted by the nucleus.

1. The table below shows the electronegativity values of the elements in Period 3 of the Periodic Table.

Element	Na	Mg	Al	Si	P	S	Cl
Electronegativity	1.0	1.2	1.5	1.8	2.1	2.5	3.0

State and explain the trend in electronegativity values of the elements

Electronegativity increases from sodium to chlorine.

This is because from sodium to chlorine, nuclear charge increases because a proton is added to nucleus from element to element. Screening effect almost remains constant,

because electrons are added to the same energy level. Effective nuclear charge increases, atomic radius reduces and the bonding electrons experience a greater nuclear attraction.

- 2. The table below shows the electronegativity values of the elements in Group II of the Periodic Table.**

Element	<i>Be</i>	<i>Mg</i>	<i>Ca</i>	<i>Sr</i>	<i>Ba</i>
Electronegativity	1.57	1.31	1.00	0.95	0.89

State and explain the trend in electronegativity values of the elements

Electronegativity decreases from Beryllium to Barium.

This is because from Beryllium to Barium, nuclear charge increases, screening effect also increases, because an extra energy level completely filled with electrons is added from element to element. Increase in screening effect outweighs increase in nuclear charge. Effective nuclear charge decreases, atomic radius increases, and the bonding electrons experience a greater repulsion than nuclear attraction.

Electropositivity

The tendency of an atom of an element to lose its valence electrons to become positively charged

The variation in electropositivity down a group or across a period is determined by the factors;

1. Nuclear charge

The higher the nuclear charge, the lower the electropositivity because the valence electrons are strongly attracted and cannot easily be lost. The lower the nuclear charge, the higher the electropositivity because the valence electrons are weakly attracted by the nucleus and can easily be lost.

2. Screening effect

The higher the screening effect, the higher the electropositivity because the valence electrons are weakly attracted by the nucleus and can easily be lost. The lower the screening effect, the lower the electropositivity because the valence electrons are strongly attracted by the nucleus and cannot easily be lost.

3. Atomic radius

The larger the atomic radius, the higher the electropositivity because the valence electrons are far and weakly attracted by the nucleus hence are easily lost. The smaller the atomic radius, the lower the electropositivity because the valence electrons are nearer and strongly attracted by the nucleus hence not easily lost.

4. Electronic configuration

Atoms with outermost sub energy levels half-filled or completely filled with electrons are thermodynamically stable hence do not easily lose the valence electrons, reducing electropositivity. Atoms whose outermost sub energy levels are neither half-filled nor completely filled with electrons are unstable. The valence electrons are weakly attracted hence easily lost, increasing electropositivity.

Variation of electropositivity across period 3

Electropositivity decreases from sodium to chlorine.

This is because from sodium to chlorine, nuclear charge increases because a proton is added to nucleus from element to element. Screening effect almost remains constant, because an electron is added to the same energy level. Effective nuclear charge increases, atomic radius reduces and the valence electrons experience a greater nuclear attraction hence not easily lost.

Variation of electropositivity across group II

Electropositivity increases from beryllium to Barium.

This is because from Beryllium to Barium, nuclear charge increases, screening effect also increases, because an extra energy level completely filled with electrons is added from element to element. Increase in screening effect outweighs increase in nuclear charge. Effective nuclear charge decreases, atomic radius increases and the valence electrons experience a lower nuclear attraction than repulsion hence easily lost.

Metallic character

Metallic character decreases from left to right across a period because electropositivity decreases for reasons already explained. Metallic character also increases down a group since electropositivity increases for reasons also already explained.

For variation in Standard electrode potential check under electrochemistry in this same book and for variation in melting and boiling points in groups and periods, check Demystifying Inorganic Chemistry by the same author,

Questions

1. The table below shows the values for atomic and ionic radii of alkali metals.

Element	Atomic number($\times 10^{-10}m$)	Ionic radius ($\times 10^{-10}m$)
Lithium	1.23	0.68
Sodium	1.57	0.97
Potassium	2.03	1.33
Rubidium	2.16	1.47
Caesium	2.35	1.67

- (a) In every case, the ionic radius is smaller than the corresponding atomic radius. Explain.
- (b) Explain the increase in atomic radius along the series Lithium to Caesium
- (c) The ions Na^+ , Mg^{2+} and Al^{3+} , have the same electronic configuration yet they have different ionic radii. Suggest a reason for this.
- (d) Which one of the alkali metal ions in the gaseous state is likely to have the highest hydration energy? Give a reason.
2. The table below shows the atomic radii and ionic radii of the elements in Group VII of the Periodic Table.

Element	F	Cl	Br	I
Atomic radius(nm)	0.072	0.099	0.114	0.133
Ionic radius(nm)	0.136	0.181	0.195	0.216

- (a) State and explain the trend in atomic radius of the elements.
- (b) Explain why the ionic radius is larger than the atomic radius of corresponding neutral atom for each element.
3. The table below shows the first ionization energies of the elements in Period 3 of the Periodic Table.

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic number	11	12	13	14	15	16	17	18
First ionization energy (kJmol ⁻¹)	496	738	578	786	1012	1000	1251	1521

- (a) Plot a graph of ionization energy against atomic number of the elements
- (b) State and explain the trend in ionization energy of the elements
- (c) Explain why the;
- (i) first ionization energy of argon is very high
 - (ii) first ionization energy of Sulphur is less than that of phosphorus
 - (iii) first ionization energy of aluminium is less than that of magnesium

4. The table below shows the first ionization energies of Group II elements

Element	<i>Be</i>	<i>Mg</i>	<i>Ca</i>	<i>Sr</i>	<i>Ba</i>
First ionisation energy (kJmol^{-1})	899	738	589	549	502

Define the term first ionisat

CHAPTER THREE

STRUCTURE AND BONDING

CHEMICAL BONDING

Chemical bonding is one of the basic fundamentals of chemistry that explain other concepts such as chemical reactions. An atom consists of the nucleus containing protons and neutrons and electrons in certain energy levels rotating around the nucleus. In chemical bonding, only the valence electrons (electrons located in the outermost energy levels) of an atom are involved.

Chemical bonds are forces that hold atoms, ions or molecules together to make compounds. During formation of a chemical bond, atoms combine in order to acquire a noble gas electronic structure. This can be achieved by either transfer of electrons from one atom to another or by sharing electrons contributed by each atom or by electrostatic attraction between delocalized electrons and positively charged ions.

Lewis Dot symbols

The American chemist **G.N. Lewis** devised a system of symbols called **Lewis electron dot symbols** that can be used to predict the number of bonds formed by most elements in their compounds. Each Lewis Dot symbol consists of the chemical symbol of the element surrounded by dots. The dots represent the valence electrons of an element.

The following steps can be followed to draw Lewis Dot symbols of different elements

1. Identify the number of valence electrons for the element. These are the total number of electrons in the outermost energy level. They can be known by the electronic configuration
2. Write the correct chemical symbol of the element
3. Put one dot in all directions; up, down, left and right of the element symbol
4. If some electrons are left, begin doubling the dots

From the Lewis Dot symbol of each element, we can predict the number of bonds an element can form during bonding.

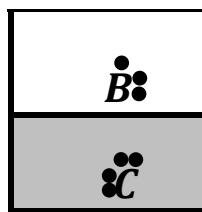
*Number of bonds formed by an element
= the number of unpaired electrons present in its Lewis Dot symbol*

Examples

Draw the Lewis Dot symbols for the elements Boron, Carbon, Nitrogen and Oxygen

Element	Atomic number	Electronic configuration	Number of Valence electrons	Lewis Dot structure	Number of bonds that can be formed
B	3	$1s^2 2s^1$	1	•B•	Three bonds
C	6	$1s^2 2s^2 2p^2$	4	•C•	Four bonds
N	7	$1s^2 2s^2 2p^3$	5	•N•	Three bonds
O	8	$1s^2 2s^2 2p^4$	6	•O•	Two bonds

Note that the Lewis Dot symbols below cannot be correct because dots have to be placed in all directions before pairing occurs.



The table below shows the electronic configuration of the first 20 elements of the Periodic Table. Use the valence electrons of each element to draw its Lewis Dot structure and predict the number of bonds the element can form

<i>Symbol</i>	<i>Atomic number</i>	<i>Electronic configuration</i>	<i>Lewis Dot structure</i>	<i>Number of bonds that can be formed</i>
<i>H</i>	1	$1s^1$		
<i>He</i>	2			
<i>Li</i>	3			
<i>Be</i>	4	$1s^2 2s^2$		
<i>B</i>	5			
<i>C</i>	6	$1s^2 2s^2 2p^2$		
<i>N</i>	7			
<i>O</i>	8			
<i>F</i>	9	$1s^2 2s^2 2p^5$		
<i>Ne</i>	10			
<i>Na</i>	11	$1s^2 2s^2 2p^6 3s^1$		
<i>Mg</i>	12			
<i>Al</i>	13	$1s^2 2s^2 2p^6 3s^2 3p^1$		
<i>Si</i>	14	$1s^2 2s^2 2p^6 3s^2 3p^2$		
<i>P</i>	15			
<i>S</i>	16			
<i>Cl</i>	17	$1s^2 2s^2 2p^6 3s^2 3p^5$		
<i>Ar</i>	18	$1s^2 2s^2 2p^6 3s^2 3p^6$		
<i>K</i>	19			
<i>Ca</i>	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$		

The octet rule and ions

Most elements, except noble gases, combine with other elements to form compounds. Compounds are the result of formation of chemical bonds between two or more atoms of different elements.

In the formation of a chemical bond, atoms lose, gain or share valence electrons to completely fill their outermost energy levels and attain a noble gas configuration. This tendency of atoms to have eight electrons in their outermost energy levels is known as the **octet rule**.

It states that; an atom is most stable when there are eight electrons in its outermost energy level.

Only the *s* and *p* electrons are involved in the octet rule. It does not apply to *d* or *f* electrons.

Atoms of metallic elements have few electrons in their outer most sub energy levels. By losing those electrons, metals can gain a noble gas configuration and satisfy the octet rule. Similarly, atoms of nonmetals have close to eight electrons in their outermost sub energy levels. They tend to readily accept electrons to achieve the noble gas configuration, satisfying the octet rule.

The octet rule is important in the following ways;

1. It explains the formation of chemical bonds in various compounds depending on the nature of the elements involved.
2. It is used to predict stability of atoms

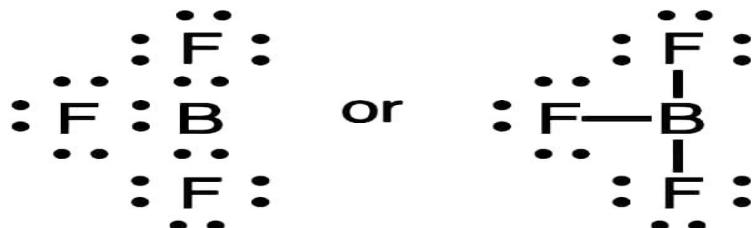
Point of thought;

1. *Outline the importance of the Octet rule in formation of ions and stability of compounds.*
2. *Identify the stable ions of the first 20 elements of the Periodic Table using the Octet rule.*

Stable ions without an Octet

There are a number of elements whose atoms can exist in stable compounds by forming bonds with less than eight valence electrons. When this occurs, the atom of the element within the molecule is said to have an incomplete octet. The examples include; hydrogen ion, beryllium ion, boron ion and aluminium ion. The boron ion and aluminium ion can

form stable ions in covalent compounds like boron trifluoride and aluminium chloride. The phosphorus atom in phosphorus pentachloride has 10 electrons and Sulphur in Sulphur hexafluoride has 12.



Ionic bond formation

An ionic bond is also called an electrovalent bond.

It is formed by *complete transfer of one or more electrons* from one atom to another to form *oppositely charged ions*.

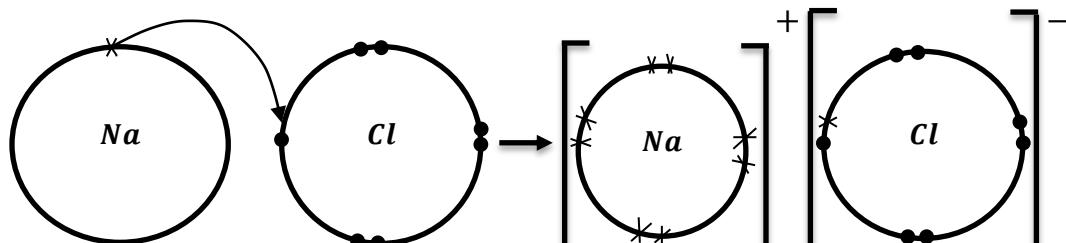
The electron or electrons are transferred from *a metallic element* to a *nonmetallic element*.

The element that *loses electrons is electropositive* since it forms *a positive ion*. The element *gaining electrons is electronegative* since it forms a *negative ion*.

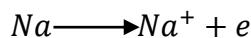
The cation and anion formed are held together by *strong electrostatic forces of attraction*.

Examples;

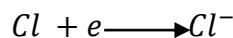
(i) Formation of sodium chloride



The sodium atom has electronic configuration, $1s^2 2s^2 2p^6 3s^1$. The $3s$ subenergy level has one electron and is unstable. This electron is transferred to the chlorine atom by sodium to form noble gas configuration, $1s^2 2s^2 2p^6$. A Sodium ion is formed.



The chlorine atom has electronic configuration, $1s^2 2s^2 2p^6 3s^2 3p^5$. The $3p$ subenergy level has five electrons and is unstable. The electron transferred from sodium occupies this sub energy level to form noble gas configuration, $1s^2 2s^2 2p^6 3s^2 3p^6$. A chloride ion is formed.



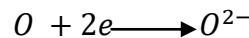
The sodium ion and chloride ion get hold together by strong electrostatic forces of attraction.

(ii) Formation of magnesium oxide

The magnesium atom has electron configuration, $1s^2 2s^2 2p^6 3s^2$. The two 3s electrons are transferred to the chlorine atom by magnesium to form noble gas configuration, $1s^2 2s^2 2p^6$. A magnesium ion is formed.



The oxygen atom has electron configuration, $1s^2 2s^2 2p^4$. The 2p sub energy level has four electrons and is unstable. The two electrons transferred from magnesium occupy this sub energy level to form noble gas configuration, $1s^2 2s^2 2p^6$. An oxide ion is formed.



The magnesium ion and oxide ion get hold together by strong electrostatic forces of attraction.



Giant ionic structures

In giant ionic structures, metallic elements combine with non-metallic elements.

The ionic bonds formed in these compounds are strong electrostatic attractions between the ions of opposite charges (cations and anions).

Each ion is surrounded by the greatest number of positive oppositely charged ions called the coordination number.

Examples of giant ionic solids include **sodium chloride**, **caesium chloride** and **zinc blende**.

Check under matter (specifically under the solid state of matter for details about giant ionic structures)

Structures of some ionic compounds

Compound	Structure
Sodium oxide	$(Na^+)_2O^{2-}$
Magnesium oxide	$Mg^{2+}O^{2-}$
Calcium chloride	$Ca^{2+}(Cl^-)_2$

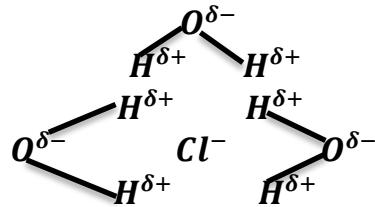
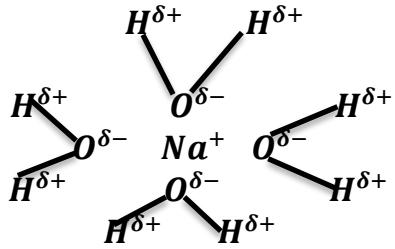
Sodium hydride	$Na^+ H^-$
Magnesium sulphate	$Mg^{2+} SO_4^{2-}$

The properties of ionic compounds

Property	Explanation
1. High melting and boiling points.	<i>There are strong electrostatic forces of attraction between the oppositely charged ions that require a high amount of energy to break.</i>
2. They are strong electrolytes in molten state or aqueous state	<i>In the ionizing solvent, the forces of attraction between the ions are greatly reduced and the oppositely charged ions become free to move in molten or aqueous state under the influence of an electric field.</i>
3. They readily dissolve polar solvents like water but insoluble in non-polar solvents like methylbenzene	<i>The ion-solvent interactions are stronger than ion-ion interactions of the compound for polar solvents. Ion-ion interaction is stronger than ion-solvent interaction and solvent-solvent interaction for non-polar solvents.</i>
4. Exist as crystalline solids at room temperature	<i>There are strong electrostatic forces of attraction between the oppositely charged ions that require a high amount of energy to break.</i>

Explain why sodium chloride is soluble in water but insoluble in benzene.

On dissolving in water, the electrostatic forces of attraction between the sodium ions and chloride ions in the crystal lattice are greatly reduced. The ions become free to move in solution. Since water is a polar molecule, the sodium ions get attracted to the negative end of water molecules and the chloride ions get attracted to the positive end of the water molecules. The formation of ion-solvent interactions releases enough energy to break the sodium-chlorine bonds. The ion-solvent interactions are stronger than ion-ion interactions in sodium chloride.



Benzene is non-polar. Ion-ion interaction is stronger than ion-solvent interaction and solvent-solvent interaction in benzene.

Covalent character in ionic compounds

The partial covalent character of an ionic bond is explained in terms of **polarising power** and **polarisability**.

1. Polarising power

Polarising power is the power of a cation to distort the electron cloud of an anion.

The greater the polarising power of the cation, the greater the tendency of the cation to form a covalent bond.

Polarising power of a cation depends on;

(i) Charge of the cation

Cations with high charges have high polarising power. The larger the positive charge on the ion, the greater the attraction of the valence electrons. The Al^{3+} ion therefore has a higher polarising power than the Na^+ due to its higher charge.

(ii) Cationic radius

The smaller the ionic radius, the higher the polarising power of the cation. The Al^{3+} ion therefore has a higher polarising power than the Na^+ due to its smaller ionic radius.

(iii) Charge density or charge-radius ratio.

Charge density is the ratio of ionic charge to ionic radius.

Ion	Na^+	Mg^{2+}	Al^{3+}
Ionic radius(nm)	0.095	0.065	0.050
Charge density	$\frac{1}{0.095} = 10.53 \text{ (nm)}^{-1}$	$\frac{2}{0.065} = 30.77 \text{ (nm)}^{-1}$	$\frac{3}{0.050} = 60 \text{ (nm)}^{-1}$

The higher the charge density, the higher the polarising power of the cation. From the table above, charge density and hence polarising power increases in the order $Na^+ < Mg^{2+} < Al^{3+}$. The ionic character of the chlorides formed by the elements increases from sodium chloride to magnesium chloride to aluminium chloride due to the increase in polarising power.

In general, compounds in which a cation has a **high charge** and **small ionic radius** tend to have a **high charge density** and **high polarising power**. This makes such compounds tend to a covalent character and exhibit properties contrary to ionic compounds

Aluminium chloride, beryllium chloride, aluminium hydride, beryllium hydride, beryllium oxide and beryllium hydroxide are partly covalent for reasons explained above.

1. Polarisability

Polarisability is the ease by which the electron cloud of the anion can be distorted.

The greater the polarisability of the anion, the greater the tendency of the anion to form a covalent bond.

Polarisability of an anion depends on the **size of the anion**

The smaller the anion, the lower it is polarizable and the larger the anion, the easier it is polarized.

If we consider the halide ions, polarisability increases in the order $F^- < Cl^- < Br^- < I^-$

Examples to show effect of polarising power of cations and polarisability of anions

- (i) The table below shows the melting points of the chlorides formed by the three Period 3 elements.

Chloride	$NaCl$	$MgCl_2$	$AlCl_3$
Melting point of the chloride ($^{\circ}C$)	801	712	180

State and explain the trend in melting points of the chlorides of the three metals.

Melting points of the chlorides decrease from sodium chloride to aluminium chloride.

Sodium chloride and magnesium chloride have **giant ionic structures held by strong ionic bonds** which require a **high amount of energy to break**. The decrease in melting point from sodium chloride to magnesium chloride is because magnesium ion has a **smaller ionic radius, higher charge density and higher polarising power** than sodium ion making magnesium chloride **less ionic** than sodium chloride. Aluminium chloride has the **lowest melting point** because among the cations, the aluminium ion has the **smallest ionic radius, highest charge density and highest polarising power**. Aluminium chloride is therefore **predominantly covalent**. Covalent bonds require a **low amount of energy to break**

- (ii) Aluminium chloride dissolves in methylbenzene but sodium chloride does not. The **aluminium ion** in aluminium chloride has a **higher charge and a smaller ionic radius** than the **sodium ion** in sodium chloride. The aluminium ion therefore has a **higher charge density and higher polarising power** than the sodium ion. The chloride ion being **greatly polarized** by the aluminium ion makes **aluminium chloride mainly covalent** hence soluble in **non-polar** methylbenzene. However, sodium chloride is **purely ionic** and **insoluble in non-polar solvents**.

- (iii) The melting point of lead(II) chloride is 500°C whereas that of tin(II) chloride is 247°C. Explain this observation.

Lead(II) ion has a larger ionic radius than tin(II) ion. Therefore the tin(II) ion has a higher charge density and polarising power than the lead(II) ion. This makes tin(II) chloride mainly covalent whereas lead(II) chloride is mainly ionic. Covalent bonds need a lower amount of energy to break than ionic bonds.

- (iv) Lead(II) chloride is insoluble in ethanol whereas lead(IV) chloride readily dissolves in ethanol.

The lead(II) ion in lead(II) chloride has a smaller charge and a larger ionic radius than the lead(IV) ion in lead(IV) chloride. Therefore the lead(II) ion has a lower charge density and lower polarising power than the lead(IV) ion. This makes lead(II) chloride mainly ionic hence insoluble in nonpolar solvents whereas lead(II) chloride is mainly covalent hence soluble in non-polar solvents.

- (v) the melting point of calcium oxide is higher than that of calcium chloride

The oxide ion in calcium oxide has a smaller ionic radius than the chloride ion in calcium chloride. Therefore the oxide ion less easily polarized by the calcium ion whereas the chloride ion is more easily polarized by the calcium ion. This makes calcium oxide more ionic than calcium chloride. The ionic bonds in calcium oxide require a higher amount of energy to break.

- (vi) The table below shows the melting points of magnesium halides.

Formula of halide	MgF_2	$MgCl_2$	$MgBr_2$	MgI_2
Melting point($^{\circ}C$)	1263	714	711	634

Explain the general trend in melting points of the halides.

The melting points of the halides increase from magnesium fluoride to magnesium iodide. This is because the anionic radius increases from the fluoride ion to the iodide ion. The degree of polarization of the anions also therefore increases from the fluoride ion to the iodide ion, increasing the covalent character of the halides. Thus a decreasing amount of energy is required to break the magnesium-halogen bonds that become increasingly more covalent.

Questions

1. Explain why
 - (a) calcium iodide is ionic whereas aluminium iodide is covalent
 - (b) Sodium chloride melts at 800 °C whereas aluminium chloride sublimes at 180 °C
 - (c) Beryllium chloride is more soluble in ethanol than in water whereas barium chloride is more soluble in water than in ethanol
 - (d) The solubility of lithium chloride in ethanol is higher than the solubility of potassium chloride in ethanol.
 - (e) aluminium fluoride sublimes at 1270°C whereas aluminium chloride sublimes at 178°C
 - (f) aluminium chloride is soluble in methylbenzene and has a low melting point yet aluminium fluoride is soluble in water and has a higher melting point.
 - (g) tin(II) chloride is a solid whereas tin(IV) chloride is a liquid at room temperature
 - (h) lead(II) fluoride has a higher melting point than lead(IV) fluoride
 - (i) iron(II) chloride is more ionic than iron(III) chloride
2. The values of lattice energies of potassium halides are given below.

Formula of halide	KF	KCl	KI
Lattice energy(kJmol ⁻¹)	-813	-710	-643

Explain the trend in these values for the potassium halides.

3. Explain why
 - (i) the solubility of lead(II) halides increases in the order; $PbI_2 < PbBr_2 < PbCl_2$
 - (ii) melting points of the halides of aluminium decrease in the order;
 $AlF_3 > AlCl_3 > AlBr_3 > AlI_3$
4. The table below shows the melting points of the chlorides of Group II elements.

Chloride	$BeCl_2$	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$
Melting point (°C)	405	714	782	875	962

Explain why;

- (i) the melting point of beryllium chloride is very low
- (ii) melting point increases from magnesium chloride to Barium chloride

Covalent bond formation

A covalent bond is formed when **electrons are shared in pairs** between **two bonded atoms**.

In a single covalent bond between two atoms, one electron is contributed by each atom and is shared as a pair of electrons.

The shared pair of electrons is called a **covalent bond**.

A simplified, well elaborated , illustrative approach to Physical Chemistry

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The shared pair of electrons occupies the same orbital with opposing spins and each of the electrons must be unpaired from the orbital in which it is got.

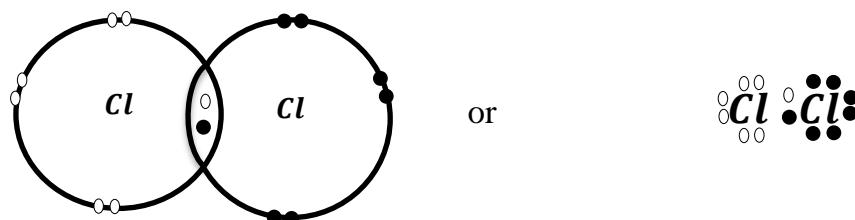
In double covalent bonds, two pairs of electrons are shared and in a triple covalent bond, three pairs of electrons are shared.

Covalent bonds may be formed between atoms of the same element ($H—H$) or atoms of different elements ($H—Cl$)

Usually the bonding atoms contribute an equal number of electrons towards formation of a normal covalent bond.

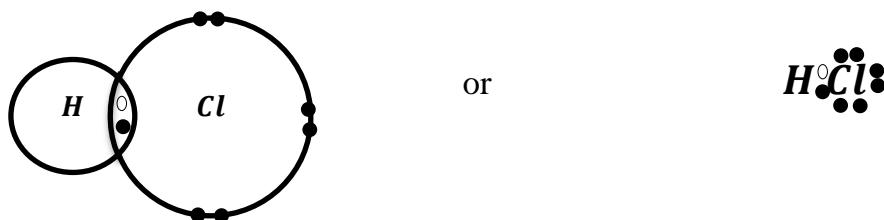
Examples

(i) Formation of chlorine molecule



The chlorine atom has electronic configuration, $1s^2 2s^2 2p^6 3s^2 3p^5$. The chlorine molecule is formed by each of the chlorine atom sharing one of its valence electrons with another atom. The two atoms approach each other closely for their atomic orbitals to overlap.

(ii) Formation of hydrogen chloride molecule

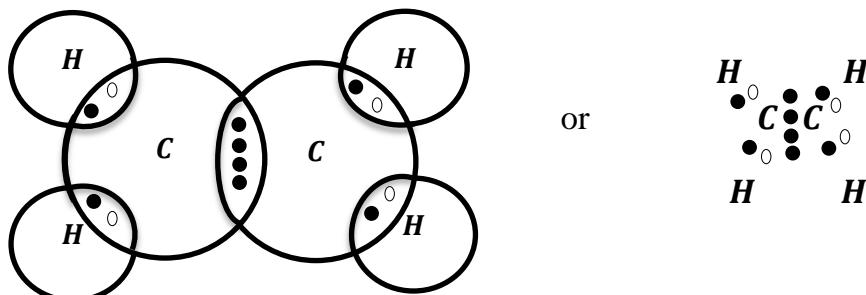


The hydrogen atom has electronic configuration $1s^1$ and the chlorine atom has electronic configuration, $1s^2 2s^2 2p^6 3s^2 3p^5$. Hydrogen contributes its only electron and chlorine contributes one of its valence electrons. The electron pair is shared to make hydrogen have a full s sub energy level and chlorine to have a full octet.

(iii) Formation of ethene

In an ethene molecule, each carbon atom shares one pair of electrons with a hydrogen atom and two pairs of electrons with the other carbon atom. When atoms share two pairs

of electrons, a double bond is formed between them. Each carbon atom forms single bonds to two hydrogen atoms and a double bond to the other carbon atom.



In a simple way, covalent bonds are usually represented by a line to indicate a pair of shared electrons, double lines to indicate two shared pairs and triple lines to indicate a three shared pairs.

Other covalent molecules include; CO_2 , CH_4 , H_2 , O_2 , N_2 , $HC \equiv CH$, NH_3 , H_2O , etc.

Types of covalent bonding

There are three types of covalent bonds which include; **normal covalent bond**, **polar covalent bond** and a **dative covalent bond**.

1. The normal covalent bond

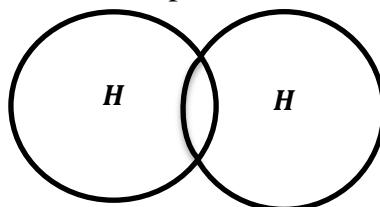
In a normal covalent bond, two atoms with very similar electronegativities or almost similar electronegativities are bonded together and the combined atoms contribute an equal number of electrons to be shared.

One electron is contributed by each atom for a single covalent bond.

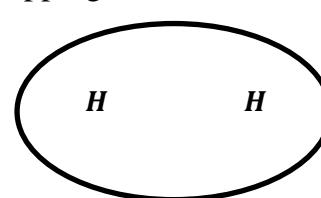
The two electrons that are shared between the atoms must be unpaired and must also have opposite spins from the orbitals from which they are got.

The normal covalent bond results from overlapping of the atomic orbital or charge cloud of one electron with another.

The two atomic orbitals produce one molecular orbital on overlapping as shown below.



Overlapping of atomic orbitals of hydrogen

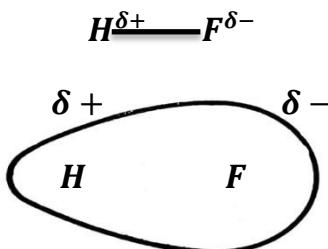


Resulting molecular orbital of hydrogen

2. Polar covalent bond

When a covalent bond is formed between two atoms whose electronegativity values are greatly different, the bond becomes polar. For example in hydrogen fluoride molecule, fluorine is more electronegative than hydrogen. The fluorine atom therefore pulls the

bonding electrons more towards its self. This makes fluorine gain a partial negative charge and hydrogen a partial positive charge, making the hydrogen fluorine bond polar.



The bonding electron density is greater towards the fluorine atom with a small negative charge than towards hydrogen with a small positive charge

Other polar covalent bonds as a results of difference in electronegativity of the bonding atoms include; $H\overset{\delta+}{\text{—}}Cl^{\delta-}$, $H\overset{\delta+}{\text{—}}Br^{\delta-}$, $H\overset{\delta+}{\text{—}}I^{\delta-}$, $H\overset{\delta+}{\text{—}}O^{\delta-}$, $C\overset{\delta+}{\text{—}}Cl^{\delta-}$, etc.

For two equal but opposite separated electrical charges, there exists an electric dipole moment. An electric dipole moment is a product of one of the charges, $\delta+$ or $\delta-$ and the distance between the atomic nuclei. Any individual polar covalent bond must have a corresponding dipole moment.

However, there are molecules in which the individual bonds in it are polar but the molecule as a whole is non-polar. This will be seen later under **polarity of molecules**.

3. Dative covalent bond

A dative covalent bond is formed is a covalent bond formed when the shared pair of electrons by only one of the bonded atoms.

A dative covalent bond is also called a **coordinate covalent bond**.

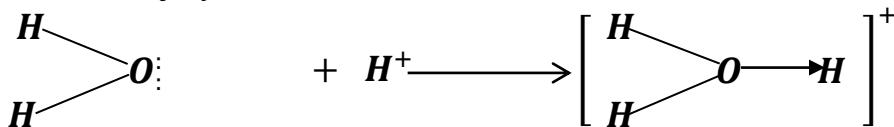
The atom that contributes the pair of the electrons is the **donor atom** and the other atom is called the **acceptor atom**. For an atom to act as a donor atom, it must have atleast one pair of unshared electrons, called a **lone pair**.

For an atom to act as an acceptor atom, it must have atleast one vacant orbital. An acceptor can be a **transition metal atom** or an **atom in a molecule**.

An arrow (\longrightarrow) is always drawn from the donor atom to the acceptor atom to show a dative bond.

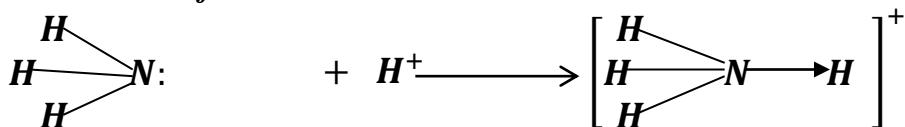
Examples

(i) Formation of hydroxonium ion.



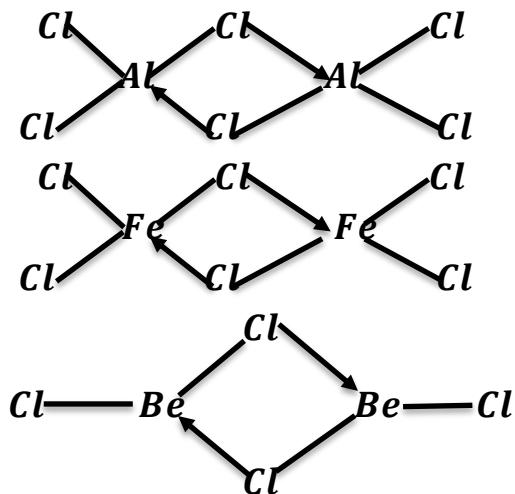
This ion is formed by coordination of water to a hydrogen ion. The oxygen atom in the water molecule has two lone pair of electrons. The hydrogen ion has electronic configuration $1s^0$.The hydrogen ion therefore accepts one of the lone pairs of electrons from oxygen to have a full 1s sub energy level. This results into formation of the hydroxonium ion.

(ii) *Formation of Ammonium ion*

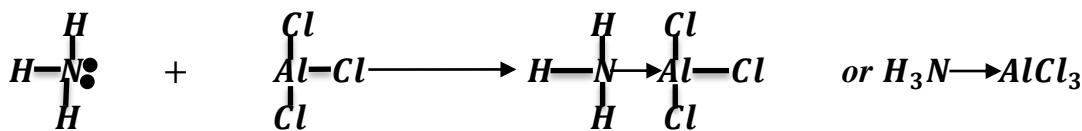


This ion is formed by coordination of ammonia to a hydrogen ion. The nitrogen atom in the ammonia molecule has a lone pair of electrons. The hydrogen ion has electronic configuration $1s^0$.The hydrogen ion therefore accepts the lone pair of electrons from nitrogen to have a full 1s subenergy level. This results into formation of the ammonium ion.

(iii) *Formation of dimerised aluminium chloride(Al_2Cl_6), dimerised iron(III) chloride(Fe_2Cl_6) and dimerised beryllium chloride(Be_2Cl_4).*



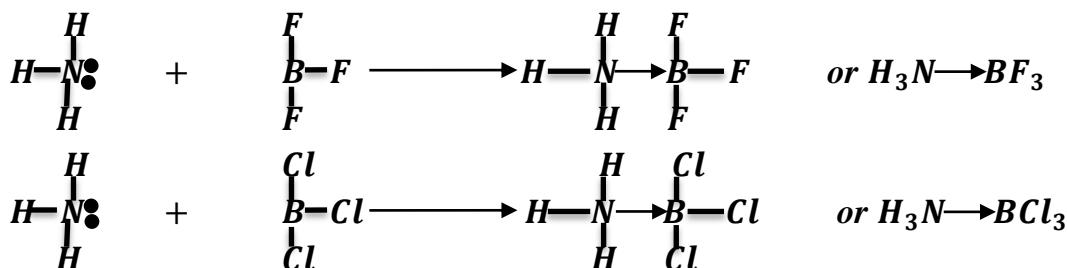
(iv) *Reaction between ammonia and anhydrous aluminium chloride*



The nitrogen atom in the ammonia molecule has a lone pair of electrons. The aluminium atom has only three valence electrons. When aluminium covalently bonds with three chlorine atoms in aluminium chloride, it has six electrons in its outermost energy level, requiring two electrons to complete its octet. Since nitrogen is more electronegative than

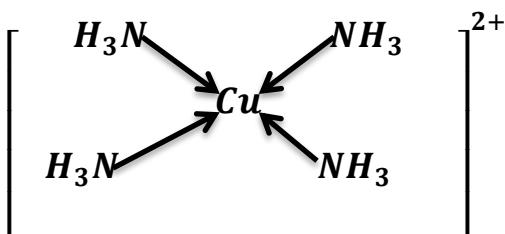
hydrogen in ammonia, it has a partial negative charge. Also aluminium is less electronegative than chlorine in aluminium chloride, hence has a partial positive charge. There is therefore an attraction between nitrogen atom and aluminium atom. The lone pair of electrons on the nitrogen atom is donated to the aluminium atom to form a dative bond.

Ammonia can also form coordinate bonds with boron trifluoride or boron trichloride



(v) Formation of transition metal complexes

In transition metal complexes, the donor atoms in ligands donate lone pairs of electrons to the central metal atoms. These electrons occupy the empty d-orbitals of the transition metal atoms. The ion formed is called a complex ion. An example is the tetraamminecopper(II) ion.



A distinction between the different types of covalent bond

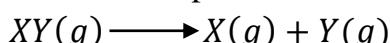
Normal covalent bond	Polar covalent bond	Dative or coordinate covalent bond
Can be formed between two similar atoms of the same element	The atoms involved must be different	A dative bond is formed between two different atoms
Can occur between atoms of the same electronegativity or almost similar electronegativities	The bond occurs between atoms with different electronegativities	
Each atom contributes an equal number of electrons to be shared		The bonding electrons are contributed by only one of the involved atoms

Covalent bond strength

The strength of a bond is represented by its **bond dissociation energy**.

Bond dissociation energy is defined as the heat change that occurs when one mole of a covalent bond is broken down into its constituent gaseous atoms.

Bond dissociation energy is an endothermic process hence denoted by a positive value.



Strength of a covalent bond depends on the following factors;

(i) Bond length

The shorter the bond length, the stronger the covalent bond and the longer the bond length, the weaker the covalent bond. This is because when bond length increases, the region of space between atoms in which electrons are shared becomes proportionally smaller as atomic radius increases.

(ii) Atomic radius

The larger the atomic radii of bonding atoms, the greater the bond length and the lower the bond dissociation energy. The lower the bond dissociation energy the lower the bond strength. The smaller the atomic radii, the smaller the bond length and the higher the bond dissociation energy. The higher the bond dissociation energy the higher the bond strength.

(iii) Electronegativity difference of bonding atoms

The greater the electronegativity difference between the atoms covalently bonded together, the greater the bond polarity and the higher the bond dissociation energy. Bond strength increases with increase in polarity of bonds

(iv) Number of bonding electron pairs

Triple bonds involve three electron pairs and are shorter and stronger than double bonds which involve two electron pairs which are also shorter and stronger than single bonds that involve one electron pair between similar atoms. The energy required to break the bonds therefore decreases as for the case of carbon-carbon bonds shown below

Bond	Bond dissociation energy(kJmol ⁻¹)
$C \equiv C$	796
$C=C$	606
$C-C$	334

Examples

1. The respective bond energies of the covalent bonds of group IV elements are given below.

Bond	$C-C$	$Si-Si$	$Ge-Ge$
Bond dissociation energy(kJmol ⁻¹)	346	175	168

State the trend in bond energy. Give a reason for your answer.

The bond energy decreases from carbon-carbon bond to silicon-silicon bond to germanium-germanium bond. This is because the atomic radius increases from carbon to germanium, bond length increases and bond strength decreases.

2. The table below gives bond energies of hydrogen halides.

Hydride	HF	HCl	HBr	HI
Bond energy(kJmol ⁻¹)	556	431	336	299

Explain the observed trend in bond energy

The bond energy decreases from hydrogen fluoride to hydrogen iodide. This is because the atomic radius increases from fluorine to iodine, bond length increases and bond strength decreases.

Question

The table below gives bond energies of Carbon-halogen bonds.

Bond	C—F	C—Cl	C—Br	C—F
Bond energy(kJmol ⁻¹)	452	351	293	234

Explain the observed trend in bond energy

Giant covalent structures

When many very strong covalent bonds link one atom to another to form an extensive three dimensional lattice, a giant covalent structure is formed.

Examples of giant covalent solids include **diamond**, **graphite**, **silicon**, **silicon(IV) oxide** and **fullerene**.

Giant covalent solids have high melting points and are non-volatile due to the strong covalent bonds holding the atoms together.

Check under matter (specifically under the solid state of matter for details about giant covalent structures)

Properties of covalent compounds

Property	Explanation
1. Low melting and boiling points.	<i>There are weak forces of attraction between the molecules thus a low amount of energy is required to break them.</i>
2. They do not conduct electricity except graphite	<i>They neither form free mobile ions nor have delocalized electrons to conduct electricity.</i>
3. Most covalent substances are insoluble in polar solvents like water but soluble in non-polar solvents like benzene, ethanol or propanone	<i>In polar solvents, the solvent-solvent interaction is much greater than interaction between the covalent molecules in the solute or the interaction between the covalent molecules and the polar molecules in the solution. Covalent compounds tend to dissolve in non-polar solvents because van der Waals' forces are the binding forces in both cases.</i>

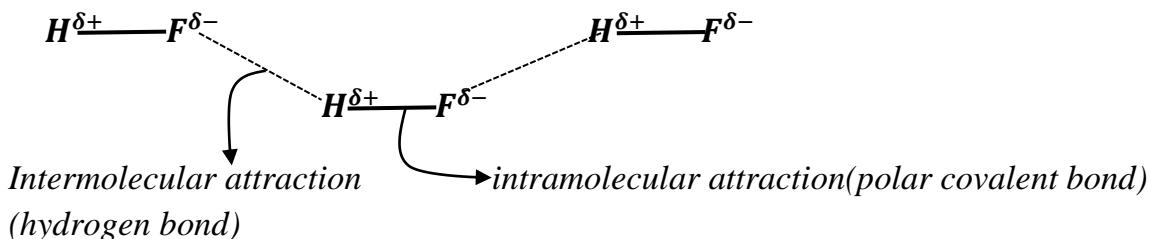
	<i>Note that some covalent compounds containing polar bonds as O—H or N—H may dissolve in water due to interaction between the polar bond and the water.</i>
4. Exist as gases or liquids at room temperature	<i>There are strong electrostatic forces of attraction between the oppositely charged ions that require a high amount of energy to break.</i>

Point of thought; Compare properties of ionic and covalent compounds.

Intermolecular forces

Intermolecular forces are forces that exist between molecules. There are a number of types of intermolecular forces. They include; **van der Waals forces** and the **hydrogen bond**. They are different from forces holding individual atoms in a molecule. The forces between atoms in a molecule are called the **intramolecular forces**.

Intermolecular forces	Intramolecular forces
van der Waals forces	Covalent bond
Hydrogen bonds	Ionic bond
	Metallic bond



Van der Waals' forces

There are forces of attraction between molecules of liquids or solids. These forces are neither ionic nor covalent. The van der Waals forces may exist between polar molecules and these are called **dipole-dipole interactions**. The van der Waals forces that exist between non-polar molecules are called **London dispersion forces (temporary dipole-dipole attractions)**.

(i) Dipole- dipole interactions

Polar molecules like hydrogen chloride and ammonia, interact to form an ordered arrangement. In this arrangement, partial positive charge in one molecules is adjacent to partial negative charge in another molecule.

The dipole-dipole attractive forces are increased by one dipole inducing a dipole in another neighbouring molecule.

(ii) **London dispersion forces (temporary dipole-dipole)**

Attractions also exist between **non-polar** molecules like the molecules of gases O_2, N_2, H_2 etc, halogens and noble gases.

This is due to momentary polarization of the molecules.

If two nonpolar molecules are very close to each other, the arrangement of electrons is on average symmetrical.

However at any given instant, the electron distribution in one molecule may be unsymmetrical and a dipole may be in that molecule at that particular instant. This dipole is called a **temporary dipole**.

The temporary dipole in one molecule can attract the electron cloud of the neighbouring molecule and this makes both molecules to have dipoles.

The dipoles are in such a way that the molecules attract each other.

Since electrons move at high speed, the dipole may be in the other molecule in the next instant. The induced dipole by one molecule into another results into an attraction.

The dipoles are temporary, but the net attraction which they produce is permanent. This attraction is due to **London dispersion forces**.

The London dispersion form of van der Waals force is usually very weak and only functions when the molecules are very close to each other.

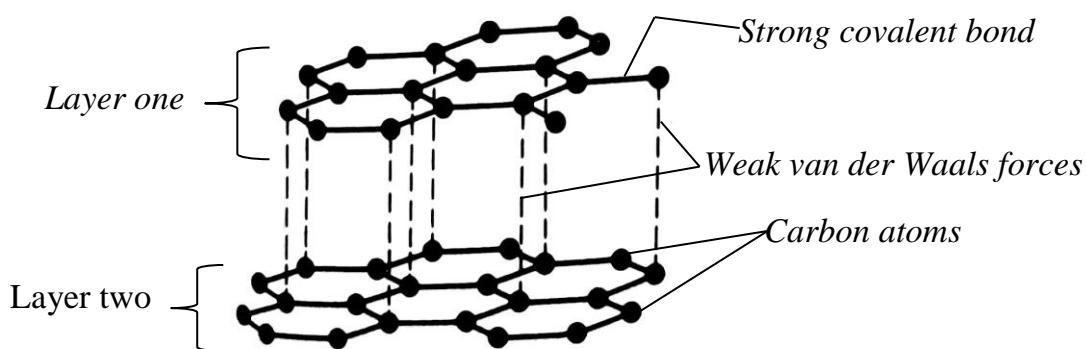
The size of the force however increases as the number of electrons in the molecules increase.

Van der Waals forces are in general very weak compared to ionic or covalent bonds. This is shown by the low melting and boiling points of substances held together by van der Waals' forces

Examples to explain the effect of van der Waals' forces

1. Explain why graphite is soft and slippery.

Each carbon atom in graphite is covalently bonded to three other carbon atoms to form two dimensional layers of hexagonal rings of carbon atoms. The hexagonal layers held together by weak Van-der-Waals' forces of attraction which allow the layers to slide over each other.



2. The table below shows the melting points of the some elements in Period 3 of the Periodic Table.

Element	P	S	Cl	Ar
Melting point($^{\circ}\text{C}$)	44.2	115.2	-101.5	-189.4

Explain the trend in the melting points the elements

Phosphorus, Sulphur, chlorine and argon have **simple molecular structures** with **weak Van-der-Waal's forces of attraction** whose magnitude **increases in strength** with **increase in molecular weight**. Sulphur is octatomic (S_8) with a higher molecular weight hence stronger Van der Waal's forces of attraction than Phosphorus which is tetratomic(P_4). Chlorine is diatomic (Cl_2), with a higher molecular weight and stronger Van-der-Waal's forces than argon which is monoatomic. The **energy required to break the Van-der-Waal's forces** therefore **decreases** from phosphorus to argon.

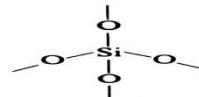
3. Silicon, phosphorus, Sulphur and chlorine are period 3 elements that form oxides whose melting points decrease in the order $\text{SiO}_2 > \text{P}_2\text{O}_5 > \text{SO}_3 > \text{Cl}_2\text{O}_7$. Explain the trend in melting points of the oxides

Silicon(IV) oxide has a **giant covalent structure** in which each silicon atom is bonded to four oxygen atoms making **very many strong covalent bonds** that require a **high amount of energy to break**. Phosphorus pentoxide, sulphur trioxide and Chlorine(VII) oxide have **simple molecular structures** whose molecules are held by **weak van der waal's forces of attraction** whose **strength decreases with decrease in polarity of the molecules** as a **result of increase in electronegativities of the atoms bonded to oxygen**

4. Briefly explain why carbon dioxide is a gas whereas silicon(IV) oxide is a solid at room temperature.

Carbon dioxide is non-polar. It has discrete molecules with a simple molecular structure held by weak van der Waals forces of attraction which are easily overcome at room temperature keeping the molecules far apart from each other.

However, in silicon(IV) oxide, each silicon atom is covalently bonded to four oxygen atoms to form a tetrahedral structure which is continuous to form a giant molecular structure with very many strong covalent bonds that are not easily broken at room temperature, keeping its molecules very close to each other.



5. The table below shows the boiling points of the hydrides of group IV elements.

Hydride	CH_4	SiH_4	GeH_4	SnH_4	PbH_4
Boiling point($^{\circ}\text{C}$)	-161.5	-111.9	-88	-52	-13

Explain the trend in variation of the melting points of the hydrides.

(Note that all these hydrides are gases)

Boiling point increases from methane to plumbane.

This is because molecules of the hydrides are held by weak van der Waals' forces of attraction whose strength increases with increase in molecular weight and molecular size.

6. Explain why fluorine and chlorine exist as gases whereas bromine and iodine exist as liquid and solid respectively at room temperature

From fluorine to iodine, atomic radius increases, molecular size and molecular mass increases, hence magnitude of Van der Waals' forces of attraction holding the molecules increases in the order; $\text{F}_2 < \text{Cl}_2 < \text{Br}_2 < \text{I}_2$. The Van der Waals' forces in bromine and iodine are strong enough to hold the molecules closer to each other existing as liquid and solid respectively. Fluorine and chlorine have weaker Van der Waals' forces due to their small size and low molecular masses. Their molecules are therefore far apart.

7. The table below shows the boiling points some alkylhalides

Element	CH_3Cl	$\text{CH}_3\text{CH}_2\text{Cl}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$
Boiling point($^{\circ}\text{C}$)	-24.0	12.5	47.0	78.5

Explain the trend in boiling points of the chloroalkanes.

Boiling point increases from chloromethane to chloroethane to chloropropane to chlorobutane.

This is because molecules of the chloroalkanes are held by weak van der Waals' forces of attraction whose strength increases with increase in molecular weight and molecular size.

8. The table below shows the boiling points some alkylhalides

Element	CH_3F	CH_3Cl	CH_3Br	CH_3I
Boiling point($^{\circ}C$)	-78.4	-24.0	5.0	43.0

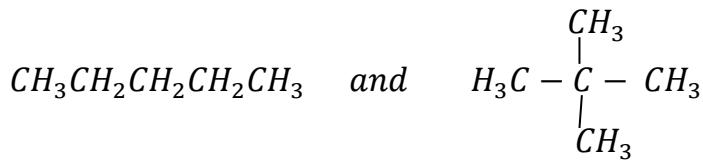
Explain the trend in boiling points of the alkylhalides

Boiling point increases from fluoromethane to chloromethane to bromomethane to iodomethane.

This is because the atomic radius of the halogen atoms increases in the order;

$F < Cl < Br < I$, molecular size and molecular mass of the alkylhalides increases, hence magnitude of Van der Waals' forces of attraction holding the molecules increases.

9. 2, 2-dimethyl propane boils at a lower temperature than n-pentane yet both are of the same molecular weight.



2, 2-dimethyl propane is a branched isomer giving it a spherical shape which reduces its size and weaker Vander Waal's forces of attraction will exist between the molecules. n-pentane is a straight chain molecule which gives the molecule an extended structure resulting into relatively stronger Vander Waal's forces.

The hydrogen bond

A hydrogen bond is a dipole- dipole attraction which occurs between a hydrogen atom attached to a strongly electronegative atom and a second strongly electronegative atom with a lone pair of electrons.

The electronegative atoms are fluorine, oxygen or nitrogen.

Fluorine has the highest electronegativity. For this reason, hydrogen fluoride forms the strongest hydrogen bonds which persist even in vapour state.

The greatest number of hydrogen bonds known are those which unite two oxygen atoms.

The hydrogen bond is weaker than a normal covalent bond.

Types of hydrogen bonding

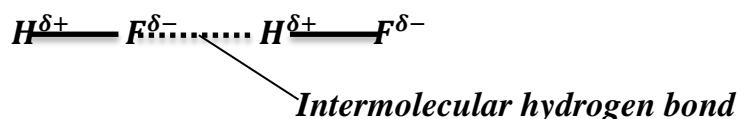
(i) Intermolecular hydrogen bonding

This is the type of hydrogen bond that occurs between two or more similar or different molecules.

Intermolecular hydrogen bonds occur in the following examples;

(a) Hydrogen fluoride , water and ammonia molecules

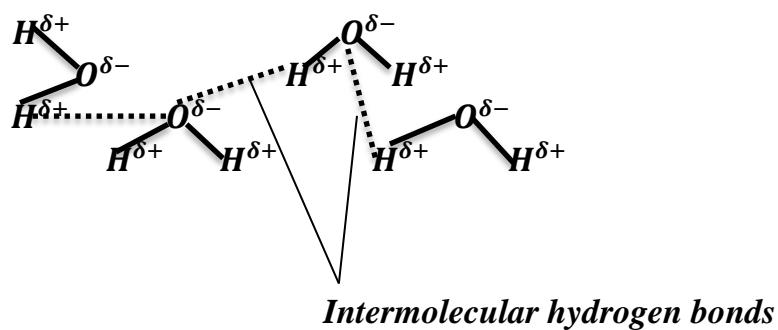
If two polar hydrogen fluoride molecules are close enough, there is an attraction between the positive end of one molecule and the negative end of the other molecule. Since the attraction between the hydrogen atom in one molecule and the fluorine atom in the other molecule is stronger than the repulsion between the two hydrogen atoms and between the two fluorine atoms, the two molecules are bonded together by a hydrogen bond.



This explains why hydrogen fluoride is a liquid whereas other group VII hydrides are gases at room temperature; hydrogen fluoride has a higher boiling point than any other hydride of group VII.

Water molecules

Water molecules also associate through intermolecular hydrogen bonding. Each water molecule forms four hydrogen bonds with other water molecules. This explains why water has higher boiling point and is a liquid whereas hydrogen sulphide has a lower melting point and is a gas although both Sulphur and oxygen are group VI elements.



Ammonia

Both ammonia (NH_3) and phosphine(PH_3) are trigonal pyramidal but ammonia has a higher boiling point($-33.4^{\circ}C$) than phosphine($-87.7^{\circ}C$). This is because nitrogen has a smaller atomic radius and is more electronegative than phosphorus. This makes the nitrogen- hydrogen bond strongly polar whereas the phosphorus- hydrogen bond is non-polar. Ammonia molecules are therefore held together by strong hydrogen bonds which require a high amount of energy to break than the weak van der Waals' forces in phosphine.

Comparison between hydrogen fluoride, water and ammonia

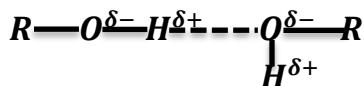
Molecule	Boiling point($^{\circ}C$)
HF	19.9
H_2O	100
NH_3	-33.4

Although fluorine is more electronegative than oxygen, meaning the hydrogen- fluorine bond is more polar than hydrogen-oxygen bond and hydrogen fluoride would have stronger hydrogen bonds than water, this is not shown by the boiling points of the two compounds. Water has a higher boiling point than hydrogen fluoride because each water molecule forms four hydrogen bonds whereas each hydrogen fluoride molecule forms two hydrogen bonds. The higher the number of hydrogen bonds a compound forms, the higher the boiling point. Since nitrogen is the least electronegative element, the nitrogen- hydrogen bond is less polar than oxygen- hydrogen bond or hydrogen-fluorine bond. Ammonia therefore forms weaker hydrogen bonds than those in water or hydrogen fluoride.

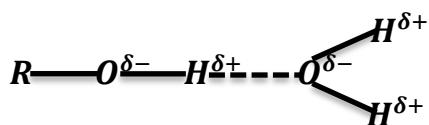
(b) Alcohols

Alcohols associate in their liquid form due to intermolecular hydrogen bonding. The boiling points of alcohols are higher than boiling points of corresponding alkanes or alkyl halides with similar molar mass because of association through hydrogen bonding.

For example the boiling point of methanol is $64.6^{\circ}C$ whereas that of methane is $-24.2^{\circ}C$.



Alcohols are also more soluble in water than alkanes or alkyl halides of similar molecular mass because of the ability to form hydrogen bonds with water.



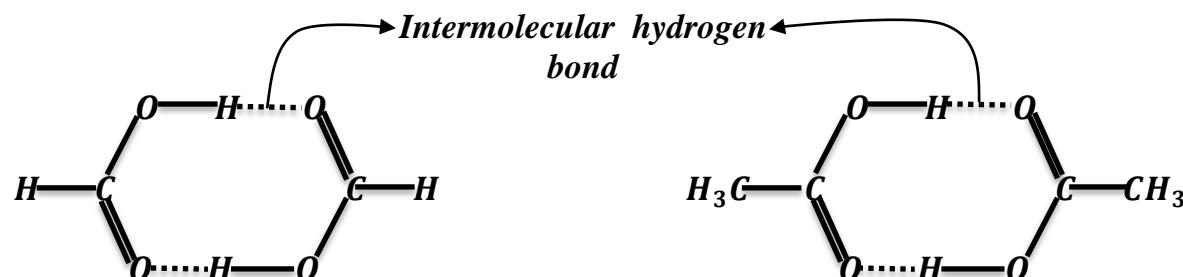
Alcohols with more hydroxyl groups have higher boiling points than alcohols with one hydroxyl group. Propane-1,2,3-triol, ethane-1,2-diol and ethanol have boiling points 290°C , 197°C and 78.4°C respectively.

Viscosity of alcohols also increases as number of hydroxyl groups increases due to increased hydrogen bonding.

(c) Carboxylic acids

When methanoic acid (HCOOH) or ethanoic acid (CH_3COOH)is dissolved in benzene or other organic solvents and the **relative molecular mass of the acid determined by cryoscopic method**, the value obtained is **normally twice the actual value**. This is because in **liquid state form or in solution in benzene**, the acids **associate through intermolecular hydrogen bonds** to form **dimers**. The same scenario happens when measurements in the vapour phase of the acids are done.

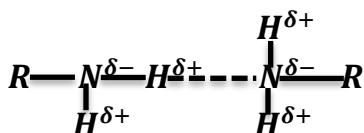
Association(dimerization of methanoic acid) *Association(dimerization of ethanoic acid)*



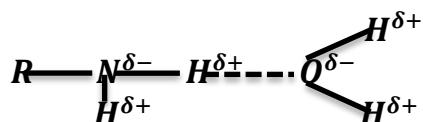
In aqueous solution however, molecules of carboxylic acids do not dimerise but form intermolecular hydrogen bonds with water. This explains their solubility in water.

(d) Amines

Amines also associate in their liquid form due to intermolecular hydrogen bonding. The boiling points of amines are higher than boiling points of corresponding alkanes with similar molar mass because of association through hydrogen bonding.



Amines are also soluble in water because of the ability to form hydrogen bonds with water.



Amines have lower boiling points than corresponding alcohols or carboxylic acids because nitrogen is less electronegative than oxygen. The nitrogen-hydrogen bonds are less polar than oxygen-hydrogen bonds so the hydrogen bonds formed in amines are weaker than in alcohols.

Primary amines have higher boiling points than secondary amines which also have higher boiling points than tertiary amines of the same molecular mass. This is because the nitrogen atom in primary amines has two hydrogen atoms hence can form more intermolecular hydrogen bonds than the nitrogen atom in secondary amines which has one hydrogen atom hence can form one intermolecular hydrogen bond. The nitrogen atom in tertiary amines has no hydrogen atom that can form hydrogen bonds.

(e) **Phenols**

Phenols associate in their liquid form due to intermolecular hydrogen bonding. The boiling points of phenols are higher than boiling points of corresponding alkanes or alkyl halides because of association through hydrogen bonding.

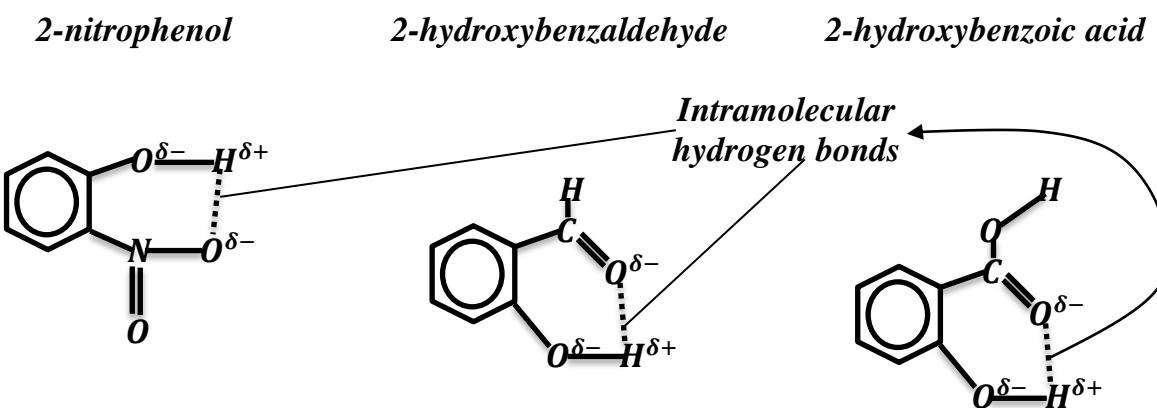


Phenols are more soluble in water than corresponding alkanes or alkyl halides because of the ability to form hydrogen bonds with water just like alcohols.

(ii) **Intramolecular hydrogen bonding**

This is the type of hydrogen bonding that occurs within the same molecule.

An example is the intramolecular hydrogen bond formed in 2-nitrophenol, 2-chlorophenol, 2-hydroxybenzaldehyde and 2-hydroxybenzoic acid



The **intramolecular hydrogen bonding** prevents **intermolecular hydrogen bonding** between two or more molecules. Intramolecular hydrogen bonding is not possible for 3- and 4- substituted isomer (para and meta isomers) because of the substituent groups are far apart. However the para and meta isomers can form **intermolecular hydrogen bonds**. The intramolecular hydrogen bonding in ortho- substituted compounds explains their difference in physical properties from their para- and meta-substituents. For example 2-nitrophenol boils at 214°C whereas 3-nitrophenol and 4-nitrophenol boil at 290°C and 279°C respectively.

Examples to explain the effect of hydrogen bonding

1. Explain why hydrogen fluoride is a liquid whereas other hydrides are gases at room temperature.

Fluorine has the smallest atomic radius and highest electronegativity among the halogens making the hydrogen-fluorine bond highly polar. The molecules of hydrogen fluoride are held by strong intermolecular hydrogen bonds which keep the molecules closer to each other. Molecules of hydrogen chloride, hydrogen bromide and hydrogen iodide are held by weak Van der Waals' forces that keep the molecules far apart.

2. The table below shows both boiling points of group VII hydrides.

Hydride	HF	HCl	HBr	HI
Boiling point(°C)	+19.9	-85.0	-66.7	-35.4

Explain the variation in boiling points, including any anomalies involved.

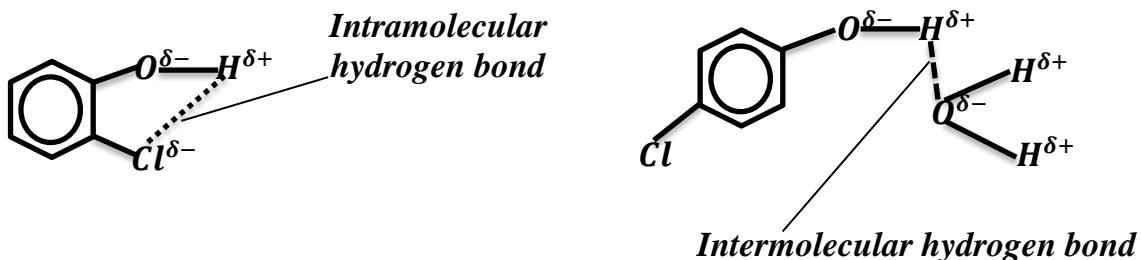
Boiling points increases from hydrogen chloride to hydrogen iodide. However, hydrogen fluoride has an abnormally high value of boiling point.

The increase in melting point from hydrogen chloride to hydrogen iodide is because the three hydrides have simple molecular structures held by weak Van der Waals' forces whose magnitude increases with the increasing molecular weight leading to an increase in amount of energy required to break the forces.

Hydrogen fluoride has an abnormally high melting point because the fluorine atom has the smallest atomic radius and the highest electronegativity, making the hydrogen-fluorine highly polar. The hydrogen fluoride molecules are therefore held by strong intermolecular hydrogen bonds which require a high amount of energy to break.

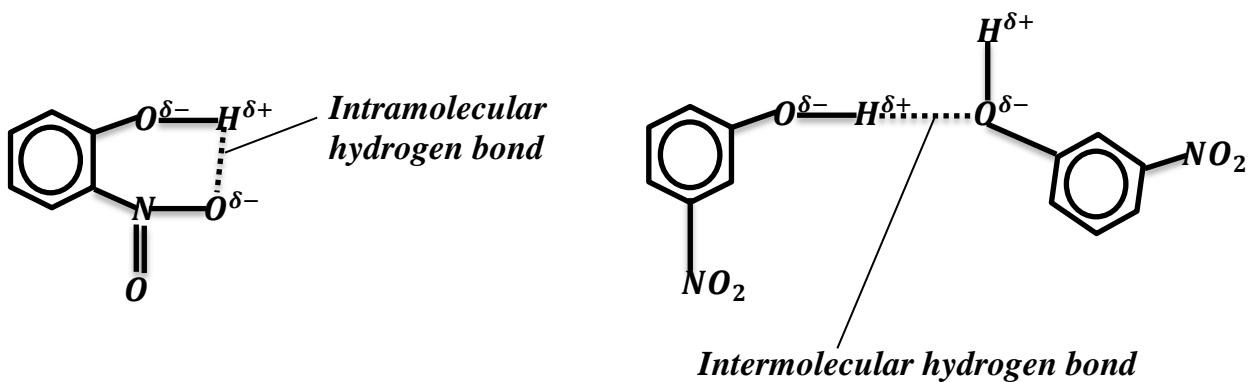
3. Explain why;

- (i) 2-chlorophenol is less soluble in water than 4-chlorophenol.



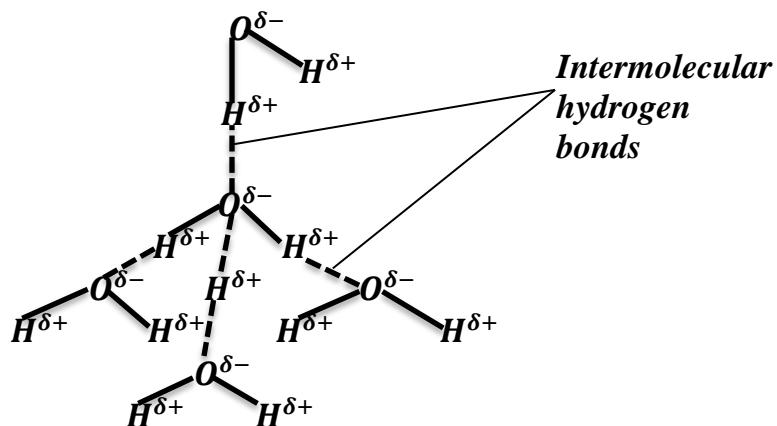
Molecules of 2-chlorophenol form intramolecular hydrogen bonds because the chloro group is nearer the hydroxyl group. This suppresses the hydroxylic character of the compound or prevents formation of intermolecular hydrogen bonds between 2-chlorophenol and water molecules reducing its solubility. However, molecules of 4-chlorophenol cannot form intramolecular hydrogen bonds because the chloro group is far from the hydroxyl group. Molecules 4-chlorophenol therefore form intermolecular hydrogen bonds with water. This increases its solubility.

- (ii) The boiling point of 2-nitrophenol is 214°C whereas that of 3-nitrophenol is 290°C .



Molecules of 2-nitrophenol form intramolecular hydrogen bonds because the nitro group is nearer the hydroxyl group. This suppresses the hydroxylic character of the compound or prevents formation of intermolecular hydrogen bonds between 2-nitrophenol molecules. However, molecules of 3-nitrophenol cannot form intramolecular hydrogen bonds because the nitro group is far from the hydroxyl group. Molecules of 3-nitrophenol therefore form intermolecular hydrogen bonds.

4. Explain why ice is less dense than water



In ice, each oxygen atom in a water molecule is surrounded tetrahedrally by four other oxygen atoms through extensive intermolecular hydrogen bonds. This gives ice an open structure. The water molecules in ice are spaced and further apart than they are in liquid water. Therefore ice occupies a bigger volume than that of liquid water of the same mass. Since density is inversely proportional to volume, ice has a lower density than water. However when ice melts, the hydrogen bonds breaks down and the molecules pack closely together so that liquid water has a lower volume hence a higher density than water.

Questions

1. Explain why

- The melting of silicon is much higher than that of phosphorus yet both silicon and phosphorus are covalent substances.
- hydrogen and helium gases show a small deviation from ideal behaviour
- For gases methane, ammonia, oxygen and carbon dioxide, the deviation from ideal behaviour increases in the order $CH_4 < NH_3 < O_2 < CO_2$.
- The boiling point of the given arylhalides increases in the order $C_6H_5I > C_6H_5Br > C_6H_5Cl > C_6H_5F$
- The boiling point of chlorobenzene is higher than benzene which is also higher than cyclohexane
- Both carbon and silicon are group IV elements. However, the melting point of carbon dioxide is -56.5 whereas that of silicon dioxide is 1700 .

2. The table below shows the boiling points some alkanes

Element	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_6H_{14}
Boiling point($^{\circ}C$)	112	185	231	273	342

Explain the trend in boiling points of the alkanes.

3. The table below shows the boiling points of halogens

Element	F_2	Cl_2	Br_2	I_2
Boiling point($^{\circ}\text{C}$)	-187.9	-34.0	58.2	+184.5

Explain the trend in boiling points of the halogens

4. Explain the following observations;

- (a) hydrogen fluoride has a higher boiling point than hydrogen chloride.
- (b) melting point of 4 – nitrophenol is much higher than that of 2 – nitrophenol
- (c) 4-nitrophenol is more soluble in water than 2-nitrophenol
- (d) 2-hydroxybenzaldehyde has a lower boiling point than 3-hydroxybenzaldehyde although the relative molecular masses of the two compounds are the same.
- (e) boiling points of the given homologous series decreases in the order; *carboxylic acids > alcohols > amines > alkanes* of the same molecular mass.
- (f) methyl amine (*molar mass = 31g*) boils at -6.3°C while methanol (*molar mass = 32g*) boils at 46°C .
- (g) 2-methylpropan-2-ol boils at a lower temperature than butan-1-ol yet they all have the same molecular weight.
- (h) ethane boils at lower temperature than butane.
- (i) water(*molar mass = 18g*) is a liquid at room temperature whereas hydrogen sulphide (*molar mass = 34g*) is a gas at room temperature

Metallic bonding

A metallic bond is the electrostatic force of attraction between positive metal ions and delocalized electrons.

A metallic solid consists of a lattice of metal ions with the outer most electrons forming a “sea” of delocalized electrons. The delocalized electrons freely move throughout the structure and can conduct electricity. Electrostatic attractions exist between the delocalized electrons and the metal ions.



Properties of metals

The metallic bond is the bond that is responsible for the properties of metals.

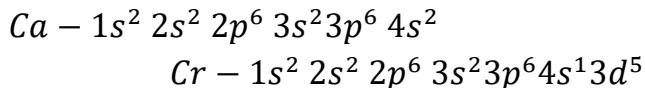
1. High melting and boiling points.

This is because of a high amount of energy is required to break the strong metallic bonds. Melting point increases as the number of electrons contributed per atom of a metal towards metallic bonding increases. Transition elements have higher melting points than main group elements because they contribute both 4s and 3d electrons towards bonding.

Qn. Explain why group II elements form metals with higher melting and boiling points than group I elements

Both group I and group II elements form metallic bonds whose strength depend on the number of electrons contributed per atom to the formation of the metallic bonds. Group II elements contribute two electrons per atom forming stronger metallic bonds that require a higher amount of energy to break than Group I elements which only contribute one electron per atom towards forming weaker metallic bonds that require a lower amount of energy to break.

Qn. Explain why the melting point of chromium is higher than that of calcium



Calcium has a larger atomic radius and only contributes the two 4s electrons per atom towards metallic bonding hence forming weaker metallic bonds that require a lower amount of energy to break than chromium which has a smaller atomic radius and contributes both the one 4s electron and the five 3d electrons forming stronger metallic bonds that require a higher amount of energy to break.

2. Electrical conductivity

Metals are good conductors of electricity and heat due to presence of free mobile electrons throughout the lattice. If a potential difference is applied between the ends of a metal, the delocalized electron cloud will move towards the positive potential.

However, electrical conductivity of a metal decreases with increase in temperature because resistance increases. This is because increase in temperature increases thermal vibration within the metal. The regularity within the metallic lattice is upset and therefore the electrons cannot easily move in the lattice.

3. Thermal conductivity

They conduct heat due to exchange of kinetic energy between free mobile electrons in the lattice. When heat is supplied to one end of a piece of a metal, the kinetic energy of the electrons is increased. This increase in kinetic energy is transmitted through the system of delocalized electrons to other parts of the metal.

4. Malleability and ductility

Metals are malleable (can be hammered-beaten into sheets) and ductile (can be drawn out under tension-pulled out into wires). This is due to the ability of layers of atoms to roll over each other into new positions without breaking the metallic bond.

5. Insoluble in polar and non-polar solvents.

The metal-metal attractions are much stronger than the metal-metal attractions or the metal-solvent attractions. The solvent molecules cannot penetrate the metal lattice.

Strength of a metallic bond

The strength of a metallic bond is determined by three factors;

1. Charge of the cation

The higher the cationic charge, the stronger the metallic bond because there will be a stronger attraction of the delocalized electrons.

2. Number of delocalised electrons per atom

The higher the number of electrons contributed per atom towards metallic bonding, the stronger the metallic bond. This is because there will be a greater attraction between the nucleus and the delocalised electrons.

3. Ionic radius

The smaller the ionic radius of the cation, the stronger the metallic bond because there will be a stronger attraction of the delocalised electrons.

VALENCE BOND THEORY

The Valence Bond Theory (VBT) is one of the theories that were developed to explain chemical bonding, along with the molecular orbital theory.

According to the theory, a covalent bond is formed between two atoms by the overlap of atomic orbitals of each atom containing an unpaired electron.

The atomic orbitals of two atoms overlap to form chemical bonds but they do not lose their identity.

The shape of a molecule depends upon the shapes of the combining atomic orbitals. Only outer atomic orbitals for a valence energy level are involved in bonding. The number of covalent bonds formed is equal to half the number of combining atomic orbitals.

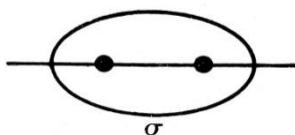
Sigma(σ) and pi (π)bonds

The nomenclature s and p used for atomic orbitals is replaced by σ and π for molecular orbitals.

Sigma(σ) bond

A sigma bond is formed by **head to head or collinear overlap of two atomic orbitals** along their **internuclear axis**.

Only one sigma bond can exist between any two atoms. It is a strong bond because orbitals can overlap to a greater extent.

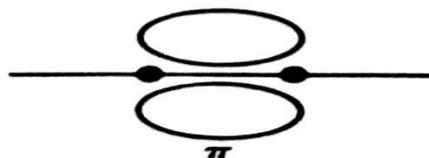


pi (π)bond

A pi bond is formed by **sideways or collateral overlap of two atomic orbitals**.

One or two π bonds can exist between any two atoms. A π bond shortens the bond length (internuclear distance). Two π bonds (as in a triple bond) shorten the bond length to a greater extent than one π bond (as in a double bond). It is a weak bond because of poor overlapping of orbitals.

It exists only when a σ bond is already present between two atoms.



Hybridisation of atomic orbitals

s , p and d orbitals of comparable energy can combine within an atom to form hybrid orbitals. The hybrid orbitals have different shapes from s , p and d orbitals and they form stronger bonds due to great overlap during bonding.

Below are some important points about hybridization:

1. Usually atomic orbitals containing one electron each are considered in hybridisation
2. In most cases, one or more electrons are promoted to the next higher energy levels so that the number of unpaired electrons becomes equal to the oxidation state of the central atom in the molecule.
3. Lone pairs are also involved in hybridization if the geometry of the molecule can be explained by involving them.
4. An orbital can accommodate a maximum of two electrons with opposite spins.
5. Hybrid orbitals have greater potential for overlapping than the ground state orbitals from which they are constructed.
6. The experimentally determined bond angles of molecules are very close to the directions of the hybrid orbitals.

Hybrid orbitals

(a) *sp*-hybridisation

This occurs when one *s* and one *p*-orbital of the same atom combine to form a set of two equivalent *sp*-hybrid orbitals which are 180° to each other.

The beryllium atom with electronic configuration $1s^2\ 2s^2$ has both the $1s$ and $2s$ subenergy levels completely filled with electrons.

	$1s^2$	$2s^2$	$2p^0$
<i>Be</i>			
	$1s^2$	$2s^1$	$2p^1$
<i>Be*</i>		↑	↑

From the configuration in the ground state of Beryllium, it may not form compounds since it has no unpaired electrons. However beryllium is known to form compounds in which it is divalent.

For beryllium to form compounds, one of the $2s$ electrons is promoted to the $2p$ subenergy level to form an excited beryllium atom, Be^* .

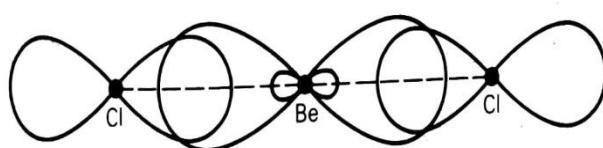
The two $2s$ and $2p$ electrons combine to form two collinear *sp* hybrid orbitals.

In formation of beryllium chloride for example, the two *sp* hybrid orbitals overlap with the two $3p_x$ orbitals of two chlorine atoms to form to form two sigma bonds.

Two collinear sp hybrid orbitals



Formation of two σ-bonds in beryllium chloride



(b) sp^2 -hybridisation

This occurs when one s and two p -orbitals of the same atom combine to form a set of three equivalent sp^2 -hybrid orbital which are **trigonal planar** with a bond angle 120° .

The boron atom with electronic configuration $1s^2 2s^2 2p^1$ has the $2p$ subenergy level having one unpaired electron.

	$1s^2$	$2s^2$		$2p^1$		
				$2p_x$	$2p_y$	$2p_z$
B				↑		
	$1s^2$	$2s^1$	$2p^1$			
B^*		↑	↑	↑		

From the configuration in the ground state of Boron, two of the three two p orbitals are unoccupied.

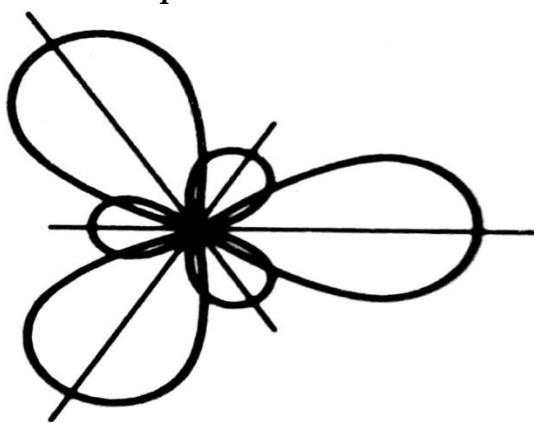
For boron to form compounds, one of the $2s$ electrons is promoted to one of the empty p orbitals to form an excited boron atom, B^* . The excited boron atom therefore has two p electrons.

Hybridization occurs between the remaining s orbital and the two p orbitals to form three equivalent sp^2 hybrid orbitals.

The axes of these orbitals lie in the same plane and at 120° to each other.

This resulting hybridization therefore implies that the BX_3 compounds of boron are trigonal planar.

Three sp^2 hybrid orbitals in the same plane at 120°



(c) sp^3 -hybridisation

This occurs when one s and three p -orbitals of the same atom combine to form a set of four equivalent sp^3 -hybrid orbitals which point towards the corners of a regular tetrahedron with a bond angle of $109^\circ 28'$ to each other.

The carbon atom with electronic configuration $1s^2 2s^2 2p^1$ has the $2p$ subenergy level having one unpaired electron.

	$1s^2$	$2s^2$		$2p^2$		
				$2p_x$	$2p_y$	$2p_z$
C			1	1		
	$1s^2$	$2s^1$	$2p^1$			
C^*		1	1	1	1	1

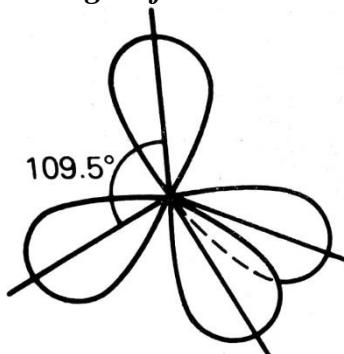
From the configuration in the ground state of carbon, two of the three two p orbitals have one unpaired electron each.

For carbon to form compounds, one of the $2s$ electrons is promoted to the empty $2p_z$ orbital to form an excited carbon atom, C^* . The excited carbon atom therefore has three p electrons.

Hybridization occurs between the s orbital and the three p orbitals to form four equivalent sp^3 hybrid orbitals.

These are directed outwards from the carbon atom at an angle of $109^\circ 28'$ with each other. This resulting hybridization therefore implies that the molecules of methane or tetrachloromethane are in a shape of a regular tetrahedron with the carbon atom at the centre and the hydrogen or chlorine atoms at the four corners.

Four sp^3 hybrid orbitals directed outwards from the carbon atom at an angle of $109^\circ 28'$



Geometry for different types of hybridisation

Type of hybridization	Spatial arrangement	Bond angle	Examples
sp	Linear	180°	$BeCl_2, N_2O, C_2H_2$
sp^2	Trigonal planar	120°	$BF_3, BCl_3, SO_2, SO_3, CO_3^{2-}, NO_3^-$
sp^3	Tetrahedral	$109^\circ 28'$	$CH_4, CCl_4, SiF_4, NH_4^+, BF_4^-$

The formation of single, double and triple bonds

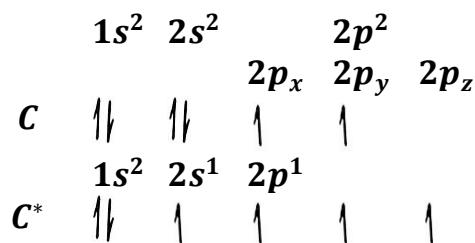
The formation of single, double and triple bonds in organic compounds is due to hybridization.

(i) *the carbon-carbon single bond*

The carbon-carbon single bonds are all σ -bonds formed by sp^3 hybridization.

(ii) *the carbon-carbon double bond*

The carbon-carbon double bond for example in ethene consists of one σ -bond and one π bond formed by sp^2 hybridization.

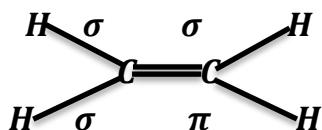


From the configuration in the ground state of carbon, two of the three two p orbitals have one unpaired electron each.

One of the $2s$ electrons is promoted to the empty $2p_z$ orbital to form an excited carbon atom, C^* .

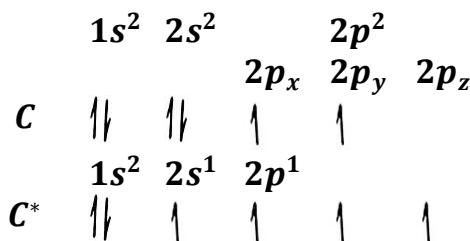
Hybridization occurs between the $2s, 2p_x$ and the $2p_y$ orbitals to form three equivalent sp^2 hybrid orbitals. Two of the sp^2 hybrid orbitals form σ -bonds with the $1s$ orbitals of hydrogen. The remaining sp^2 hybrid orbital forms a σ -bond between the carbon atoms. The unhybridised $2p_z$ orbital forms a π bond between the carbon atoms.

The two carbon atoms and four hydrogen atoms are all in the same plane and the bond angle is 120° . This gives ethene a trigonal planar shape.



(iii) the carbon-carbon triple bond

The carbon-carbon triple bond for example in ethyne consists of one σ -bond and two $\pi -$ bonds formed by sp hybridization.



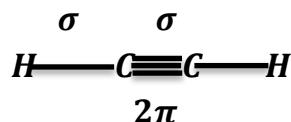
From the configuration in the ground state of carbon, two of the three two p orbitals have one unpaired electron each.

One of the $2s$ electrons is promoted to the empty $2p_z$ orbital to form an excited carbon atom, C^* .

Hybridization occurs between the $2s$ and the $2p_x$ orbitals to form two equivalent sp hybrid orbitals. One of these two sp hybrid orbitals forms a σ -bond with the $1s$ orbital of hydrogen. The remaining sp hybrid orbital forms a σ -bond between the carbon atoms.

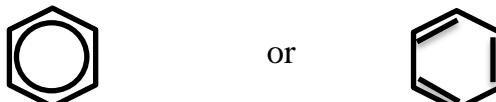
The two unhybridised $2p_y$ and $2p_z$ orbitals form two $\pi -$ bonds between the carbon atoms.

This gives ethyne a linear shape.



The double bond formation in benzene

Benzene has the structure as shown below;



Between each pair of adjacent carbon atoms is a sigma bond formed by overlapping sp^2 hybrid orbitals.

Because sp^2 orbitals are planar, all the six carbon atoms and six hydrogen atoms lie in the same plane and the bond angles are 120° .

There are unhybridised p orbitals for each of the carbon atoms with an axis at right angles to the plane of the carbon atoms.

These six p orbitals overlap with each other all around the ring to form delocalised bonds.

The electrons in these $p -$ orbitals are free to move between all the carbon atoms in the ring and they are described as delocalised electrons.

NOTE: Benzene, just like ethene is formed by sp^2 hybridisation but the difference is what happens with the unhybridised p orbitals.

DRAWING LEWIS STRUCTURES OF MOLECULES AND POLYTATOMIC IONS

Lewis structures

A Lewis structure is a simplified representation of the arrangement of the outermost electrons of each atom in a molecule and the lone pairs of electrons that may exist in the molecule or polyatomic ions.

The electrons are shown as dots or as lines (for bonding electrons between two atoms). For example when two chlorine atoms combine to form a chlorine molecule, the following Lewis structure can be drawn;



The Lewis structure of a chlorine molecule shows 3 unshared electron pairs for each atom (**lone pairs**) and one shared pair of electrons (**bonding pair**).

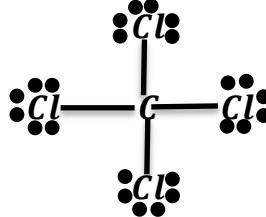
A line is sometimes used to indicate a shared pair of electrons.

The single shared pair of electrons is called a **single bond**.



Drawing Lewis structures of some simple molecules

Molecule	Description	Lewis structure
Ammonia (NH_3)	<i>It is known from the Lewis Dot symbol of Nitrogen that it has one lone pair and can form three bonds. Hydrogen can form one bond and has no lone pair</i>	
Water(H_2O)	<i>It is known from the Lewis Dot symbol of Oxygen that it has two lone pairs and can form two bonds. Hydrogen can form one bond and has no lone pair</i>	

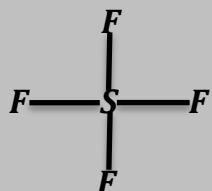
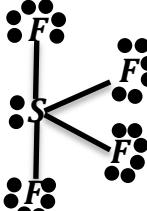
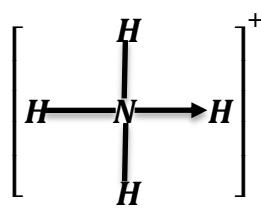
<i>Sulphur dioxide (SO_2)</i>	<i>It is known from the Lewis Dot symbol of Sulphur that it can form two bonds and has two lone pairs. Each oxygen atom also has two lone pairs and can form two bonds. But for oxygen to form the two bonds, one lone pair of Sulphur must be used.</i>	
<i>Carbon tetrachloride (CCl_4)</i>	<i>It is known from the Lewis Dot symbol of Carbon that it has no lone pair and can form four bonds. Each Chlorine atom has three lone pairs and can form one bond.</i>	

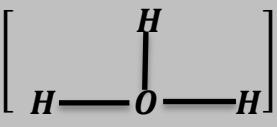
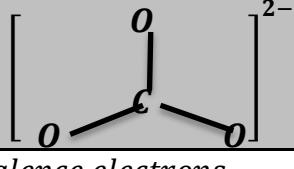
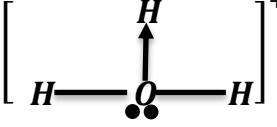
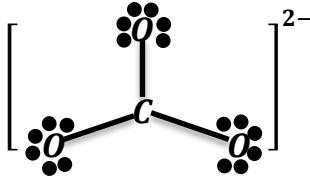
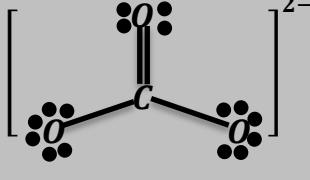
Steps for writing Lewis structures for more complex molecules/polyatomic ions

1. Write the skeleton structure of the molecule or ion. The central atom is usually the least electronegative element in the compound and then place a bonding pair of electrons between each pair of adjacent atoms or draw a line to indicate a single bond. In the water molecule for example, there is a bonding pair of electrons between each oxygen atom and each hydrogen atom.
2. Determine the total number of Valence electrons for the atoms in the molecule or ion. For a neutral molecule, this is the sum of valence electrons on each atom. This can be got from the Lewis Dot symbol of the atom or its electronic configuration. For a negatively charged ion, add one electron for each negative charge.
For a positively charged ion, subtract one electron for each positive charge.
3. Subtract two valence electrons for each bond formed in the skeleton structure.
4. Beginning with the terminal atoms, add enough electrons of the remaining electrons as valence electrons to satisfy the octets of the atoms (two for hydrogen). These electrons are the lone pairs.
5. The remaining electrons are then placed on the central atom (some central atoms can accommodate more than eight electrons)
6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet. This will not change the number of electrons on the terminal atoms.

Examples

In this table, we are using each of the steps 1-7 for different molecules or polyatomic ions to draw their Lewis structures.

	SF_4	NO	NH_4^+
1		$N - O$	$\left[\begin{array}{c} H \\ \\ H - N - H \\ \\ H \end{array} \right]^+$
2	<p>Number of valence electrons for Sulphur is 6 Number of valence electrons for the fluorine atoms $= (7 \times 4) = 28$ Total number of valence electrons $= 6 + 28 = 34$</p>	<p>Number of valence electrons for Nitrogen is 5 Number of valence electrons for oxygen = 6 Total number of valence electrons $= 5 + 6 = 11$</p>	<p>Number of valence electrons for Nitrogen is 5 Number of valence electrons for the hydrogen atoms $= (4 \times 1) = 4$ Total number of valence electrons $= 5 + 4 = 9$ Since there is a positive charge, the total electrons remain $(9 - 1) = 8$</p>
3	<p>For each of the four bonds (4×2) $= 8$ electrons are used Remaining electrons $= 34 - 8 = 26$</p>	<p>For the bond shown $(2 \times 1) = 2$ electrons are used Remaining electrons $= 11 - 2 = 9$</p>	<p>For each of the four bonds (4×2) $= 8$ electrons are used Remaining electrons $= 8 - 8 = 0$</p>
4			
5			
6	Not applicable	 <i>Nitrogen cannot get an octet for reasons explained later.</i>	

	H_3O^+	CO_3^{2-}
1		
2	<p>Number of valence electrons for Oxygen is 6 Number of valence electrons for the hydrogen atoms = $(1 \times 3) = 3$ Total number of valence electrons = $6 + 3 = 9$ Since there is a positive charge, the total electrons remain $(9 - 1) = 8$</p>	<p>Number of valence electrons for carbon is 4 Number of valence electrons for the oxygen atoms = $(3 \times 6) = 18$ Total number of valence electrons = $18 + 4 = 22$ Since there are 2 negative charges, the total electrons becomes $(22 + 2) = 24$</p>
3	<p>For each of the three bonds $(3 \times 2) = 6$ electrons are used Remaining electrons = $8 - 6 = 2$</p>	<p>For each of the three bonds $(3 \times 2) = 6$ electrons are used Remaining electrons = $24 - 6 = 18$</p>
4		
5		 <p>All the remaining 18 electrons have been used but carbon doesn't have a full octet yet. Rule 6 must be satisfied.</p>
6	Not applicable	 <p>More resonance structures can be made for this ion as we shall see later.</p>

Exceptions of the Octet rule

We already have an idea about the octet rule and we have applied it in many bonding situations in this topic. We have equally used it in drawing Lewis structures.

However, there are three exceptions of the Octet rule, which include;

- (a) *Incomplete octet*
- (b) *Expanded octet*
- (c) *Odd number electron*

(a) Incomplete octet

Molecules with atoms containing an incomplete octet of electrons generally contain the lighter s-block and p-block elements especially beryllium with just four electrons around the central atom and boron, typically with six electrons. Examples include;

- Beryllium chloride
- Boron trichloride

(b) Expanded octet

This is the most exception of the Octet rule. It applies to a molecule or an ion with at least one atom that possesses more than an octet of electrons.

This applies commonly to compounds in period 3 and beyond. Examples from the p-block elements include;

- Sulphur hexafluoride(SF_6)
- Sulphate ion(SO_4^{2-})
- Phosphate ion (PO_4^{3-})
- Phosphorus pentafluoride (PF_5)

Try to come up with probable Lewis structures of the above molecules/ ions

(c) Odd number electron

There are molecules such as nitrogen monoxide that have an odd number of electrons. This is seen in one of the examples above.

Molecules of most s-block and p-block elements contain an even number of electrons. Their bonding can therefore easily be described using the rules stated above.

However, molecules or ions containing d-block elements commonly contain an odd number of electrons. Their bonding cannot adequately be explained using the rules seen above.

There also a few molecules however for the p-block elements that have an odd number of electrons. These include;

<i>Molecule</i>	<i>Total number of electrons</i>
Nitrogen monoxide(NO)	$5 + 6 = 11$
Nitrogen dioxide(NO_2)	$5 + (2 \times 6) = 17$
Chlorine dioxide (ClO_2)	$7 + (2 \times 6) = 19$

Questions

Write the Lewis structures for the following species

1. NCI_3	9. H_2
2. CO_2	10. PCl_3
3. SCl_2	11. N_2
4. CH_4	12. CO
5. HF	13. BF_4^-
6. NCI_3	14. PO_4^{3-}
7. CO_2	15. SO_3^{2-}
8. SCl_2	16. BH_2^-

Formal charges

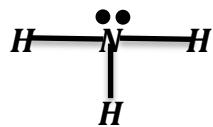
A formal charge compares the number of electrons around a neutral atom and the number of electrons around an atom in a molecule.

A formal charge is assigned to an atom in a molecule on assumption that the electrons in all chemical bonds are shared equally between atoms regardless of relative electronegativity.

$$\text{Formal charge} = \left(\frac{\text{number of valence electrons in free atom}}{} \right) - \left(\frac{\text{nonbonding electrons}}{\text{number of bonding electrons}} + \frac{1}{2} \right)$$

Examples

1. Calculate the formal charges of the atoms in ammonia.

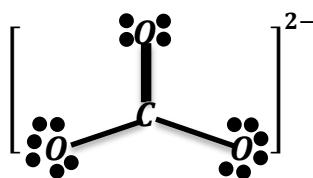


$$FC = V - (N + \frac{B}{2})$$

$$\text{Formal charge of nitrogen} = 5 - \left(2 + \frac{1}{2} \times 6 \right) = 0$$

$$\text{Formal charge of one hydrogen atom} = 1 - \left(0 + \frac{1}{2} \times 2 \right) = 0$$

2. Calculate the formal charges of the atoms in the carbonate ion



$$FC = V - \left(N + \frac{B}{2} \right)$$

$$\text{Formal charge of carbon} = 4 - \left(0 + \frac{1}{2} \times 8 \right) = 0$$

$$\text{Formal charge of one oxygen atom bonded with single bond} = 6 - \left(6 + \frac{1}{2} \times 2 \right) = -1$$

$$\text{Formal charge of the oxygen atom bonded with a double bond} = 6 - \left(4 + \frac{1}{2} \times 4 \right) = 0$$

Note;

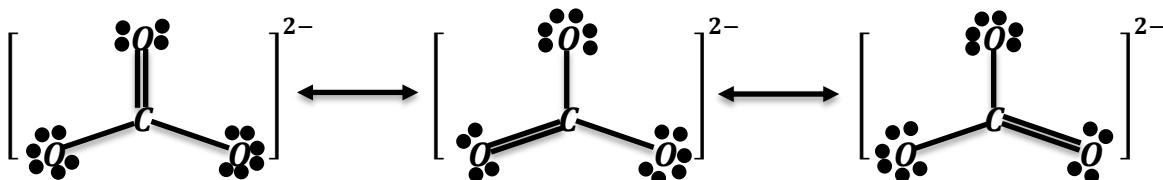
- (a) When formal charges on each of the atoms in a molecule are added, they must give the total charge on the molecule.
- (b) The structure with the most formal charges of zero on its atoms is the most stable Lewis structure.
- (c) In the case where there must be either positive or negative formal charges on various atoms, the most stable structures have negative formal charges on the more electronegative atoms and positive charges on the less electronegative atoms.

Resonance

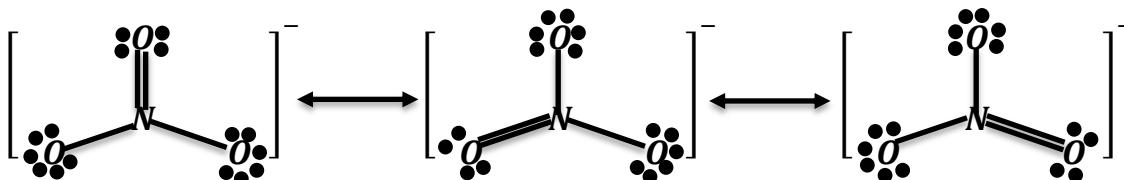
This is the situation in which two or more Lewis structures can be written. Resonance is used when a single Lewis structure cannot fully describe the bonding in a molecule or ion. Resonance structures arise when there are more than one way to draw a Lewis structure that satisfies the Octet rule. They are drawn by placing double bonds between different atoms and lone pairs on different atoms. Molecules with multiple resonance structures are more stable than those with fewer resonance structures. Some resonance structures contribute more to the stability of a molecule than others. This can be determined using the concept of formal charges. The most stable resonance structure is one with the least formal charge.

An illustration of how resonance structures arise

The carbonate ion



The nitrate ion



VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

Beryllium chloride (BeCl_2) is a linear molecule without a dipole moment whereas tin(II) chloride(SnCl_2) is a bent molecule with a dipole moment. Boron trichloride (BCl_3) is trigonal planar whereas ammonia(NH_3) is trigonal pyramidal.

A theory was put forward to explain the differences in shapes of molecules and ions. This theory is known as the **Valence Shell Electron Pair Repulsion Theory**.

The theory points out that the arrangement of electron pairs around a central atom in a molecule depends of the number of electron pairs.

Between any electron pair and any other electron pair, there is a force of electrostatic repulsion.

The electron pairs can be bonding or shared pairs which constitute the covalent bonds or unshared (lone pairs).

Any lone pairs of electrons on the central atom repel the bonding pairs of electrons and this affects the geometry (bond angle and shape) of the molecule.

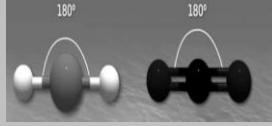
For the purpose of determining electron geometry, the VSEPR theory considers the electron pairs in a double bond or a triple bond are treated as one pair

Since the lone pairs are closer to the central atom, they cause greater repulsion than bonding pairs and the repulsions are in the order;

Lone pair – lone pair repulsion > lone pair – Bonding pair repulsion > bonding pair – bonding pair repulsion.

Predicting the shapes of molecules and ions

Note; In some of the three dimensional structures, the lone pairs of electrons are not shown. These will be shown in further examples.

Number of valence electrons	Total electron pairs	Number of bonding pairs	Number of lone pairs	Shape of molecule	3-dimensional presentation	Examples
4	2	2	0	Linear		$BeCl_2$, $H-C\equiv C-H$, BH_2 , CO_2 , HCN , CS_2 , $Ag(NH_3)_2^+$, $Ag(CN)_2^-$, $[CuCl_2]^-$
6	3	2	1	Bent or V-shaped		$SnCl_2$, $PbCl_2$, $GeCl_2$, SO_2 , O_3 , $NOCl$, NO_2^-
6	3	3	0	Trigonal planar		BCl_3 , BF_3 , SO_3 , $HCHO$, NO_3^- , CO_3^{2-} , HCO_3^-
8	4	4	0	Tetrahedral		CCl_4 , $SiCl_4$, $GeCl_4$, $SnCl_4$, CH_4 , SiH_4 , GeH_4 , SnH_4 , $CHCl_3$, H_2SO_4 , H_3PO_4 , $HClO_4$, SO_2Cl_2 , $POCl_3$, NH_4^+ , SO_4^{2-} , PO_4^{3-} , ClO_4^- , CrO_4^{2-} , MnO_4^{2-} , MnO_4^- , $Zn(NH_3)_4^{2+}$

8	4	3	1	Trigonal pyramidal		$NH_3, PCl_3, PF_3, PH_3, H_2SO_3, (CH_3)_3N, H_3PO_3, HClO_3, SO_3^{2-}, H_3O^+, ClO_3^-$
8	4	2	2	Bent or V-shaped		$H_2O, H_2S, Cl_2O, ClO_2^-, OF_2, SCl_2, HOCl$
10	5	5	0	Trigonal bipyramidal		$PF_5, PCl_5, PBr_5, PI_5, Fe(CO)_5$
10	5	4	1	Irregular tetrahedral		SF_4
10	5	3	2	T-shaped		ClF_3, ICl_3
10	5	2	3	Linear		ICl_2^-, I_3^-
12	6	6	0	Octahedral		$SF_6, SCl_6, SBr_6, Cr(NH_3)_6^{3+}, Co(NH_3)_6^{3+}, Fe(CN)_6^{4-}, Al(H_2O)_6^{3+}$
12	6	5	1	Square pyramidal		IF_5, BrF_5

12	6	4	2	Square planar		ICl_4^-
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(a) Steps followed to draw the structure of molecules and cations

- Determine the *number of valence electrons on the central atom* from its electronic configuration or the number of its group in the Periodic Table.
- If the structure is for a cation, subtract an electron for each positive charge on the number of valence electrons.
- If the central atom is a transition element, calculate the oxidation state and use it as number of valence electrons.

Molecule or ion	Electronic configuration of central atom	Number of valence electrons for central atom
PBr_3	2: 8: 5	5
NH_4^+	2: 5	$5 - 1 = 4$
SBr_6	2: 8: 6	6
Cl_2O	2: 6	6

- Add one electron to the valence electrons in (1) above for each atom/ligand bonded to the central atom as shown below.

Molecule or ion	Number of valence electrons on central atom	Total number of valence electrons
PBr_3	5	$5 + 3 = 8$
NH_4^+	4	$4 + 4 = 8$
SBr_6	6	$6 + 6 = 12$
Cl_2O	6	$6 + 2 = 8$

- Divide the *total number of valence electrons by two* to get the *total number of electron pairs*. This is because electrons bond in pairs

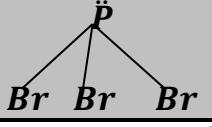
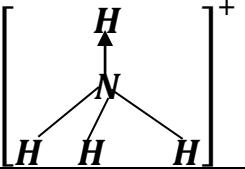
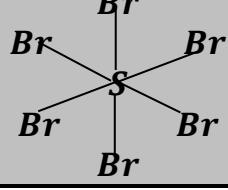
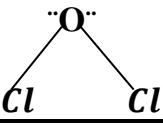
Molecule or ion	Total number of valence electrons	Total number of electron pairs
PBr_3	8	$\frac{8}{2} = 4$
NH_4^+	8	$\frac{8}{2} = 4$
SBr_6	12	$\frac{12}{2} = 6$

Cl_2O	8	$\frac{8}{2} = 4$
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4. From the **total number of electron pairs**, subtract the **number of bonding pairs** to get the number of **lone pairs**. The number of bonding pairs corresponds to the number of bonded atoms to the central atom.

Molecule or ion	Total number of electron pairs	Number of bonding pairs	Number of lone pairs
PBr_3	4	3	$4 - 3 = 1$
NH_4^+	4	4	$4 - 4 = 0$
SBr_6	6	6	$6 - 6 = 0$
Cl_2O	4	2	$4 - 2 = 2$

5. Then draw the structure of the molecule using the summary in the table above, **showing prediction of shapes of molecules**. The lone pairs are shown as two dots around the central atom for each electron pair. Put the **VSEPR** theory into consideration as you draw the molecule/ion.

Molecule or ion	Number of bonding pairs	Number of lone pairs	Structure	Shape
PBr_3	3	1		Trigonal pyramidal
NH_4^+	4	0		Tetrahedral
SBr_6	6	0		Octahedral
Cl_2O	2	2		Bent

NOTE:

- (i) *It is strictly that number of bonding pairs and lone pairs that guide us on the geometry of the molecule.*
- (ii) *Bond angles and bond lengths should be put into consideration when drawing the structures*
- (iii) *The lines that represent the bonds should strictly not leave a lot of space between the atoms.*

(b) Steps followed to draw the structure of oxy-anions and oxy-molecules

These are molecules or anions containing oxygen atoms. They are treated in a special way since they contain --OH bonds, $=\text{O}$ bonds and $-\text{O}^-$ bonds.

1. Determine the *number of valence electrons on the central atom* from its electronic configuration or the number of its group in the Periodic Table.
- *If the central atom is a transition element, calculate the oxidation state and use it as number of valence electrons.*
- *The number of valence electrons is used to deduce the expected number of bonds to be formed by the central atom.*

Molecule or ion	Electronic configuration of central atom	Number of valence electrons on central atom
SO_3	2: 8: 6	6
H_2SO_3	2: 8: 6	6
H_3PO_4	2: 8: 5	5
NO_2^-	2: 5	5
SO_4^{2-}	2: 8: 6	6
HCO_3^-	2: 4	4
MnO_4^{2-}	Oxidation state of Mn is +6	6

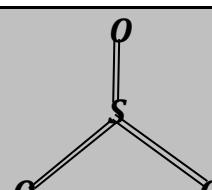
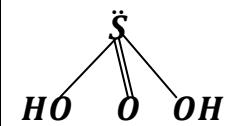
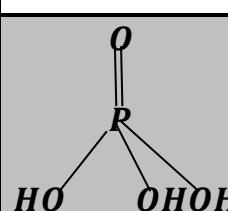
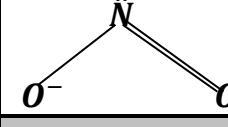
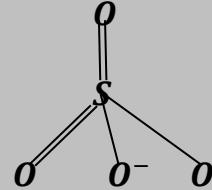
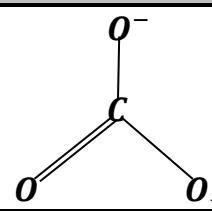
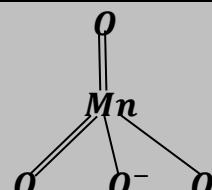
6. Deduce the nature of bonds in the ion or molecule. Begin with $-\text{O}^-$ bonds, followed by $\text{O} - \text{H}$ bonds and then $=\text{O}$ bonds.
 - (i) For every negative charge in the anion, there is one $-\text{O}^-$ bond.
 - (ii) For every hydrogen atom, there is one $\text{O} - \text{H}$ bond.
 - (iii) All the remaining oxygen atoms are double bonded after (i) and (ii) or if (i) and (ii) do not apply to the molecule.

<i>Molecule or ion</i>	<i>Expected number of bonds formed by central atom</i>	<i>Nature of bonds</i>
SO_3	6	$3 S = O$ bonds
H_2SO_3	6	2 $O - H$ bonds one $S = O$ bond
H_3PO_4	5	3 $O - H$ bonds one $P = O$ bond
NO_2^-	5	one $N - O^-$ bond one $N = O$ bond
SO_4^{2-}	6	2 $S - O^-$ bonds 2 $S = O$ bonds
HCO_3^-	4	one $O - H$ bond one $C - O^-$ bond one $C = O$ bond
MnO_4^{2-}	6	2 $Mn - O^-$ bonds 2 $Mn = O$ bonds

7. Since for each single bond, one electron of the valence electrons of the central atom is used, and two for a double bond, the unbounded electrons are the lone pairs. The lone pairs are obtained by subtracting the number of bonds formed from the number of valence electrons.

<i>Molecule or ion</i>	<i>Number of valence electrons of central atom</i>	<i>Nature of bonds</i>	<i>Number of valence electrons involved in bonds</i>	<i>Number of non-bonding electrons (lone pairs)</i>
SO_3	6	$3 S = O$ bonds	$(3 \times 2) = 6$	$6 - 6 = 0$
H_2SO_3	6	2 $O - H$ bonds one $S = O$ bond	$(2 + 2) = 4$	$6 - 4 = 2$ (1 lone pair)
H_3PO_4	5	3 $O - H$ bonds one $P = O$ bond	$(3 + 2) = 5$	$5 - 5 = 0$
NO_2^-	5	one $N - O^-$ bond one $N = O$ bond	$(1 + 2) = 3$	$5 - 3 = 2$ (1 lone pair)
SO_4^{2-}	6	2 $S - O^-$ bonds 2 $S = O$ bonds	$2 + (2 \times 2) = 6$	$6 - 6 = 0$
HCO_3^-	4	one $O - H$ bond one $C - O^-$ bond one $C = O$ bond	$(1 + 1 + 2) = 4$	$4 - 4 = 0$
MnO_4^{2-}	6	2 $Mn - O^-$ bonds 2 $Mn = O$ bonds	$2 + (2 \times 2) = 6$	$6 - 6 = 0$

8. Draw the structure of the molecule/ion using the nature of bonds and lone pairs. Where no lone pairs in the molecule/ ion, the bonds are symmetrically placed around the molecule.

Molecule or ion	Nature of bonds	Number of lone pairs	Structure	Shape
SO_3	$3 S = O$ bonds	0		Trigonal planar
H_2SO_3	2 $O - H$ bonds one $S = O$ bond	1		Trigonal pyramidal
H_3PO_4	3 $O - H$ bonds one $P = O$ bond	0		Tetrahedral
NO_2^-	one $N - O^-$ bond one $N = O$ bond	1		Bent
SO_4^{2-}	2 $S - O^-$ bonds 2 $S = O$ bonds	0		Tetrahedral
HCO_3^-	one $O - H$ bond one $C - O^-$ bond one $C = O$ bond	0		Trigonal planar
MnO_4^-	2 $Mn - O^-$ bonds 2 $Mn = O$ bonds	0		Tetrahedral

(a) Molecules or ions with a linear shape

Linear molecules have *two bonding pairs* and *no lone pairs*. The molecules are *linear* with a **bond angle of 180°** because the *bonding pairs greatly repel themselves*.

The molecules in gaseous beryllium chloride are linear because the two bonded pairs around the beryllium atom repel each other as fully as possible giving the molecule a bond angle of 180°.

For example in CO_2 ,

- *It is treated as an oxy-molecule.*
- *The carbon (central) atom has 4 valence electrons from its electronic configuration.*
- *Carbon is therefore expected to form 4 bonds with the oxygen atoms.*
- *Each oxygen atom forms a double bond to the carbon atom and no lone pair remains.*
- *The two bonding pairs greatly repel themselves greatly to form a linear molecule, bond angle 180°.*

Some ions also form a linear structure. These have *two bonding pairs* and *three lone pairs*.

For example in ICl^-_2 ,

- *The iodine (central) atom has 7 valence electrons from its electronic configuration.*
- *Since the structure is for an anion with negative charge one, the total electrons are $(7 + 1) = 8$.*
- *2 of these electrons are used for bonding with the chlorine atoms.*
- *This leaves 6 electrons not used for bonding and form the three lone pairs.*
- *The geometry of two bonding pairs and three lone pairs corresponds to a linear molecule, bond angle 180°.*

In $HOCl$ or ClO^- , there are three lone pairs and one bond pair surrounding the central oxygen atom. They are also linear species.

Molecule	Structure	Shape
$BeCl_2$	$Cl—Be—Cl$	<i>Linear</i>
CO_2	$O=C=O$	
ICl^-_2	$[Cl—..I..—Cl]^-$	

(b) Molecules or ions with a bent shape

Bent molecules or ions are also called **V-shaped** molecules or ions. They either have;

- (i) two bonding pairs and one lone pair or
- (ii) two bonding pairs and two lone pairs

For example in H_2S ,

- The sulphur (central) atom has 6 valence electrons from its electronic configuration.
- Since it is bonded to two hydrogen atoms, the total number of valence electrons in the molecule is 8 .
- The total number of valence electrons divided by two gives four electron pairs.
- Of the four electron pairs, there are two bonding pairs since Sulphur is bonded to two hydrogen atoms and two lone pairs.
- The repulsion between the two lone pairs of electrons is greater than the repulsion between lone pairs and bonding pairs of electrons which is also greater the repulsion between the bonding pairs of electrons.
- This reduces the bond angle to 92° making the molecule V-shaped.

For example in $PbBr_2$,

- The lead atom has 4 valence electrons from its electronic configuration.
- Since it is bonded to two chlorine atoms, the total number of valence electrons in the molecule is 6 .
- The total number of valence electrons divided by two gives three electron pairs.
- Of the three electron pairs, there are two bonding pairs since lead is bonded to two chlorine atoms and one lone pair.
- The two bonding pairs of electrons repel each other but the lone pair-bond pair repulsion is greater.
- This reduces the bond angle to a value smaller than 120° making the molecule V-shaped.

Some ions also form a bent structure.

For example in ClO_2^- ,

- It is an oxy-anion
- The chlorine atom has 7 valence electrons from its electronic configuration.
- Chlorine is therefore expected to form seven bonds.
- The negative charge in the anion means there is one $Cl - O^-$ bond.
- The remaining oxygen atom is doubly bonded to chlorine $Cl = O$

- This implies that 3 of the 7 electrons are used for bonding and the remaining 4 form two lone pairs.
- The repulsion between the two lone pairs of electrons is greater than the repulsion between lone pairs and bonding pairs of electrons which is also greater the repulsion between the bonding pairs of electrons.
- This reduces the bond angle making the molecule V-shaped.

Molecule	Structure	Shape
H_2S		V-shaped
$PbBr_2$		
ClO_2^-		

(c) Molecules or ions with a trigonal planar shape

Trigonal planar molecules have *three bonding pairs of electrons* and *no lone pairs*. The *three bonding pairs lie in the same plane* and the molecules have a *bond angle of 120°* because the *bonding pairs greatly repel each other equally*.

For example in BF_3 ,

- The boron atom has 3 valence electrons from its electronic configuration.
- Since it is bonded to three fluorine atoms, the total number of valence electrons in the molecule is 6 .
- The total number of valence electrons divided by two gives three electron pairs.
- All the three electron pairs are used in bonding to form three bonding pairs since boron is bonded to three fluorine atoms and there is no lone pair.
- The three bonding pairs of electrons repel each other equally.
- This makes the bond angle 120°making the molecule trigonal planar.

For example in $HCHO$,

- The carbon atom has 4 valence electrons from its electronic configuration.
- Two of these are used to bond to each hydrogen atom and two to form a double bond with oxygen .No lone pair remains.
- This gives the molecule three bonding pairs and no lone pair.
- The three bonding pairs of electrons repel each other equally.

- This makes the bond angle 120° making the molecule trigonal planar.

Molecule	Structure	Shape
BF_3		Trigonal planar
$HCHO$		

(d) Molecules or ions with a tetrahedral shape

Tetrahedral molecules or ions have *four bonding pairs of electrons* and *no lone pairs*. They have a *bond angle of $109^\circ 28'$* because the *bonding experience mutual repulsion*.

For example in $SiCl_4$,

- The silicon atom has 4 valence electrons from its electronic configuration.
- Since it is bonded to four chlorine atoms, the total number of valence electrons in the molecule is 8 .
- The total number of valence electrons divided by two gives four electron pairs.
- All the four electron pairs are bonding pairs since silicon is bonded to four chlorine atoms and no lone pairs.
- The four bonding pairs of electrons mutually repel each other, resulting into a bond angle of $109^\circ 28'$ making the molecule tetrahedral.

Some ions also form a tetrahedral structure.

For example in PO_4^{3-} ,

- It is an oxy-anion
- The phosphorus atom has 5 valence electrons from its electronic configuration.
- Phosphorus is therefore expected to form five bonds.
- The three negative charges in the anion means there are three $P - O^-$ bonds.
- The remaining oxygen atom is doubly bonded to phosphorus $P = O$
- This gives a total of five bonds, and all the electrons are used for bonding. There is no lone pair.
- The four bonding pairs of electrons mutually repel each other, resulting into a bond angle of $109^\circ 28'$ making the molecule tetrahedral.

Some complexes also form a tetrahedral structure.

For example in $Zn(NH_3)_4^{2+}$,

Molecule	Structure	Shape
$SiCl_4$		
PO_4^{3-}		Tetrahedral
$Zn(NH_3)_4^{2+}$		

(e) Molecules or ions with a trigonal pyramidal shape

Trigonal pyramidal molecules or ions have *three bonding pairs of electrons* and *one lone pair*. They have a *bond angle smaller than $109^\circ 28'$, which is observed in the tetrahedral molecules*. This is due to increased repulsion caused by the lone pair.

For example in PH_3 ,

- *The phosphorus atom has 5 valence electrons from its electronic configuration.*
- *Since it is bonded to three hydrogen atoms, the total number of valence electrons in the molecule is 8 .*
- *The total number of valence electrons divided by two gives four electron pairs.*
- *Of the four electron pairs, there are three bonding pairs since phosphorus is bonded to three hydrogen atoms and one lone pair.*
- *The three bonding pairs of electrons repel each other but the lone pair-bond pair repulsion is greater.*
- *This reduces the bond angle to $93^\circ 20'$ making the molecule trigonal pyramidal.*

For example in $HClO_3$,

- *It is an oxy-molecule/ oxy-acid*
- *The chlorine atom has 7 valence electrons from its electronic configuration.*

- Phosphorus is therefore expected to form seven bonds.
- For the hydrogen atom present, there is one O – H bond.
- The two other oxygen atoms form two Cl = O bonds.
- This gives a total of five bonds, and two electrons are not used for bonding. There is one lone pair therefore.
- The three bonding pairs of electrons repel each other but the lone pair-bond pair repulsion is greater.
- This reduces the bond angle making the molecule trigonal pyramidal.

Some ions also form a trigonal pyramidal structure.

For example in SO_3^{2-} ,

- It is an oxy-anion
- The Sulphur atom has 6 valence electrons from its electronic configuration.
- Phosphorus is therefore expected to form six bonds.
- The two negative charges in the anion mean there are two $S - O^-$ bonds.
- The remaining oxygen atom is doubly bonded to Sulphur, $S = O$.
- This gives a total of four bonds, and two electrons are not used for bonding. There is one lone pair therefore.
- The three bonding pairs of electrons repel each other but the lone pair-bond pair repulsion is greater.
- This reduces the bond angle making the molecule trigonal pyramidal.

Molecule	Structure	Shape
PH_3		
$HClO_3$		Trigonal pyramidal
SO_3^{2-}		

(f) Molecules or ions with a trigonal bipyramidal shape

Trigonal bipyramidal molecules have *five bonding pairs of electrons* and *no lone pairs*.

For example in PF_5 ,

- The phosphorus atom has 5 valence electrons from its electronic configuration.
- Since it is bonded to five fluorine atoms, the total number of valence electrons in the molecule is 10 .
- The total number of valence electrons divided by two gives five electron pairs.
- All the five electron pairs are used in bonding as bonding pairs.

The $Fe(CO)_5$ complex also has a trigonal bipyramidal shape,

Molecule	Structure	Shape
PF_5		
$Fe(CO)_5$		Trigonal bipyramidal

(g) Molecules or ions with an irregular tetrahedral shape

Irregular or distorted tetrahedral molecules have *four bonding pairs of electrons* and *one lone pair*.

For example in SF_4 ,

- The Sulphur atom has 6 valence electrons from its electronic configuration.
- Since it is bonded to four fluorine atoms, the total number of valence electrons in the molecule is 10 .
- The total number of valence electrons divided by two gives five electron pairs.
- Four of the five electron pairs are used as bonding pairs to bond with the four fluorine atoms.
- One electron pair remains as a lone pair.
- The four bonding pairs of electrons repel each other but the lone pair-bond pair repulsion is greater.

Molecule	Structure	Shape
SF_4		Irregular tetrahedral

(h) Molecules or ions with an octahedral shape

Octahedral molecules have *six bonding pairs of electrons*.

For example in SCl_6 ,

- *The sulphur atom has 6 valence electrons from its electronic configuration.*
- *Since it is bonded to six chlorine atoms, the total number of valence electrons in the molecule is 12 .*
- *The total number of valence electrons divided by two gives six electron pairs.*
- *All the six electron pairs are used in bonding as bonding pairs.*

The $Cr(NH_3)_6^{3+}$ complex also has an octahedral shape,

Molecule	Structure	Shape
SCl_6		
$Cr(NH_3)_6^{3+}$		Octahedral

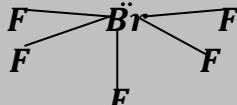
(i) Molecules with a square pyramidal shape

Square pyramidal molecules have *five bonding pairs of electrons and one lone pair*.

For example in BrF_5 ,

- *The bromine atom has 7 valence electrons from its electronic configuration.*
- *Since it is bonded to five fluorine atoms, the total number of valence electrons in the molecule is 12 .*
- *The total number of valence electrons divided by two gives six electron pairs.*

- Five of the six electron pairs are used in bonding as bonding pairs.
- One electron pair remains as a lone pair.
- The five bonding pairs of electrons repel each other but the lone pair-bond pair repulsion is greater.

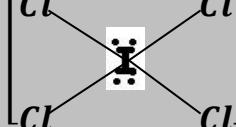
Molecule	Structure	Shape
BrF_5		Square pyramidal

(j) Molecules or ions with a square planar shape

Square planar molecules have *four bonding pairs of electrons and two lone pairs*.

For example in ICl_4^- ,

- The iodine (central) atom has 7 valence electrons from its electronic configuration.
- Since the structure is for an anion with negative charge one, the total electrons are $(7 + 1) = 8$.
- 4 of these electrons are used for bonding with the chlorine atoms.
- This leaves 4 electrons not used for bonding and form the two lone pairs.
- The lone pair-lone pair repulsion is greater than lone pair-bond pair repulsion which is also greater than bond pair- bond pair repulsion.

Molecule	Structure	Shape
ICl_4^-		Square planar

Qn. Draw the structure and name the shapes of the following molecules or ions

Molecule	Structure	Shape
H_2O		
PCl_3		
CCl_4		
$SnCl_2$		
NH_3		
$SnCl_4$		
NO_3^-		
PCl_5		
$GeCl_4$		
H_3O^+		

CS_2		
$(CH_3)_3N$		
PBr_5		
I_3^-		
CH_4		
PF_3		
$NOCl$		
ClO_4^-		
BCl_3		
SiH_4		
$Fe(CN)_6^{4-}$		
BH_2		

$CHCl_3$		
H_3PO_3		
HCN		
OF_2		
PI_5		
H_2SO_4		
SCL_2		
CO_3^{2-}		
C_2H_2		
SF_6		
SO_2		
IF_5		

HCl		
$Ag(NH_3)_2^+$		
O_3		
$Co(NH_3)_6^{3+}$		
$POCl_3$		
ClO_3^-		
Cl_2O		
$Ag(CN)_2^-$		
$HClO_4$		
$GeCl_2$		
SO_2Cl_2		
CrO_4^{2-}		

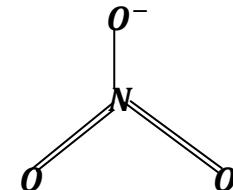
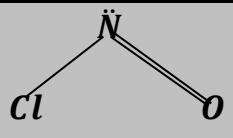
$Al(H_2O)_6^{3+}$		
NH_2^-		
$S_2O_3^{2-}$		
NO_2^+		

The effect of lone pairs on Molecular Geometry

The effect of lone pairs on molecular geometry is explained basing on the **VSEPR** theory.

1. Explain the structures of the following species;

- (i) *beryllium chloride*
- (ii) *nitrate ion*
- (iii) *NOCl*
- (iv) *Chlorate(V) ion*
- (v) *Hydrogen sulphide*

Molecule / ion	Structure	Explanation
$BeCl_2$	$Cl—Be—Cl$	Beryllium chloride molecule has two bonding pairs of electrons and no lone pair . The two bonding pairs repel each other greatly to form a linear molecule with a bond angle of 180° .
NO_3^-		The nitrate ion possesses three bonding pairs of electrons and no lone pair . The three bonding pairs which lie in the same plane and repel each other equally to form a trigonal planar shape with a bond angle of 120° .
$NOCl$		Nitrosyl chloride molecule has two bonding pairs of electrons and one lone pair . The two bonding pairs of electrons repel each other but the lone pair-bond pair repulsion is greater. This reduces the bond angle making the molecule V-shaped .
		The chlorate(V) ion possesses three bonding pairs of electrons and one lone pair . The three bonding pairs which lie in the same plane and repel each other equally to form a trigonal planar shape with a bond angle of 120° .

ClO_3^-		<i>electrons and one lone pair. The three bonding pairs of electrons repel each other but the lone pair-bond pair repulsion is greater. This reduces the bond angle making the molecule trigonal pyramidal.</i>
H_2S		<i>The hydrogen sulphide molecule has two bonding pairs and two lone pairs. The repulsion between the two lone pairs of electrons is greater than the repulsion between lone pairs and bonding pairs of electrons which is also greater the repulsion between the bonding pairs of electrons alone. This reduces the bond angle to 92°making the molecule V-shaped.</i>

2. Explain why;

- (i) Beryllium bromide has a bond angle of 180° but tin(II) bromide has a bond angle less than 120°



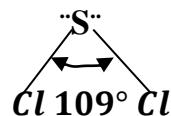
Beryllium bromide molecule has two bonding pairs of electrons and no lone pair. The two bonding pairs repel each other greatly to form a linear molecule with a bond angle of 180° . Tin(II) bromide molecule has two bonding pairs of electrons and one lone pair. The two bonding pairs of electrons repel each other but the lone pair-bond pair repulsion is greater. This reduces the bond angle making the molecule V-shaped.

- (ii) The sulphate ion is tetrahedral but the sulphite ion is trigonal pyramidal



The sulphate ion has four bonding pairs and no lone pairs. The four bonding pairs of electrons mutually repel each other, resulting into a bond angle of $109^\circ 28'$ making the molecule tetrahedral. The sulphite ion possesses three bonding pairs of electrons and one lone pair. The three bonding pairs of electrons repel each other but the lone pair-bond pair repulsion is greater. This reduces the bond angle making the molecule trigonal pyramidal.

- (iii) Sulphur dioxide has a bond angle of 120° while Sulphur dichloride has bond angle of 109° although both are V-shaped molecules.



The Sulphur dioxide molecule has two bonding pairs and one lone pair. The two bonding pairs of electrons repel each other but the lone pair-bond pair repulsion is greater. This makes the bond angle 120° . The Sulphur dichloride molecule also possesses two bonding pairs of electrons but has two lone pairs. Since the Sulphur dichloride molecule has more lone pairs than the Sulphur dioxide molecule, there exists lone pair-lone pair repulsion, and the lone pair-bond pair repulsion is also greater than in Sulphur dioxide. This reduces the bond angle in Sulphur dichloride.

The effect of electronegativity on size of bond angles

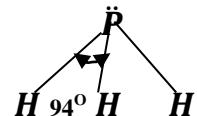
For two molecules or ions in which the central atoms are different but the bonded atoms are the same, the increase in electro negativity increases the attraction for the bonding electrons by the central atoms in their molecules. This makes the bonding pairs of electrons closer to the more electronegative atom than to the less electronegative element. This implies that the bonding pairs of electrons are closer to the central atom leading to an increased repulsion between them, which increases the bond angle.

For two molecules or ions in which the central atoms are similar but the bonded atoms are the different, the increase in electro negativity of the bonded atoms increases the attraction for the bonding electrons by the bonded atoms in their molecules. This makes the bonding pairs of electrons closer to the more electronegative atom than to the less electronegative element. This implies that the bonding pairs of electrons far apart leading to a decreased repulsion between them, which reduces the bond angle.

Examples

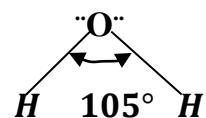
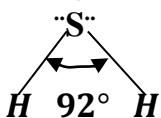
Explain why;

- (i) the bond angle in ammonia is 107° while that in phosphine is 94° .



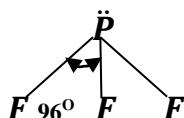
Both ammonia and phosphine molecules adopt a trigonal pyramidal shape. However, the nitrogen atom is more electronegative than the phosphorus atom. The bonding pairs of electrons are closer to the nitrogen atom in ammonia than they are to the phosphorus atom in phosphine. This causes an increased repulsion between the bonded pairs of electrons in ammonia than it is in phosphine, therefore ammonia has a bigger bond angle than phosphine.

- (ii) the bond angle in hydrogen sulphide is 92° while that in water is 105° .



Both hydrogen sulphide and water molecules adopt a V- shaped structure. However, the oxygen atom is more electronegative than the sulphur atom. The bonding pairs of electrons are closer to the oxygen atom in water than they are to the sulphur atom in hydrogen sulphide. This causes an increased repulsion between the bonded pairs of electrons in water than it is in hydrogen sulphide, therefore the water molecule has a bigger bond angle than hydrogen sulphide.

- (iii) the bond angle in phosphorus trifluoride is 96° while that of phosphorus trichloride is 100° .



Both phosphorus trifluoride and phosphorus trichloride molecules adopt a trigonal pyramidal shape. However, the fluorine atom is more electronegative than the chlorine atom. The fluorine atom therefore withdraws away the bonded pairs of electrons from the phosphorus atom more than the chlorine atom does. This makes the bonded pairs to be far apart in phosphorus trifluoride than they are in phosphorus trichloride, reducing the repulsion between them. Therefore phosphorus trifluoride has a smaller bond angle than phosphorus trichloride.

Polarity of molecules

Polarity is a condition of a molecule to have positive and negative charges. Polarity of molecules is related to the electronegativity difference of the bonding atoms and bond symmetry.

Factors that determine the polarity of molecules

- (i) electronegativity difference of atoms in the molecule

- (ii) bond symmetry or spatial arrangement of various bonds in the molecule

Polar covalent bonds are formed as a result of difference in electronegativity of the bonding atoms. These include; $H^{\delta+}-Cl^{\delta-}$, $H^{\delta+}-Br^{\delta-}$, $H^{\delta+}-I^{\delta-}$, $H^{\delta+}-O^{\delta-}$, $C^{\delta+}-Cl^{\delta-}$, etc.

For two equal but opposite separated electrical charges, there exists an electric dipole moment. An electric dipole moment is a product of one of the charges, $\delta +$ or $\delta -$ and the distance between the atomic nuclei. Any individual polar covalent bond must have a corresponding dipole moment.

However, there are molecules in which the individual bonds in it are polar but the molecule as a whole is non-polar. An example is tetrachloromethane which has a zero dipole moment, although the individual carbon-chlorine bonds in it have dipole moments. This is due to the symmetrical distribution of the chlorine atoms around the carbon atom such that the effects of the four dipoles cancel each other. Another example is the carbon dioxide molecule.

All molecules in which the atoms are symmetrically distributed around the central atom are non polar. This is only possible if all the symmetrically distributed atoms around the central atom are the same. These include;

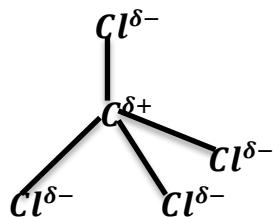
- (i) *linear molecules*
- (ii) *trigonal planar molecules*
- (iii) *square planar molecules*
- (iv) *tetrahedral molecules*
- (v) *trigonal bipyramidal molecules*
- (vi) *octahedral molecules*

Explain why;

- (a) Carbon tetrachloride is non-polar yet the carbon-chlorine bond is polar.

Chlorine is more electronegative than carbon. The chlorine atom therefore tends to attract the bonding electrons towards itself hence acquires a partial negative charge (δ^-) and the carbon atom gains a partial positive charge (δ^+). This makes the carbon- chlorine bond polar.

However, the whole molecule is non-polar because it has a tetrahedral structure in which the chlorine atoms are symmetrically distributed about the carbon atom. This creates equal and opposite dipole moments in all directions that cancel out making the resultant dipole moment zero.



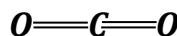
Note; For the same reason, a stream of tetrachloromethane is not deflected by a charged rod while that of chloroform is deflected.

- (b) The carbon- oxygen bond is polar but carbon dioxide is non-polar.

Oxygen is more electronegative than carbon. The oxygen atom therefore tends to attract the bonding electrons towards itself hence acquires a partial negative charge (δ^-) and the carbon atom gains a partial positive charge (δ^+). This makes the

carbon-oxygen bond polar.

However, the whole molecule is non-polar because it has a linear structure in which the oxygen atoms are symmetrically distributed about the carbon atom. This creates equal and opposite dipole moments in all directions that cancel out making the resultant dipole moment zero.



Molecules in which the bonded atoms are not symmetrically distributed around the central atom like chloromethane, dichloromethane, trichloromethane, water and ammonia have an overall dipole moment over the molecule. Therefore both the individual bonds and the whole molecule are polar.

Differences between polar and non-polar molecules

Polar molecules	Non-polar molecules
Asymmetrical	Symmetrical
One end of the molecule is positive whereas the other has a positive charge	Does not have distribution of charges at opposite ends
Can interact through hydrogen bonds	There are van der Waals forces between non polar molecules
Have a dipole moment	Have no dipole moment

Miscellaneous Questions

1. Use dot and cross diagrams to show how the following atoms can combine

- (a) Lithium and fluorine
- (b) Hydrogen and fluorine
- (c) Magnesium and fluorine
- (d) Lithium and oxygen
- (e) Sodium and fluorine
- (f) Aluminium and fluorine
- (g) Calcium and oxygen

2. (a) What is meant by the term hydrogen bonding?

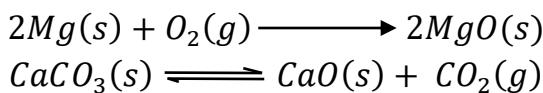
- (b) Explain how hydrogen bonding arises in;
- (i) hydrogen fluoride
- (ii) ice
- (iii) Methylamine
- (iv) Ethanoic acid

CHAPTER SIX

CHEMICAL EQUILIBRIA

THE CONCEPT OF CHEMICAL EQUILIBRIUM

Chemical reactions, just like physical changes can reach a state of equilibrium. Although some reactions take place in one direction, like the when magnesium burns in air to form magnesium oxide, other reactions take place in both forward and backward directions at comparable rates for example the thermal dissociation of calcium carbonate.



The products of thermal dissociation of calcium carbonate are calcium oxide, a base and carbon dioxide, an acidic gas which can react to form calcium carbonate again.

Apart from thermal dissociation of calcium carbonate, many other reactions do not go to completion and then stop, since the products of the reaction themselves react to form original reactants. Such reactions are called **reversible reactions**. Therefore, for equilibrium to be established there is both a **forward** and **backward reaction**.

The characteristics of a chemical equilibrium

- (i) *The reaction in which it occurs should be reversible*
- (ii) *The reaction should occur in a closed system*
- (iii) *Temperature should be constant*
- (iv) *Rate of forward reaction should be equal to the rate of backward reaction*

Reversible and irreversible reactions

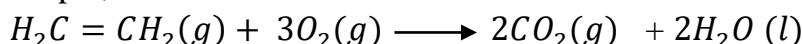
A reversible reaction is a reaction takes place in both forward and backward directions such that both the reactants and products are present in the equilibrium hence does not go to completion.

For example;

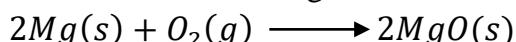
- (i) the reaction between hydrogen gas and gaseous iodine to form hydrogen iodide
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
- (ii) the esterification reaction for formation of ethylethanoate from ethanoic acid and ethanol
$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$
- (iii) reaction between heated iron and steam to form iron(II) diiron(III) oxide and hydrogen
$$3Fe(s) + 4H_2O(l) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

An irreversible reaction is a reaction takes place only in the forward direction, such that only the products are formed during the reaction hence the reaction can never be at equilibrium.

- (i) For example, the combustion of ethene to form carbon dioxide and water



- (ii) Burning magnesium in air to form magnesium oxide



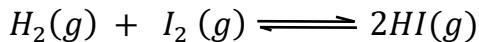
- (iii) Alkaline hydrolysis of an ethylethanoate to form ethanoate ions and ethanol



Dynamic equilibrium

A dynamic equilibrium is the equilibrium established when the rate of forward reaction is equal to the rate of backward reaction, such that the concentration of reactants and products remains constant.

For the reaction between known amounts of hydrogen and iodine in a sealed glass tube heated to a higher constant temperature and then allowed to cool, the equilibrium mixture formed contains hydrogen, iodine and hydrogen iodide.



This implies that both forward and backward reactions are still taking place and the rate of formation of hydrogen iodide is equal to rate of dissociation of hydrogen iodide and the concentrations of each species remains constant and the system is said to be in dynamic equilibrium.

This can be proven by injecting iodine containing a small quantity of radioactive iodine-131 into the equilibrium mixture. Radioactive iodine appears in the hydrogen iodide. This confirms that both forward reaction and backward reaction are still occurring.

Types of chemical equilibria

There are two types equilibrium systems namely;

- (i) Homogeneous equilibrium systems
- (ii) Heterogeneous equilibrium systems

A homogeneous equilibrium system is one in which all the reactants and products of a reaction are in the same phase.

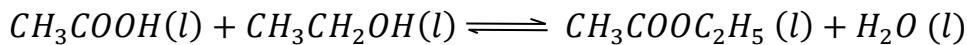
They can all gases, all liquids or all in solution.

For example;

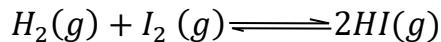
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- (i) the reaction between ethanol and ethanoic acid to form ethyl ethanoate /diethyl ether (esterification)



- (ii) the reaction between hydrogen gas and gaseous iodine to form hydrogen iodide



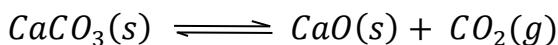
- (iii) Dissociation of dinitrogen tetroxide to form nitrogen dioxide.



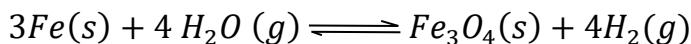
A heterogeneous equilibrium system is one in which two or more phases are involved.

For example;

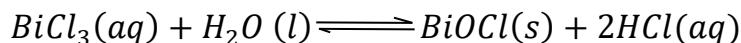
- (i) Dissociation of calcium carbonate to form calcium oxide and carbon dioxide.



- (ii) Reaction between iron and steam to form triiron tetraoxide and hydrogen



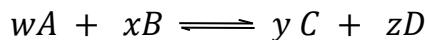
- (iii) Reaction between bismuth chloride and water to form bismuth oxychloride and hydrochloric acid



Note; if only ions are involved in an equilibrium, an ionic equilibrium (check next chapter) is established.

THE LAW OF MASS ACTION OR EQUILIBRIUM LAW

For a homogeneous equilibrium, represented as;



$$\frac{[C]^y[D]^z}{[A]^w[B]^x} = \text{a constant at a given temperature} = K_c$$

Where [] represents molar concentration at equilibrium and

K_c is the concentration equilibrium constant

The equilibrium law/ law of mass action therefore states that if a reversible reaction is allowed to reach equilibrium at a particular temperature, the product of the molar concentrations of the products raised to appropriate powers divided by the product of the molar concentrations of the reactants raised to appropriate powers is a constant

or

The law of mass action states that the in a reversible reaction, there is a fixed relationship at a given temperature between the molar concentrations of the products and those of the reactants in the equilibrium mixture.

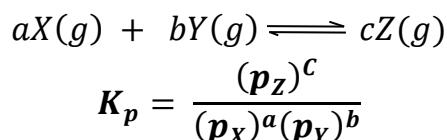
The concentration equilibrium constant, K_c

Equilibrium constant is the ratio of the product of molar concentration of products raised to their appropriate powers to the product of molar concentration or reactants raised to their appropriate powers in a stoichiometric equation of a reversible reaction at constant temperature.

The pressure equilibrium constant, K_p

For reactions involving gases, it is often more convenient to measure and express the gas concentrations in partial pressures in atmospheres. If this is done, the equilibrium constant is known as K_p

For example;



Using the law of mass action to write equilibrium constant expressions (K_c or K_p) and units

When writing expressions for equilibrium constants, the following should be noted;

1. Check whether **only the concentrations /moles in a given volume** are given or total pressure at equilibrium
2. If **only concentration/ moles** are given, then an expression for K_c should be written.
3. If **total pressure** at equilibrium is given, then expression for K_p should be written.
4. Solids **do not** appear in the equilibrium constant expression since their concentration is assumed to be constant.
5. For a K_p expression, only gaseous reactants and products appear.
6. If water is **one of the reactants**, and its **concentration is not given**, or remains unchanged, it is assumed to be present in a large excess hence does not appear in the equilibrium constant expression. If water is in gaseous state, then include it in the expression.
7. When only the expression is required, do not write the equation also as part of the answer
8. In the case of K_c , strictly square brackets must be used.
9. Sometimes the question may specify for you whether to write a K_c or K_p expression.

In each of the cases below, write the equation for the equilibrium, the equilibrium constant expression in terms of either K_c and K_p or both , depending on what is indicated in brackets and state the units.

1. Reaction between ethanol and ethanoic acid in presence of an acid catalyst (K_c)
2. The reaction between hydrogen gas and gaseous iodine.(both K_c and K_p)
3. Dissociation of dinitrogen tetroxide to form nitrogen dioxide.(both K_c and K_p)
4. Reaction between iodine solution and potassium iodide. (K_c)
5. Thermal dissociation of calcium carbonate.(both K_c and K_p)
6. Reaction between iron and steam to form triiron tetraoxide and hydrogen .
(both K_c and K_p)
7. Hydrolysis of bismuth(III) chloride. (K_c)
8. Reaction between hydrogen and nitrogen.(both K_c and K_p)
9. Hydrolysis of ethylethanoate using dilute hydrochloric acid. (K_c)
10. Reaction of phosphorus trichloride and chlorine.(both K_c and K_p)
11. Reaction between nitrogen and oxygen.(both K_c and K_p)
12. Conversion of Sulphur dioxide to Sulphur trioxide.(both K_c and K_p)
13. Reaction between carbon monoxide and hydrogen to form gaseous methanol.(both K_c and K_p)
14. Dissociation of hydrogen iodide.(both K_c and K_p)
15. Dissociation of phosphorus(V) chloride to phosphorus(III) chloride and chlorine.(both K_c and K_p)
16. Dissociation of Sulphur trioxide.(both K_c and K_p)
17. Reaction between carbon disulphide and hydrogen to form methane and hydrogen sulphide. .(both K_c and K_p)
18. Reaction between ammonia and oxygen to form nitrogen monoxide and water. (both K_c and K_p)
19. Redox reaction between iron metal and chromium(III) ions. (K_c)
20. Hydrogenation of nitrogen dioxide to form ammonia and water.(both K_c and K_p)

$$(y + z) - (w + x) = \Delta n$$

$$K_p = K_c (RT)^{\Delta n}$$

Where Δn is the total number of moles of gaseous products – total number of moles of gaseous reactants in a balanced equation.

EXPERIMENTS ON CHEMICAL EQUILIBRIUM

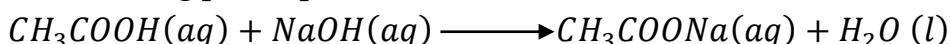
(a) Experiment to determine the equilibrium constant for the hydrolysis of ethylethanoate using hydrochloric acid.

A known amount of ethylethanoate (a moles) is mixed with a known amount of water (b moles)

A known volume of concentrated hydrochloric acid is added to catalyze the reaction.

The mixture is kept in a sealed glass tube at a constant temperature for a week.

The tube is broken in cold water and the solution titrated with a standard solution of sodium hydroxide using phenolphthalein indicator



The amount of ethanoic acid present at equilibrium is obtained (x moles)

Treatment of results

Let V be the volume of the solution in dm^3

If there are x moles of ethanoic acid at equilibrium, there are also x moles of ethanol at equilibrium since mole ratio of $CH_3COOH : CH_3CH_2OH = 1:1$

Moles of ester hydrolysed and moles of water used are both equal to x , since mole ratio is also 1:1

$CH_3COOCH_2CH_3(l) + H_2O(l) \rightleftharpoons CH_3COOH(l) + CH_3CH_2OH(l)$				
Initial moles	a	b	0	0
Moles reacted/formed	x	x	x	x
Moles at equilibrium	$a - x$	$b - x$	x	x
concentration	$\frac{a - x}{v}$	$\frac{b - x}{v}$	$\frac{x}{v}$	$\frac{x}{v}$

$$K_c = \frac{[CH_3COOH][CH_3CH_2OH]}{[CH_3COOCH_2CH_3][H_2O]}$$

$$K_c = \frac{(x/v)(x/v)}{\left(\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)\right)}$$

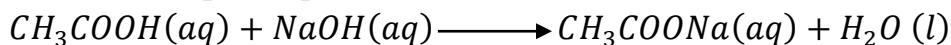
$$K_c = \frac{x^2}{(a-x)(b-x)}$$

(b) Experiment to determine the equilibrium constant for the esterification reaction between ethanoic acid and ethanol

A known amount of ethanoic acid (a moles) is mixed with a known amount of ethanol (b moles) and put in a sealed glass tube.

The sealed tube and its contents is left in a water bath at 60°C to 70°C for 7 hours

The tube is broken in cold water and the solution titrated with a standard solution of sodium hydroxide using phenolphthalein indicator



The amount of ethanoic acid present at equilibrium is obtained (x moles)

Treatment of results

Let V be the volume of the solution in dm³

moles of ethanoic acid at equilibrium=x

moles of ethanoic acid converted to ester and water =(a-x)

since mole ratio of CH₃COOH: CH₃COOCH₂CH₃: H₂O = 1: 1: 1

(a-x) moles of CH₃COOH form (a-x) moles of H₂O and (a-x) moles of CH₃COOCH₂CH₃ at equilibrium.

Since mole ratio of CH₃COOH : CH₃CH₂OH = 1: 1

Moles of ethanol that react=(a-x)

Moles of ethanol at equilibrium=b-(a-x) =(b-a+x)

$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$				
Initial moles	a	b	0	0
Moles reacted/ formed	a - x	a - x	a - x	a - x
Moles at equilibrium	x	b - a + x	a - x	a - x
Concentration	$\frac{x}{v}$	$\frac{b - a + x}{v}$	$\frac{a - x}{v}$	$\frac{a - x}{v}$

$$K_c = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$

$$K_c = \frac{\left(\frac{a-x}{v}\right)\left(\frac{a-x}{v}\right)}{\left(\frac{x}{v}\right)\left(\frac{b-a+x}{v}\right)}$$

$$K_c = \frac{(a-x)^2}{x(b-a+x)}$$

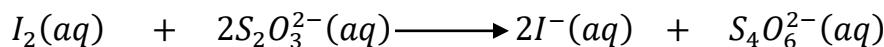
(c) Experiment to determine the equilibrium constant for the dissociation of hydrogen iodide to hydrogen and iodine.

A known amount of hydrogen iodide (n moles) is put in a sealed glass bulb of a fixed volume ($v \text{ dm}^3$) and kept in a thermostat at a temperature of 450°C until equilibrium is established.

At equilibrium, the bulb is removed and rapidly cooled to stop the reaction and fix the equilibrium such that the equilibrium does not adjust itself to the equilibrium value at a lower temperature.

The tube is then broken under an aqueous solution of potassium iodide to dissolve the iodine present at equilibrium.

The resultant mixture is titrated with a standard solution of sodium thiosulphate using starch indicator



The amount of iodine present at equilibrium is obtained.

Treatment of results

Total volume of the bulb= $v \text{ dm}^3$

Number of moles of hydrogen iodide heated= c moles

Degree of dissociation of hydrogen iodide= α

	$2\text{HI}(g)$	$\rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$	
<i>Initial moles</i>	n	0	0
<i>Moles dissociated/formed</i>	$n\alpha$	$\frac{n\alpha}{2}$	$\frac{n\alpha}{2}$
<i>Moles at equilibrium</i>	$n - n\alpha$	$\frac{n\alpha}{2}$	$\frac{n\alpha}{2}$
<i>Concentration at equilibrium</i>	$\frac{n(1-\alpha)}{v}$	$\frac{n\alpha}{2v}$	$\frac{n\alpha}{2v}$

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$$

$$K_c = \frac{\left(\frac{n\alpha}{2v}\right)^2}{\left(\frac{n(1-\alpha)}{v}\right)^2}$$

$$K_c = \frac{\alpha^2}{4(1-\alpha)^2}$$

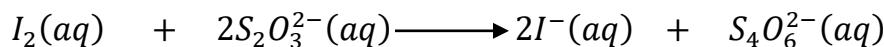
(d) Experiment to determine the equilibrium constant for the reaction between hydrogen and iodine to form hydrogen iodide.

A known amount of hydrogen (a moles) and a known amount of iodine (b moles) are put in a sealed glass bulb of a fixed volume ($v \text{ dm}^3$), kept in a thermostat at a temperature of 450°C until equilibrium is established.

At equilibrium, the bulb is removed and rapidly cooled to stop the reaction and fix the equilibrium such that the equilibrium does not adjust itself to the equilibrium value at a lower temperature.

The tube is then broken under an aqueous solution of potassium iodide to dissolve the iodine present at equilibrium.

The resultant mixture is titrated with a standard solution of sodium thiosulphate using starch indicator



The amount of iodine present at equilibrium is obtained.

Treatment of results

Total volume of the bulb = $v \text{ dm}^3$

Let number of moles of iodine converted to hydrogen iodide = x moles

Moles of hydrogen iodide formed = $2x$ moles

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2\text{HI}(\text{g})$
<i>Initial moles</i>	a		b		0
<i>Moles reacted/formed</i>	x		x		$2x$
<i>Moles at equilibrium</i>	$a - x$		$b - x$		$2x$
<i>Concentration at equilibrium</i>	$\frac{(a-x)}{v}$		$\frac{b-x}{v}$		$\frac{2x}{v}$

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

$$K_c = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)}$$

$$K_c = \frac{4x^2}{(a-x)(b-x)}$$

CALCULATIONS INVOLVING CONCENTRATION EQUILIBRIUM CONSTANT AND PRESSURE EQUILIBRIUM CONSTANT

(a) Equilibria for esterification.

Examples

1. When 60g of ethanoic acid were heated with 46g of ethanol until equilibrium was established, 12g of water and 58.7g of ethylethanoate were formed. Calculate;
 - (a) the equilibrium constant for the reaction
 - (b) the mass of ethylethanoate that would be formed under the same conditions if 90g of ethanoic acid and 92g of ethanol were heated.

(a) Molar mass of CH_3COOH = $(2 \times 12) + (2 \times 16) + (4 \times 1) = 60\text{g}$

Molar mass of $\text{CH}_3\text{CH}_2\text{OH}$ = $(2 \times 12) + (6 \times 1) + (1 \times 16) = 46\text{g}$

$$\text{Moles of } \text{CH}_3\text{COOH} = \frac{60}{60} = 1.0 \text{ moles}$$

$$\text{Moles of } \text{CH}_3\text{CH}_2\text{OH} = \frac{46}{46} = 1.0 \text{ moles}$$

Molar mass of H_2O = $2 + 16 = 18\text{g}$

Molar mass of $\text{CH}_3\text{COOCH}_2\text{CH}_3$ = $(4 \times 12) + (8 \times 1) + (2 \times 16) = 88\text{g}$

$$\text{Moles of } \text{H}_2\text{O at equilibrium} = \frac{12}{18} = 0.667 \text{ moles}$$

$$\text{Moles of } \text{CH}_3\text{COOCH}_2\text{CH}_3 \text{ at equilibrium} = \frac{58.7}{88} = 0.6670 \text{ moles}$$

$\text{CH}_3\text{COOH(l)} + \text{CH}_3\text{CH}_2\text{OH(l)} \rightleftharpoons \text{CH}_3\text{COOCH}_2\text{CH}_3(l) + \text{H}_2\text{O(l)}$				
Initial moles	1.0	1.0	0	0
Moles reacted/formed	0.667	0.667	0.667	0.667
Moles at equilibrium	$1 - 0.667$ = 0.333	$1 - 0.667$ = 0.333	0.667	0.667

$$K_c = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]}$$

$$K_c = \frac{(0.667)^2}{(0.333)^3}$$

$$K_c = 4.01$$

(b)

$$\text{Moles of } \text{CH}_3\text{COOH} = \frac{90}{60} = 1.5 \text{ moles}$$

$$\text{Moles of } \text{CH}_3\text{CH}_2\text{OH} = \frac{92}{46} = 2.0 \text{ moles}$$



<i>Initial moles</i>	1.5	2.0	0	0
<i>Moles reacted/ formed</i>	x	x	x	x
<i>Moles at equilibrium</i>	$1.5 - x$	$2.0 - x$	x	x

$$K_c = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]}$$

$$4.01 = \frac{x^2}{(1.5 - x)(2.0 - x)}$$

$$3.01x^2 - 14.035x + 12.03 = 0$$

$$x = \frac{-(-14.035) \pm \sqrt{(-14.035)^2 - (4 \times 3.01 \times 12.03)}}{2 \times 3.01}$$

$$x = 3.48 \text{ or } 1.14$$

But x cannot be 3.48 since number of reacted moles cannot be greater than original moles

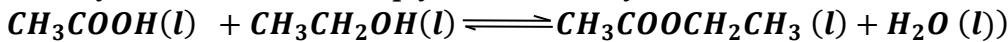
$$x = 1.14$$

$$\text{Moles of } \text{CH}_3\text{COOCH}_2\text{CH}_3 \text{ at equilibrium} = x = 1.14 \text{ moles}$$

$$\text{Mass of } \text{CH}_3\text{COOCH}_2\text{CH}_3 \text{ at equilibrium} = (1.14 \times 88) = 100.32 \text{ g}$$

2. A 10.0 cm^3 mixture initially contained 0.0515 moles of ethanol, 0.0525 moles of ethanoic acid, 0.0314 moles of ester, 0.0167 moles of water and 0.001 moles of hydrochloric acid. If at equilibrium 0.0255 moles of ethanoic acid were found. Calculate the equilibrium constant for the reaction.

Hydrochloric acid is simply added to catalyse the reaction



<i>Initial moles</i>	0.0525	0.0515	0.0314	0.0167
<i>Moles reacted/ formed</i>	$0.0525 - 0.0255$	0.027	0.027	0.027
<i>Moles at equilibrium</i>	0.0255	$0.0515 - 0.027$	$0.0314 + 0.027$	$0.0167 + 0.027$

$$K_c = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]}$$

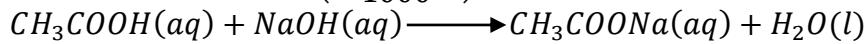
$$K_c = \frac{0.0437 \times 0.0584}{0.0255 \times 0.0245}$$

$$K_c = 4.08$$

3. 1 mole of ethanoic acid was mixed with 5 moles of ethanol in a sealed glass tube left in a water bath at 60°C for some hours. The tube was then broken in cold water and the resultant solution required 289 cm^3 of 0.2 M sodium hydroxide for complete neutralisation. Calculate the equilibrium constant, K_c for the reaction.

Moles of NaOH that reacted with CH_3COOH present at equilibrium

$$= \left(\frac{289 \times 0.2}{1000} \right) = 0.0578 \text{ moles}$$



Mole ratio of $\text{CH}_3\text{COOH} : \text{NaOH} = 1 : 1$

Moles of CH_3COOH present at equilibrium = $(0.0578 \times 1) = 0.0578 \text{ moles}$

$\text{CH}_3\text{COOH}(l) + \text{CH}_3\text{CH}_2\text{OH}(l) \rightleftharpoons \text{CH}_3\text{COOCH}_2\text{CH}_3(l) + \text{H}_2\text{O}(l)$				
Initial moles	1.0	5.0	0	0
Moles reacted/formcd	1 - 0.0578 = 0.9422	0.9422	0.9422	0.9422
Moles at equilibrium	0.0578	5 - 0.9422 = 4.0578	0.9422	0.9422

$$K_c = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]}$$

$$K_c = \frac{(0.9422)^2}{(0.0578 \times 4.0578)}$$

$$K_c = 3.79$$

(b) Equilibria involving hydrogen, iodine and hydrogen iodide.

NOTE: All dissociations will be treated in terms involving degree of dissociation for calculations.

The degree of dissociation (α) is the fraction or percentage of the original undissociated molecules which have dissociated.

Examples

1. (a) 3 moles of hydrogen and 1 mole of iodine were heated together in a sealed tube at 500°C until equilibrium was established. Calculate the number of moles of hydrogen iodide present in the equilibrium mixture at 500°C . (The equilibrium constant , K_c for the reaction between hydrogen and iodine is 50)
 (b) Describe briefly how the concentration of iodine at equilibrium can be obtained.

(a)	$\text{H}_2(g)$	+	$\text{I}_2(g)$	\rightleftharpoons	$2\text{HI}(g)$
Initial moles	3		1		0
Moles reacted/formcd	x		x		$2x$
Moles at equilibrium	$3 - x$		$1 - x$		$2x$

Taking volume of vessel to be one litre;

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$50 = \frac{(2x)^2}{(3-x)(1-x)}$$

$$46x^2 - 200x + 150 = 0$$

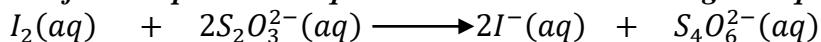
$$x = \frac{-(-200) \pm \sqrt{(-200)^2 - (4 \times 46 \times 150)}}{2 \times 46}$$

$x_1 = 3.384$ and $x_2 = 0.964$
but x cannot be 3.384, because it gives a negative value for moles of hydrogen and iodine at equilibrium
therefore $x = 0.964$

Moles of hydrogen iodide at equilibrium
 $= 2x = 2 \times 0.964 = 1.938$ moles

(b) The tube is broken under an aqueous solution of potassium iodide to dissolve the iodine present at equilibrium.

The resultant mixture is titrated with a standard solution of sodium thiosulphate using starch indicator. The amount of iodine present at equilibrium is calculated using the equation below.



2. (a) State three characteristics of a chemical equilibrium.

- (b) 25 moles of hydrogen and 18 moles of iodine vapour were heated in a 1 litre sealed tube at 465 °C. When equilibrium was attained, the tube was rapidly cooled and found to contain 30.8 moles of hydrogen iodide.
- Give a reason why the tube was rapidly cooled.
 - Calculate the value of the equilibrium constant for the reaction taking place in the flask and the degree of dissociation of hydrogen iodide.

(b) (i) Tube is rapidly cooled to stop the reaction and fix the equilibrium such that the equilibrium does not adjust itself to the equilibrium value at a lower temperature.

(ii)	$H_2(g)$	+	$I_2(g)$	\rightleftharpoons	$2HI(g)$
Initial moles	25		18		0
Moles reacted/formed		x		x	2x
Moles at equilibrium	$25 - x$		$18 - x$		30.8

$$2x = 30.8, \quad x = 15.4$$

$$[HI] = 30.8$$

$$[H_2] = 25 - 15.4 = 9.6$$

$$[I_2] = 18 - 15.4 = 2.6$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$K_c = \frac{(30.8)^2}{9.6 \times 2.6}$$

$$K_c = 38$$

Note that K_c for the dissociation of HI is the reciprocal of K_c for reaction between hydrogen and iodine to form HI

For dissociation of hydrogen iodide,



<i>Initial moles</i>	c	0	0
<i>Moles dissociated/formed</i>	$c\alpha$	$\frac{c\alpha}{2}$	$\frac{c\alpha}{2}$
<i>Moles at equilibrium</i>	$c - c\alpha$	$\frac{c\alpha}{2}$	$\frac{c\alpha}{2}$
<i>Concentration at equilibrium</i>	$\frac{c(1-\alpha)}{v}$	$\frac{c\alpha}{2v}$	$\frac{c\alpha}{2v}$

$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

$$K_c = \frac{\left(\frac{c\alpha}{2v}\right)^2}{\left(\frac{c(1-\alpha)}{v}\right)^2}$$

$$K_c = \frac{\alpha^2}{4(1-\alpha)^2}$$

$$\text{But } K_c \text{ for dissociation of HI} = \frac{1}{38}$$

$$\frac{1}{38} = \frac{\alpha^2}{4(1-\alpha)^2}$$

$$4 - 8\alpha + 4\alpha^2 = 38\alpha^2$$

$$34\alpha^2 + 8\alpha - 4 = 0$$

$$\alpha = \frac{-(8) \pm \sqrt{(8)^2 - (4 \times 34 \times 4)}}{2 \times 34}$$

$$\alpha = -0.48 \text{ or } 0.24$$

But α cannot be negative

Therefore $\alpha = 0.24$

3. When stoichiometric amounts of hydrogen and iodine were allowed to reach equilibrium in a 1 litre vessel at 450 °C and $1.01 \times 10^5 \text{ Nm}^{-2}$, 1.56 moles of hydrogen iodide were formed at equilibrium. Calculate the equilibrium constant, K_p .

Note that stoichiometric amounts mean amounts of moles as shown by the balanced equation



<i>Initial moles</i>	1	1	0
<i>Moles reacted/formed</i>		x	$2x$
<i>Moles at equilibrium</i>	$1 - x$	$1 - x$	1.56

$$2x = 1.56, \quad x = 0.78$$

$$\text{Total moles at equilibrium} \\ = 1 - x + 1 - x + 2x = 2$$

$$p_{H_2} = \left(\frac{1 - 0.78}{2}\right) \times 1.01 \times 10^5 \\ = 1.111 \times 10^4 \text{ Nm}^{-2}$$

$$p_{I_2} = \left(\frac{1 - 0.78}{2}\right) \times 1.01 \times 10^5 \\ = 1.111 \times 10^4 \text{ Nm}^{-2}$$

$$p_{HI} = \left(\frac{1.56}{2}\right) \times 1.01 \times 10^5 \\ = 7.878 \times 10^4 \text{ Nm}^{-2}$$

$$K_p = \frac{(p_{HI})^2}{p_{H_2} \times p_{I_2}} = \frac{(7.878 \times 10^4)^2}{(1.111 \times 10^4)^2}$$

$$K_p = 50.28$$

4. The equilibrium constant for the dissociation of hydrogen iodide is 0.02. 1 mole of hydrogen and $\frac{1}{3}$ moles of iodine are heated together at 450 °C. Calculate the mass of hydrogen iodide present in the equilibrium mixture at that temperature.

	$H_2(g)$	+	$I_2(g)$	\rightleftharpoons	$2HI(g)$
Initial moles	1			$\frac{1}{3}$	0
Moles reacted/formed		x		x	$2x$
Moles at equilibrium	$1 - x$			$\frac{1}{3} - x$	$2x$

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$K_c \text{ for the reaction} = \frac{1}{K_c \text{ for dissociation of HI}}$$

$$\frac{1}{0.02} = \frac{(2x)^2}{(1-x)\left(\frac{1}{3}-x\right)}$$

$$69x^2 - 100x + 25 = 0$$

$$x = \frac{-(-100) \pm \sqrt{(-100)^2 - (4 \times 69 \times 25)}}{2 \times 69}$$

$$x = 0.321 \text{ or } 1.128$$

But x cannot be 1.128 since it gives negative values of $(1-x)$ and $\left(\frac{1}{3}-x\right)$

Therefore $x = 0.321$

$$\text{Moles of } HI \text{ at equilibrium} = 2x \\ = 2 \times 0.321 = 0.642$$

$$\text{Molar mass of } HI = (1 + 127) \\ = 128g$$

$$\text{Mass of } HI \text{ present at equilibrium} \\ = (128 \times 0.642) = 82.176g$$

5. 1g of hydrogen and 127g of iodine are allowed to attain equilibrium in an evacuated container of volume $10dm^3$ at a temperature of $450 ^\circ\text{C}$. If the equilibrium constant at the same temperature, K_c is 50. Calculate the;

- (i) the value of K_p
- (ii) the total pressure in the container
- (iii) the partial pressure of hydrogen in the container

$$(i) \text{ Molar mass of } H_2 = (2 \times 1) = 2g$$

$$\text{Molar mass of } I_2 = (2 \times 127) = 254g$$

$$\text{Mole ratio of } H_2 : HI = 1 : 2$$

$$\text{Moles of } HI = (2 \times 0.5) = 1 \text{ mole}$$

$$K_c = 50$$

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$V = 10 \times 10^{-3} m^3$$

$$\text{Moles of } H_2 = \frac{1}{2} = 0.5 \text{ moles}$$

$$\text{Moles of } I_2 = \frac{127}{254} = 0.5 \text{ moles}$$

$$T = (450 + 273) = 723K$$

$$\Delta n = 1 - (0.5 + 0.5) = 0$$

$$K_p = K_c (RT)^{\Delta n}$$

$$K_p = 50 (8.314 \times 723)^0 = 50$$

	$H_2(g)$	+	$I_2(g)$	\rightleftharpoons	$2HI(g)$
Initial moles	0.5		0.5		0
Moles reacted/formed		x		x	$2x$
Moles at equilibrium	$0.5 - x$		$0.5 - x$		$2x$

(ii) Total moles equilibrium mixture,

$$n = 0.5 - x + 0.5 - x + 2x = 1$$

$$pV = nRT$$

$$p = \frac{1 \times 8.314 \times 723}{10 \times 10^{-3}}$$

$$p = 6011022.2 \text{ Nm}^{-2}$$

(iii)

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$50 = \frac{(2x)^2}{(0.5-x)^2}$$

$$92x^2 - 100x + 25 = 0$$

$$x = \frac{-(-100) \pm \sqrt{(-100)^2 - (4 \times 92 \times 25)}}{2 \times 92}$$

$$x = 0.390 \text{ or } 0.697$$

But x cannot be 0.697 since it gives

negative values of $(0.5 - x)$

Therefore $x = 0.390$

Partial pressure of hydrogen

$$= \left(\frac{0.5 - x}{1} \right) \times 6011022.2$$

$$= \left(\frac{0.5 - 0.390}{1} \right) \times 6011022.2$$

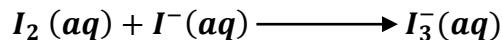
$$p_{H_2} = 661212.442 \text{ Nm}^{-2}$$

6. 3.20g of hydrogen iodide were heated at 450 °C in a glass bulb of volume 800cm³. When equilibrium was attained, the bulb was rapidly cooled to room temperature and then broken under a solution of potassium iodide. The iodine formed required 36.0 cm³ of a 0.2M sodium thiosulphate solution in the presence of starch indicator for complete reaction.

(i) Explain why the bulb broken under potassium iodide solution

(ii) Calculate the equilibrium constant for the reaction at 450 °C

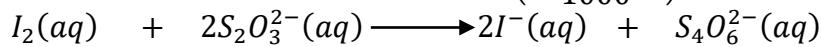
(i) The bulb is broken under an aqueous solution of potassium iodide to dissolve the iodine present at equilibrium.



(ii) Molar mass of HI = $(1 + 127) = 128\text{g}$

$$\text{Moles of HI} = \frac{3.20}{128} = 0.025 \text{ moles}$$

$$\text{Moles of Na}_2\text{S}_2\text{O}_3 \text{ that reacted with } I_2 = \left(\frac{0.2 \times 36.0}{1000} \right) = 0.0072 \text{ moles}$$



Mole ratio of $S_2O_3^{2-}: I_2 = 2:1$

$$\text{Moles of } I_2 = \left(\frac{1}{2} \times 0.0072 \right) = 0.0036 \text{ moles}$$



Initial moles	0.025	0	0
Moles dissociated/formed	0.025α	$\frac{0.025\alpha}{2}$	$\frac{0.025\alpha}{2}$
Moles at equilibrium	$0.025 - 0.025\alpha$	$\frac{0.025\alpha}{2}$	$\frac{0.025\alpha}{2}$

$$\frac{0.025\alpha}{2} = 0.0036$$

$$\alpha = 0.288$$

moles of HI at equilibrium

$$= 0.025(1 - 0.288) = 0.0178$$

$$[HI] = \left(\frac{0.0178 \times 1000}{800} \right) = 0.02225M$$

Note: The volume was given in cm^3 .
Multiplying moles in $800cm^3$ by 1000 converts the concentration to moles per litre

$$[H_2] = \left(\frac{0.0036 \times 1000}{800} \right) = 0.0045M$$

$$[I_2] = \left(\frac{0.0036 \times 1000}{800} \right) = 0.0045M$$

$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

$$K_c = \frac{(0.0045)^2}{(0.02225)^2}$$

$$K_c = 0.04$$

7. The degree of dissociation of 0.5 moles of hydrogen iodide was found to be 25% at a certain temperature in a $1.5dm^3$ vessel. Calculate the equilibrium constant, K_p

	$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
<i>Initial moles</i>	0.5 0 0
<i>Moles dissociated/formed</i>	$\frac{0.5\alpha}{2}$ $\frac{0.5\alpha}{2}$
<i>Moles at equilibrium</i>	$0.5 - 0.5\alpha$ $\frac{0.5\alpha}{2}$ $\frac{0.5\alpha}{2}$

$$\alpha = \frac{25}{100} = 0.25$$

Total moles at equilibrium

$$= 0.5 - 0.5\alpha + \frac{0.5\alpha}{2} + \frac{0.5\alpha}{2} = 0.5$$

moles of HI at equilibrium

$$= 0.5(1 - 0.25) = 0.375$$

moles of H_2 at equilibrium = $\frac{0.5}{2} \times 0.25$

$$= 0.0625$$

moles of I_2 at equilibrium = 0.0625

Let the total pressure at equilibrium be P

$p_{HI} = \left(\frac{0.375}{0.5} \right) P$

$$p_{H_2} = \left(\frac{0.0625}{0.5} \right) P$$

$$p_{I_2} = \left(\frac{0.0625}{0.5} \right) P$$

$$K_p = \frac{p_{H_2} \times p_{I_2}}{(p_{HI})^2}$$

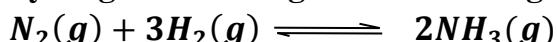
$$K_p = \frac{\left(\frac{0.0625}{0.5} P \right)^2}{\left(\frac{0.375}{0.5} P \right)^2} = \frac{0.015625P^2}{0.5625P^2}$$

$$K_p = 0.0278$$

(c) Equilibria involving hydrogen, nitrogen and ammonia.

Examples

1. Nitrogen reacts with hydrogen according to the following equation



(a) Write expression for equilibrium constant, K_c

(b) Stoichiometric amounts of nitrogen and hydrogen were reacted in a 2 litre vessel. At equilibrium, 0.8moles of ammonia was formed. Calculate:

(i) the amount of hydrogen at equilibrium.

(ii) the value of equilibrium constant, K_c .

$$(a) \quad K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

(b)(i)

Initial moles

$N_2(g)$

+

$3H_2(g)$

$\rightleftharpoons 2NH_3(g)$

1

3

0

Moles dissociated/formed

x

$3x$

$2x$

Moles at equilibrium

$1 - x$

$3 - 3x$

$2x$

$$2x = 0.8. \text{ Therefore } x = 0.4$$

$$\begin{aligned} \text{moles of } H_2 \text{ at equilibrium} &= 3(1 - 0.4) \\ &= 1.8 \end{aligned}$$

$$\begin{aligned} \text{moles of } N_2 \text{ at equilibrium} &= (1 - 0.4) \\ &= 0.6 \end{aligned}$$

$$\begin{aligned} \text{moles of } NH_3 \text{ at equilibrium} &= (2 \times 0.4) \\ &= 0.8 \end{aligned}$$

$$[N_2] = \left(\frac{0.6}{2}\right) = 0.3M$$

$$[H_2] = \left(\frac{1.8}{2}\right) = 0.9M$$

$$[NH_3] = \left(\frac{0.8}{2}\right) = 0.4M$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$K_c = \frac{(0.4)^2}{0.3 \times (0.9)^3} \frac{mol^2 dm^{-6}}{mol dm^{-3} \times mol^3 dm^{-9}}$$

$$K_c = 0.732 \text{ mol}^{-2} \text{ dm}^6$$

2. 0.8 moles of nitrogen and 0.9 moles of hydrogen were heated in a 1500cm^3 closed vessel. At equilibrium, the mixture contained 20% hydrogen. Find the value of equilibrium constant, K_c .

Initial moles

$N_2(g)$

+

$3H_2(g)$

$\rightleftharpoons 2NH_3(g)$

0.8

0.9

0

Moles dissociated/formed

x

$3x$

$2x$

Moles at equilibrium

$0.8 - x$

$0.9 - 3x$

$2x$

$$\begin{aligned} \text{Total moles at equilibrium} \\ = 0.8 - x + 0.9 - 3x + 2x = 1.7 - 2x \end{aligned}$$

$$\text{But } \left(\frac{0.9 - 3x}{1.7 - 2x}\right) \times 100 = 20$$

$$\begin{aligned} 0.9 - 3x &= 0.2(1.7 - 2x) \\ x &= 0.215 \end{aligned}$$

moles of H_2 at equilibrium

$$= 0.9 - (3 \times 0.215) = 0.255$$

$$\begin{aligned} \text{moles of } N_2 \text{ at equilibrium} &= (0.8 - 0.215) \\ &= 0.585 \end{aligned}$$

$$\begin{aligned} \text{moles of } NH_3 \text{ at equilibrium} &= (2 \times 0.215) \\ &= 0.430 \end{aligned}$$

$$[N_2] = \left(\frac{0.585 \times 1000}{1500}\right) = 0.39M$$

$$[H_2] = \left(\frac{0.255 \times 1000}{1500}\right) = 0.17M$$

$$[NH_3] = \left(\frac{0.430 \times 1000}{1500}\right) = 0.287M$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$K_c = \frac{(0.287)^2}{0.39 \times (0.17)^3} \frac{mol^2 dm^{-6}}{mol dm^{-3} \times mol^3 dm^{-9}}$$

$$K_c = 42.99 \text{ mol}^{-2} \text{ dm}^6$$

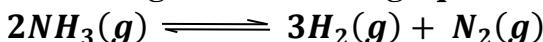
3. When 3 moles of hydrogen and 1 mole of nitrogen were mixed and allowed to attain equilibrium at 100 atm and 400°C, the equilibrium mixture contained 25% of ammonia by volume. Calculate;

(i) Number of moles of nitrogen and hydrogen at equilibrium.

(ii) Value of K_p at 400°C

<p>(i)</p> <table style="margin-left: 20px; border-collapse: collapse;"> <tr><td style="padding-right: 20px;"><i>Initial moles</i></td><td style="text-align: center;">1</td><td style="text-align: center;">+</td><td style="text-align: center;">$3H_2(g) \rightleftharpoons 2NH_3(g)$</td></tr> <tr><td><i>Moles dissociated/formed</i></td><td style="text-align: center;">x</td><td style="text-align: center;">3</td><td style="text-align: center;">0</td></tr> <tr><td><i>Moles at equilibrium</i></td><td style="text-align: center;">$1 - x$</td><td style="text-align: center;">$3x$</td><td style="text-align: center;">$2x$</td></tr> <tr><td></td><td></td><td style="text-align: center;">$3 - 3x$</td><td style="text-align: center;">$2x$</td></tr> </table> <p>Total moles at equilibrium $= 1 - x + 3 - 3x + 2x = 4 - 2x$</p> <p>But $\left(\frac{2x}{4 - 2x}\right) \times 100 = 25$</p> $2x = 1 - 0.5x$ $x = 0.4$ <p>moles of H_2 at equilibrium = $3(1 - 0.4)$ $= 1.8$ moles</p> <p>(ii) moles of N_2 at equilibrium = $(1 - 0.4) = 0.6$ moles</p> <p>moles of NH_3 at equilibrium = (2×0.4) $= 0.8$ moles</p>	<i>Initial moles</i>	1	+	$3H_2(g) \rightleftharpoons 2NH_3(g)$	<i>Moles dissociated/formed</i>	x	3	0	<i>Moles at equilibrium</i>	$1 - x$	$3x$	$2x$			$3 - 3x$	$2x$	<p>Total moles at equilibrium $= 4 - 2(0.4) = 3.2$</p> $p_{N_2} = \left(\frac{0.6}{3.2} \times 100\right) = 18.75 \text{ atm}$ $p_{H_2} = \left(\frac{1.8}{3.2} \times 100\right) = 56.25 \text{ atm}$ $p_{NH_3} = \left(\frac{0.8}{3.2} \times 100\right) = 25 \text{ atm}$ $K_p = \frac{(p_{NH_3})^2}{p_{N_2} \times (p_{H_2})^3}$ $K_p = \frac{25^2}{18.75 \times 56.25^3} \frac{\text{atm}^2}{\text{atm} \times \text{atm}^3}$ $K_p = 1.87 \times 10^{-4} \text{ atm}^{-2}$
<i>Initial moles</i>	1	+	$3H_2(g) \rightleftharpoons 2NH_3(g)$														
<i>Moles dissociated/formed</i>	x	3	0														
<i>Moles at equilibrium</i>	$1 - x$	$3x$	$2x$														
		$3 - 3x$	$2x$														

4. Ammonia dissociates according to the following equation



Calculate the equilibrium constant, K_c for the reaction given 3.0 moles of ammonia were found to be 15% dissociated.

<table style="margin-left: 20px; border-collapse: collapse;"> <tr><td style="padding-right: 20px;"><i>Initial moles</i></td><td style="text-align: center;">3.0</td><td style="text-align: center;">+</td><td style="text-align: center;">$N_2(g)$</td><td style="text-align: center;">$+ 3H_2(g)$</td></tr> <tr><td><i>Moles dissociated/formed</i></td><td style="text-align: center;">3α</td><td style="text-align: center;">0</td><td style="text-align: center;">0</td><td style="text-align: center;">$\frac{3\alpha}{2}$</td></tr> <tr><td><i>Moles at equilibrium</i></td><td style="text-align: center;">$3 - 3\alpha$</td><td style="text-align: center;">$\frac{3\alpha}{2}$</td><td style="text-align: center;">$3\left(\frac{3\alpha}{2}\right)$</td><td style="text-align: center;">$\frac{9\alpha}{2}$</td></tr> </table> <p>But $\alpha = \frac{15}{100} = 0.15$</p> <p>moles of H_2 at equilibrium = $\frac{9 \times 0.15}{2}$ $= 0.675$ moles</p>	<i>Initial moles</i>	3.0	+	$N_2(g)$	$+ 3H_2(g)$	<i>Moles dissociated/formed</i>	3α	0	0	$\frac{3\alpha}{2}$	<i>Moles at equilibrium</i>	$3 - 3\alpha$	$\frac{3\alpha}{2}$	$3\left(\frac{3\alpha}{2}\right)$	$\frac{9\alpha}{2}$	<p>Assuming volume is one litre</p> $[N_2] = 0.255M$ $[H_2] = 0.675M$ $[NH_3] = 2.55M$ $K_c = \frac{[N_2][H_2]^3}{[NH_3]^2}$
<i>Initial moles</i>	3.0	+	$N_2(g)$	$+ 3H_2(g)$												
<i>Moles dissociated/formed</i>	3α	0	0	$\frac{3\alpha}{2}$												
<i>Moles at equilibrium</i>	$3 - 3\alpha$	$\frac{3\alpha}{2}$	$3\left(\frac{3\alpha}{2}\right)$	$\frac{9\alpha}{2}$												

$$\begin{aligned} \text{moles of } N_2 \text{ at equilibrium} &= \frac{3 \times 0.15}{2} \\ &= 0.225 \text{ moles} \\ \text{moles of } NH_3 \text{ at equilibrium} &= 3(1 - 0.15) = 2.55 \text{ moles} \end{aligned}$$

$$K_c = \frac{0.225 \times (0.675)^3}{(2.55)^2} \frac{mol dm^{-3} \times mol^3 dm^{-9}}{mol^2 dm^{-6}}$$

$$K_c = 0.012 \text{ mol}^2 \text{ dm}^{-6}$$

5. 1.75 moles of ammonia were heated in a 1 litre vessel and the equilibrium mixture was found to contain 42.9% hydrogen. Calculate the equilibrium constant, K_c .

	$2NH_3(g)$	\rightleftharpoons	$N_2(g)$	$+$	$3H_2(g)$
Initial moles	1.75		0		0
Moles dissociated/formed	1.75α		$\frac{1.75\alpha}{2}$		$3\left(\frac{1.75\alpha}{2}\right)$
Moles at equilibrium	$1.75 - 1.75\alpha$		$\frac{1.75\alpha}{2}$		$\frac{5.25\alpha}{2}$

$$\begin{aligned} \text{Total moles at equilibrium} &= 1.75 - 1.75\alpha + 0.875\alpha + 2.625\alpha \\ &= 1.75 + 1.75\alpha \end{aligned}$$

$$\text{But } \frac{2.625\alpha}{1.75 + 1.75\alpha} \times 100 = 42.9 \\ 1.87425\alpha = 0.75075$$

$$\alpha = 0.4$$

$$\begin{aligned} \text{moles of } H_2 \text{ at equilibrium} &= (2.625 \times 0.4) \\ &= 1.05 \text{ moles} \end{aligned}$$

$$\begin{aligned} \text{moles of } N_2 \text{ at equilibrium} &= (0.875 \times 0.4) = 0.35 \text{ moles} \end{aligned}$$

$$\begin{aligned} \text{moles of } NH_3 \text{ at equilibrium} &= 1.75(1 - 0.4) \\ &= 1.05 \text{ moles} \end{aligned}$$

Since volume is one litre

$$[N_2] = 0.35M \quad [H_2] = 1.05M$$

$$[NH_3] = 1.05M$$

$$K_c = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

$$K_c = \frac{0.35 \times (1.05)^3}{(1.05)^2} \frac{mol dm^{-3} \times mol^3 dm^{-9}}{mol^2 dm^{-6}}$$

$$K_c = 0.3675 \text{ mol}^2 \text{ dm}^{-6}$$

(d) Equilibria involving phosphorus, chlorine and phosphorus(V) chloride Examples

1. Phosphorus(V) chloride dissociates at high temperatures according to the equation



83.4 g of phosphorus(V) chloride were placed in a vessel of 9.23 dm^3 . At equilibrium at a certain temperature, 11.1g of chlorine were formed at a total pressure of 250 kPa .

- (a) Calculate the number of moles of phosphorus(V) chloride and chlorine in the vessel at equilibrium.
- (b) Determine the equilibrium constant, K_c , for the reaction and state its units.
- (c) Calculate the value of the equilibrium constant, K_p , for the reaction and state its units.

(a)

$$\text{Molar mass of } PCl_5 = 31 + (5 \times 35.4) = 208$$

$$\text{moles of } PCl_5 \text{ before equilibrium} = \frac{83.4}{208} = 0.401$$

$$\text{Molar mass of } Cl_2 = (35.4 \times 2) = 70.8$$

$$\text{moles of chlorine at equilibrium} = \frac{11.1}{70.8} = 0.15678 \text{ moles}$$

$$\text{Molar concentration of } Cl_2 = \frac{0.1186}{9.0} = 0.0132M$$



Initial moles

$$0.401 \quad 0 \quad 0$$

Moles dissociated/formed

$$0.401\alpha \quad 0.401\alpha \quad 0.401\alpha$$

Moles at equilibrium

$$0.401(1 - \alpha) \quad 0.401\alpha \quad 0.401\alpha$$

$$\text{But } 0.401\alpha = 0.15678$$

$$\alpha = 0.391$$

$$\begin{aligned} \text{moles of } PCl_5 \text{ at equilibrium} \\ &= 0.401(1 - 0.391) \\ &= 0.24421 \text{ moles} \end{aligned}$$

$$\begin{aligned} \text{moles of } Cl_2 \text{ at equilibrium} \\ &= 0.15679 \text{ moles} \end{aligned}$$

$$\text{(b) moles of } PCl_3 \text{ at equilibrium} = (0.401 \times 0.391) = 0.15679 \text{ moles}$$

Since volume is 9.23 litres

$$[PCl_5] = \left(\frac{0.24421}{9.23} \right) = 0.0265M$$

$$[Cl_2] = \left(\frac{0.15679}{9.23} \right) = 0.0170M$$

$$[PCl_3] = 0.0170M$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$K_c = \frac{0.0170 \times 0.0170}{0.0265} \frac{mol^2 dm^{-6}}{mol dm^{-3}}$$

$$K_c = 0.011 mol dm^{-3}$$

(c) Total moles at equilibrium

$$\begin{aligned} &= 0.24421 + 0.15679 + 0.15679 \\ &= 0.55779 \end{aligned}$$

$$p_{Cl_2} = \left(\frac{0.15679}{0.55779} \times 250 \right) = 70.27 kPa$$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$$

$$K_p = \frac{70.27 \times 70.27}{109.45} \frac{kPa^2}{kPa}$$

$$K_p = 45.13 kPa$$

2. 1.0 mole of phosphorus(V) chloride was strongly heated in a one litre closed bulb until equilibrium was obtained. The glass bulb was then rapidly broken under potassium iodide solution. The bulb was found to contain 40.70% of chlorine.

(a) Write equations for the reactions that took place when:

(i) the glass bulb was strongly heated

(ii) the glass bulb was broken under potassium iodide solution.

(b) State the reasons why the bulb;

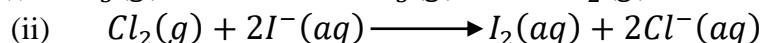
(i) was rapidly broken

(ii) was broken under potassium iodide solution

(c) Determine the;

(i) degree of dissociation of phosphorus(V) chloride

(ii) equilibrium constant for the reaction.



(b) (i) Bulb was rapidly broken to stop the reaction and fix the equilibrium such that the equilibrium does not adjust itself to the equilibrium value at a lower temperature.

(ii) Bulb is broken under potassium iodide to dissolve and oxidise chlorine present at equilibrium to chloride ions as the potassium iodide is reduced to iodine.

(c) (i)



Initial moles

1 0 0

Moles dissociated/formed

α α α

Moles at equilibrium

$(1 - \alpha)$

α α

Total moles at equilibrium

$$= 1 - \alpha + \alpha + \alpha = (1 + \alpha)$$

$$\text{But } \frac{\alpha}{1 + \alpha} \times 100 = 40.70$$

$$0.593\alpha = 0.407$$

$$\alpha = 0.686$$

moles of PCl_5 at equilibrium

$$= (1 - 0.686) = 0.314 \text{ moles}$$

moles of Cl_2 at equilibrium = 0.686 moles

moles of PCl_3 at equilibrium

$$= 0.686 \text{ moles}$$

Since volume is 1 litre

$$[PCl_5] = 0.314M$$

$$[Cl_2] = 0.686M$$

$$[PCl_3] = 0.686M$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$K_c = \frac{0.686 \times 0.686}{0.314} \frac{mol^2 dm^{-6}}{mol dm^{-3}}$$

$$K_c = 1.499 mol dm^{-3}$$

3. 2.085g of phosphorus(V) chloride was heated in a 1 litre vessel until equilibrium was attained. The vessel was then broken under excess potassium iodide solution. The iodine liberated required 40 cm³ of 0.1M sodium thiosulphate solution. Calculate the equilibrium constant, K_c , for the reaction.

$$\text{Molar mass of } PCl_5 = 31 + (5 \times 35.4) = 208$$

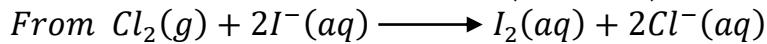
$$\text{moles of } PCl_5 \text{ before equilibrium} = \frac{2.085}{208} = 0.01$$

$$\text{Moles of } Na_2S_2O_3 \text{ that reacted with } I_2 = \left(\frac{40 \times 0.1}{1000} \right) = 0.004 \text{ moles}$$



$$\text{Mole ratio of } S_2O_3^{2-}:I_2 = 2:1$$

$$\text{Moles of } I_2 \text{ that were formed from KI} = \left(\frac{1}{2} \times 0.004 \right) = 0.002 \text{ moles}$$



1 mole of I_2 is formed from 1 mole of Cl_2

Therefore moles of Cl_2 at equilibrium = 0.002 moles



Initial moles

1 0 0

Moles dissociated/formed

0.002 0.002 0.002

Moles at equilibrium

(1 - 0.002) 0.002 0.002

$$\text{moles of } PCl_5 \text{ at equilibrium} = (1 - 0.002) \\ = 0.998 \text{ moles}$$

$$[Cl_2] = 0.002M$$

$$[PCl_3] = 0.002M$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$K_c = \frac{0.002 \times 0.002}{0.998} \frac{mol^2 dm^{-6}}{moldm^{-3}}$$

$$K_c = 4.01 \times 10^{-6} moldm^{-3}$$

$$\text{moles of } Cl_2 \text{ at equilibrium} = 0.002 \text{ moles}$$

$$\text{moles of } PCl_3 \text{ at equilibrium} \\ = 0.002 \text{ moles}$$

Since volume is 1 litre

$$[PCl_5] = 0.998 M$$

4. 2.00 g of phosphorus(V) chloride were allowed to reach equilibrium at 200°C in a 1 dm³ capacity vessel. If the equilibrium constant of the above reaction is 0.008 moldm⁻³ at this temperature and in the conditions stated. Calculate the percentage dissociation of phosphorus pentachloride at equilibrium.

$$\text{Molar mass of } PCl_5 = 31 + (5 \times 35.4) = 208g$$

$$\text{moles of } PCl_5 \text{ before equilibrium} = \frac{2.00}{208} = 0.009615$$



Initial moles

0.009615 0 0

Moles dissociated/formed

0.009615 α 0.009615 α 0.009615 α

Moles at equilibrium

0.009615(1 - α) 0.009615 α 0.009615 α

Since volume is 1 litre

$$[PCl_5] = (0.009615(1 - \alpha)) M$$

$$[Cl_2] = (0.009615\alpha)M$$

$$[PCl_3] = (0.009615\alpha)M$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$0.008 = \frac{(0.009615\alpha)^2}{0.009615(1 - \alpha)}$$

$$9.244\alpha^2 + 7.962\alpha - 7.962 = 0$$

$$\alpha = \frac{-(7.962) \pm \sqrt{(7.962)^2 - (4 \times 9.244 \times -7.962)}}{2 \times 9.244}$$

$$\alpha = -1.454 \text{ or } 0.592$$

But α cannot be negative.
Therefore $\alpha = 0.592$

Percentage dissociation of PCl_5
 $= 0.592 \times 100 = 59.2\%$

5. 3.6 moles of phosphorus(V) chloride in a vessel of volume 2 litres was found to be 38% dissociated. Calculate the equilibrium constant, K_c , for the reaction.

	$PCl_5(g)$	\rightleftharpoons	$PCl_3(g)$	$+$	$Cl_2(g)$
Initial moles	3.6		0		0
Moles dissociated/formed	3.6α		3.6α		3.6α
Moles at equilibrium	$3.6(1 - \alpha)$		3.6α		3.6α

But $\alpha = \frac{38}{100} = 0.38$

Moles of PCl_5 at equilibrium
 $= 3.6(1 - 0.38)$
 $= 2.232 \text{ moles}$

moles of Cl_2 at equilibrium $= (3.6 \times 0.38)$
 $= 1.368 \text{ moles}$

moles of PCl_3 at equilibrium $= 1.368 \text{ moles}$

Since volume is 2 litres

$$[PCl_5] = \left(\frac{\frac{2.232}{2}}{2}\right) = 1.116 M$$

$$[Cl_2] = \left(\frac{1.368}{2}\right) = 0.684 M$$

$$[PCl_3] = 0.684 M$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$K_c = \frac{(0.684)^2}{1.116} \frac{mol^2 dm^{-6}}{moldm^{-3}}$$

$$K_c = 0.419 moldm^{-3}$$

6. Calculate the percentage of chlorine is the equilibrium mixture formed when 0.4 moles of phosphorus(V) chloride were heated in a one litre vessel. (The equilibrium constant is $0.02 moldm^{-3}$).

	$PCl_5(g)$	\rightleftharpoons	$PCl_3(g)$	$+$	$Cl_2(g)$
Initial moles	0.4		0		0
Moles dissociated/formed	0.4α		0.4α		0.4α
Moles at equilibrium	$0.4(1 - \alpha)$		0.4α		0.4α

Since volume is 1 litre

$$[PCl_5] = (0.4(1 - \alpha)) M$$

$$[Cl_2] = (0.4\alpha) M$$

$$[PCl_3] = (0.4\alpha) M$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$0.02 = \frac{(0.4\alpha)^2}{0.4(1 - \alpha)}$$

$$\alpha^2 + 0.05\alpha - 0.05 = 0$$

$$\alpha = \frac{-(0.05) \pm \sqrt{(0.05)^2 - (4 \times 1 \times -0.05)}}{2 \times 1}$$

$$\alpha = -0.25 \text{ or } 0.2$$

But α cannot be negative.

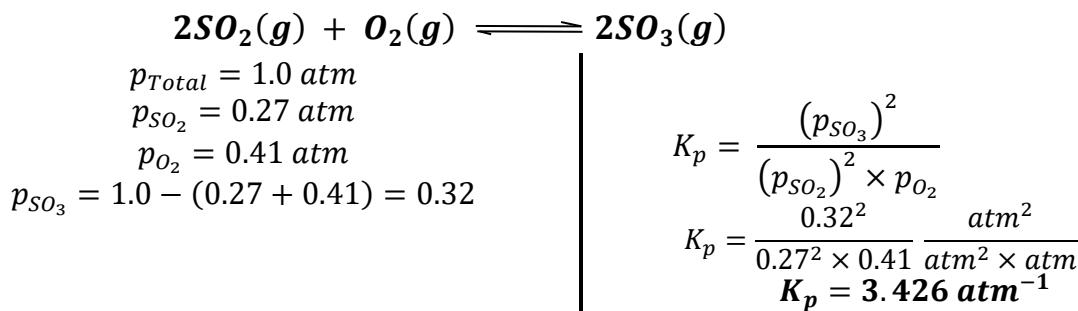
Therefore $\alpha = 0.2$

Total moles at equilibrium
 $= 0.4(1 - 0.2) + 0.4(0.2) + 0.4(0.2) = 0.48$

Percentage of chlorine
 $= \left(\frac{0.4 \times 0.2}{0.48} \right) \times 100 = 16.67\%$

(e) Equilibria involving sulphur trioxide, sulphur dioxide and oxygen Examples

1. At 700°C, and total pressure of 1.0 atm, the partial pressure at equilibrium for sulphur dioxide and oxygen are 0.27 and 0.41 atm respectively. Calculate the equilibrium constant, K_p for the reaction.



2. 0.425 moles of sulphur dioxide and 0.294 moles of oxygen were heated in a 1.6 litre vessel and at equilibrium, it was found that 52% of oxygen had reacted. Calculate the value of equilibrium constant, K_c .

	$2SO_2(g)$	$+ O_2(g) \rightleftharpoons 2SO_3(g)$
Initial moles	0.425	0.294 0
Moles reacted/formed	$2x$	x $2x$
Moles at equilibrium	$(0.425 - 2x)$	$(0.294 - x)$ $2x$

Total moles at equilibrium
 $= 0.425 - 2x + 0.294 - x + 2x = (0.719 - x)$

Moles of O_2 that reacted = x
 $x = \frac{52}{100} \times 0.294 = 0.15288$

Since volume is 1.6 litres,

$$[O_2] = \left(\frac{0.14112}{1.6} \right) = 0.0882M$$

$$[SO_2] = \left(\frac{0.11924}{1.6} \right) = 0.0745M$$

$$[SO_3] = \left(\frac{0.30576}{1.6} \right) = 0.1911M$$

$$\begin{aligned} \text{Moles of } O_2 \text{ at equilibrium} &= 0.294 - 0.15288 \\ &= 0.14112 \end{aligned}$$

$$\begin{aligned} \text{Moles of } SO_2 \text{ at equilibrium} \\ &= 0.425 - 2(0.15288) = 0.11924 \end{aligned}$$

$$\begin{aligned} \text{Moles of } SO_3 \text{ at equilibrium} \\ &= 2(0.15288) = 0.30576 \end{aligned}$$

$$\begin{aligned} K_c &= \frac{[SO_3]^2}{[SO_2]^2 [O_2]} \\ K_c &= \frac{(0.1911)^2}{(0.0745)^2 \times 0.0882} \frac{mol^2 dm^{-6}}{mol^3 dm^{-9}} \\ K_c &= 74.6 \text{ mol}^{-1} dm^3 \end{aligned}$$

3. 1 mole of sulphur trioxide was introduced into a $1dm^3$ vessel. The vessel was heated to 1000K until equilibrium was attained. At equilibrium, 0.35 moles of sulphur trioxide was present.

- (i) Write equation for the dissociation of sulphur trioxide.
- (ii) Write an expression for the equilibrium constant, K_c .
- (iii) Calculate the value of K_c .

(i)



(ii) $K_c = \frac{[SO_2]^2 [O_2]}{[SO_3]^2}$

<i>Initial moles</i>	1	0	0
<i>Moles dissociated/formed</i>	α	α	$\frac{\alpha}{2}$
<i>Moles at equilibrium</i>	$1 - \alpha$	α	$\frac{\alpha}{2}$

Total moles at equilibrium
 $= 1 - \alpha + 2\alpha + \alpha = 1 + 0.5\alpha$

But $1 - \alpha = 0.35$

$\alpha = 0.65$

Moles of O_2 at equilibrium

$$= \frac{0.65}{2} = 0.325$$

Moles of SO_2 at equilibrium = 0.65

Moles of SO_3 at equilibrium = 0.35

Since volume is one litre

$$[O_2] = 0.325M \quad [SO_2] = 0.65M$$

$$[SO_3] = 0.35M$$

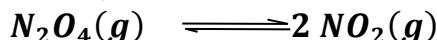
$$K_c = \frac{[SO_2]^2 [O_2]}{[SO_3]^2}$$

$$K_c = \frac{0.65^2 \times 0.325}{(0.35)^2} \frac{mol^3 dm^{-9}}{mol^2 dm^{-6}}$$

$$K_c = 1.12 \text{ moldm}^{-3}$$

(f) Examples involving other equilibria systems

1. Dinitrogen tetroxide and nitrogen dioxide exist in the following equilibrium.



When 11.04g of dinitrogen tetroxide were placed in a vessel of volume $4.80dm^3$ at a fixed temperature, 5.52g of nitrogen dioxide were produced at equilibrium under a pressure of 100kPa. Calculate the:

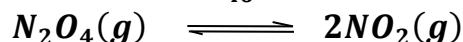
- (a) equilibrium number of moles of each gas
- (b) equilibrium constant, K_c .
- (c) equilibrium constant, K_p .

(a) Molar mass of $N_2O_4 = (2 \times 14) + (4 \times 16) = 92g$

$$\text{Initial moles of } N_2O_4 = \frac{11.04}{92} = 0.12 \text{ moles}$$

$$\text{Molar mass of } NO_2 = (1 \times 14) + (2 \times 16) = 46g$$

$$\text{Moles of } NO_2 \text{ at equilibrium} = \frac{5.52}{46} = 0.12 \text{ moles}$$



Initial moles

0.12

0

Moles dissociated/formed

0.12 α

2(0.12 α)

Moles at equilibrium

0.12(1 - α)

0.24 α

But $0.24\alpha = 0.12$

$$\alpha = 0.5$$

Moles of NO_2 at equilibrium = 0.12 moles

Moles of N_2O_4 at equilibrium

$$= 0.12(1 - 0.5) = 0.06 \text{ moles}$$

(b) $[N_2O_4] = \frac{0.06}{4.8} = 0.0125M$

$$[NO_2] = \frac{0.12}{4.8} = 0.025 M$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_c = \frac{(0.025)^2}{0.0125} \frac{\text{mol}^2 \text{dm}^{-6}}{\text{mol dm}^{-3}}$$

$$K_c = 0.05 \text{ mol dm}^{-3}$$

(c) Total moles at equilibrium

$$= 0.12 + 0.06 = 0.18 \text{ moles}$$

$$p_{N_2O_4} = \frac{0.06}{0.18} \times 100 = 33.333 \text{ kPa}$$

$$p_{NO_2} = \frac{0.12}{0.18} \times 100 = 66.667 \text{ kPa}$$

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}}$$

$$K_p = \frac{(66.667)^2}{33.333} \frac{(\text{kPa})^2}{\text{kPa}}$$

$$K_p = 133.336 \text{ kPa}$$

2. For the following gas equilibrium, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ at 333K, the equilibrium constant, K_p is 1.33 atmospheres. Calculate the degree of dissociation of one mole of dinitrogen tetroxide at 333K if the total pressure of the system is 2 atmospheres.



Initial moles

1

0

Moles dissociated/formed

α

2α

Moles at equilibrium

$(1 - \alpha)$

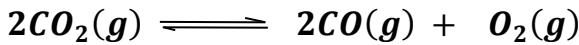
2α

Total moles at equilibrium	$= 1 - \alpha + 2\alpha = (1 + \alpha)$
$p_{N_2O_4} = \frac{1 - \alpha}{1 + \alpha} \times 2 = \frac{2(1 - \alpha)}{1 + \alpha} \text{ atm}$	
$p_{NO_2} = \frac{2\alpha}{1 + \alpha} \times 2 = \frac{4\alpha}{1 + \alpha} \text{ atm}$	
$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}}$	$= 1.33$
$\frac{\left(\frac{4\alpha}{1 + \alpha}\right)^2}{\frac{2(1 - \alpha)}{1 + \alpha}} = 1.33$	

$$\begin{aligned} \left(\frac{16\alpha^2}{(1 + \alpha)^2} \right) \times \left(\frac{1 + \alpha}{2(1 - \alpha)} \right) &= 1.33 \\ \frac{16\alpha^2}{2(1 + \alpha)(1 - \alpha)} &= 1.33 \\ 16\alpha^2 &= 2.66(1 - \alpha^2) \\ 16\alpha^2 + 2.66\alpha^2 &= 2.66 \\ 18.66\alpha^2 &= 2.66 \\ \alpha^2 &= 0.142551 \\ \alpha &= 0.378 \end{aligned}$$

The degree of dissociation of N_2O_4 is 0.378

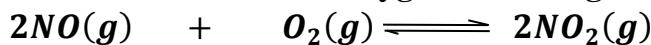
3. When heated, carbon dioxide dissociates according to the equation:



If at a certain temperature and a pressure of one atmosphere, 60% of the original carbon dioxide remained undissociated. Calculate the equilibrium constant K_p for the reaction.

$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$			
Initial moles	n	0	0
Moles dissociated/formed	$n\alpha$	$n\alpha$	$\frac{n\alpha}{2}$
Moles at equilibrium	$n(1 - \alpha)$	$n\alpha$	$\frac{n\alpha}{2}$
<hr/>			
But $\frac{n(1 - \alpha)}{n} \times 100 = 60$			$p_{CO} = \frac{0.4n}{1.2n} \times 1 = 0.333 \text{ atm}$
$1 - \alpha = 0.6$			$p_{O_2} = \frac{0.2n}{1.2n} \times 1 = 0.167 \text{ atm}$
$\alpha = 0.4$			
Total moles at equilibrium			
$= n(1 - \alpha) + n\alpha + \frac{n\alpha}{2}$			$K_p = \frac{(p_{CO})^2 \times p_{O_2}}{(p_{CO_2})^2}$
$= n(1 - \alpha + \alpha + \frac{\alpha}{2})$			$K_p = \frac{(0.333)^2 \times 0.167}{(0.5)^2} \frac{\text{atm}^3}{\text{atm}^2}$
$= n\left(1 + \frac{\alpha}{2}\right) = 1.2n$			$K_p = 0.0741 \text{ atm}$
$p_{CO_2} = \frac{0.6n}{1.2n} \times 1 = 0.5 \text{ atm}$			

4. Nitrogen monoxide reacts with oxygen according to the reaction:

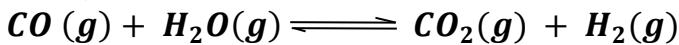


At equilibrium, the equilibrium constant is $375 \text{ mol}^{-1}l$ at a given temperature in a container of volume, 755cm^3 . The equilibrium mixture was found to contain

0.0148 moles of oxygen. Calculate the ratio of $[NO]$ to $[NO_2]$ in the equilibrium mixture.

$2NO(g)$ <i>Moles at equilibrium</i> ?	$O_2(g)$ 0.0148 ?	$\rightleftharpoons 2NO_2(g)$
<i>Since volume is 755 cm³,</i> $[O_2] = \left(\frac{0.0148 \times 1000}{755} \right) = 0.0196M$ $[NO] = ? \quad [NO_2] = ?$ $K_c = \frac{[NO_2]^2}{[NO]^2[O_2]} = 375$ $\frac{[NO_2]^2}{[NO]^2} = 375[O_2]$	$\frac{[NO_2]^2}{[NO]^2} = 375 \times 0.0196$ $\frac{[NO_2]}{[NO]} = \sqrt{375 \times 0.0196}$ $\frac{[NO_2]}{[NO]} = 2.711$ $\frac{[NO]}{[NO_2]} = \frac{1}{2.711} = 0.3689$	

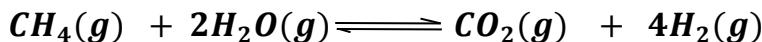
5. For the equilibrium system below:



- (a) Write the expression for the equilibrium constant, K_p .
- (b) When 1 mole of steam and 1 mole of carbon monoxide are allowed to reach equilibrium, 33.3% of the equilibrium mixture is hydrogen. Calculate the value of K_p and state its units.

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$				
<i>Initial moles</i>	1	1	0	0
<i>Moles reacted/formed</i>	x	x	x	x
<i>Moles at equilibrium</i>	$1 - x$	$1 - x$	x	x
Total moles at equilibrium $= 1 - x + 1 - x + x + x = 2$ But $\frac{x}{2} \times 100 = 33.3$ $x = 0.666$ Let the total pressure be P $p_{CO} = \frac{1 - 0.666}{2}P = 0.167 \text{ units}$ $p_{H_2O} = \frac{1 - 0.666}{2}P = 0.167 \text{ units}$			$p_{CO_2} = \frac{0.666}{2}P = 0.333 \text{ units}$ $p_{H_2} = \frac{0.666}{2}P = 0.333 \text{ units}$ $K_p = \frac{p_{CO_2} \times p_{H_2}}{p_{CO} \times p_{H_2O}}$ $K_p = \frac{(0.333)^2}{(0.167)^2}$ $K_p = 3.976$	

6. Methane reacts with steam according to the equation



When 0.18 moles of methane and 0.22 moles of steam were heated in a 5 litre vessel, 0.1 mole of carbon dioxide was found to be present at equilibrium. Calculate the value of K_c .

$CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$				
Initial moles	0.18	0.22	0	0
Moles reacted/formed	x	$2x$	x	$4x$
Moles at equilibrium	$0.18 - x$	$0.22 - 2x$	x	$4x$
<p>But number of moles of CO_2 at equilibrium = 0.1 Therefore $x = 0.1$</p> <p>Moles of CH_4 at equilibrium = $0.18 - 0.1 = 0.08$</p> <p>Moles of H_2O at equilibrium = $0.22 - 2(0.1) = 0.02$</p> <p>Moles of CO_2 at equilibrium = 0.1</p> <p>Moles of H_2 at equilibrium = $4(0.1) = 0.4$</p>		<p>Since volume is 5 litres,</p> <p>$[CH_4] = \left(\frac{0.08}{5}\right) = 0.016M$</p> <p>$[H_2O] = \left(\frac{0.02}{5}\right) = 0.004M$</p> <p>$[CO_2] = \left(\frac{0.1}{5}\right) = 0.02M$</p> <p>$[H_2] = \left(\frac{0.4}{5}\right) = 0.08M$</p> <p>$K_c = \frac{[CO_2][H_2]}{[CH_4][H_2O]}$</p> <p>$K_c = \frac{0.02 \times 0.08}{0.016 \times 0.004}$</p> <p>$K_c = 25$</p>		

7. Sulphonyl dichloride dissociates when heated according to the following equation: $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

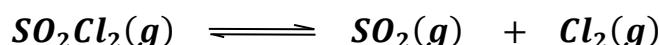
When 67.5g of Sulphonyl dichloride was heated in a 1 litre vessel at 120°C and 3.6 atmospheres, it was found that at equilibrium, 45% of it had dissociated.

- (i) Write the expression for the equilibrium constant, K_p .
- (ii) Calculate the number of moles of each substance present at equilibrium.
- (iii) Calculate the equilibrium constant, K_c .

$$(i) K_p = \frac{p_{SO_2} \times p_{Cl_2}}{p_{SO_2Cl_2}}$$

$$(ii) Molar mass of $SO_2Cl_2 = 32 + (2 \times 16) + (2 \times 35.4) = 134.8g$$$

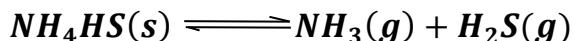
$$\text{Initial moles of } SO_2Cl_2 = \frac{67.5}{134.8} = 0.5$$



Initial moles	0.5	0	0
Moles dissociated/formed	0.5α	0.5α	0.5α
Moles at equilibrium	$0.5(1 - \alpha)$	0.5α	0.5α

$\text{But } \alpha = \frac{45}{100} = 0.45$ $\text{Moles of } SO_2Cl_2 \text{ at equilibrium} \\ = 0.5(1 - 0.45) = 0.275$ $\text{Moles of } SO_2 \text{ at equilibrium} \\ = (0.5 \times 0.45) = 0.225$ $\text{Moles of } Cl_2 \text{ at equilibrium} = 0.225$	(iii) Since volume is 1 litre $[SO_2Cl_2] = 0.275 M$ $[SO_2] = 0.225 M$ $[Cl_2] = 0.225 M$ $K_c = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]} = \frac{(0.225)^2}{0.275} = 0.184 \text{ moldm}^{-3}$
---	--

8. The equilibrium constant, K_p for the reaction below at 250°C is $1.08 \times 10^{-1} \text{ atm}^2$:



Calculate the:

- (i) total pressure of the system at equilibrium.
(ii) degree of dissociation of ammonium hydrogen sulphide

$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$	
Initial moles	n
Moles dissociated/formed	$n\alpha$
Moles at equilibrium	$n(1 - \alpha)$
Total moles at equilibrium	
$= n(1 - \alpha) + n\alpha + n\alpha$	0
$= n(1 - \alpha + \alpha + \alpha)$	0
$= n(1 + \alpha)$	$n\alpha$
Let the total pressure at equilibrium be P	
$p_{NH_3} = p_{H_2S} = \frac{n\alpha}{n(1 + \alpha)} P = \frac{\alpha}{(1 + \alpha)} P$	
$K_p = p_{NH_3} \times p_{H_2S}$	
Since $p_{NH_3} = p_{H_2S}$:	
$K_p = (p_{NH_3})^2$	

$$1.08 \times 10^{-1} = (p_{NH_3})^2$$

$$p_{NH_3} = \sqrt{1.08 \times 10^{-1}}$$

$$p_{NH_3} = 0.3286 \text{ atm}$$

$$P = p_{NH_3} + p_{H_2S}$$

$$= 2(0.3286) = 0.6572 \text{ atm}$$

From

$$p_{NH_3} = \frac{\alpha}{(1 + \alpha)} P$$

$$0.3286 = \frac{\alpha}{(1 + \alpha)} \times 0.6572$$

$$\frac{\alpha}{(1 + \alpha)} = \frac{0.3286}{0.6572} = 0.5$$

$$\alpha = 1$$

General questions involving calculations on chemical equilibria

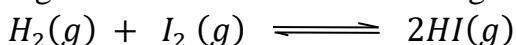
1. When 3.12g of ethanoic acid and 2.07g of ethanol were reacted in a 1 litre closed vessel at 50°C. 0.36g of water was found at equilibrium. Calculate the value of equilibrium constant for the reaction, K_c .
2. When 8.28g of ethanol were heated with 60g of ethanoic acid, 49.74g of the acid remained at equilibrium. Calculate the;
 - (i) value of the equilibrium constant, K_c .
 - (ii) mass of ester present in the equilibrium mixture formed from 13.8g of ethanol and 12g of ethanoic acid.
3. When equimolar quantities of ethanoic acid and ethanol were heated, one third of each reactant remained at equilibrium. Calculate the equilibrium constant for the reaction
4. 1 mole of ethanol was reacted with 2 moles of ethanoic acid at 60°C. If the equilibrium constant for the reaction at the same temperature is 4. Calculate the mass of ethylethanoate in the equilibrium mixture.
5. 5moles of ethanol, 6 moles of ethanoic acid, 6 moles of ethylethanoate and 4moles of water were mixed together in a stoppered bottle at 15°C. At equilibrium, the bottle was found to contain 4 moles of ethanoic acid.
 - (a) (i) Write an equation for the reaction between ethanol and ethanoic acid to form ethylethanoate and water.
 - (ii) Suggest a mechanism for the reaction
 - (b) Write an expression for the equilibrium constant, K_c for this reaction
 - (c) Determine the number of moles of ethanol, ethylethanoate and water present in the equilibrium mixture hence the value of K_c for this reaction
 - (d) If 1moleof ethanol, 1mole of ethanoic acid, 3 moles of ethylethanoate and 3 moles of water are mixed together in a stoppered flask at 15°C. Determine the number of moles of each compound present in the equilibrium mixture.
6. 3.0g of ethanoic acid and 2.3g of ethanol were equilibrated at 100°C for an hour and then quickly cooled in an ice bath. 50 cm^3 of 1.0 M sodium hydroxide solution were added. When the mixture was titrated with 1.0M hydrochloric acid, 33.3cm^3 of the acid were required for complete reaction.
 - (a) Explain why the mixture was cooled in an ice bath.
 - (b) Calculate the equilibrium constant, K_c for the reaction.
7. 4.6g of ethanol and 12.0g of ethanoic acid were mixed in a stoppered flask with 20cm^3 of 1M hydrochloric acid as catalyst at 20°C. The mixture was left for a week to attain equilibrium, and then titrated with 137cm^3 of 1.0M sodium hydroxide. (Of the total volume of base used, only 20 cm^3 were used to react with hydrochloric acid)
 - (a)Work out the concentrations of the equilibrium mixture
 - (b) Calculate the value of equilibrium constant, K_c .

8. When 60g of ethanoic acid and 46g of ethanol were made to react to equilibrium at 100°C, the percentage of esterification was 54%
- Write equation for the esterification reaction.
 - Calculate the value of the concentration equilibrium constant, K_c .
 - Outline the mechanism for the reaction between ethanoic acid and ethanol.
9. When 6.22cm^3 of hydrogen were heated with 5.71cm^3 of iodine in a sealed tube at 356 °C, it was found out that 9.60 cm^3 of hydrogen iodide were present at equilibrium. Calculate the:
- equilibrium constant
 - volume of hydrogen iodide in the equilibrium mixture formed by reacting together 6.41cm^3 of hydrogen and 10.40cm^3 of iodine at 356 °C.

(*Hint: Number of moles of a gas is directly proportional to volume*)

10. A mixture of 0.8 mole of hydrogen and 0.6 mole of iodine was allowed to react in a sealed tube at 450°C. At equilibrium, 0.2 mole of iodine had reacted.
- Write an expression for the equilibrium constant, K_c , for the reaction
 - Calculate the value of K_c , at 450°C.

11. Hydrogen reacts with iodine according to the equation



- (a) Calculate the equilibrium concentration of each of the following when:

- 0.2 mole of iodine and 0.3 moles of hydrogen are reacted in a one litre vessel.
 - 0.5 mole of iodine and 0.8 mole of hydrogen are reacted in a 4 litre vessel
(*The equilibrium constant, K_c , for the reaction is 50*)
- (b) Equimolar quantities of hydrogen and iodine were heated in a 1 litre vessel until equilibrium was attained. The equilibrium mixture was found to contain 20.5% hydrogen iodide Determine the equilibrium constant, K_c .

12. (a) State the **law of mass action**

- (b) Explain what is meant by the following terms:

- equilibrium constant**
- dynamic equilibrium**

- (c) Describe an experiment to determine the equilibrium constant for the reaction between hydrogen and iodine

- (d) 1.54g of hydrogen iodide were heated in a 600cm^3 bulb at 530 °C. When equilibrium was attained, the bulb was rapidly cooled to room temperature and broken under potassium iodide solution. The iodine formed required 67 cm^3 of 0.1M sodium thiosulphate solution for complete reaction. Calculate ;

- Number of moles of hydrogen iodide in 1.54g
- Number of moles of iodine formed

(iii) Value of K_c at 530 °C

13. 1.0g of hydrogen iodide was heated to a certain temperature in a sealed vessel and the products rapidly cooled. The iodine which had been liberated required 15.0 cm^3 of 0.1M sodium thiosulphate for complete reaction. Calculate the percentage by mass of hydrogen iodide which remained undissociated at that temperature.

14. (a) 3.4 moles of hydrogen iodide at 460°C are found to be 20% dissociated. Calculate the:

(i) number of moles of hydrogen iodide, hydrogen and iodine formed at equilibrium

(ii) equilibrium constant for the dissociation reaction.

(b) A mixture containing 28 moles of hydrogen and 22 moles of iodine was heated in a sealed tube at 460 °C until equilibrium was attained and 36 moles of hydrogen iodide was obtained. Calculate the degree of dissociation of hydrogen iodide at 460°C

15. (a) The equilibrium constant for the dissociation of hydrogen iodide into hydrogen and iodine is 0.02. Calculate the equilibrium composition of the following if they are heated.

(i) 0.05 mole of hydrogen iodide.

(ii) 0.2 mole of hydrogen iodide.

(b) When 0.4 mole of hydrogen iodide was heated to equilibrium, it dissociated. Determine the degree of dissociation of hydrogen iodide, given that the equilibrium constant is 0.025

16. (a) 1 mole of hydrogen iodide gas at 25°C was introduced into a container of volume 20 litres. Calculate the pressure of the gas assuming ideal behaviour. (*1 mole of an ideal gas occupies 22.4 litres under standard conditions*)

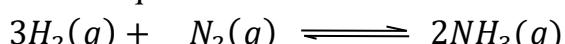
(b) The sample of hydrogen iodide, considered above was raised to a temperature of 300°C and it partially dissociated into hydrogen and iodine. At equilibrium, 1 mole of iodine was found to be present.

(i) Write an equation for the dissociation

(ii) Calculate the pressure of the equilibrium mixture at 300°C assuming no change in volume.

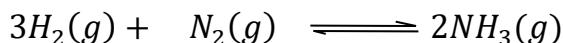
(iii) Calculate the equilibrium constant at 300°C

17. Derive an expression for the equilibrium constant for the reaction;



in terms of a , b , x and P , where a and b are the original number of moles of hydrogen and nitrogen respectively, and x is the number of moles of nitrogen which react at a total pressure of P Pa.

18. When 0.2 moles and 0.47 moles of nitrogen and hydrogen respectively were heated to equilibrium in a 1 litre vessel, 0.18 moles of ammonia were formed. Calculate the equilibrium constant, K_c .
19. When 1.65 moles of hydrogen and 0.6 moles of nitrogen were heated to 150°C in a 1.5 litre closed vessel, equilibrium was attained when 0.9 moles of ammonia were formed. Calculate the value of equilibrium constant, K_c for the reaction.
20. Nitrogen and hydrogen are mixed in a ratio 1:3. At equilibrium at 600°C and 10 atmospheres, the percentage of ammonia in the mixture of gases is 15%
- (a) Write equation for the reaction
 - (b) Write an expression for the equilibrium constant.
 - (c) Calculate the equilibrium constant at that temperature and state its units.
21. Stoichiometric amounts of hydrogen and nitrogen were reacted at 50 atm. At equilibrium, 0.8 moles of ammonia were formed. Calculate:
- (i) Amount of hydrogen and nitrogen present at equilibrium
 - (ii) Value of the equilibrium constant
22. (a) For the reaction,



Calculate the molar percentage of ammonia in the equilibrium mixture formed at 400°C and at a pressure of 3×10^7 Pa, when gaseous hydrogen and nitrogen are mixed in a 3:1 ratio and there is 61% conversion of nitrogen to ammonia.

- (b) (i) Determine the equilibrium constant, K_p of the reaction.
- (ii) Given that the value of K_p at a given temperature is $2.0 \times 10^{-14} Pa^2$, calculate the pressure at which ammonia is 95% dissociated into its elements at that temperature.

23. (a) Write equation for the reaction leading to formation of ammonia
- (b) The value of the pressure equilibrium constant, K_p for the reaction in (a) above is $1.5 \times 10^{-5} atm^{-2}$ at 500°C . Calculate the percentage of a 1:3 mixture of nitrogen and hydrogen that would be converted to ammonia at 500 atmospheres.
24. (a) Write an equation for the reaction between hydrogen and nitrogen.
- (b) At 500 °C, the equilibrium concentration of hydrogen is $0.250 mol l^{-1}$ and that of nitrogen is $2.7 mol l^{-1}$ Calculate the equilibrium concentration of ammonia at the same temperature given that $K_c = 6 \times 10^{-2} mol^{-2} l^2$ at 500 °C.
25. When nitrogen was reacted with hydrogen at 690K, the total pressure of the system at equilibrium was 32 atmospheres and the partial pressures of hydrogen and nitrogen were 8 and 3 atmospheres respectively. Calculate the:
- (i) partial pressure of ammonia in equilibrium mixture.
 - (ii) equilibrium constant for the reaction

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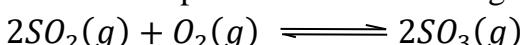
26. At a certain temperature, the equilibrium constant for the reaction between nitrogen and hydrogen, K_p , is $4.82 \times 10^{-2} \text{ atm}^{-2}$ and the partial pressures of nitrogen and hydrogen are 30 and 120 atm respectively.
- Write the expression for the equilibrium constant, K_p .
 - Calculate the partial pressure of ammonia at equilibrium.
27. When 80.4 g of phosphorus(V) chloride were placed in a 9.0 litre vessel and heated at a certain pressure, 8.4 g of chlorine were formed at equilibrium. Calculate the:
- amount of phosphorus(V) chloride and phosphorus(III) chloride at equilibrium in moles per litre.
 - equilibrium constant, K_c , for the reaction and state its units.
28. (a) When 2.6 mole of phosphorus(V) chloride was heated in a 1.5 dm^3 vessel, equilibrium was established when 1.04 mole of phosphorus(III) chloride was formed. Calculate the value of equilibrium constant, K_c .
- (b) 3.0 mole of phosphorus pentachloride was heated in a 1 litre vessel and when equilibrium was attained, it was found to contain 1.14 mole of chlorine gas. Determine the value of equilibrium constant, K_c .
29. **75.06g** of phosphorus(V) chloride were heated to 200°C in a vessel of volume 1000 cm^3 at a pressure of 170kPa. Calculate the;
- degree of dissociation of phosphorus(V) chloride
 - value of equilibrium constant, K_p , at 200°C
30. 0.2 moles of phosphorus pentachloride were heated at 500K in 5 litre flask. At equilibrium, 60% of phosphorus pentachloride was found to have dissociated and the total pressure was found to be 300mmHg.
- Calculate the equilibrium constant, K_p .
 - What will be the total pressure if phosphorus pentachloride dissociated only by 35%
31. When 2.4 moles of phosphorus pentachloride were heated in a 1.5 dm^3 vessel and at equilibrium, it was found to contain 23.53% phosphorus trichloride.
- Write equation for the dissociation of phosphorus pentachloride
 - Write the expression for the equilibrium constants, K_c , and K_p , for the reaction.
 - Determine the value of equilibrium constant, K_c .
32. (a) 2.6 mole of phosphorus pentachloride was heated in a 500 cm^3 closed vessel. At equilibrium, it was found to contain 1.04 mole of phosphorus trichloride. Determine the value of equilibrium constant, K_c .
- (b) 3.0 mole of phosphorus pentachloride was heated in a 750 cm^3 vessel until equilibrium was established. The vessel contained 1.14 moles of chlorine. Determine the value of equilibrium constant, K_c .

33. Determine the mass of each of the components of the equilibrium mixture formed when 0.52 moles of phosphorus(V) chloride is heated at equilibrium.
(*The equilibrium constant is 0.043 mol dm⁻³*)

34. 0.04 moles of sulphur trioxide were allowed to dissociate at 900K in a flask of volume 3.04 litres. At equilibrium, 0.0289 moles of sulphur trioxide were found to be present.

- (i) Derive the relationship between K_c and K_p for this reaction. Show clearly how you arrive at your answer.
- (ii) Calculate equilibrium constants K_c and K_p .

35. At 700°C and total pressure of one atmosphere, the partial pressures at equilibrium for sulphur dioxide and oxygen are 0.27 and 0.41 atmospheres respectively. Sulphur dioxide is oxidized to sulphur trioxide according to the following equation:



Calculate the equilibrium constant, K_p , for the reaction

36. When 0.6 and 0.425 moles of sulphur dioxide and oxygen respectively were reacted in a 1 litre vessel to equilibrium, the equilibrium mixture contained 18.75% sulphur dioxide. Calculate the equilibrium constant value, K_p .

37. Dinitrogen tetraoxide dissociates at 40 °C and 1 atm according to the following equation.



- (i) Write an equation for the equilibrium constant, K_p .
- (ii) Draw a well labelled energy level diagram for the reaction in (i) above
- (iii) The reaction mixture of the reaction was found to contain 60% by volume of nitrogen dioxide at equilibrium. Calculate the equilibrium constant K_p at 40 °C for the reaction.

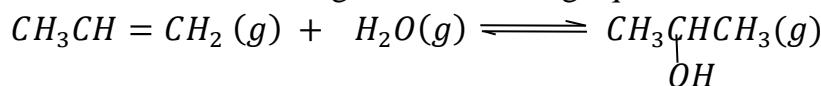
38. (a) At 40°C and under a pressure of 1 atmosphere, dinitrogen tetraoxide contains 60% by volume of nitrogen dioxide molecules. Calculate the percentage dissociation of dinitrogen tetraoxide and equilibrium constant in terms of the partial pressures of the two gases.

(b) Deduce the:

- (ii) percentage dissociation of dinitrogen tetraoxide at the same temperature when the gases are under a pressure of 6 atm.
- (iii) the pressure at which dinitrogen tetraoxide would be dissociated to an extent of 80% at the same temperature.

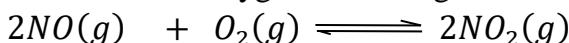
39. 1 mole of dinitrogen tetra oxide was allowed to dissociate to nitrogen dioxide in a 5 litre flask at 50°C. At equilibrium one mole of nitrogen dioxide was found to be present. Calculate equilibrium constant for the reaction.

40. Propene reacts with steam according to the following equation.



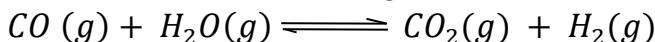
At a certain temperature and total pressure of 197.38 atmospheres, the equilibrium partial pressures of propene and steam are 74.02 and 93.76 atmospheres respectively. Calculate the value of K_p at this temperature and state its units.

41. Nitrogen monoxide combines with oxygen according to the equation



A closed vessel of 500 cm^3 containing 0.33 moles of nitrogen monoxide and 0.355 moles of oxygen was heated. Equilibrium was established when 0.105 moles of oxygen had reacted. Calculate the value of K_c .

42. Carbon monoxide reacts with steam according to the reaction;



When 6.5 cm^3 of carbon monoxide were heated with 4.8 cm^3 of steam at 45°C until equilibrium, 4.6 cm^3 of carbon dioxide was formed. Calculate the;

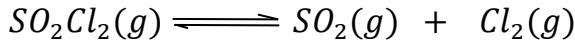
(a) volume of carbon monoxide and steam left at equilibrium.

(b) equilibrium constant, K_c .

43. At 700°C , the equilibrium constant for the reaction

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ is 1.4. Calculate the percentage by volume of the gases in the equilibrium mixture at the same temperature when one volume of carbon monoxide and two volumes of steam are mixed.

44. Sulphur dioxide dichloride dissociates when heated according to the equation:



When 1.33 moles of sulphur dioxide dichloride were heated in a 2 litre vessel, equilibrium mixture contained 5.98% sulphur dioxide dichloride. Calculate the value of equilibrium constant, K_c .

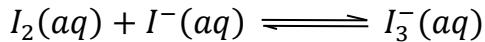
45. Ammonium hydrogen sulphide was allowed to dissociate into ammonia and hydrogen sulphide gases at $500K$. At equilibrium the total pressure was measured and found to be 0.6 atm. Calculate the:

(i) partial pressure of each gas at equilibrium.

(ii) pressure equilibrium constant

Determining equilibrium constants using partition coefficients

Iodine reacts with potassium iodide to form potassium triiodide according to the equation;



The equilibrium constant for the above reaction is given by the expression below and is measured by partition method.

$$K_c = \frac{[I_3^-]}{[I_2][I^-]}$$

A known mass of iodine is dissolved in a standard solution of potassium iodide and the resultant mixture shaken with trichloromethane or benzene or carbon disulphide. Some iodine forms a complex with potassium iodide according to the above equation and some iodine remains free in the solution. The free iodine then distributes itself between the aqueous layer and the organic solvent used.



The concentration of iodine in the organic layer is obtained by titrating a portion of a known volume of it with standard sodium thiosulphate solution.

The concentration of free iodine in the aqueous layer is then got from the expression below, if the partition coefficient value is known;

$$K_D = \frac{[I_2] \text{ in free aqueous layer}}{[I_2] \text{ free in organic layer}}$$

$$[I_2]_{\text{total in aqueous layer}} = [I_2]_{\text{free(aqueous layer)}} + [I_3^-]$$

The total concentration of iodine in the aqueous layer, $[I_2]_{\text{total}}$ is obtained by titrating a portion of a known volume of it with standard sodium thiosulphate solution.

$$[I_2]_{\text{total in aqueous layer}} = [I_2]_{\text{free(aqueous layer)}} + [I_3^-]$$

Since $[I_2]_{\text{free(aqueous layer)}}$ is known, then $[I_3^-]$ can be obtained.

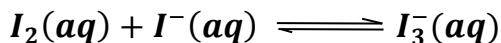
The total iodide ion concentration in the aqueous layer is obtained from the concentration of potassium iodide used.

$$[I^-]_{\text{total}} = [I^-]_{\text{aqueous}} + [I_3^-]$$

Since $[I_3^-]$ is known, then $[I^-]_{\text{aqueous}}$ can be obtained and the value of K_c then determined.

Example

4g of potassium iodide was dissolved in 500cm^3 of water and about 1g of iodine was dissolved in 100cm^3 of benzene. The two solutions were then mixed and allowed to stand. 10 cm^3 of the benzene layer required 5.1cm^3 of 0.1M sodium thiosulphate solution while 50 cm^3 of the aqueous layer required 2.9 cm^3 of 0.1M sodium thiosulphate solution for complete reaction. The distribution coefficient of iodine between benzene and water is 130. Calculate the value of the equilibrium constant for the reaction:



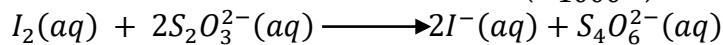
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$$\text{Molar mass of } KI = 39 + 127 = 166\text{g}$$

$$\text{Moles of } Na_2S_2O_3 \text{ that reacted with } I_2 \text{ in benzene layer} = \left(\frac{5.1 \times 0.1}{1000} \right) = 0.00051 \text{ moles}$$



$$\text{Mole ratio of } S_2O_3^{2-} : I_2 = 2 : 1$$

$$\text{Moles of } I_2 \text{ in } 10 \text{ cm}^3 \text{ of benzene layer} = \frac{1}{2} \times 0.00051 = 0.000255 \text{ moles}$$

10 cm³ of benzene layer contain 0.000255 moles of I₂

$$1000 \text{ cm}^3 \text{ of benzene layer contain } \left(\frac{1000 \times 0.000255}{10} \right) \text{ moles of } I_2$$

$$[I_2] \text{ in benzene layer} = 0.0255M$$

$$K_D = \frac{[I_2] \text{ free in benzene}}{[I_2] \text{ free in aqueous layer}} = 130$$

$$[I_2] \text{ free in aqueous layer} = \frac{0.0255}{130} = 0.000196M$$

$$\text{Moles of } Na_2S_2O_3 \text{ that reacted with free } I_2 \text{ in aqueous layer} = \left(\frac{2.9 \times 0.1}{1000} \right) = 0.00029 \text{ moles}$$

$$\text{Mole ratio of } S_2O_3^{2-} : I_2 = 2 : 1$$

$$\text{Moles of total } I_2 \text{ in } 50 \text{ cm}^3 \text{ of aqueous layer} = \frac{1}{2} \times 0.00029 = 0.000145 \text{ moles}$$

50 cm³ of aqueous layer contain 0.000145 moles of total I₂

$$1000 \text{ cm}^3 \text{ of aqueous layer contain } \left(\frac{1000 \times 0.000145}{50} \right) \text{ moles of total } I_2$$

$$[I_2] \text{ total in aqueous layer} = 0.0029M$$

$$[I_2] \text{ total in aqueous layer} = [I_2] \text{ free} + [I_3^-]$$

$$[I_2] \text{ free} + [I_3^-] = 0.0029$$

$$[I_3^-] = 0.0029 - 0.000196 = 0.0027$$

$$\text{Moles of } KI \text{ in } 500 \text{ cm}^3 = \frac{4}{166} = 0.0241 \text{ moles}$$

$$\text{Molar concentration of } KI \text{ solution} = \left(\frac{1000 \times 0.0241}{500} \right) = 0.0482 M$$

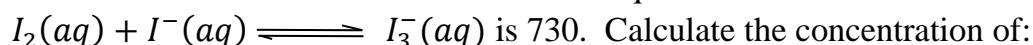
$$[I^-]_{\text{total}} = [I^-]_{\text{aqueous}} + [I_3^-]$$

$$[I^-]_{\text{aqueous}} = 0.0482 - 0.0027 = 0.0455$$

$$K_c = \frac{[I_3^-]}{[I_2][I^-]} = \frac{0.0027}{0.000196 \times 0.0455} = 302.8 \text{ mol}^{-1} \text{ dm}^3$$

Questions

1. A solution containing 12.7g of iodine and 166.1g of potassium iodide in 1 litre of water was shaken with 1 litre of benzene. If the partition coefficient of iodine between benzene and water is 400 and the equilibrium constant for the reaction:



- (i) iodine in benzene
 (ii) triiodide ions in water

Compare concentration equilibrium constant, K_c and pressure equilibrium constant, K_p

Concentration equilibrium constant, K_c	Pressure equilibrium constant, K_p
It can be measured for any reversible reaction	Measured for only reversible reactions involving gases
Expressed in terms of molar concentrations	Expressed in terms of partial pressures
N.B The two equilibrium constants are always the same value at a given temperature for equilibria where $\Delta n = 0$ <i>(where total number of moles of products – total number of moles of reactants is zero)</i>	

Interpretation of magnitude of K_c or K_p in relation to equilibrium position

Consider the reversible reaction, $wA + xB \rightleftharpoons yC + zD$

The proportion of products to reactants in the equilibrium mixture is described as the **position of the equilibrium**.

The magnitude of the equilibrium constant, K_c or K_p indicates the extent to which a reaction will proceed and the position of the equilibrium.

When K_c or K_p is small ($k < 1$), it implies that the conversion of A and B into C and D is small and the position of the equilibrium lies to the left.

When K_c or K_p is large ($k > 1$), it implies that the equilibrium mixture is largely composed of C and D is small and the position of the equilibrium lies to the right.

If K is about 1, the equilibrium is reached at some intermediate mixture.

Comparing the reaction quotient (Q) and K_c to determine direction of a chemical reaction

The reaction quotient(Q) is defined as the ratio of the molar concentrations of the product species over those of the reactant species involved in the chemical reaction,

taking stoichiometric coefficients of the reaction into account as powers of the concentrations.

The **reaction quotient**, Q , has the same mathematical form as the equilibrium-constant expression, but Q is a ratio of the actual concentrations (not a ratio of equilibrium concentrations).

For a given reaction, $wA + xB \rightleftharpoons yC + zD$

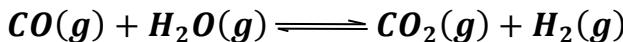
The reaction quotient is given as;

$$Q = \frac{[C]^y [D]^z}{[A]^w [B]^x}$$

- At equilibrium, $K_c = Q$, and this is defined as the **equilibrium condition**.
- If $K_c < Q$, the backward reaction is favoured, the reaction moves from right to left, until equilibrium is established.
- If $K_c > Q$, the forward reaction is favoured, the reaction moves from left to right, until equilibrium is established.

Examples

1. In the water–gas shift reaction, carbon monoxide produced by steam-reforming reaction of methane reacts with steam at elevated temperatures to produce more hydrogen:



If $K_c = 0.64$ at 900 K and 0.010 moles of carbon monoxide and 0.010 moles of water, 0.0080 moles of carbon dioxide, and 0.012 moles of hydrogen are injected into a 4.0 litre reactor and heated to 900 K, will the reaction proceed to the left or to the right ?

$$[CO] = \frac{0.01}{4} = 0.0025M$$

$$[H_2O] = \frac{0.01}{4} = 0.0025M$$

$$[CO_2] = \frac{0.008}{4} = 0.002M$$

$$[H_2] = \frac{0.012}{4} = 0.003M$$

$$Q = \frac{[CO_2] \times [H_2]}{[CO] \times [H_2O]}$$

$$Q = \frac{0.002 \times 0.003}{0.0025 \times 0.0025}$$

$$Q = 0.96$$

Since $Q > K_c$, the reaction proceeds from right to left, until equilibrium is established.

2. Consider the following reversible reaction; $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$. At a certain temperature, the partial pressure were measured and found to be 0.57 atm for sulphur trioxide, 0.4 atm for sulphur dioxide and 0.16 atm for oxygen. Predict the direction in which the reaction should proceed in order to attain equilibrium.

$$(K_p = 3.4 \text{ atm}^{-1})$$

$$p_{SO_3} = 0.57 \text{ atm}$$

$$p_{SO_2} = 0.4 \text{ atm}$$

$$p_{O_2} = 0.16 \text{ atm}$$

$$Q = \frac{(p_{SO_3})^2}{(p_{SO_2})^2 \times p_{O_2}}$$

$$Q = \frac{0.57^2}{0.4^2 \times 0.16}$$

$$Q = 12.69 \text{ atm}^{-1}$$

Since $Q > K_p$, the reaction proceeds from right to left, until equilibrium is established.

Questions

- For the reaction: $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, the equilibrium constant, K_c , is 1.0×10^{-5} at 1500 K. Predict the direction the reaction will move in if the reactants and products have the following concentrations: $[N_2] = 0.05 \text{ mol l}^{-1}$, $[O_2] = 0.02 \text{ mol l}^{-1}$, and $[NO] = 0.30 \text{ mol l}^{-1}$.
- For the reaction: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the equilibrium constant, K_c , is 5.0×10^{-1} at 100°C. Predict the direction the reaction will move in if the concentration of N_2O_4 is 0.02 mol l^{-1} and the concentration of NO_2 is 0.10 mol l^{-1}
- 1 mole of Sulphur trioxide was introduced into a 1 dm^3 vessel. The vessel was heated to 1000K until equilibrium was attained. At equilibrium, 0.35 mole of Sulphur trioxide was present.
 - Write:
 - equation for the decomposition of Sulphur trioxide
 - an expression for the equilibrium constant, K_c
 - Calculate the value of K_c .
 - 0.2 mole of Sulphur dioxide, 0.1 mole of oxygen and 0.7 mole of Sulphur trioxide, were introduced into the vessel in (a) at 1000K. Calculate the new K_c value for the reaction.
 - Using your answers in (b) and (c) above, state how the position of the equilibrium was affected.

Lé CHATELIER'S PRINCIPLE AND THE EFFECTS OF VARIOUS FACTORS ON THE EQUILIBRIUM OF REVERSIBLE CHEMICAL REACTIONS

Lé Chatelier's Principle

The principle states that if a system in equilibrium is subjected to any change, the equilibrium will shift if possible, to a direction which causes an opposite change.

or

If a system in equilibrium is subjected to a constraint, that change takes place which tends to remove the constraint

The system cannot completely cancel the change in the external factor, but it will move in a direction that will minimize the change.

The external factor may be **pressure, temperature, concentration, adding a noble gas or a catalyst**.

(a) Effect of pressure

Since pressure has a negligible effect on the volumes of solids and liquids, it only affects reactions in which gases are involved.

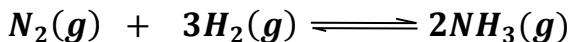
Any reaction that occurs with an increase in volume is favoured by a decrease in pressure.

A reaction that occurs with a decrease in volume is favoured by an increase in pressure.

Any change in pressure of the system **changes the position of the equilibrium** and the **rate of attainment of the equilibrium** but has **no effect on the equilibrium constant**.

Sample questions

1. Nitrogen and hydrogen react according to the equation



Explain how the position of the equilibrium, value of the equilibrium constant and the rate of attainment of equilibrium would be affected if ;

- (i) the pressure was decreased

Note that **1 volume of N_2 + 3 volumes of H_2 (a total of 4 volumes) produce 2 volumes of ammonia**

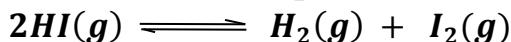
There forward reaction occurs by a reduction in volume, hence favoured by an increase in pressure.

A decrease in pressure shifts equilibrium from right to left since backward reaction occurs by an increase in volume. Ammonia dissociates to form nitrogen and hydrogen, keeping the equilibrium constant value unchanged. Rate of attainment of equilibrium decreases because there are fewer gas molecules in a given volume, molecules are far apart hence there are fewer chances of successful collisions between particles.

- (ii) the pressure was increased

Increase in pressure shifts equilibrium from left to right since forward reaction occurs by a decrease in volume. Nitrogen will react with hydrogen to form ammonia so as to keep the equilibrium constant value unchanged. Rate of attainment of equilibrium increases because there are more gas molecules in a given volume, molecules are closer together hence there are more chances of successful collisions between particles.

2. When hydrogen iodide is heated it decomposes according to the equation



Explain how the position of the equilibrium, value of the equilibrium constant and the rate of attainment of equilibrium would be affected if the pressure of the reaction was increased

Note that **2 volumes of HI produce 1 volume of H_2 + 1 volume of I_2 = 2 volumes of products**

Increase in pressure has no effect on position of equilibrium since both forward and backward reactions proceed with no change in volume. Equilibrium constant remains unchanged but the rate of attainment of equilibrium increases because there are more gas molecules in a given volume, molecules are closer together hence there are more chances of successful collisions between particles.

(b) Effect of concentration

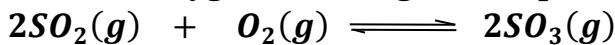
Increasing concentration of any reagent in an equilibrium mixture shifts the equilibrium in the direction that converts some of the reagent into other products.

Addition of a reagent that reacts with one of the reactants/products, reduces the concentration of the reactant/product in an equilibrium mixture and shifts the equilibrium in the direction to which the reactant/ product is removed so that it is replaced.

Any change in concentration of one of the species in an equilibrium mixture **changes the position of the equilibrium** and the **rate of attainment of the equilibrium** but has **no effect on the equilibrium constant**.

Sample question

1. Sulphur dioxide reacts with oxygen according to the equation;



Explain how the position of the equilibrium, value of the equilibrium constant and the rate of attainment of equilibrium would be affected if;

(i) more Sulphur dioxide was added

The concentration of sulphur dioxide increases and the excess sulphur dioxide reacts with oxygen to produce sulphur trioxide, so as to keep the equilibrium constant value the same. Equilibrium therefore shifts from left to right and equilibrium constant value remains unchanged. The rate of attainment of equilibrium increases since there is an increase in the number of particles in the reaction vessel.

(ii) Sulphur trioxide was added.

The concentration of sulphur trioxide increases and the excess sulphur trioxide dissociates to produce sulphur dioxide and oxygen, so as to keep the equilibrium constant value the same. Equilibrium therefore shifts from right to left and equilibrium constant value remains unchanged. The rate of attainment of equilibrium increases since there is an increase in the number of particles in the reaction vessel.

(iii) Removing the Sulphur trioxide formed

Removing sulphur trioxide makes the sulphur dioxide to react with oxygen so as to replace sulphur trioxide removed, keeping the equilibrium constant value unchanged. Equilibrium therefore shifts from left to right. The rate of attainment of equilibrium reduces since there is a reduction in the number of particles in the reaction vessel.

(c) Effect of temperature.

The effect of temperature on an equilibrium depends on whether the reaction is endothermic (ΔH is positive) or exothermic (ΔH is negative).

If the reaction is endothermic, increase in temperature favours it

If the reaction is exothermic, then it is favoured by lowering temperature.

Any change in temperature changes the position of the equilibrium, rate of attainment of the equilibrium and also the value of the equilibrium constant.

Among all the factors, it is only temperature that affects the value of the equilibrium constant.

For an exothermic reaction, increase in temperature favours backward reaction, reducing the equilibrium constant value.

For an endothermic reaction, increase in temperature favours forward reaction, increasing the equilibrium constant value.

Sample question

- Ammonia is formed from nitrogen and hydrogen at 25°C and 10 atm.

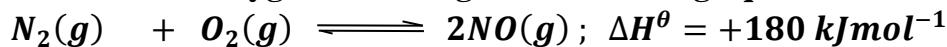


Explain how the position of the equilibrium, value of the equilibrium constant and the rate of attainment of equilibrium would be affected if the reaction is carried out at a temperature of 250°C , while the pressure remains at 10 atm.

Since forward reaction is exothermic, increase in temperature from 25°C to 250°C will make equilibrium shift from right to left, favouring the backward reaction which is endothermic. The ammonia dissociates to form nitrogen and hydrogen according to Lé Chatelier's Principle. This reduces the concentration of ammonia but increases the concentrations of nitrogen and hydrogen, reducing the equilibrium constant.

The rate of attainment of equilibrium increases because increase in temperature will increase both the forward reaction rate and the reverse reaction rate and the collision frequency between colliding particles.

2. Nitrogen reacts with oxygen according to the following equation



Explain how the position of the equilibrium, value of the equilibrium constant and the rate of attainment of equilibrium would be affected if;

- (i) the temperature was increased.

Increase in temperature will make equilibrium shift from left to right, favouring the forward reaction which is endothermic. The nitrogen reacts with oxygen to form nitrogen monoxide according to Lé Chatelier's Principle. This reduces the concentration of nitrogen and oxygen but increases the concentration of nitrogen monoxide, increasing the equilibrium constant.

The rate of attainment of equilibrium increases because increase in temperature will increase both the forward reaction rate and the reverse reaction rate the collision frequency between colliding particles.

- (ii) the temperature was decreased.

Decrease in temperature will make equilibrium shift from right to left, favouring the backward reaction which is exothermic. The nitrogen monoxide dissociates to form oxygen and nitrogen according to Lé Chatelier's Principle. This increases the concentration of nitrogen and oxygen but decreases the concentration of nitrogen monoxide, reducing the equilibrium constant.

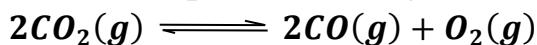
The rate of attainment of equilibrium decreases because decrease in temperature will reduce the collision frequency between colliding particles.

(d) Effect of adding a noble gas

Addition of an inert gas for example argon to an equilibrium system does not affect the equilibrium constant.

The noble gas effect can be investigated under two conditions i.e. constant volume (where total pressure of the system increases) and at constant pressure(where the total volume of the system increases).

When heated, carbon dioxide decomposes according to the equation:



Explain the effect on the equilibrium position and equilibrium constant and the rate of attainment of equilibrium when;

- (i) argon is added to the equilibrium at constant volume

Argon being a noble gas, when added, the total pressure of the system increases, but there is no change in partial pressure/ concentrations of the reactants and products. The position of the equilibrium is not affected.

Since the concentration of argon does not apply in the K_c or K_p expression, the equilibrium constant also remains unchanged.

The rate of attainment of equilibrium reduces since some of the particles on collision do not react.

N.B Hence, when an inert gas is added to the system in equilibrium at constant volume there will be no effect on the equilibrium position or equilibrium constant but reduces the rate of attainment of equilibrium.

(ii) **neon is added to the equilibrium at constant pressure**

Neon being a noble gas, when added to the system at constant pressure, leads to an increase in the total volume. As a result, partial pressures/ concentrations of the reactants and products decrease. According to Le Chatelier's Principle, the equilibrium will be shifted from left to right (in that direction where there is an increase in number of moles). The equilibrium constant remains unchanged since the partial pressure/concentration of neon does not apply in the equilibrium constant expression. The rate of attainment of equilibrium reduces as some of the particles on collision do not react.

N.B Hence, when an inert gas is added to the system in equilibrium at constant pressure, there will be a shift of the equilibrium position to a direction where the number of moles increases, no effect on equilibrium constant but reduces the rate of attainment of equilibrium.

(e) Effect of adding a catalyst

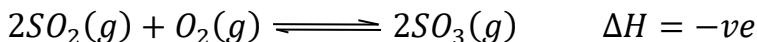
A catalyst is a substance which alters the rate of a chemical reaction but remains unchanged in quantity at the end of the reaction or at equilibrium.

A catalyst has **no effect on position of equilibrium** and **no effect on the value of equilibrium constant** but only alters the rate of backward and forward reaction equally. A catalyst therefore **increases the rate of attainment of equilibrium** by decreasing the activation energy.

The explanations given above are general. A question may require you just to state the effect of a constraint. This may not require you to go into details of explaining.

Questions

1. Sulphur dioxide reacts with oxygen according to the following equation.



(a) State what would happen to the **concentration of sulphur(VI) oxide** in the equilibrium mixture and give a reason for your answer if;

- (i) the temperature was increased
- (ii) nitrogen gas was added to the mixture at a constant pressure.
- (iii) pressure was increased
- (iv) more oxygen was added to system at equilibrium
- (v) volume of the vessel increased

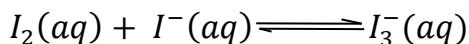
2. The reaction between nitrogen and hydrogen at 25°C and 10 atm takes place according to the following equation.



What would happen to the **concentration of ammonia** and the **value of the equilibrium constant** if;

- (i) Helium was added to the equilibrium mixture at constant pressure?
- (ii) the temperature was increased to 250°C but the pressure remains at 10 atm?
- (iii) Argon is added to the equilibrium mixture at constant volume?
- (iv) some iron is added to the equilibrium mixture

3. Iodine is sparingly soluble in water but readily dissolves in potassium iodide according to the following equilibrium



- (a) Explain why iodine is sparingly soluble in water but very soluble in potassium iodide
 - (b) (i) Write an expression for the concentration equilibrium constant, K_c .
 (ii) State any **three** characteristics of the above equilibrium.
 - (c) State and explain the effect of adding sodium thiosulphate solution to **the position of equilibrium**.
4. Phosphorus pentachloride decomposes at high temperatures according to the following equation.



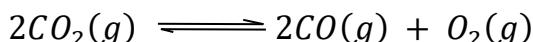
State how the **position of the equilibrium** and the **value of the equilibrium constant** would be affected and in each case give a reason for your answer if ;

- (i) the pressure was increased
- (ii) some chlorine was added to the equilibrium
- (iii) some phosphorus(III) chloride was removed from the equilibrium mixture
- (iv) the temperature was increased

- (v) volume of the container was decreased
 - (vi) adding a catalyst
5. (a) State three characteristics of a chemical equilibrium.
- (b) Phosphorus(V) chloride when heated decomposes according to the following equation.



- (i) Write the expression for the equilibrium constant, K_c .
 - (ii) When 1 mole of phosphorus(V) chloride was heated in a closed vessel at 350°C, the equilibrium mixture was found to contain 38.4% of chlorine. Calculate the equilibrium constant at 350°C.
 - (iii) The equilibrium constant at 250°C was found to be 1.54. State whether the reaction is exothermic or endothermic. Give a reason for your answer.
 - (c) State what would happen to the concentration of chlorine if the pressure in the vessel was decreased while the temperature maintained at 350°C. Give a reason for your answer.
6. When heated at 1atm, carbon dioxide decomposes according to the equation:



State and explain the effect of ;

- (i) heating the carbon dioxide at 2 atmospheres on the equilibrium concentration of oxygen
 - (ii) carrying out the decomposition at a lower temperature on the value of the equilibrium constant, K_p .
7. Hydrogen and iodine were heated in a 1 litre vessel. Explain what would happen to the equilibrium position of the reaction, equilibrium constant, and rate of attainment of equilibrium if;
- (i) sodium thiosulphate solution was added to the vessel.
 - (ii) the pressure was increased
 - (iii) concentration of iodine was increased
 - (iv) helium gas was added at constant volume.
8. The esterification reaction for formation of ethylethanoate from ethanoic acid and ethanol is shown by the equation below.

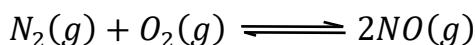


State how the amount of ethylethanoate and position of the equilibrium would be affected if:

- (i) some ethanol is added to the system
- (ii) some water is removed from the system
- (iii) concentrated sulphuric acid is added
- (iv) some sodium hydroxide solution is added

(v) the temperature was increased

9. Nitrogen and oxygen react endothermically at high temperatures according to the equation;



The equilibrium constant for the reaction at 2680K and 1 atm total pressure is 3.6×10^{-3} . Equal volumes of nitrogen and oxygen were mixed at 2680K and 1 atm total pressure and allowed to react until equilibrium is reached.

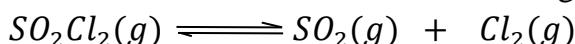
(a) Calculate the:

- (i) fraction of the original nitrogen used in the reaction
- (ii) fraction of nitrogen(II) oxide in the reaction mixture

(b) State what will happen to the value in (a)(ii) above and give a reason(s) if:

- (i) the pressure is increased to 10 atm
- (ii) the temperature is raised to 2780K
- (iii) a catalyst is added

10. Sulphur dioxide dichloride dissociates when heated according to the equation:

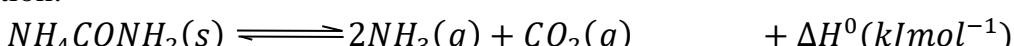


(a) At a temperature of 375°C and an overall pressure of $101325Nm^{-2}$, a sample of sulphur dioxide dichloride in the gas phase was found to be 84% dissociated. Calculate the value of equilibrium constant, K_p .

(b) State, at constant temperature, the effect on the position of equilibrium and the value in (a) above of:

- (i) adding a catalyst
- (ii) compressing the system

11. Ammonium carbamate (NH_4CONH_2) decomposes according to the following equation:



(a) Write the expression for the equilibrium constant (K_p)

(b) At equilibrium, the total pressure of the system is 0.36 atm. at 40°C. Calculate the value of K_p for the reaction at 40°C and indicate its units.

(c) State what happens to the K_p calculated in (a) if :

- (i) more solid ammonium carbamate is added to the equilibrium mixture.
- (ii) the temperature is increased to 80°C.

12. Discuss the effect of each of the following factors on the position of equilibrium of a reversible reaction, the rate of attainment of equilibrium and the value of equilibrium constant.

- (i) Temperature
- (ii) Pressure
- (iii) Catalyst
- (iv) Concentration.

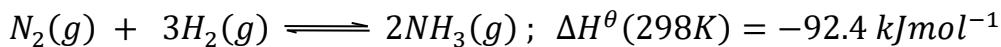
INDUSTRIAL APPLICATION OF CHEMICAL EQUILIBRIUM

The knowledge of chemical equilibrium is applied industrially in the following processes;

- Haber process
- Contact process
- Ostwald process

1. Manufacture of ammonia (the Haber process)

The reaction between dry hydrogen (*obtained from natural gas*) and dry nitrogen (*from fractional distillation of liquid air*) to form ammonia is **exothermic** and occurs with a **decrease in volume**



According to Lé Chatelier's Principle , the yield of ammonia will be greatest at **low temperature** and **high pressure**.

At a low temperature however, rate of attainment of equilibrium is low and at high temperature, the position of the equilibrium is over to the left.

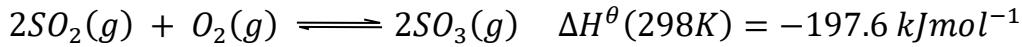
At high pressure, the cost of the equipment and running costs are high.

Therefore, in practice, a compromise has to be struck. The conditions used in this process are therefore;

- *Pressures between 200-1000 atmospheres*
- *Temperature of about 450-550°C*
- *Finely divided iron catalyst*

2. Manufacture of sulphuric acid (the Contact process)

The conversion of Sulphur dioxide (obtained by burning Sulphur in air, roasting iron pyrites, copper pyrites or oxidation of zinc blende or burning hydrogen sulphide from crude oil in air) and oxygen (obtained from fractional distillation of liquid air) to Sulphur trioxide is an **exothermic reaction** and occurs with a **decrease in volume**.



According to Lé Chatelier's Principle , the yield of ammonia will be greatest at **low temperature** and **high pressure**.

At a low temperature however, the rate of attainment of equilibrium is very slow.

Increase in pressure gives an increased yield of Sulphur trioxide but the effect is small and the yield is good even at pressures just above atmospheric pressure but not as high as those used in the Haber Process.

Still, at high pressures, sulphur dioxide liquefies.

Therefore, in practice, a compromise has to be struck. The conditions used in this process are therefore;

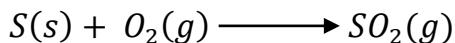
- Pressures between 1-3 atmospheres
- Temperature of about 450-500 °C
- Vanadium(V) oxide catalyst

Question

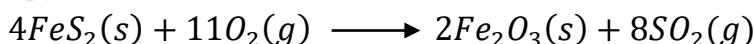
Sulphur dioxide is a raw material used in manufacture of sulphuric acid by the contact process.

- (a) With relevant equations, describe the various ways how sulphur dioxide used in this process may be obtained on a large scale.
- (b) Describe how sulphuric acid can be manufactured using one of the sources above.
- (c) Briefly describe how the sulphuric acid can be converted to superphosphate fertilizer.

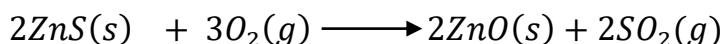
(a) Sulphur dioxide can be obtained by burning sulphur in air



or by roasting iron pyrites in air



or roasting zinc blende in air



or roasting copper pyrites



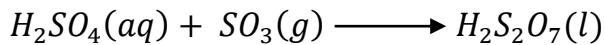
(b) Iron pyrites are roasted in air to form iron(III) oxide and sulphur dioxide.



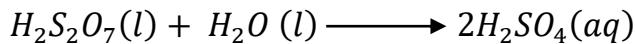
The sulphur dioxide obtained above and oxygen obtained by fractional distillation of liquid air are purified to clear them off any dust that may poison the catalyst and dried. The purified gases are passed over Vanadium(V) oxide catalyst at temperatures about 450-500 °C and pressures between 1-3 atmospheres to form sulphur trioxide.



The sulphur trioxide is dissolved in concentrated sulphuric acid to form a fuming liquid called oleum.



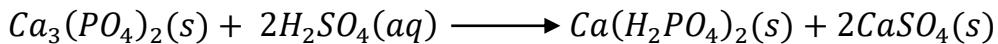
The oleum is carefully diluted with a correct amount of water to form 98% concentrated sulphuric acid.



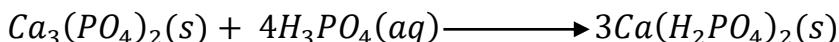
N.B. 1. Vanadium pentoxide is preferred over Platinum as catalyst because it is cheaper and not commonly poisoned by impurities

2. The sulphur trioxide is not dissolved in water because its reaction with water is **highly exothermic** and it leads to **formation of sulphuric acid sprays** that damage plants and animals

(c) Calcium phosphate is dissolved and stirred in about 65% sulphuric acid to form a mixture calcium sulphate and calcium dihydrogen phosphate. The product is dried and forms the superphosphate fertilizer.



N.B; The Single Superphosphate(SSP) fertilizer made above is less efficient because it is contaminated with Calcium sulphate. A more efficient fertilizer called Triple Superphosphate fertilizer is formed by using concentrated sulphuric acid instead.



Details of these process for conversion of ammonia formed by Haber process to nitric acid are discussed in DEMISTIFYING INORGANIC CHEMISTRY under chemistry of period 3 elements by the same author)

Questions

1. Ammonia is manufactured from hydrogen and nitrogen by the Haber process.
 - (a) Write the equation for the reaction.
 - (b) State one source of hydrogen and one source of nitrogen used in the above process
 - (c) Write an expression for the equilibrium constant, K_p for the reaction.
 - (d) State **Le Chatelier's principle**.
 - (e) The reaction in (a) above is exothermic. State and explain the effect on the above equilibrium of:
 - (i) increasing pressure
 - (ii) removing ammonia from the mixture of gases
 - (f) Explain why the synthesis of ammonia is operated at a temperature of 400°C.
 - (g) (i) Name the catalyst used in the Haber process
(ii) Describe how the catalyst works
(iii) Explain the effect of the catalyst on the position of the equilibrium.
 - (h) Write equations to show how ammonia is converted to nitric acid.
2. Sulphur dioxide is a raw material used in manufacture of sulphuric acid by the contact process. It is initially converted exothermically to sulphur trioxide during the process. On industrial scale, this conversion carried out at 450°C and 2 atmospheres in presence of a catalyst.
 - (a) Write equation for formation of sulphur trioxide in the contact process
 - (b) Name the catalyst used
 - (c) State the reasons for the choice of the temperature and pressure used to convert sulphur dioxide to sulphur trioxide.

(d) Sulphur trioxide reacts with water to form sulphuric acid.

(i) Write equation for the reaction.

(ii) State the hazard of the reaction in d(i) above and describe how it is avoided in the contact process.

(e) Concentrated sulphuric acid contains 98% of the acid. Calculate the mass of concentrated sulphuric acid required to make 500cm^3 of 1.5M solution of sulphuric acid.

(f) Name one reagent that can be used to identify the anion in sulphuric acid. State what would be observed and write the equation for the reaction that takes place when the reagent you have named is used.

(g) State two large scale uses of sulphuric acid.