DEMYSTIFYING PHYSICAL CHEMISTRY (A’LEVEL)

A simplified, well elaborated and illustrative approach to the physical chemistry

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PREFACE

The author has an inexorable curiosity in streamlining the chemistry concepts that majority of the students in Uganda consider a nut to crack.

He has taught Chemistry and Mathematics in various schools in Entebbe, Kampala, Wakiso and Butambala. This means that he has analysed the problems students at A’ level face in Chemistry.

This physical chemistry collation has been substantially organised and fully compatible with the NCDC Chemistry syllabus-2013

The author is contented that this edition contains more than enough material as regards A’ level physical chemistry and the subject matter has been arranged and structured so that it can be tackled by students of different abilities and the text is in a readable font to all kinds of eyes.

Indeed this book is vital for a student to teach him/herself even in absence of a teacher. However, the teacher is as well vital in cases where you may not well interprete the content. The author has tried to link physical chemistry with inorganic and organic concepts where he feels it is necessary.

Variety of examples are given, more than one methods of solving a problem illustrated and a diversity of typical examinable revision questions in each subtopic but no answers such that research and consultation is enhanced.

Also feel free to contact the author using contacts or social media platforms at the back cover of the book for clarity, recommendations, guidance or advice.

This is the only book that you will not regret to have come across.

DEDICATION

All my parents and friends for their support, discipline and a spiritual guidance

My dear students in the various schools I have worked for their encouragement and courage

Lastly to my lovely daughters **Joselyne Fortunate Kayiira** and **Jacqueline Franches Kayiira**

ACKNOWLEDGEMENTS

I wish to thank the following people without whom I would not be able to produce this book.

First, my parents; **Mrs. Nakavuma Harriet** and **Mr. Ssentume Fahad** who thought it wise that they should transmit some of the traits they are gifted with through me to the next generations and my dear spouse, **Noeline Nakasumba** for giving me ample time to make this wonderful compilation.

Senior teachers like **Mr.Opia Richard**, **Mr.Mawejje Henry** and **Mr. Sseruuma** for the inspiration I got from them to write this book. Through their wonderful lessons, I was guided and directed throughout my course of studying and applying chemistry.

All colleagues in the profession, with whom we shared online or by a call for solving some problems before we incorporated them in this text

I am finally grateful to **Mr. Kibira Ivan**, **Hajj Sulait Kato Kasagga** and **Hajj Mukasa Ibrahim** for their guidance and encouragement in releasing this edition.

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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

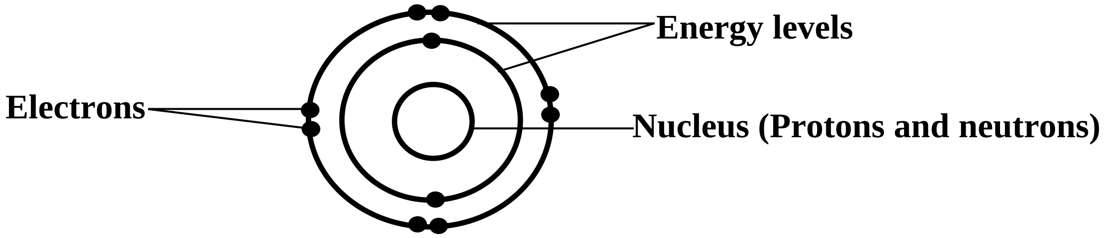
An atom is spherical in shape and has a small region in the center called the nucleus. The atom contains **protons** and **neutrons**, and **electrons** as fundamental particles.

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 charges) 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

Leptons		*Hadrons*			
		baryons		***mesons***	
electron	e^-	proton	p^+	pions	π^+
					π^0
muon	μ^-	neutron	n	kaons	K^+
					K^0
neutrino	v	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

An electron has a mass of $^1/_{1836}$ 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**
Electron	-	$^1/_{1836}$
Proton	+	*1*
Neutron	*No charge*	*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_ZX 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	${}^{1}_{1}H$	1	1	0
	Deuterium	${}^{2}_{1}H$	1	1	1
	Tritium	${}^{3}_{1}H$	1	1	2
Carbon	Carbon-12	${}^{12}_{6}C$	6	6	6
	Carbon-14	${}^{14}_{6}C$	6	6	8
Oxygen	Oxygen-16	${}^{16}_{8}O$	8	8	8
	Oxygen-17	${}^{17}_{8}O$	8	8	9
	Oxygen-18	${}^{18}_{8}O$	8	8	10
Chlorine	Chlorine-35	${}^{35}_{17}Cl$	17	17	18
	Chlorine-37	${}^{37}_{17}Cl$	17	17	20
Uranium	Uranium-234	${}^{234}_{92}U$	92	92	142
	Uranium-235	${}^{235}_{92}U$	92	92	143
	Uranium-238	${}^{238}_{92}U$	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

$$Na \xrightarrow{loses\ one\ electron} Na^{+} + e$$

(ii) Formation of Aluminium ion

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

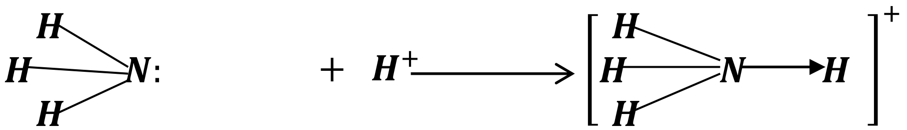
The atom therefore has three electrons more than the stable configuration of a noble gas, $2:8$.

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

$$Al \xrightarrow{loses\ three\ electrons} Al^{3+} + 3e$$

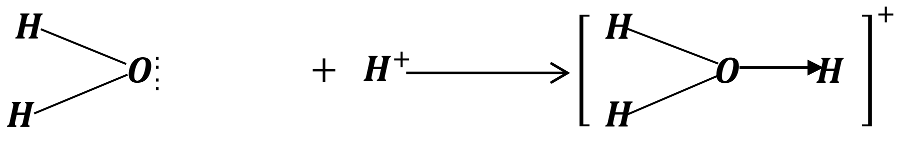
(iii) Formation of Ammonium ion

This is an ion formed by coordination of ammonia to a hydrogen ion. The formation of this ion is possible because 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 because 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

$$Cl + e \xrightarrow{gains\ one\ electron} Cl^{-}$$

(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

$$O + 2e \xrightarrow{gains\ two\ electrons} O^{2-}$$

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^{-}	Hydr**ide**
N^{3-}	Nitr**ide**
B^{3-}	Bor**ide**
C^{4-}	Carb**ide**
Si^{4-}	Silic**ide**
O^{2-}	Ox**ide**
Cl^{-}	Chlor**ide**
I^{-}	Iod**ide**
Br^{-}	Brom**ide**
F^{-}	Fluor**ide**
S^{2-}	Sulph**ide**
P^{3-}	Phosph**ide**

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
$CH_3COO\bar{O}$	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 ion
I_3^-	Triiodide ion

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 state 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) 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
$NaCO_3.10H_2O$	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	*Tin has more than one oxidation states (+2 and +4). Therefore its exact oxidation state in the compound should be depicted*
Tin (IV) sulphate	*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*
Tin(IV)sulphate	*There should some little space between name of the cation with its charge, and name of the anion*
Tin(iv) sulphate	*Roman numerals do not have dots (.) above them.*
Tin(IIII) sulphate	*Roman numeral is wrong*

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.

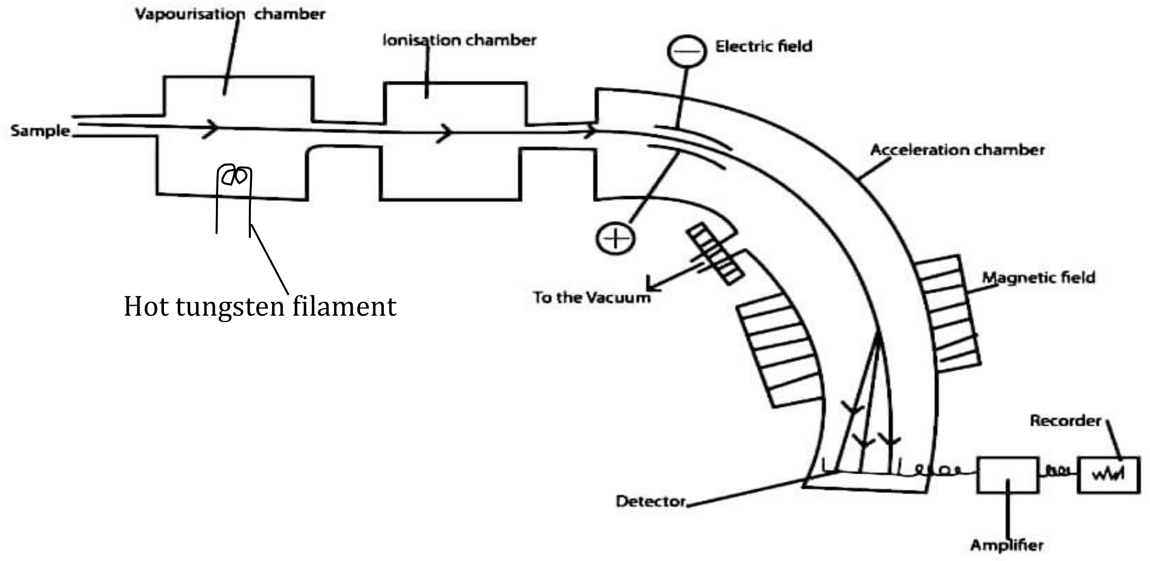
The earliest experiments of mass spectroscopy by J. J. Thomson used a stream of positive ions from a discharge tube, which were deflected by parallel electric and magnetic fields at right angles to the beam. Each type of ion formed a parabolic trace on a photographic plate (a mass spectrograph). In modern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

$$X(g) \longrightarrow X^{+}(g) + e \qquad for\ 1\ electron$$
$$X(g) \longrightarrow X^{2+}(g) + e \qquad for\ 2\ electrons$$

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;***

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

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.

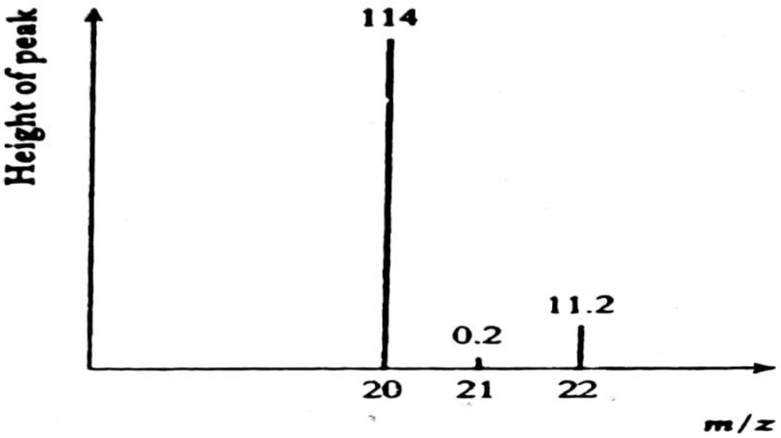
Interpreting a mass spectrum

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 $^{20}Ne^{+}$, $^{21}Ne^{+}$ and $^{22}Ne^{+}$ respectively. These ions are formed by bombardment of the gaseous atoms by electrons as shown below;

$$^{20}Ne(g)+e \longrightarrow {}^{20}Ne^+(g)$$
$$^{21}Ne(g)+e \longrightarrow {}^{21}Ne^+(g)$$
$$^{22}Ne(g)+e \longrightarrow {}^{22}Ne^+(g)$$

The height of each peak is related to the relative abundance of each isotope of neon.
$^{20}Ne^+$has the highest peak so ^{20}Ne is the most abundant isotope.
$^{21}Ne^+$has the lowest peak so ^{21}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

$$Total\ height = 114 + 0.2 + 11.2 = 125.4$$

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

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

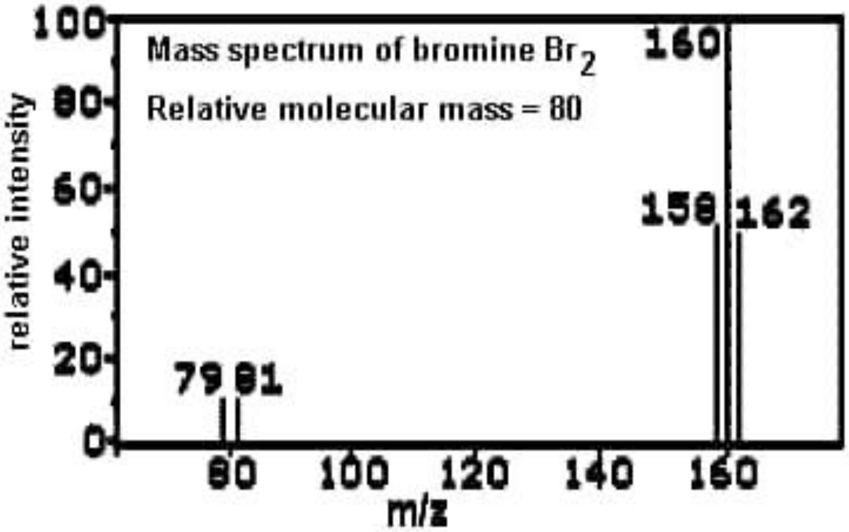
$$Percentage\ abundance\ of\ Neon - 22 = \left(\frac{11.2}{125.4} \times 100\right) = 8.93$$

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

$$R.A.M = \left(20 \times {}^{90.91}/_{100}\right) + \left(21 \times {}^{0.16}/_{100}\right) + \left(22 \times {}^{8.93}/_{100}\right)$$

$$\boldsymbol{R.A.M = 20.18}$$

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

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.

Peak at $^{m}/_{z}$ value of;	Formula of ion
158	$[{}^{79}Br — {}^{79}Br]^+$
160	$[{}^{79}Br — {}^{81}Br]^+$
162	$[{}^{81}Br — {}^{81}Br]^+$

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

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

$$Total\ ratio = 1 + 1 = 2$$

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

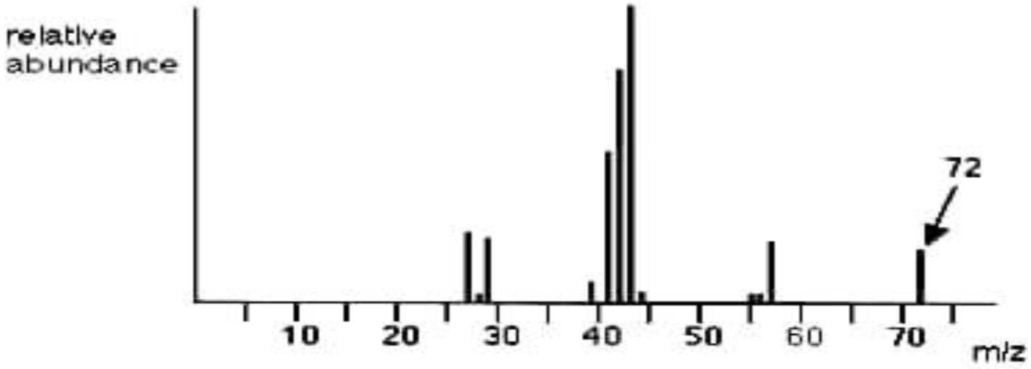
$$Percentage\ abundance\ of\ Bromine - 81 = \left(\frac{1}{2} \times 100\right) = 50$$

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

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

$$\boldsymbol{R.A.M = 80}$$

Consider the mass spectrum below for pentane $(CH_3CH_2CH_2CH_2CH_3)$



The largest mass-to-charge ratio value is 72. The line at this $^{m}/_{z}$ represents the original molecular ion, $CH_3CH_2CH_2CH_2CH_3^+$. It is formed by the reaction;

$$CH_3CH_2CH_2CH_2CH_3 + e \longrightarrow CH_3CH_2CH_2CH_2CH_3^+ + 2e$$

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.

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.

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

$$where\ f\ is\ the\ the\ natural\ abundance\ of\ the\ isotope$$

$$M\ is\ the\ mass\ number\ of\ the\ isotope$$

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;

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

$$Average\ atomic\ mass = \left(\frac{(75.77 \times 35) + (24.23 \times 37}{100}\right)$$

$$Average\ atomic\ mass = 35.48\ amu$$

Relative atomic mass(Ar)

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

or

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

$$Relative\ atomic\ mass(A_r) = \frac{average\ mass\ of\ atom}{\frac{1}{12} \times mass\ of\ {}^{12}_{6}C}$$

Relative molecular mass(Mr)

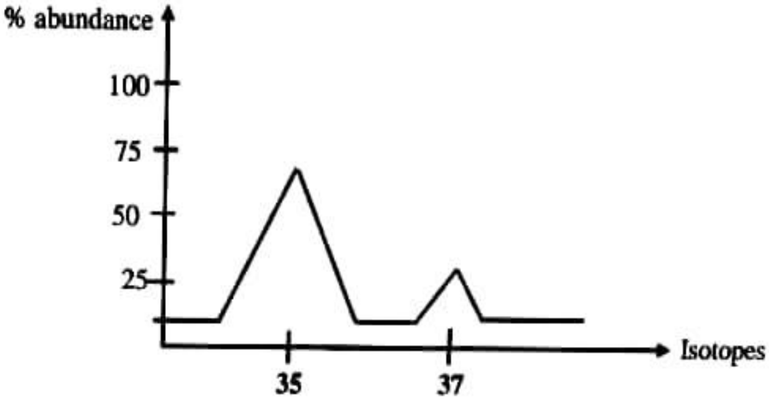
Relative is the average mass of one molecule of a compound to $^{1}/_{12}$ th of the mass of an atom of the carbon-12 isotope.

$$Relative\ molecular\ mass(M_r) = \frac{mass\ of\ one\ molecule\ of\ a\ compound}{\frac{1}{12} \times mass\ of\ {}^{12}_{6}C}$$

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

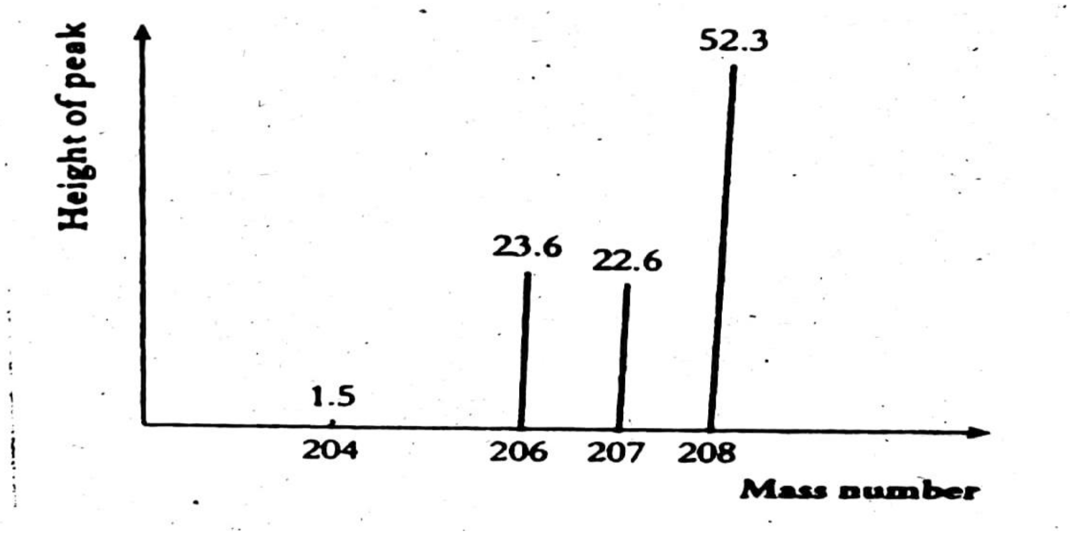
$$\boldsymbol{R.A.M = \sum Relative\ isotopic\ mass \times proportion\ of\ isotope}$$

$$\boldsymbol{R.A.M = \left(35 \times {}^{75}/_{100}\right) + \left(37 \times {}^{25}/_{100}\right)}$$

$$\boldsymbol{R.A.M = 35.5}$$

---

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) $\boldsymbol{Total\ height = 1.5 + 23.6 + 22.6 + 52.3 = 100}$

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

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

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

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

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

$$\boldsymbol{R.A.M = \left(204 \times {}^{1.5}/_{100}\right) + \left(206 \times {}^{23.6}/_{100}\right) + \left(207 \times {}^{22.6}/_{100}\right) + \left(208 \times {}^{52.3}/_{100}\right)}$$

$$\boldsymbol{R.A.M = 207.242}$$

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

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) $let\ the\ percentage\ abundance\ of\ neon-20\ be\ y$

$$The\ percentage\ abundance\ of\ neon-22 = (100-\ y)$$

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

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

$$2018 = 2200 - 2y$$

$$y = 91$$

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

(b) $number\ of\ moles\ on\ neon\ in\ 13.2\ g = {}^{13.2}/_{20.18} = 0.654$

$$number\ of\ neon\ atoms\ in\ 0.654\ mole = 0.654 \times 6.022 \times 10^{23}$$

$$= 3.938 \times 10^{23}\ atoms$$

$$number\ of\ neon-22\ atoms\ present = {}^{9}/_{100} \times 3.938 \times 10^{23}$$

$$= \mathbf{3.544 \times 10^{22}} \boldsymbol{atoms}.$$

---

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.

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

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

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

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

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

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

$$\boldsymbol{R.A.M = \left(204 \times {}^{1.42}/_{100}\right) + \left(206 \times {}^{24.07}/_{100}\right) + \left(207 \times {}^{22.12}/_{100}\right) + \left(208 \times {}^{52.4}/_{100}\right)}$$

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

---

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 and are in a ratio of 9:6:1.**

   Chlorine has two isotopes; chlorine-35 and chlorine-37.
   The peak at 84 is due to the ion $[CH_2{}^{35}Cl^{35}Cl]^+$
   The peak at 86 is due to the ion $[CH_2{}^{35}Cl^{37}Cl]^+$
   The peak at 88 is due to the ion $[CH_2{}^{37}Cl^{37}Cl]^+$

The peak with mass to charge ratio 84 is longest because chlorine-35 is the most abundant isotope followed by the peak with mass to charge ratio 86 whose ion still has chlorine-35 in it. The peak with mass to charge ratio 88 is shortest because chlorine-37 is less abundant than chlorine-35.

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)

Peak at $m/_Z$ value of	***Formula of ion***
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.

3. (a) Define the term relative atomic mass.
   (b) The table below shows the mass numbers and relative intensities of an element R.

Mass number	*Relative intensity*
20	0.91
21	0.0026
22	0.088

Calculate the relative atomic mass of R

(c) State two advantages of using a mass spectrometer in measuring relative atomic mass.

4. (a) Define the term relative atomic mass.
   (b) The mass spectrum of a sample of strontium contains four peaks with mass to charge ratios $\left(\frac{\mu}{z}\right)$ and relative abundances shown below

$\left(\frac{\boldsymbol{\mu}}{\boldsymbol{z}}\right)$	84	86	87	88
Relative abundance	0.60	9.90	7.00	82.50

(i) Explain why strontium shows three peaks in its mass spectrum

(ii) Use the information in the table to calculate the relative atomic mass of strontium.

5. The mass spectrum of a sample of magnesium contains three peaks with mass-charge ratios and relative intensities show below.

$\boldsymbol{m/z}$	24	25	26
Relative intensity	1	0.127	0.139

(i) Explain why magnesium gives three peaks in its spectrum.

(ii) Use the information in the table to calculate an accurate value for the relative atomic mass of magnesium.

6. The relative atomic mass of magnesium is 24.3. Naturally occurring magnesium has three isotopes Mg-24, Mg-25 and Mg-26. If the percentage abundance of magnesium-24 is eight times that of magnesium-26. Calculate the percentage abundances of each magnesium isotope in the sample.
7. (a) Explain what is meant by each of the following terms;
   - (i) Atomic number
   - (ii) Mass number

(iii) Relative atomic mass
(iv) Isotope

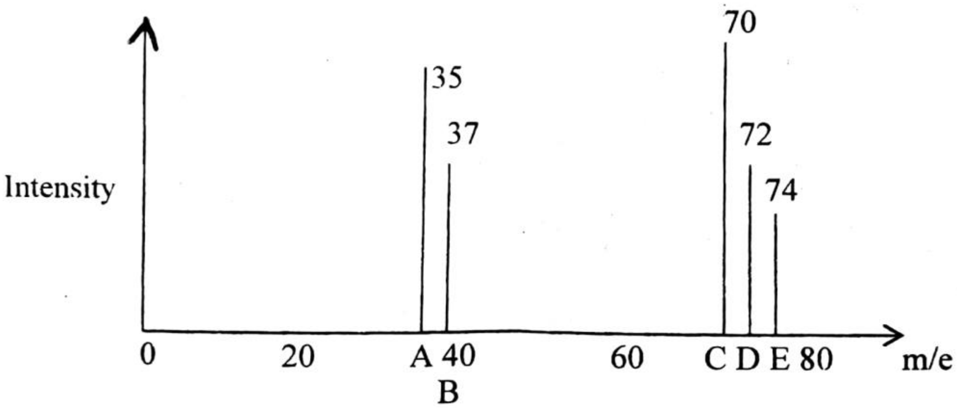
(b) A mass spectrometer measures the relative abundance of ions with different values of m/z. Explain the meaning of the symbols m and z.

(c) A sample of nickel was analysed in a mass spectrometer. Three peaks were observed with the properties shown in the table below.

Relative abundance	69	27	4
m/z	58	60	62

(i) Write the full symbol, including the mass number and atomic number for the ion responsible for the peak at m/z value 58.
(ii) Calculate the relative atomic mass of this sample of nickel.

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



(a) State the ions responsible for each of the peaks.
(b) State why the peaks of height 35 and 70 are relatively longer than other peaks.
(c) Use the spectrum to calculate the relative atomic mass of chlorine.
(d) When chloromethane is analysed in the mass spectrometer, two peaks are observed having an abundance ratio of 3:1. Explain this observation.
(e) The mass spectrum of C_2H_5Cl shows peaks corresponding to ^{1}H, ^{2}H, ^{12}C, ^{13}C, ^{35}Cl and ^{37}Cl. Calculate the mass number of the
  (i) most abundant molecular ion
  (ii) heaviest molecular ion
(f) Write the formulae of all the possible ions that contribute to the peak at a mass number 66.

9. The mass spectrum of neon consists of three lines corresponding to relative mass/charge ratios of 20, 21 and 22 with relative intensities in a ratio 0.91 : 0.0026 : 0.088 respectively. Calculate the relative atomic mass of neon.
10. Chlorine has two isotopes of relative atomic masses 34.97 and 36.96 respectively and relative abundances of 75.77% and 24.23% respectively. Calculate the relative atomic mass of chlorine.
11. Chlorine has two isotopes; chlorine-35 and chlorine-37. If the relative atomic mass of chlorine is 35.5. Calculate the ratio of the two isotopes in a natural sample.
12. Natural oxygen consists of 99.76% of an isotope of mass 16, 0.04% of an isotope of mass 17 and 0.20% of an isotope of mass 18. Calculate the average mass of an atom of natural oxygen.
13. Copper, relative atomic mass 63.55 has two isotopes of mass numbers 63 and 65. Calculate the percentage abundance of the isotopes.

THE MOLE CONCEPT

The number of atoms in 1 mole of ^{12}C is obtained by dividing 12g by the mass of an individual atom of ^{12}C . The answer has a value 6.022×10^{23} and is known as the ***Avogadro constant (L)***. It is this value that is used to define an amount of a substance known as a mole.

A mole is therefore defined as the amount of substance containing as many elementary particles as those in 12 g of carbon-12

or

A mole is the amount of substance which contains $\mathbf{6.022 \times 10^{23}}$ ***elementary particles.***
The particles may be molecules, atoms, ions, radicals, electrons or any other specified particle.

Summary

Substance	***Atomic mass/ molecular mass***	***Number of particles***
1 mole of C atoms	12g	6.022×10^{23}atoms
1 mole of Mg^{2+}ions	24g	6.022×10^{23}ions
1 mole of H_2SO_4	98g	6.022×10^{23}molecules
1 mole of N atoms	14g	6.022×10^{23}atoms
1 mole of N_2 gas	28g	6.022×10^{23}molecules

Calculating molar masses of elements and compounds

Molar mass(M) is the mass of one mole of a substance.
Its unit is grams. The molar mass of carbon is 12 g. Molar mass has units but relative molecular mass has no units.

Number of moles of a substance $= \frac{\boldsymbol{mass\ of\ a\ substance}}{\boldsymbol{molar\ mass\ of\ the\ substance}}$

Molar mass of an element= relative atomic mass expressed in grams

Molar mass of a compound = relative molecular mass expressed in grams

Examples

Calculate the molar masses of the following

- **(i)** **Ethanol**
- **(ii)** **Carbon dioxide**
- **(iii)** **Potassium iodate**
- **(iv)** **Sodium thiosulphate-5-water**

A similar approach as that of O level is used. But take note that molar mass has units

Consider a compound Z whose molecular formula is $P_pQ_qR_r$, with atomic masses $P = s, Q = t, R = u$

The molar mass of Z is given as

$$(Atomic\ mass\ of\ P \times p) + (Atomic\ mass\ of\ Q \times q) + (Atomic\ mass\ of\ R \times r)$$

$$\text{Molar mass} = (s \times p) + (t \times q) + (u \times r)$$

(i) Ethanol ($\boldsymbol{CH_3CH_2OH}$) $Molar\ mass = (12 \times 2) + (6 \times 1) + (1 \times 16)$ $= \boldsymbol{46g}$	(ii) Carbon dioxide($\boldsymbol{CO_2}$) $Molar\ mass = (12 \times 1) + (2 \times 16) \ = \boldsymbol{44g}$
(iii) Potassium iodate($\boldsymbol{KIO_3}$) $Molar\ mass$ $= (39 \times 1) + (127 \times 1) + (3 \times 16)$ $= \boldsymbol{214g}$	(iv) Sodium thiosulphate-5-water($Na_2S_2O_3.5H_2O$) $Molar\ mass = (23 \times 2) + (32 \times 2)$ $+ (3 \times 16) + (5 \times 18)$ $= \boldsymbol{248g}$

Molar mass-mole conversions

In order to make these conversions, molar mass should be calculated from the molecular formula of the compound. It should be ascertained that a correct formula of the compound in terms of number of atoms is written. If the formula is wrong, then the molar mass cannot be correct

1 mole of a compound weighs the relative molecular mass in grams.

Number of moles of a substance $= \frac{mass\ of\ a\ substance}{molar\ mass\ of\ the\ substance}$

Molar mass of a substance$= \frac{mass\ of\ a\ substance}{number\ of\ moles\ of\ the\ substance}$

Mass of a substance$=$ $number\ of\ moles\ of\ a\ substance \times molar\ mass\ of\ the\ substance$

Although the above formulae are well known and ease calculation work, it is advisable to use first principles in the examination work.

Examples

(a) Calculate the number of moles in;

- **(i) 3.16g of potassium manganate(VII)**
- **(ii) 0.5g of potassium persulphate**

(i) Molar mass of potassium manganate(VII) ($KMnO_4$)

$$Molar\ mass = (39 \times 1) + (55 \times 1) + (4 \times 16) = 158g$$

$$158g\ of KMnO_4\ contain\ 1\ mole$$

$$3.16g\ \ of KMnO_4\ contain\ \left(\frac{3.16 \times 1}{158}\right) mole$$

$$= 0.02\ mole$$

(ii) Molar mass of potassium persulphate ($K_2S_2O_8$)

$$Molar\ mass = (39 \times 2) + (32 \times 2) + (16 \times 8) = 270g$$

$$270g\ of K_2S_2O_8\ contain\ 1\ mole$$

$$0.5g\ \ of K_2S_2O_8\ contain\ \left(\frac{0.5 \times 1}{270}\right) mole$$

$$= 1.852 \times 10^{-3}\ mole$$

(b) Calculate the mass contained in 3.9375×10^{-3} moles of potassium chlorate

Molar mass of potassium chlorate ($KClO_3$)

$$Molar\ mass = (39 \times 1) + (35.5 \times 1) + (3 \times 16) = 122.5g$$

$$1\ mole\ of\ KClO_3\ weighs\ 122.5g$$

$$3.9375 \times 10^{-3}\ moles\ weigh\ \left(\frac{3.9375 \times 10^{-3} \times 122.5}{1}\right) g$$

$$= 0.482g$$

Questions

1. Work out the molar masses of each of the following

$$(H = 1;\ B = 11;\ C = 12;\ N = 14;\ O = 16;\ Na = 23; S = 32;\ Cl = 35.5;\ K = 39; Cr = 52;\ Mn = 55;\ Fe = 56;\ I = 127)$$

(i) Chlorine gas
(ii) Iodine molecule
(iii) Oxalic acid crystal
(iv) Sodium ethanedioate
(v) Sodium carbonate decahydrate
(vi) Sodium hydrogencarbonate
(vii) Sodium hydroxide
(viii) Disodium tetraborate decahydrate($\boldsymbol{Na_2B_4O_7.10H_2O}$)
(ix) Potassium chlorate
(x) Potassium iodate
(xi) Potassium persulphate(potassium peroxodisulphate)
(xii) Potassium dichromate(VI)
(xiii) Potassium manganate(VII)
(xiv) Hydrochloric acid
(xv) Hydrogen peroxide
(xvi) Sulphuric acid
(xvii) Iron(II) sulphate-7-water
(xviii) Diammonium iron(II) sulphate hexahydrate ($\boldsymbol{(NH_4)_2SO_4FeSO_4.6H_2O}$)

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2. Calculate the number of moles in;
   (i) 1.0g of potassium iodate
   (ii) 19.1g of disodium tetraborate decahydrate
   (iii) 1.0g of sodium ethanedioate
   (iv) 6.0g of Diammonium iron(II) sulphate-6-water
   (v) 1.2g of potassium dichromate
   (vi) 6.2g of copper(II) sulphate pentahydrate
3. Determine the mass of;
   (i) 0.01288 moles of chlorine gas
   (ii) 1.312×10^{-3} moles of potassium iodate
   (iii) 7.76×10^{-2} moles of sodium hydrogencarbonate
   (iv) 0.025 mole of sodium ethanedioate
   (v) 0.00833 mole of copper(II) ions

Limiting reactants and excess reactants

In a perfect reaction, we would have exactly as much of each reactant that we need to convert everything to a product. However in real practice, it is much more likely that we have non-stoichiometric amounts of reactants.

Consider a scenario where we are making grilled cheese sandwiches.

$$1\ slice\ of\ cheese + 2\ slices\ of\ bread \longrightarrow 1\ sandwich.$$

Stoichiometric amounts of cheese and bread required are in a ratio 1:2. If we are provided with 28 slices of bread and 11 slices of cheese, one would prepare 11 sandwiches using all the provided cheese and 22 slices of bread. This leaves six slices of bread not used. In this scenario, the number of sandwiches prepared is limited by the number of cheese slices and the bread slices have been provided in excess.

A limiting reactant is that reactant which is completely used up in a chemical reaction and limits the quantities of the products formed.

An excess reactant is that reactant that remains after a chemical reaction due to the limiting reactant being used up.

Percentage yields in a chemical reaction

The amount of product that may be produced by a chemical reaction under specified conditions, as calculated per the stoichiometry of an appropriate balanced chemical equation is called **theoretical yield** of the reaction. In practice, the amount of product obtained is called the **actual yield**, and is often less than the theoretical yield for a number of reasons. This is because some reactions are inherently inefficient, being accompanied by side reactions which produce other products. Others by nature are incomplete. Some products are difficult to collect without some loss, and so less than perfect recovery will reduce the actual yield.

The extent to which a reaction’s theoretical yield is expressed as **percentage yield**.

$$percentage\ yield = \left(\frac{actual\ yield}{theoretical\ yield}\right) \times 100$$

Experiment to demonstrate concept of limiting and excess reactants, theoretical yield, actual yield and percentage yield.

Weigh a beaker and record its mass (m_b).
Then weigh accurately 1.00g of iron powder into the beaker.
Measure 30cm^3 of 1.0M copper(II) sulphate solution using a measuring cylinder and slowly add it to the beaker above.
Stir the solution until the solution has completely turned colour from blue and a brown copper solid formed.

$$CuSO_4(aq) + Fe(s) \longrightarrow Cu(s) + FeSO_4(aq)$$

Decant off the resultant solution carefully and do not lose any copper formed.
The copper formed is washed several times with distilled water, and then with acetone, and dried.
The beaker together with dried copper is weighed (m_c).

Treatment of results;

$$mass\ of\ copper\ formed = (m_c - m_b)$$

$$number\ of\ moles\ of\ iron\ used = {}^{1.00}/_{56} = 0.017857.$$

$$number\ of\ moles\ of\ copper\ formed = {}^{(m_c - m_b)}/_{63.5}$$

$$number\ of\ moles\ of\ copper(II)\ sulphate\ used = \left(\frac{30 \times 1}{1000}\right) = 0.03$$

$$from\ equation;\ mole\ ratio\ of\ CuSO_4\!:\!Fe\ is\ 1\!:\!1,\ since\ moles\ of\ copper(II)\ sulphate\ are\ more\ than\ those\ of\ iron\ used,\ copper(II) sulphate\ is\ the\ \boldsymbol{excess}\ reagent\ and\ iron\ is\ \boldsymbol{limiting}.$$

$$Actual\ yield\ of\ copper = {}^{(m_c - m_b)}/_{63.5}$$

$$using\ mole\ ratio\ Cu\!:\!Fe\ is\ also\ 1\!:\!1,\ then\ theoretical\ yield\ of\ copper = 0.017857$$

$$percentage\ yield\ of\ copper\ is\ got\ from = \left(\frac{actual\ yield}{0.017857}\right) \times 100$$

Examples

1. **What mass of aluminium chloride can be formed from 34.0g of aluminium and 12320 cm^3 of chlorine gas?**

(*1 mole of a gas occupies 22.4 litres at s.t.p;* $\boldsymbol{Al = 27, Cl = 35.5}$)

$$number\ of\ moles\ of\ aluminium = {}^{34.0}/_{27} = 1.259$$

$$number\ of\ moles\ of\ chlorine = {}^{12320}/_{22400} = 0.55$$

$$2Al(s) + 3Cl_2(g) \longrightarrow 2AlCl_3(s)$$

$$2\ moles\ of\ Al\ react\ with\ 3\ moles\ of\ Cl_2$$

$$1.259\ moles\ of\ Al\ react\ with\ \left(\frac{1.259 \times 3}{2}\right)\ moles\ of\ Cl_2$$

$$= 1.8885\ moles\ of\ Cl_2$$

$$but\ this\ number\ of\ moles\ of\ chlorine\ is\ greater\ than\ the\ available\ number\ of\ moles. This\ implies\ that\ aluminium\ is\ an\ excess\ reagent.$$

$$3\ moles\ of\ Cl_2\ react\ with\ 2\ moles\ of\ Al$$

$$0.55\ moles\ of\ Cl_2\ react\ with\ \left(\frac{0.55 \times 2}{3}\right)\ moles\ of\ Al$$

$$= 0.3667\ moles\ of\ Al$$

$$2\ moles\ of\ Al\ form\ 2\ moles\ of\ AlCl_3$$

$$0.3667\ moles\ of\ Al\ form\ \left(\frac{0.3667 \times 2}{2}\right) moles$$

$$= 0.3667\ moles\ of\ AlCl_3$$

$$molar\ mass\ of\ AlCl_3 = (27 \times 1) + (3 \times 35.5) = 133.5g$$

$$\boldsymbol{mass\ of\ AlCl_3\ formed} = (\boldsymbol{133.5 \times 0.3667}) = \boldsymbol{48.95g}$$

2. Sodium carbonate reacts with calcium chloride to form calcium carbonate and sodium chloride. In an experiment, 53g of sodium carbonate and 44.4 g of calcium chloride were mixed forming 23.6g of calcium carbonate.

(i) What is the limiting reagent of the reaction?

(ii) Calculate the percentage yield of calcium carbonate.

$$Na_2CO_3(aq) + CaCl_2(aq) \longrightarrow 2NaCl(aq) + CaCO_3(s)$$
$$molar\ mass\ of\ Na_2CO_3 = (2 \times 23) + (12 \times 1) + (3 \times 16) = 106g$$
$$molar\ mass\ of\ CaCl_2 = (1 \times 40) + (2 \times 35.5) = 110g$$
$$number\ of\ available\ moles\ of\ \ Na_2CO_3 = {}^{53}/_{106} = 0.5$$
$$number\ of\ available\ moles\ of\ CaCl_2 = {}^{44.4}/_{111} = 0.4$$
$$from\ equation;$$
$$1\ mole\ of\ CaCl_2\ reacts\ with\ 1\ mole\ of\ Na_2CO_3$$
$$0.4\ mole\ of\ CaCl_2\ reacts\ with\ 0.4\ mole\ of\ Na_2CO_3$$
$$There\ is\ an\ excess\ of\ (0.5 - 0.4) = 0.1\ mole\ of\ Na_2CO_3$$
$$\boldsymbol{therefore\ calcium\ chloride\ is\ the\ limiting\ reagent}.$$

The limiting reagent is used to calculate percentage yield.

$$Actual\ yield\ of\ calcium\ carbonate = 23.6g$$

$$1\ mole\ of\ CaCl_2\ yields\ with\ 1\ mole\ of\ CaCO_3$$
$$0.4\ mole\ of\ CaCl_2\ yield\ 0.4\ mole\ of\ CaCO_3$$
$$molar\ mass\ of\ CaCO_3 = (1 \times 40) + (12 \times 1) + (3 \times 16) = 100g$$

$$theoretical\ mass\ of\ CaCO_3\ formed = (100 \times 0.4) = 40g$$

$$percentage\ yield\ of\ calcium\ carbonate = \left(\frac{actual\ yield}{theoretical\ yield}\right) \times 100$$

$$percentage\ yield\ of\ calcium\ carbonate = \left(\frac{23.6}{40}\right) \times 100$$

$$\boldsymbol{percentage\ yield\ of\ calcium\ carbonate = 59}\%$$

3. 0.50g of a fertilizer containing ammonium sulphate was warmed with sodium hydroxide solution to expel all ammonia gas which was trapped and absorbed in 100cm^3 of 0.10M hydrochloric acid solution. The excess acid required 55.90 cm^3 of 0.1M sodium hydroxide solution for neutralisation. Calculate the percentage of ammonium sulphate in the sample.

Theory; *Warming any ammonium salt with an alkali liberates ammonia gas. All the ammonia formed reacted with hydrochloric acid but the acid was as excess reactant and ammonia was limiting. So the excess hydrochloric acid(that did not react with ammonia) was neutralized with sodium hydroxide.*

Moles of $NaOH$ that reacted with excess acid

$$= \left(\frac{0.1 \times 55.90}{1000}\right) = 0.00559$$

$$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

$$Since\ mole\ ratio\ of NaOH : HCl = 1:1$$

$$moles\ of\ excess\ HCl = 0.00559$$

Original number of moles of hydrochloric acid

$$= \left(\frac{0.1 \times 100}{1000}\right) = 0.01$$

Number of moles of hydrochloric acid that reacted with ammonia

$$= 0.01 - 0.00559 = 0.00441$$

$$NH_3(g) + HCl(aq) \longrightarrow NH_4Cl(aq)$$

$$Since\ mole\ ratio\ of\ NH_3 : HCl = 1:1$$

$$number\ of\ moles\ of\ NH_3\ that\ reacted\ with\ HCl\ = 0.00441$$

$$(NH_4)_2SO_4(s) + 2NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2NH_3(g) + 2H_2O(l)$$

$$2\ moles\ of\ NH_3\ are\ evolved\ from\ 1\ mole\ of\ (NH_4)_2SO_4$$

$$0.00441\ mole\ of\ NH_3\ are\ evolved\ from \left(\frac{0.00441 \times 1}{2}\right)$$

$$= 0.002205\ moles$$

$$molar\ mass\ of\ (NH_4)_2SO_4 = (2 \times 14) + (8 \times 1) + (32 \times 1) + (16 \times 4) \qquad = 132g$$

$$mass\ of\ (NH_4)_2SO_4\ present\ in\ the\ fertiliser = (132 \times 0.002205) = 0.291g$$

$$percentage\ of (NH_4)_2SO_4 = \left(\frac{mass\ of\ (NH_4)_2SO_4\ present}{mass\ of\ fertiliser}\right) \times 100$$

$$= \left(\frac{0.291}{0.50}\right) \times 100$$

$$= \mathbf{58.2}\%$$

Questions

1. What is the limiting reagent when 5.00g of hydrogen and 10.0g of oxygen react to form water?
2. Toluene is oxidised by air under carefully controlled conditions to benzoic acid. Benzoic acid is used to prepare the food preservative, sodium benzoate. What is the percentage yield of a reaction that converts 1.000 kg of toluene to 1.21kg of benzoic acid?

3. In a laboratory experiment, the reaction of 3 moles of hydrogen with 2 moles of iodine produced 1 mole of hydrogen iodide. Determine the theoretical yield in grams and percentage yield.
4. 1.274g of copper(II) sulphate was reacted with excess zinc metal to produce 0.392g of copper. Calculate the percentage yield.
5. 1.07g of anhydrous sodium carbonate was dissolved in 50cm^3 of an acid solution. The resultant solution required 24.6cm^3 of 0.237M sodium hydroxide for complete neutralisation. Calculate the molarity of the acid solution.
6. 27.825g of a normal carbonate of a univalent metal Y, was dissolved in 320.0cm^3 of a 2.5M monobasic acid solution. The resultant solution was boiled, cooled and diluted to one litre of solution. 25cm^3 of this solution required 34.375cm^3 of 0.2M potassium hydroxide for complete neutralisation. Calculate the relative atomic mass of Y.
7. 50cm^3 of a concentrated solution of hydrochloric acid was added to 200cm^3 of 0.5M sodium hydroxide solution. The excess base required 35.0cm^3 of 0.2M nitric acid solution for complete neutralisation. Calculate the molarity of the concentrated hydrochloric acid solution.
8. 50cm^3 of concentrated potassium hydroxide solution was diluted to 250cm^3. 25cm^3 of this solution was reacted with 100cm^3 of 0.5M hydrochloric acid. If 26.42cm^3 of 0.125M sodium hydroxide solution was needed to neutralise the excess acid. Determine the molarity of the potassium hydroxide in the original 50cm^3.

Avogadro's law

The Italian scientist Avogadro, in 1811 suggested that in gaseous elements like chlorine and hydrogen, the atoms joined to form larger particles containing two or more atoms. He called the larger particles **molecules**. *A molecule is therefore defined as a group of like or unlike atoms, chemically combined together*.

Avogadro came up with a hypothesis that then became a theory to now a law which states that;

Equal volumes of all gases measured at the same conditions of temperature and pressure contain the same number of molecules.

If hydrogen and chlorine were to combine therefore;

$$1\,volume\ of\ H_2 + 1\,volume\ of\ Cl_2 \longrightarrow 2\,volumes\ of\ HCl$$

can be interpreted as;

$$1\,molecule\ of\ H_2 + 1\,molecule\ of\ Cl_2 \longrightarrow 2\,molecules\ of\ HCl$$

$$n\,molecules\ of\ H_2 + n\,molecules\ of\ Cl_2 \longrightarrow 2n\,molecules\ of\ HCl$$

$$equation; \quad H_2 + Cl_2 \longrightarrow 2HCl$$

It follows from Avogadro's hypothesis that if equal volumes of gases contain equal numbers of molecules then the volume occupied by one mole of molecules of gases must be the same for all gases. It is called **molar gas volume**.

The value is

$$22.4\ dm^3 or\ litres\ or\ 22400 cm^3\ at\ stp (0°C\ and\ 1\ atm)\ \textbf{or}\ 24\ dm^3 or\ litres\ or\ 24000 cm^3\ at\ room\ temperature\ (20°C\ and\ 1\ atm)$$

It also therefore follows that ***the total number of moles of a gas is directly proportional to the volume occupied by a gas at constant temperature***.

$$\boldsymbol{V \propto n}\ (n = number\ of\ moles\ of\ a\ gas)$$

$$\boldsymbol{V = kn}$$

$$\boldsymbol{\frac{V}{n} = k}\ ;\ \ where\ V\ is\ volume\ of\ a\ gas$$

$$k\ is\ a\ constant.$$

$$\boldsymbol{\frac{V_1}{n_1} = \frac{V_2}{n_2}}$$

However, Avogadro's law cannot be true at all pressures. It only holds if the gases behave as perfect gases, that is, at very low pressures.

Examples

1. **One mole of helium gas fills up an empty balloon to a volume of 1.5 litres. What would be the volume of the balloon if an additional 2.5 moles of helium gas is added? (Assume that the temperature and the pressure are kept constant)**

$$\boldsymbol{V_1 = 1.5\ l, n_1 = 1}$$

$$\boldsymbol{V_2 = ?, n_2 = (1 + 2.5)}$$

$$\boldsymbol{= 3.5\ moles}$$

$$\boldsymbol{\frac{V_1}{n_1} = \frac{V_2}{n_2}}$$

$$\boldsymbol{V_1 n_2 = V_2 n_1}$$

$$\boldsymbol{V_2 = \frac{V_1 n_2}{n_1}}$$

$$\boldsymbol{= \frac{1.5 \times 3.5}{1} = 5.25\ litres}$$

2. **50g of nitrogen gas are contained in a 3000cm^3 container. The gas exerts a pressure of 3 atmospheres on the container. If the pressure and temperature are kept constant, calculate the mass of nitrogen that can be added the container until the volume reaches 5000cm^3. ($N = 14$)**

$$molar\ mass\ of\ N_2 = (14 \times 2) = 28g$$

$$number\ of\ moles\ (n_1) of\ N_2 = \frac{50}{28}$$

$$= 1.7857$$

$$V_1 = 3000cm^3$$

$$pressure\ and\ temperature\ are\ constant$$

$$n_2 = ?$$

$$V_2 = 5000cm^3$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$n_2 = \frac{V_2 n_1}{V_1} = \frac{5000 \times \frac{50}{28}}{3000}$$

$$= 2.9762\ moles$$

$$extra\ moles\ of\ gas\ added$$

$$= (2.9762 - 1.7857) = 1.1905$$

$$extra\ mass\ of\ gas\ added$$

$$= (28 \times 1.1905) = 33.334g$$

Gay-Lussac's law

In 1808, French Chemist Gay-Lussac provided the result of a series of experiments on the volumes of combining gases. He summarized his results in a law which states that;

When gases combine together at constant temperature and pressure, they do so in volumes which bear a simple ratio to each other, and to the volume of any gaseous product.

$$1\ volume\ of\ H_2 + 1\ volume\ of\ Cl_2 \longrightarrow 2\ volumes\ of\ HCl$$

$$2\ volumes\ of\ H_2 + 1\ volume\ of\ O_2 \longrightarrow liquid\ water$$

$$2\ volumes\ of\ H_2 + 1\ volume\ of\ O_2 \longrightarrow 2\ volumes\ of\ steam$$

$$1\ volume\ of\ N_2 + 3\ volumes\ of\ H_2 \longrightarrow 2\ volumes\ of\ ammonia$$

Just like Avogadro's law, Gay-Lussac's law is only approximately true. It is only valid when gases are at very low pressures.

We shall not look at calculation probles involving this law since you Ordinary Level teacher must have looked at them in detail.

LABORATORY APPARATUS AND CHEMICALS

Laboratory equipment can be hazardous if they are not used or handled properly. This is to reduce accidents and prevent injury.

When using gas burners for example, they should be placed away from other equipment, remove all papers, notebooks and other combustible materials and containers of flammable chemicals from the area surrounding the burner. Long hair should be tied back. Rubber tubing should be inspected for cracks, holes or any other defects and the hose should be securely connected on the gas valve and the burner.

Most glass ware can only be exposed to certain high and low temperatures. Usage outside of those ranges may cause damage or breakage to the glassware. Always watch evaporation closely. A vessel, heated after evaporation has already occurred, may crack. Do not put hot glassware on cold or wet surfaces as it may break with temperature change. Never heat glassware that is cracked. It's advisable to use wire gauze when heating glass ware.

Selection of apparatus for different experiments

Glass ware is designed for a specific purpose. It should only be used for that purpose. When selecting glassware, it's wise to determine the compatibility of the glass ware with the chemicals. Some chemicals react with glass ware or cause damage. If the process in which glassware is to be used involves temperature or pressure changes, ensure that the glassware can withstand the changes. Use the right size and type of glassware for any given experiment.

Laboratory rules and regulations for handling chemicals and apparatus

A laboratory is a well specialized room or place where scientific experiments are done from.

Great care must be taken while in the laboratory so that danger or accidents are avoided.

There are therefore rules and regulations that must be followed while in the laboratory. These include;

1. Students should not enter the laboratory before the teacher tells them to do so
2. Students should not remove anything from the laboratory without the teacher's permission
3. Do not taste anything in the laboratory without being instructed
4. Never handle chemicals with bare hands because come chemicals are corrosive and others flammable
5. Bottles should never be handled by the necks
6. Unnecessary movements in the laboratory are prohibited
7. Any burn or cut or material that is accidentally swallowed should be reported to the teacher immediately.
8. Broken glass should be discarded in a separate designated container.
9. Report any damage of the laboratory equipment to the laboratory supervisor immediately.
10. Do not return chemicals to their original packaging. An incompatible mixture may be accidentally formed.
11. Keep chemical containers closed. Vapour may escape from an open container or atmospheric gases may enter the containers, changing the nature of the chemical to change.

12. Never use the wrong or unmarked reagent. If you are unsure about the compound, do not use it.
13. Corks or stoppers once removed from the bottle or glass, they must be placed on a clean surface with the opening facing down. This is to avoid contamination of the compound and unnecessary exposure.
14. Special precautions should be taken when handling concentrated acids. Dilution of acids should be performed by pouring the acid into water.

Concentration

Concentration is the amount of substance, solid or liquid in a known quantity of solution. The amount of substance can be mass, moles or number of particles. The quantity in which the amount of substance exists is normally volume.

Concentration is therefore the amount of a substance in a known volume of solvent. The volume commonly used is 1 litre (1000cm^3 or 1 dm^3).

Concentration is therefore expressed in terms of grams per litre $(g\ l^{-1} or\ g\ dm^{-3})$ and moles per litre $(mol\ l^{-1} or\ mol\ dm^{-3})$

Molarity (M)

Molarity is also a measure of concentration. It is the number of moles of a substance in one litre of a solution. It is abbreviated as M and expressed in the units of moles per litre $(mol\ l^{-1} or\ mol\ dm^{-3})$

Try to find the concentration of the following solutions in both moles per litre and grams per litre

(i) 0.025 moles of sodium ethanedioate in 750cm^3 of water
(ii) 3.5g of Diammonium iron(II) sulphate-6-water in 250cm^3 of solution
(iii) 4.0g of sodium hydroxide in 500cm^3 of solution
(iv) 0.0085 moles of potassium peroxodisulphate in 500cm^3 of solution
(v) 19.1g of disodium tetraborate decahydrate in 1000cm^3 of solution
(vi) 0.0456 moles of copper(II) sulphate-5-water in 500cm^3 of water
(vii) 49.0g of sulphuric acid in 2.5dm^3 of solution

Difference between molarity and molality

The molar concentration(or molarity; symbol *M*) is the number of moles of a substance in one litre of a solution, commonly given in units of moles per litre $(mol\ l^{-1} or\ mol\ dm^{-3})$

The molal concentration (or molality; symbol *m*) is the amount of substance per unit mass of solvent, commonly given in units of $mol\ kg^{-1}\ or\ mol\ g^{-1}$.

$$molarity = \left(\frac{number\ of\ moles\ of\ solute}{volume\ of\ solution} \times 1000\right) M$$

$$molality = \left(\frac{number\ of\ moles\ of\ solute}{mass\ of\ solvent}\right) mol\ kg^{-1}\ or\ mol\ g^{-1}$$

Percentage by mass (% w/w)

Mineral acids are always kept in the laboratory using stock bottles and certain specifications under certain conditions are displayed on the bottles.

The specifications include;

(i) Chemical formula
(ii) Relative formula mass
(iii) Specific gravity (density)
(iv) Percentage by mass (w/w) value of the acid

The percentage by mass is got by the expression;

$$percentage\ by\ mass(w/w) = \frac{mass\ of\ solute(g)}{mass\ of\ solution(g)} \times 100\%$$

Sulphuric acid is commonly $98\%\ w/w$ and hydrochloric acid is commonly $(35 - 38\%)\ w/w$. The Specific gravity (density) of sulphuric acid is normally ranging from $(1.80 - 1.86\ gcm^{-3})$

The statement $98\%\ w/w$ means that 100cm^3 of stock solution contains 98 cm^3 of sulphuric acid.

Similarly; the statement $1.84\ gcm^{-3}$ implies that $1cm^3\ of\ solution\ weighs\ 1.84g$.

Below is a table summarizing the approximated information about some stock solutions

Reagent	Sulphuric acid	Hydrochloric acid	Nitric acid	Phosphoric acid	Ammonia
Density(specific gravity) (gcm^{-3})	1.84	1.18	1.41	1.75	0.89
Percentage by mass (w/w)	98	37.3	70	90	29
Molecular weight	98	36.5	63	97	17

The above information can be used to find the molarity of the stock solution which can then be used to prepare solutions of any other known concentration (standard solutions) using the steps below.

***(i)* Determine the mass of acid in 1 cm^3 of stock solution**
***(ii)* Calculate the mass of the same acid in 1000cm^3 of solution**

(iii)* *Using the molar mass of the acid, convert the mass got in step (ii) to moles. This gives the molarity(M_1) of the acid in the stock solution

(iv)* *Use the expression $M_1V_1 = M_2V_2$ to get the volume (V_1) of the stock solution needed to prepare a volume (V_2) of a solution of known concentration (M_2)

Examples

1. **Calculate the volume of concentrated sulphuric acid needed to prepare 500cm^3 of 0.25M sulphuric acid solution.(*The stock specifications of the acid are 98% w/w and specific gravity 1.84gcm^{-3}*)**

$$1\ cm^3\ of\ stock\ solution\ weighs\ 1.84g$$
$$But\ only\ 98\%\ of\ the\ 1.84g\ is\ H_2SO_4$$
$$Therefore\ 1\ cm^3\ of\ stock\ solution\ contains\left({}^{98}\!/_{100} \times 1.84\right)g\ of H_2SO_4$$
$$1000\ cm^3\ of\ solution\ contain\left({}^{98}\!/_{100} \times 1.84 \times 1000\right)g\ of H_2SO_4$$
$$= 1803.2g\ of\ H_2SO_4$$
$$molar\ mass\ of\ H_2SO_4 = (2 \times 1) + (32 \times 1) + (16 \times 4) = 98g$$
$$molarity\ of H_2SO_4 = \left({}^{1803.2}\!/_{98}\right) = 18.4M$$

Let the volume of stock solution required be V_1 cm^3

$$M_1V_1 = M_2V_2$$
$$18.4V_1 = 0.25 \times 500$$
$$V_1 = \frac{0.25 \times 500}{18.4} \approx 6.8cm^3$$

500cm^3 of 0.25M sulphuric acid solution is therefore prepared by putting 6.8cm^3 of the concentrated acid in a measuring cylinder and adding 493.2cm^3 such that the total volume in the cylinder is 500cm^3

2. **A solution is made by dissolving 11g of glucose in 250cm^3 of water at 30°C. What is the percentage by mass of glucose in the solution? The density of water is 0.996gcm^{-3}.**

$$1\ cm^3\ of\ water\ weighs\ 0.996g$$
$$250\ cm^3\ of\ water\ weighs\ (250 \times 0.996)g = 249g$$
$$percentage\ by\ mass\ of\ glucose = \left(\frac{mass\ of\ glucose}{mass\ of\ solution} \times 100\right)$$
$$= \left(\frac{11}{11 + 249} \times 100\right)$$
$$= \mathbf{4.23}\%$$

Percentage by volume (% v/v)

This is a measure of concentration of a substance in solution. It is expressed as the ratio of the volume of the solute to the total volume of the solution, and this ratio multiplied by 100.

The percentage by volume is got by the expression;

$$percentage\ by\ volume(v/v) = \frac{volume\ of\ solute(ml)}{volume\ of\ solution(ml)} \times 100\%$$

It is used when preparing solutions of two liquids.

Wine, for example is 12% *v/v* ethanol. This means that there is 12cm^3 of ethanol for every 100cm^3 of wine.

70% *v/v* ethanol solution means that there is 70cm^3 of ethanol in every 100cm^3 of water.

Example

How to prepare 750cm^3 of 70% ethanol

$$percentage\ by\ volume(v/v) = \frac{volume\ of\ solute}{volume\ of\ solution} \times 100\%$$

$$70 = \frac{volume\ of\ solute}{750} \times 100$$

$$volume\ of\ solute = \frac{70 \times 750}{100}$$

$$volume\ of\ solute = 525cm^3$$

***525 cm^3 of ethanol are added to a measuring cylinder and water added up to the 750 cm^3 mark*.**

Questions

1. Determine the volume of 85% concentrated phosphoric acid, density 1.70 gcm^{-3} needed to prepare 25cm^3 of 0.1M phosphoric acid solution.
2. If concentrated sulphuric acid contains 98% by mass of the acid and has a density of 1.84gcm^{-3} , calculate the volume of the concentrated sulphuric acid that is required to prepare a litre of 2M solution of sulphuric acid.
3. Concentrated hydrochloric acid contains 37.3% by mass of the acid and has a specific gravity of 1.18gcm^{-3}. Calculate the volume of the concentrated acid that is required to prepare a litre of 2M solution of sulphuric acid.
4. Concentrated ammonia has a density of 0.880gcm^{-3}. What volume of 29% concentrated ammonia is required to prepare a litre of 2M ammonia solution?
5. A solution is prepared by dissolving 5g of urea in 95g of water. Calculate the percentage by mass of urea in the solution.
6. A solution of naphthalene in benzene is 2% naphthalene. What is its mass by percentage of benzene?

$$(H = 1;\ N = 14;\ O = 16;\ S = 32;\ P = 30;\ Cl = 35.5;)$$

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)	$H_2C_2O_4.2H_2O$
Sodium oxalate	$Na_2C_2O_4$
Butane-1,4-dioic acid	$HOOCCH_2CH_2COOH$
Disodium tetraborate decahydrate (Borax)	$Na_2B_4O_7.10H_2O$
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(s) 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	$Na_2S_2O_3.5H_2O$	Potassium iodate Potassium bromate

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

1. ***During weighing, it absorbs water vapour from the air.***
2. ***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 concentrations of their concentrated solutions are not accurately known.*** Nitric acid is not a suitable primary standard because it always ***contain 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;

1. ***It forms coloured solutions so it acts as own indicator***
2. ***It oxidises a wide range of substances***
3. ***It is not affected by the atmosphere while being weighed***
4. ***It is fairly soluble in water***
5. ***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****.*

$$2MnO_4^-(aq) + 16H^+(aq) + 10Cl^-(aq) \longrightarrow 2Mn^{2+}(aq) + 5Cl_2(g) + 8H_2O(l)$$

$$or\ 2KMnO_4(s) + 16HCl(aq) \rightarrow 2KCl(aq) + 2MnCl_2(aq) + 8H_2O(l) + 5Cl_2(g)$$

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 yellow solid deposit and bubbles of a colourless gas****.*

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,*** *which is* ***insoluble****.*

$$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(s) + SO_2(g) + H_2O(l)$$

Preparation of standard solutions by weighing and dissolving in water

Preparing a standard solution of anhydrous sodium carbonate (for example 250cm^3 of 0.2M sodium carbonate solution)

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

250cm^3 of 0.2M sodium carbonate solution

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

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

$$1\ mole\ of\ Na_2CO_3\ weighs\ 106g$$

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

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

(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 250cm^3). 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 500cm^3 of a 0.01M solution.

(c) Describe how you would prepare the solution in (b) above as accurately as possible.

VOLUMETRIC ANALYSIS

Common terms used in volumetric analysis

Titrant

This is a reagent of known concentration that is added to another solution to determine the concentration of the second chemical species.

Titrand/ Analyte

This is a reagent whose concentration is not known and has to be determined by titration.

Equivalence point

This is the point when the number of moles titrant is equal to number of moles of analyte. It occurs before end point, which signals the completion of the reaction.

End point

A point in a titration at which the reaction is complete, observed by the colour change of an indicator and occurs when small amount of solution of known concentration is added to a solution whose concentration is to be determined. It occurs after equivalence point.

Standard solution

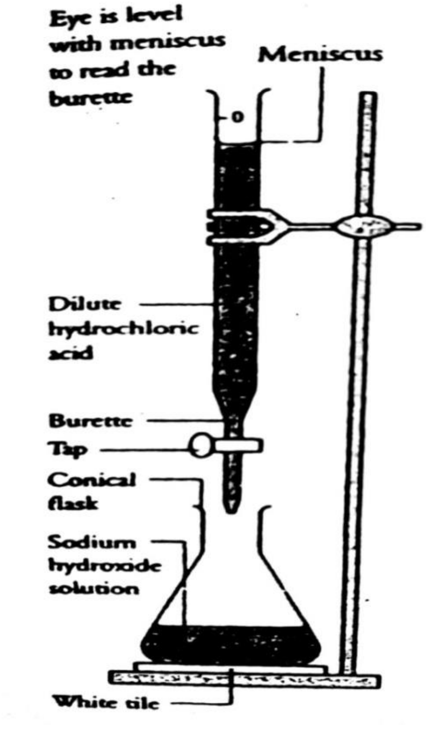
A standard solution is a solution whose concentration is accurately known i.e. one that contains a known amount of solute in a known volume of solution.

Volumetric analysis is a means of finding the concentration of a solution. In this method, a solution of an acid is added to a solution of a base until there is just enough of the acid to neutralize the base. This is done by titration.

The concentration of one of the two solutions should be known, and the volumes of both the solutions must be measured.

A standard solution of a base may be used to find the concentration of the solution of an acid. The volume of the acid solution of unknown concentration required to neutralise a known volume, usually 25.0 cm^3 of a standard solution of the base is determined. An indicator is used to determine when the right volume of a solution has been added to another solution for complete neutralisation.

Set up of apparatus for volumetric analysis



Acid-base titrations and use of data obtained

Acid-base titrations may involve one- indicator titrations or double indicator titrations. Double indicator titrations will be exploited more in practical lessons by your teacher.

One indicator titrations involve standardizing an acid or base using a standard solution of a base or acid with the aid of a suitable indicator. Calculation problems involving standardisation involve the following steps;

(i) ***Calculating the moles of the standard solution in the total volume of solution(commonly the total volume is 250cm^3 of the solution but can be any other value)***

(ii) ***Calculating the moles of the standard solution used during the reaction (usually 25.0, 20.0 or can be 10.0cm^3)***

(iii) ***Calculating moles of the solution that is standardized using equation of the reaction(mole ratio)***

(iv) ***Determining the molarity of the solution that is standardized.***

Examples

1. Standardization of hydrochloric acid using Borax

5.7g of disodium tetraborate decahydrate(Borax)($Na_2B_4O_7.10H_2O$) were dissolved in 100 cm^3 distilled water in a 250cm^3 volumetric flask, shaken to dissolve and the mixture made up to the mark with distilled water. 25.0 cm^3 of the resultant solution is pipetted into a clean conical flask and titrated against dilute hydrochloric acid solution which was approximately 0.1M using phenolphthalein indicator. 18.0 cm^3 of the acid was required for complete neutralisation. Calculate the molarity of the hydrochloric acid solution used.

(i) ***Moles of $Na_2B_4O_7.10H_2O$ in the 250cm^3 of the solution***

$$molar\ mass\ of\ Na_2B_4O_7.10H_2O = (23 \times 2) + (11 \times 4) + (16 \times 7) + (10 \times 18) = 382g$$

$$moles\ of\ Na_2B_4O_7.10H_2O\ in\ 250\ cm^3 = \frac{5.7}{382} = 0.0149$$

(ii) ***moles of $Na_2B_4O_7.10H_2O$ used during the reaction (moles in 25.0cm^3)***

$$250\ cm^3 of\ solution\ contain\ \frac{5.7}{382}\ moles$$

$$25.0\ cm^3 contain\ \left(\frac{5.7 \times 25.0}{382 \times 250}\right)\ moles$$

(iii) ***moles of the solution that is standardized using equation of the reaction(mole ratio)***

Equation;

$$B_4O_7^{2-}(aq) + 2H^+(aq) + 5H_2O(l) \longrightarrow 4H_3BO_3(aq)$$

$$1\ mole\ of B_4O_7^{2-}\ reacts\ with\ \ 2\ moles\ of\ H^+$$

$$\left(\frac{5.7 \times 25.0}{382 \times 250}\right)\ moles\ of\ B_4O_7^{2-}\ react\ with\ \left(\frac{5.7 \times 25.0 \times 2}{382 \times 250}\right)\ moles\ of\ acid$$

(iv) ***molarity of hydrochloric acid***

$$18.0\ cm^3\ of\ acid\ solution\ contain\ \left(\frac{5.7 \times 25.0 \times 2}{382 \times 250}\right)\ moles$$

$$1000\ cm^3 of\ solution\ contain\ \left(\frac{5.7 \times 25.0 \times 2 \times 1000}{382 \times 250 \times 18.0}\right)\ moles = \mathbf{0.166M}$$

Note; The concentration of the acid given in the question is approximate hence used nowhere in the calculation. Remember standardizing means we are ascertaining the actual concentration of the acid.

Over rounding should be avoided before getting the final answer to minimize errors in calculation.

2. Standardisation of hydrochloric using anhydrous sodium carbonate.

You are provided with the following:
FA1 which is 60 cm^3 of hydrochloric acid solution
Solid **Y** which is anhydrous sodium carbonate
Methyl orange indicator
You are required to determine the molarity of **FA1** using a standard solution of anhydrous sodium carbonate.

PROCEDURE:
Accurately measure 40 cm^3 of **FA1** and add exactly 60 cm^3 of distilled water. Label the resultant solution **FA3.**
Weigh accurately 1.5g of solid **Y** into a clean 250cm^3 volumetric flask and add about 100 cm^3 of distilled water. Shake well to dissolve. Add more distilled water to fill up to the mark and label the resultant solution **FA2**
Pipette 25.0 cm^3 (or 20.0 cm^3) of **FA2** into a clean conical flask. Add 2 or 3 drops of methyl orange indicator.
Titrate the resultant mixture against **FA3** from the burette until the endpoint is reached.
Repeat the titration until you obtain consistent results.
Record your results in the table below.

Sample Results:
Mass of **Y** and weighing bottle ....**41.50**............g
Mass of empty weighing bottle............**40.00**............g
Mass of **Y** used ....**1.50**............g
Volume of pipette used ....**20.0**............cm^3

Final burette reading(cm^3)	***27.50***	***37.40***	***32.50***
Initial burette reading(cm^3)	*0.00*	*10.00*	*5.00*
Volume of **FA3** used(cm^3)	*27.50*	*27.40*	*27.50*

Record the titre values used to calculate the average volume of **FA3** used.
............27.50 *and* 27.50............cm^3

Average volume of **FA3** used= $\frac{27.50+27.50}{2} = 27.50$ cm^3

Questions:

Calculate the molarity of hydrochloric acid in **FA1**.

*We should begin the treatment of results with the standard solution which is in this case **FA2.***

(i) ***Moles of solid Y (Na_2CO_3) in the 250cm^3 of FA2.***
Since the same mass of Y(1.5g) in 100cm^3 of FA2 is also in the 250cm^3 of FA2, the moles of anhydrous sodium carbonate in both volumes is the same.

$$molar\ mass\ of\ Na_2CO_3 = (23 \times 2) + (12 \times 1) + (16 \times 3) = 106g$$

$$moles\ of\ Na_2CO_3\ in\ 250\ cm^3 of FA2\ = \frac{1.50}{106} = 0.014151$$

(ii) ***moles of Na_2CO_3 used during the reaction (moles in 20.0cm^3)***

$$250\ cm^3 of\ solution\ contain\ \frac{1.50}{106}\ moles$$

$$20.0\ cm^3 contain\ \left(\frac{1.50 \times 20.0}{106 \times 250}\right)\ moles$$

(iii) ***moles of hydrochloric acid in FA3 that reacted with Na_2CO_3 in FA2 Equation;***

$$Na_2CO_3(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

$$1\ mole\ of Na_2CO_3\ reacts\ with\ \ 2\ moles\ of\ HCl$$

$$\left(\frac{1.50 \times 20.0}{106 \times 250}\right)\ moles\ of\ Na_2CO_3\ react\ with\ \left(\frac{1.50 \times 20.0 \times 2}{106 \times 250 \times 1}\right)\ moles\ of\ HCl$$

(iv) ***molarity of FA1***

Note that in the experiment, FA1 is not directly used but instead the diluted solution which is FA3. Moles of HCl in the volume used of FA3 should be calculated first. Then moles of the acid in the diluted solution (60+40)cm^3

$$27.50\ cm^3\ of\ FA3\ contain\ \left(\frac{1.50 \times 20.0 \times 2}{106 \times 250}\right)\ moles\ of\ HCl$$

$$100\ cm^3 of\ FA3\ contain\ \left(\frac{1.50 \times 20.0 \times 2 \times 100}{106 \times 250 \times 27.50}\right)\ moles\ of\ HCl$$

Dilution does not change number of moles in a given solution. Therefore moles of HCl in 100cm^3 of FA3 are the same as those in 40cm^3 of FA1

$$40\ cm^3 of\ FA1\ contain\ \left(\frac{1.50 \times 20.0 \times 2 \times 100}{106 \times 250 \times 27.50}\right)\ moles\ of\ HCl$$

$$1000\ cm^3 of\ FA1\ contain\ \left(\frac{1.50 \times 20.0 \times 2 \times 100 \times 1000}{106 \times 250 \times 27.50 \times 40}\right)\ moles\ of\ HCl$$

$$= \mathbf{0.2058M}$$

Exercise on dilution and standardisation

1. During a titration, 20cm^3 of 0.2M sodium hydrogencarbonate solution reacted completely with 32.80cm^3 of a solution of nitric acid. Calculate the molarity of nitric acid.
2. 30 cm^3 of sodium hydroxide solution reacted completely with 25.0 cm^3 of 0.5M hydrochloric acid solution. Determine the molarity of sodium hydroxide solution.
3. 25.0 cm^3 of 0.2M sodium ethanedioate solution was warmed up to 65℃ and titrated against a solution of potassium manganate(VII). Calculate the molarity of potassium manganate(VII) if 17.20 cm^3 of the oxidant was used.
4. 1.50g of anhydrous sodium carbonate were dissolved in 100 cm^3 distilled water in a 250cm^3 volumetric flask, shaken to dissolve and the mixture made up to the mark with distilled water. 20.0 cm^3 of the resultant solution is pipetted into a clean conical flask and titrated against dilute hydrochloric acid solution using methyl orange indicator. 27.50 cm^3 of the acid was required for complete neutralisation. Calculate the molarity of the hydrochloric acid solution used.

Practical exercises on standardisation

1. You are provided with:

FA1 which is approximately 0.1M hydrochloric acid solution

Solid **Q** which is hydrated disodium tetraborate (Borax)$(Na_2B_4O_7.10H_2O)$

Phenolphthalein indicator

You are required to standardise hydrochloric acid in **FA1** using a standard solution of Borax.

PROCEDURE:

Weigh accurately 4.7g of solid **Q** into a clean 250cm^3 volumetric flask and add about 100 cm^3 of distilled water. Shake well to dissolve. Add more distilled water to fill up to the mark and label the resultant solution **FA3**

Pipette 25.0 cm^3 (or 20.0 cm^3) of **FA3** into a clean conical flask. Add 2 or 3 drops of phenolphthalein indicator and shake the flask carefully.

Titrate the solution carefully against **FA1** from the burette until the endpoint is reached.

Repeat the titration until you obtain consistent results.

Record your results in the table below.

Results:

Mass of **Q** and weighing bottle...g

Mass of empty weighing bottle...g

Mass of **Q** used...g

Volume of pipette used...cm^3

Final burette reading(cm^3)			

Initial burette reading(cm^3)			
Volume of **FA1** used(cm^3)			

Record the titre values used to calculate the average volume of **FA1** used.

....cm^3

Average volume of **FA1** used.. cm^3

Questions:

Calculate the concentration of hydrochloric acid in **FA1** per litre of solution.

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2. You are provided with:

FA1 which is approximately 0.2M hydrochloric acid solution
Solid **M** which is anhydrous sodium carbonate
Methyl orange indicator

You are required to standardise hydrochloric acid in **FA1** using a standard solution of anhydrous sodium carbonate.

PROCEDURE:

Weigh accurately 2.7g of solid **M** into a clean 250cm^3 volumetric flask and add about 100 cm^3 of distilled water. Shake well to dissolve. Add more distilled water to fill up to the mark. Label this solution **FA2**

Pipette 25.0 cm^3 (or 20.0 cm^3) of **FA2** into a clean conical flask. Add 2 or 3 drops of methyl orange indicator and shake the flask carefully.

Titrate the solution against **FA1** from the burette until the solution just turns orange.

Repeat the titration until you obtain consistent results.

Record your results in the table below.

Results:

Mass of **M** and weighing bottle...g
Mass of empty weighing bottle...g
Mass of **M** used..g
Volume of pipette used...cm^3

Final burette reading(cm^3)			
Initial burette reading(cm^3)			
Volume of **FA1** used(cm^3)			

Record the titre values used to calculate the average volume of **FA1** used.

....cm^3

Average volume of **FA1** used... cm^3

Questions:

Calculate the percentage error in the concentration of hydrochloric acid in **FA1.**

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NOTE:

(i) *Volume of pipette is recorded to 1 decimal place.*
(ii) *Titre values in the table must be recorded to 2 decimal places*
(iii) *Titre values chosen to obtain average volume should be within* ± 0.1 *difference*
(iv) *All steps in your calculations should be shown and strictly use first principles.*

Back titrations

Back titration is a technique in volumetric analysis in which a known volume of an excess standard solution is added to the solution to be analysed. The amount of the unreacted standard solution is then determined by titration with another standard solution.

For example an excess of a solution of iron(II) ions of known concentration can be added to a solution of potassium peroxodisulphate or potassium chlorate(V). Some of the iron(II) ions are oxidised to iron(III) ions as shown by the equations below;

$$S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \longrightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$$

$$or\ ClO_3^-(aq) + 6H^+(aq) + 6Fe^{2+}(aq) \longrightarrow Cl^-(aq) + 6Fe^{3+}(aq) + 3H_2O(l)$$

The resultant solution which then contains unreacted iron(II) ions can then be titrated against a standardised potassium manganate(VII) solution in acidic medium or any other oxidising agent.

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \longrightarrow 2Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

The analysis usually flows by the steps below;

- **(i)** ***Calculate the number of moles of permanganate that reacted with the excess iron(II) ions.***
- **(ii)** ***Use mole ratio to determine the number of moles of excess moles of iron(II) ions. (moles of iron(II) ions that did not react with peroxodisulphate/chlorate(V).***
- **(iii)** ***Calculate the number of moles of iron(II) ions in the original solution***
- **(iv)** ***By subtraction, obtain the number of moles that reacted with the peroxodisulphate/ chlorate(V)***
- **(v)** ***Moles ratio of the reaction, percentage purity or formula mass can then be determined using the usual approaches.***

Example

(a) A solution was made by dissolving 39.2g of ammonium ferrous sulphate, $(NH_4)_2SO_4.FeSO_4.6H_2O$ in a litre of distilled water. 25.0cm^3 of this solution was pipetted into a conical flask. To it was added 20 cm^3 of 2M sulphuric acid and titrated against potassium manganate(VII) solution. 25.00cm^3 of the permanganate was required for complete reaction. Calculate the concentration of manganate(VII) ions in moles per litre.

(b) 0.5g of a solid QS_2O_8 was accurately weighed and put in a beaker. 50 cm^3 of distilled water was added and the mixture stirred to dissolve. The resultant solution was transferred into a 250cm^3 volumetric flask and 150 cm^3 of the same ammonium ferrous sulphate used in (a) was added. The solution in the flask was made up to the mark with distilled water, shaken and allowed to stand for about 5 minutes. 25.0cm^3 of this solution was pipetted into a conical flask and to it was added 10cm^3 of 2M sulphuric acid and titrated with the same potassium manganate(VII) solution used in (a). 11.30 cm^3 of the permanganate was required for complete reaction. Calculate the number of moles of:

- **(i)** **excess iron(II) ions in 250cm^3 of the solution in the volumetric flask**
- **(ii)** **iron(II) ions that reacted with QS_2O_8**
- **(iii)** **molar mass of QS_2O_8**
- **(iv)** **formula mass of Q**

(a) $Molar\ mass\ of\ (NH_4)_2SO_4.FeSO_4.6H_2O = 2(14+2)+(32\times 1)+(16\times 4)+(56\times 1)+(32\times 1)+(16\times 4)+(6\times 18)$

$$= 392g$$

$$moles\ of (NH_4)_2SO_4.FeSO_4.6H_2O\ in\ 1000cm^3 of\ solution = \frac{39.2}{392}$$

$$molarity\ of (NH_4)_2SO_4.FeSO_4.6H_2O\ \ solution = 0.1M$$
$$1000cm^3\ \ of\ solution\ \ contain\ 0.1\ moles\ of\ (NH_4)_2SO_4.FeSO_4.6H_2O$$
$$25.0cm^3\ \ of\ solution\ \ contain\ \left(\frac{25.0\times 0.1}{1000}\right)\ moles\ of\ (NH_4)_2SO_4.FeSO_4.6H_2O$$
$$= 0.0025\ moles\ of\ (NH_4)_2SO_4.FeSO_4.6H_2O$$

***The sulphuric acid is just used to provide acidic medium for the redox reaction but its volume and concentration is not used anywhere in the calculation*.**

~~$(MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) \quad + \quad 4H_2O(l))$~~

~~$(Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e) \times 5$~~

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$
$$5\ moles\ of\ Fe^{2+}\ react\ with\ \ 1\ mole\ of\ MnO_4^-$$
$$0.0025\ moles\ of\ Fe^{2+}\ react\ with\ \left(\frac{0.0025\times 1}{5}\right) moles\ of\ MnO_4^-$$
$$= 0.0005\ moles\ of MnO_4^-$$
$$25.00\ cm^3\ of\ solution\ contain\ 0.0005\ moles\ of MnO_4^-$$
$$1000\ cm^3\ of\ solution\ contain\ \left(\frac{0.0005\times 1000}{25.00}\right) moles\ of MnO_4^-$$
$$\boldsymbol{= 0.02\ moles\ per\ litre}$$

(b)

(i) **number of moles of excess iron(II) ions in 250cm^3 of the solution in the volumetric flask**

$$moles\ of\ excess\ iron(II)\ ions\ that\ reacted\ with\ manganate(VII)\ ions;$$
$$1000\ cm^3\ of\ solution\ contain\ 0.02\ moles\ of MnO_4^-$$
$$11.30\ cm^3\ of\ solution\ contain\ \left(\frac{11.30\times 0.02}{1000}\right) moles\ of MnO_4^-$$
$$= 2.26\times 10^{-4}\ moles\ of MnO_4^-$$
$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$
$$1\ mole\ of\ MnO_4^-\ reacts\ \ with\ 5\ moles\ of\ Fe^{2+}$$
$$2.26\times 10^{-4}\ moles\ of MnO_4^-\ react\ with\ \left(\frac{5\times 2.26\times 10^{-4}}{1}\right)\ moles\ of\ Fe^{2+}$$
$$= 1.13\times 10^{-3}\ \ moles\ of\ excess\ Fe^{2+}$$

***Note that* $\boldsymbol{1.13\times 10^{-3}\ moles}$ *are the moles of excess iron(II) ions that reacted with manganate(VII) ions but they are the excess moles in 25.0cm^3 of solution*.**

$$25.0\ cm^3\ of\ solution\ contain\ 1.13\times 10^{-3}\ \ moles\ of\ excess\ Fe^{2+}$$
$$250\ cm^3\ of\ solution\ contain\ \left(\frac{250\times 1.13\times 10^{-3}}{25.0}\right) moles\ of excess\ Fe^{2+}$$
$$= 0.0113\ moles\ of\ excess\ Fe^{2+}$$

(ii) **number of moles of iron(II) ions that reacted with $\mathbf{QS_2O_8}$**

$$Original\ moles\ of Fe^{2+}\ \ added;$$
$$1000\ cm^3\ of\ solution\ contain\ 0.1\ moles\ of\ Fe^{2+}$$
$$150\ cm^3\ of\ solution\ contain\ \left(\frac{0.1\times 150}{1000}\right)\ moles\ of\ Fe^{2+}$$
$$=\ 0.015\ moles\ of\ Fe^{2+}$$
$$moles\ of\ Fe^{2+}that\ reacted\ with\ QS_2O_8 = (0.015 - 0.0113)$$
$$= 0.0037\ moles$$

Note that $150\ cm^3$ of $0.1M$ of iron(II) ions were added to the persulphate solution. Some of these reacted with the persulphate and the excess moles calculated above did not react.

(iii) **molar mass of QS_2O_8**

$$\boldsymbol{S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \longrightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)}$$
$$2\ moles\ of\ \ Fe^{2+}\ \ react\ with\ 1\ mole\ of\ S_2O_8^{2-}$$
$$0.0037\ moles\ of\ \ Fe^{2+}\ \ react\ with\ \left(\frac{1\times 0.0037}{2}\right)\ moles\ of\ S_2O_8^{2-}$$
$$= 0.00185\ \ moles\ of\ S_2O_8^{2-}$$
$$0.00185\ moles\ of\ QS_2O_8\ weigh\ 0.5g$$
$$1\ mole\ of\ QS_2O_8\ weighs\ \ \left(\frac{0.5\times 1}{0.00185}\right)g$$
$$= 270.27\ g$$
$$\boldsymbol{molar\ mass\ of\ QS_2O_8\ \approx 270g}$$

(iv) **formula mass of Q**

$$QS_2O_8 =\ \ 270$$
$$(Q\times 1) + (2\times 32) + (8\times 16) = 270$$
$$Q + 64 + 128 = 270$$
$$\boldsymbol{Q = 78}$$

Question

(a) 10.0cm^3 of a solution of ammonium iron(II) sulphate-6-water, of unknown concentration was pipetted into a conical flask. To it was added an equal volume of 2M sulphuric acid and then titrated against a solution made by dissolving 3.16g of potassium manganate(VII) in a litre of distilled water. 9.90cm^3 of the permanganate solution was required for complete reaction. Calculate the molar concentration of the solution of ammonium iron(II) sulphate-6-water.

(b) 0.5g of an impure solid potassium chlorate was accurately weighed and put in a beaker. 100 cm^3 of distilled water was added and the mixture stirred to dissolve. The resultant solution was transferred into a 250cm^3 volumetric flask and the solution was made up to the mark with distilled water. 10.0cm^3 of this solution was pipetted into a conical flask and to it was added 35.0 cm^3 of the same ammonium iron(II) sulphate-6-

water solution used in (a) followed by an equal volume of 2M sulphuric acid. The mixture was heated to about 85℃ and then cooled in cold water for 3 minutes and the cold mixture titrated with the same permanganate solution used in (a). 25.20 cm^3 of the permanganate was required for complete reaction. Calculate the number of moles of:

(i) excess iron(II) ions that reacted with manganate(VII) ions.
(ii) iron(II) ions that reacted with the 10 cm^3 of chlorate(V) ions.
(iii) Percentage purity of the potassium chlorate.

OXIDATION NUMBER (OXIDATION STATE)

Oxidation number the net charge that would remain on an atom in a given compound when all the other atoms bonded to it are removed one by one, each in its normal valency state.

Oxidation number can also mean the combining power of a substance with oxygen.

Calculating oxidation state

Rules to consider

- *Oxidation numbers must be written with symbols (+ or -) to distinguish them from valency. Superscripts ($^+3$), subscripts ($_+3$), and mere numbers (3) or words(three) are not allowed*
- *Atoms in the elementary state have an oxidation number of zero.*
- *The molecules such as H_2O, NH_3, CO, NO, etc are assigned an oxidation number of zero.*
- *In the case of simple atoms but in the combined state, the element has an oxidation number with the same size and sign of the charge on its ion. For example Na, Mg, Al have oxidation numbers of +1, +2 and +3 respectively and Cl, Br, F, I, have oxidation number of -1.*
- *Atoms that are monoatomic can be assigned an oxidation number equal to their charge*
- *The oxidation number of H is +1 in most of its compounds but -1 in metallic hydrides.*
- *When two or more atoms of the same element occur in a compound, the oxidation number of the element is an average of the oxidation number of the group.*
- *The oxidation state of the atom that is required is assigned an unknown letter say, x, and the sum of the oxidation numbers on all atoms in the species is equated to the overall charge on the species.*

Examples

Calculate the oxidation state of the stated atom in the following species.

- (i) Oxygen in H_2O
- (ii) Oxygen in H_2O_2
- (iii) Chorine in $HClO_3$
- (iv) Manganese in K_2MnO_4
- (v) Chromium in $Cr_2O_7^{2-}$
- (vi) Sulphur in $S_2O_8^{2-}$
- (vii) Iron in $[Fe(H_2O)_5(OH)]^{2+}$
- (viii) Cobalt in $[Co(NH_3)_4Cl_2]Br$

(i) Let the oxidation state of *O* in H_2O be *x*.

$$(2 \times charge\ of H) + (1 \times x) = 0$$
$$(2 \times 1) + (1 \times x) = 0$$
$$x + 2 = 0$$
$$x = -2$$

The oxidation state of O is therefore -2.

(ii) Let the oxidation state of *O* in $\boldsymbol{H_2O_2}$ be *m*.

$$(2 \times charge\ of H) + (2 \times m) = 0$$
$$(2 \times 1) + (2 \times m) = 0$$
$$2 + 2m = 0$$
$$m = -1$$

The oxidation state of O is therefore -1.

(iii) Let the oxidation state of *Cl* in $HClO_3$ be *n*.

$$(1 \times charge\ of H) + (1 \times n) + (3 \times charge\ on\ O) = 0$$
$$(1 \times 1) + (1 \times n) + (3 \times -2) = 0$$
$$n - 5 = 0$$
$$n = +5$$

The oxidation state of Cl is therefore +5.

(iv) Let the oxidation state of *Mn* in K_2MnO_4 be *p*.

$$(2 \times charge\ of K) + (1 \times p) + (4 \times charge\ on\ O) = 0$$

(v) Let the oxidation state of *Cr* in $Cr_2O_7^{2-}$ be *t*.

$$(2 \times t) + (7 \times charge\ on\ O) = -2$$
$$2t + (7 \times -2) = -2$$
$$2t - 14 = -2$$
$$t = +6$$

The oxidation state of Cr is therefore +6.

(vi) Let the oxidation state of *S* in $S_2O_8^{2-}$ be *a*.

$$(2 \times a) + (8 \times charge\ on\ O) = -2$$
$$2a + (8 \times -2) = -2$$
$$2a - 16 = -2$$
$$a = +7$$

The oxidation state of S is therefore +7.

(vii) Let the oxidation state of *Fe* in $[Fe(H_2O)_5(OH)]^{2+}$ be y.

$$y + (5 \times charge\ of H_2O) + (1 \times charge\ of\ OH) = +2$$
$$y + (5 \times 0) + (1 \times -1) = +2$$
$$y - 1 = +2$$
$$y = +3$$

The oxidation state of Fe is therefore +3.

(viii) Let the oxidation state of *Co* in $[Co(NH_3)_4Cl_2]Br$ be q

$(2\times 1)+(1\times p)+(4\times -2)=0$ $p-6=0$ $p=+6$ *The oxidation state of Mn is therefore +6.*	$q+(4\times charge\ of NH_3)$ $+(2\times charge\ on\ Cl)+(1\times charge\ on\ Br)=0$ $q+(4\times 0)+(2\times -1)+(1\times -1)=0$ $q-3=0$ $q=+3$ *The oxidation state of Co is therefore +3.*

Questions

Calculate the oxidation state of the stated atom in the following species.

(i) Sulphur in H_2SO_4	(ii) Sulphur in SO_4^{2-}
(iii) Sulphur in SO_3^{2-}	(iv) Sulphur in SO_3
(v) Copper in $Cu(H_2O)_4^{2+}$	(vi) Chromium in $Cr(OH)_4^-$
(vii) Chromium in $[Cr(H_2O)_5Cl]^{2+}$	(viii) Chromium in $[Cr(NH_3)_3(H_2O)_3]^{3+}$
(ix) Manganese in $[Mn(CN)_6]^{4-}$	(x) Manganese in $[MnO_4]^{2-}$
(xi) Iron in $[Fe(NO)(H_2O)_5]^{2+}SO_4^{2-}$	(xii) Iron in $Fe(CO)_5$
(xiii) Iron in $K_4[Fe(CN)_6]$	(xiv) Iron in $[Fe(CN)_6]^{3-}$
(xv) Iron in $[Fe(CN)_6]^{3-}$	(xvi) Cobalt in $[CoCl_4]^{2-}$
(xvii) Nickel in $[Ni(CN)_4]^{2+}$	(xviii) Chromium in $[Cr(NH_3)_6]^{3+}$
(xix) Chromium in $[Cr(H_2O)_5Cl]^{2+}2Cl^-$	(xx) Iron in $[Fe(H_2O)_5SCN]^{2+}$
(xxi) Cobalt in $[Co(NH_3)_4Cl_2]Cl$	(xxii) Chromium in $[CrCl_2(H_2O)_4]^+$
(xxiii) Chromium in $[Cr(H_2O)_6]^{3+}(Cl^-)_3$	(xxiv) Nickel in $Ni(CO)_5$
(xxv) Platinum in $[PtCl(NO_2)(NH_3)_4]^+$	(xxvi) Cobalt in $Co(NH_3)_5(H_2O)Cl_3$
(xxvii) Copper in $[Cu(NH_2CH_2CH_2NH_2)_2]^{2+}$	(xxviii) Chromium in $[Cr(NH_2CH_2CH_2NH_2)_3]^{3+}$
(xxix) Chromium in $[Cr(H_2O)_5Cl]Cl_2.H_2O$	(xxx) Chromium in $[Cr(C_2O_4)_3]^{3-}$
(xxxi) Silver in $Ag(NH_3)_2^+$	(xxxii) Nickel in $[Ni(NH_3)_6](NO_3)_3$

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 reactions below

$$Cu^{2+}(aq) + 2e \longrightarrow Cu(s) \ldots\ldots\ldots\ldots\ldots\ldots\ldots (i)$$
$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e \ldots\ldots\ldots\ldots\ldots\ldots\ldots (ii)$$

In the first half 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 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.

$$Cu^{2+}(aq) + \cancel{2e} \longrightarrow Cu(s)$$
$$Zn(s) \longrightarrow Zn^{2+}(aq) + \cancel{2e}$$
$$overall\ reaction\ ;\ Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

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** – **O**xidation **i**s **l**oss of electrons, **R**eduction **i**s **g**ain of electrons*

***LEORA** says **GEROA**- **l**oss of **e**lectrons is **o**xidation (**R**educing **a**gent). **G**ain of **e**lectrons is **r**eduction (**O**xidising **a**gent)*

Oxidizing species and their reduction products

No.	Oxidizing agent	Colour	Reduction product	Colour
1	$MnO_4^-(aq)$	Purple solution	$Mn^{2+}(aq)$	Colourless
2	$Cr_2O_7^{2-}(aq)$	Orange solution	$Cr^{3+}(aq)$	Green
3	$MnO_2(s)$	Black solid	$Mn^{2+}(aq)$	Colourless
4	$ClO^-(aq)$	Yellow solution	$Cl^-(aq)$	■
5	$ClO_3^-(aq)$	Yellow solution	$Cl^-(aq)$	■
6	$PbO_2(s)$	Dark brown solid	$Pb^{2+}(aq)$	Colourless
7	$IO_3^-(aq)$	Colourless	$I_2(aq)$	Brown
8	$H_2SO_4(aq)$	Colourless	$SO_2(g)$	Colourless gas
9	$HNO_3(aq)$	Colourless	$NO_2(g)$	Brown fumes
10	$H_2O_2(aq)$	Colourless	$H_2O(l)$	Colourless
11	$Fe^{3+}(aq)$	Yellow or brown solution	$Fe^{2+}(aq)$	Green
12	$Sn^{4+}(aq)$	Colourless	$Sn^{2+}(aq)$	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.

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

1. $MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) \quad + \quad 4H_2O(l)$
2. $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \longrightarrow 2Cr^{3+}(aq) \quad + \quad 7H_2O(l)$

3. $MnO_2(s) + 4H^+(aq) + 2e \longrightarrow Mn^{2+}(aq) \quad + \quad 2H_2O(l)$
4. $ClO_3^-(aq) + 6H^+(aq) + 6e \longrightarrow Cl^-(aq) \quad + \quad 3H_2O(l)$

Reducing agents and their oxidation products

No.	Reducing agent	Colour	Oxidation product	Colour
1	$SO_3^{2-}(aq)$	[redacted]	$SO_4^{2-}(aq)$	[redacted]
2	$NO_2^-(aq)$	[redacted]	$NO_3^-(aq)$	[redacted]
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	$Cl^-(aq)$	[redacted]	$Cl_2(g)$	Greenish yellow gas
7	$Br^-(aq)$	[redacted]	$Br_2(aq)$	Reddish brown solution
8	$I^-(aq)$	[redacted]	$I_2(aq)$	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.

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

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

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 both the oxidation and reduction processes. Make sure the equations are balanced both in terms of atoms and charge.***
   The atoms are balanced the usual way 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 make the number of electrons in each equation equal.***
4. ***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 H_2O. 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. Once electrons still appear in this equation, then something is not correct***
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. Half equations can only be written if required by examiner.***
   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;

$$MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) \quad + \quad 4H_2O(l)$$

   Oxidation half equation;

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e$$

Step 3;

$$MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) \quad + \quad 4H_2O(l)$$
$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e$$

The first equation is mutiplied 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 multipy only the electrons but also every other species in the equation.

$$(MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) \quad + \quad 4H_2O(l)) \times \mathbf{2}$$
$$(2Cl^-(aq) \longrightarrow Cl_2(g) + 2e) \times \mathbf{5}$$

This now gives;

$$2MnO_4^-(aq) + 16H^+(aq) + 10e \longrightarrow 2\,Mn^{2+}(aq) \quad + \quad 8H_2O(l)$$
$$10Cl^-(aq) \longrightarrow 5Cl_2(g) + 10e$$

Step 4;

The electrons are equal and crossed out.

$$2MnO_4^-(aq) + 16H^+(aq) + \cancel{10e} \longrightarrow 2\,Mn^{2+}(aq) \;+\; 8H_2O(l)$$
$$10Cl^-(aq) \longrightarrow 5Cl_2(g) + \cancel{10e}$$

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.

$$2MnO_4^-(aq) + 16H^+(aq) + 10Cl^-(aq) \longrightarrow 2Mn^{2+}(aq) + 5Cl_2(g) + 8H_2O(l)$$

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

   Step 1; Oxidizing species is $Cr_2O_7^{2-}(aq)$ from potassium dichromate and reducing species is H_2S

   Step 2;

   Reduction half equation;

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \longrightarrow 2Cr^{3+}(aq) \quad + \quad 7H_2O(l)$$

   Oxidation half equation;

$$H_2S(g) \longrightarrow S(s) + 2H^+(aq) + 2e$$

   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.

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$(H_2S(g) \longrightarrow S(s) + 2H^+(aq) + 2e) \times \mathbf{3}$$

This now gives;

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$
$$3H_2S(g) \longrightarrow 3S(s) + 6H^+(aq) + 6e$$

Step 4;

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

$$Cr_2O_7^{2-}(aq) + \boldsymbol{14H^+(aq)} + \cancel{6e} \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$
$$3H_2S(g) \longrightarrow 3S(s) + \boldsymbol{6H^+(aq)} + \cancel{6e}$$

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.

$$Cr_2O_7^{2-}(aq) + 8H^+(aq) + 3H_2S(g) \longrightarrow 2Cr^{3+}(aq) + 3S(s) + 7H_2O(l)$$

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;

$$MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) \quad + \quad 4H_2O(l)$$

Oxidation half equation;

$$NH_2NH_2(aq) \longrightarrow N_2(g) + 4H^+(aq) + 4e$$

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;

$$4MnO_4^-(aq) + 32H^+(aq) + 20e \longrightarrow 4Mn^{2+}(aq) \quad + \quad 16H_2O(l)$$
$$5NH_2NH_2(aq) \longrightarrow 5N_2(g) + 20H^+(aq) + 20e$$

Step 4;

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

$$4MnO_4^-(aq) + \boldsymbol{32H^+(aq)} + \cancel{20e} \longrightarrow 4Mn^{2+}(aq) \quad + \quad 16H_2O(l)$$
$$5NH_2NH_2(aq) \longrightarrow 5N_2(g) + \boldsymbol{20H^+(aq)} + \cancel{20e}$$

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.

$$4MnO_4^-(aq) + 12H^+(aq) + 5NH_2NH_2(aq) \longrightarrow 4Mn^{2+}(aq) + 5N_2(g) + 16H_2O(l)$$

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;

$$Cl_2(g) + 2e \longrightarrow 2Cl^-(aq)$$

Oxidation half equation;

$$NO_2^-(aq) + H_2O(l) \longrightarrow NO_3^-(aq) + 2H^+(aq) + 2e$$

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.

$$Cl_2(g) + \cancel{2e} \longrightarrow 2Cl^-(aq)$$

$$NO_2^-(aq) + H_2O(l) \longrightarrow NO_3^-(aq) + 2H^+(aq) + \cancel{2e}$$

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. $Cl_2(g) +$

$$NO_2^-(aq) + 3H_2O(l) \longrightarrow 2Cl^-(aq) + NO_3^-(aq) + 2H^+(aq)$$

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

Step 1; Oxidizing species is $MnO_2(s)$ and reducing species is $C_2O_4^{2-}(aq)$.

Step 2;

Reduction half equation;

$$MnO_2(g) + 4H^+(aq) + 2e \longrightarrow Mn^{2+}(aq) + 2H_2O(l)$$

Oxidation half equation;

$$C_2O_4^{2-}(aq) \longrightarrow 2CO_2(g) + 2e$$

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.

$$MnO_2(g) + 4H^+(aq) + \cancel{2e} \longrightarrow Mn^{2+}(aq) + 2H_2O(l)$$

$$C_2O_4^{2-}(aq) \longrightarrow 2CO_2(g) + \cancel{2e}$$

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.

$$MnO_2(g) + 4H^+(aq) + C_2O_4^{2-}(aq) \longrightarrow Mn^{2+}(aq) + 2CO_2(g) + 2H_2O(l)$$

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;

$$MnO_4^-(aq) + 2H_2O(aq) + 3e \longrightarrow MnO_2(s) \ + \ 4\bar{O}H(aq)$$

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)

$$(MnO_4^-(aq) + 2H_2O(aq) + 3e \longrightarrow MnO_2(s) \ + \ 4\bar{O}H(aq) \times 2$$

$$I^-(aq) + 3H_2O(l) \longrightarrow IO_3^-(aq) + 6H^+(aq) + 6e$$

Then;

$$2MnO_4^-(aq) + \boldsymbol{4H_2O(aq)} + \cancel{6e} \longrightarrow 2MnO_2(s) \ + \ \boldsymbol{8\bar{O}H(aq)}$$

$$I^-(aq) + \boldsymbol{3H_2O(l)} \longrightarrow IO_3^-(aq) + \boldsymbol{6H^+(aq)} + \cancel{6e}$$

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

$$2MnO_4^-(aq) + \boldsymbol{7H_2O(aq)} + I^-(aq) \longrightarrow 2MnO_2(s) + \boldsymbol{6H_2O(aq)} + \boldsymbol{2\bar{O}H(aq)} + IO_3^-(aq)$$

The $\boldsymbol{6H_2O(aq)}$ *on the right hand side are as a result of complete neutralisation of the* $\boldsymbol{6H^+(aq)}$ *by 6 of the* $\boldsymbol{8\bar{O}H(aq)}$ *leaving a remainder of* $\boldsymbol{2\bar{O}H(aq)}$**.** *Subtraction leaves only one water molecule on the reactant side.*

Observation;

Purple solution forms a colourless solution and black solid deposited.

Equation

$$2MnO_4^-(aq) + I^-(aq) + H_2O(l) \longrightarrow 2MnO_2(s) + \ IO_3^-(aq) + 2\bar{O}H(aq)$$

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;

$$H_2O_2(aq) + 2\bar{O}H(aq) \longrightarrow O_2(g) + 2H_2O(l) + 2e$$

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.

$$H_2O_2(aq) + 2\bar{O}H(aq) \longrightarrow O_2(g) + 2H_2O(l) + 2e$$
$$(Fe^{3+}(aq) + e \longrightarrow Fe^{2+}(aq)) \times 2$$

Then;

$$H_2O_2(aq) + 2\bar{O}H(aq) \longrightarrow O_2(g) + 2H_2O(l) + \cancel{2e}$$
$$2Fe^{3+}(aq) + \cancel{2e} \longrightarrow 2Fe^{2+}(aq)$$

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

***Equation*;**

$$2Fe^{3+}(aq) + H_2O_2(aq) + 2\bar{O}H(aq) \longrightarrow 2Fe^{2+}(aq) + O_2(g) + 2H_2O(l)$$

Questions

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

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)
40. Potassium nitrite was added to acidified potassium permanganate solution.

Titration of redox reactions

Redox reactions are used in titrimetric analysis. A solution of unknown concentration of a reducing agent is titrated against a standard solution of an oxidizing agent. From the volumes of the two solutions used and the overall equation of the reaction, the unknown concentration of one of the solutions can be determined. The process involves transfer of electrons from the reducing agent to the oxidizing agent. The half-cell reactions may be given to generate the overall reaction or the student may be required to derive it oneself during practical assignments and examinations. It is very important to check the overall equation to make sure it is well balanced by both mass and charge. When the equation is not balanced, many marks are lost because the mole ratio is important in the subsequent calculation work.

Common redox titrimetric reactions include;

1. **Potassium manganate(VII) titrations in acidic medium**
2. **Sodium thiosulphate titrations**

Potassium manganate(VII) titrations in acidic medium

In these reactions, no indicator is used because the coloured potassium permanganate acts as own indicator. The permanganate ion is reduced to manganese(II) ions in acidic medium as shown by the half reaction below;

$$MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) \quad + \quad 4H_2O(l)$$

Examples

1. **1.50g of an impure potassium manganate(VII) was dissolved in water to make 250cm^3 of solution. 20.0cm^3 of this solution was acidified with dilute sulphuric acid, warmed and titrated against sodium ethanedioate solution made by dissolving 1.70g of anhydrous sodium ethanedioate to make 250cm^3. 24.0cm^3 of the ethanedioate solution was required. Calculate the percentage of impurity in the potassium manganate(VII).**

   Sodium ethanedioate is the standard solution and our treatment of results should begin with this!

$$molar\ mass\ of\ Na_2C_2O_4 = (23 \times 2) + (12 \times 2) + (16 \times 4) = 134g$$

$$moles\ of\ sodium\ ethanedioate\ \ in\ \ 250cm^3 of\ solution = \left(\frac{1.70}{134}\right)$$

$$250cm^3\ of\ \ solution\ contain\ \left(\frac{1.70}{134}\right) moles\ of\ Na_2C_2O_4$$

$$24.0cm^3\ of\ \ solution\ contain\ \left(\frac{1.70 \times 24.0}{134 \times 250}\right) moles\ of\ Na_2C_2O_4$$

~~$(MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) \quad + \quad 4H_2O(l)) \times 2$~~

~~$(C_2O_4^{2-}(aq) \longrightarrow 2CO_2(g) + 2e) \times 5$~~

$$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$$

$$5\ moles\ of\ C_2O_4^{2-}\ react\ with\ 2\ moles\ of\ MnO_4^-$$

$$\left(\frac{1.70 \times 24.0}{134 \times 250}\right) moles\ of\ \ C_2O_4^{2-}\ react\ with\ \left(\frac{1.70 \times 24.0 \times 2}{134 \times 250 \times 5}\right) moles\ of\ MnO_4^-$$

$$20.0cm^3\ contain\ \left(\frac{1.70 \times 24.0 \times 2}{134 \times 250 \times 5}\right) moles\ of\ MnO_4^-$$

$$250cm^3\ contain\ \left(\frac{1.70 \times 24.0 \times 2 \times 250}{134 \times 250 \times 5 \times 20.0}\right) moles\ of\ MnO_4^-$$

$$= \mathbf{0.00609\ moles}$$

$$Molar\ mass\ of\ KMnO_4 = (39 \times 1) + (55 \times 1) + (4 \times 16) = 158g$$

$$1\ mole\ of\ KMnO_4\ weighs\ 158g$$

$$0.00609\ \ moles\ of\ KMnO_4\ weigh\ \left(\frac{0.00609 \times 158}{1}\right)g$$

$$= 0.962g$$

$$mass\ of\ impurity\ in\ KMnO_4 = (1.50 - 0.962) = 0.538g$$

$$percentage\ impurity = \frac{0.538}{1.50} \times 100 = \mathbf{35.87}\%$$

2. **Bronze is an alloy of copper and tin. 9.40g of powdered bronze was warmed with an excess dilute sulphuric acid. The mixture was filtered and the resultant solution made up to 250 cm^3 using distilled water. 25.0cm^3 of the filtrate required 19.20cm^3 of 0.02M potassium manganate(VII) for oxidation.*(Sn=119)***

   (a) Explain why;

   - **(i) the bronze was warmed with excess dilute sulphuric acid**
   - **(ii) the mixture obtained from bronze was filtered**

   (b) Calculate the percentage by mass of tin in the bronze.

(a) (i) *Bronze was warmed with excess dilute sulphuric acid to dissolve the all tin available as tin(II) sulphate. It is the tin(II) ions in this solution that are oxidised to tin(IV) ions by manganate(VII) ions in acidic medium.*

$$Sn(s) + 2H^+(aq) \longrightarrow Sn^{2+}(aq) + H_2(g)$$

(ii) *Copper does not react with dilute sulphuric acid hence it is filtered off as residue to remain with a filtrate of tin(II) sulphate.*

(b) *The standard solution in this case is potassium manganate(VII)*

$$1000\ cm^3\ of\ solution\ contain\ 0.02\ moles\ of\ KMnO_4$$

$$19.20\ cm^3\ of\ solution\ contain\ \left(\frac{19.20 \times 0.02}{1000}\right)\ moles\ of\ KMnO_4$$

~~$(MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) \quad + \quad 4H_2O(l)) \times 2$~~

~~$(Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2e) \times 5$~~

$$2MnO_4^-(aq) + 16H^+(aq) + 5Sn^{2+}(aq) \longrightarrow 2Mn^{2+}(aq) + 5Sn^{4+}(aq) + 8H_2O(l)$$

$$2\ moles\ of\ MnO_4^-\ react\ with\ \ 5\ moles\ of\ Sn^{2+}$$

$$\left(\frac{19.20 \times 0.02}{1000}\right)\ moles\ of\ MnO_4^-\ react\ with\ \left(\frac{19.20 \times 0.02 \times 5}{1000 \times 2}\right)\ moles\ of\ Sn^{2+}$$

$$25.0cm^3 of\ solution\ contain\ \left(\frac{19.20 \times 0.02 \times 5}{1000 \times 2}\right) moles\ of\ Sn^{2+}$$

$$250cm^3 of\ solution\ contain\ \left(\frac{19.20 \times 0.02 \times 5 \times 250}{1000 \times 2 \times 25.0}\right) moles\ of\ Sn^{2+}$$

$$= 0.0096\ moles\ of\ Sn^{2+}$$

$$mass\ of\ tin\ present = (0.0096 \times 119) = 1.1424g$$

$$percentage\ of\ tin = \left(\frac{1.1424}{9.40} \times 100\right) = \mathbf{12.15}\%$$

Questions

1. Calculate the volume of 0.01M potassium manganate(VII) solution required to oxidise 50.0cm^3 of a 0.02M acidified iron(II) ethanedioate solution
2. 25.0cm^3 of an acidified solution of iron(II) sulphate required 17.5cm^3 of 0.025M potassium manganate(VII) solution for complete oxidation. Calculate the molarity of the iron(II) sulphate solution.
3. 25.0cm^3 of a solution of hydrogen peroxide required 27.5 cm^3 of a solution made by dissolving 1.58g of potassium permanganate in 500cm^3 of distilled water. Calculate the;
   (i) concentration of hydrogen peroxide in grams per litre
   (ii) volume of oxygen at s.t.p evolved during the reaction.
4. 1.93g of a sample of an ethanedioate salt was dissolved in water and made up to 250cm^3. 25.0cm^3 of this solution when warmed required 30.4 cm^3 of acidified 0.02M potassium permanganate solution. Calculate the percentage by mass of ethanedioate ions in the original salt.
5. 20.0cm^3 of a 0.01M solution of manganate(VII) ions required exactly 16.65cm^3 of a solution containing 4.8gl^{-1} of an oxalate $(COO^-Y^+)_2.2H_2O$. Calculate the relative atomic mass of Y.
6. A sample of potassium nitrate was decomposed by heating. The residue was dissolved in water and the volume of the solution made up to 250cm^3. 25.0cm^3 of this solution required 28.9cm^3 of acidified potassium manganate(VII) solution of concentration 0.015 moldm^{-3}. Calculate the;
   (i) mass of the residue obtained after decomposition
   (ii) percentage conversion of potassium nitrate to the residue
7. Air contaminated with Sulphur dioxide was bubbled through an acidified solution of potassium manganate(VII). It was found that 500dm^3 of air decolourised 100cm^3 of 0.01M potassium permanganate. Calculate the mass of Sulphur dioxide in the 500 dm^3 of air.
8. Steel is an alloy of mainly iron and carbon. 0.20g of steel was warmed with an excess dilute sulphuric acid. The resultant solution required 34.00cm^3 of 0.02M potassium manganate(VII) for oxidation. Calculate the percentage by mass of iron in the steel.
9. 5.76g of crystals a mixed salt of iron; diammonium iron(II) sulphate, $(NH_4)_2SO_4.FeSO_4.XH_2O$ were accurately weighed and dissolved in dilute sulphuric acid. The solution was made up to the 250 cm^3 mark with more dilute sulphuric acid. 20.0cm^3 of this solution required 23.5cm^3 of a 0.01M solution of potassium manganate(VII) solution for complete reaction. Calculate the value of X in $(NH_4)_2SO_4.FeSO_4.XH_2O$.

Sodium thiosulphate titrations

Sodium thiosulphate ($Na_2S_2O_3.5H_2O$) is a reducing agent. If it is standardized, it is used in titrimetric analysis for reducing iodine to iodide ions as it is oxidised to sodium tetrathionate. Starch indicator is used to give an intense blue colour in presence of iodine. At the end point when all the iodine has been converted to iodide ions, the blue colour varnishes. Sodium thiosulphate cannot be used as a primary standard because it is efflorescent.

The reactions occur by the two half reaction equations shown below and therefore the overall equation.

$$2S_2O_3^{2-}(aq) \longrightarrow S_4O_6^{2-}(aq) + 2e$$

$$I_2(aq) + 2e \longrightarrow 2I^-(aq)$$

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

The thiosulphate can be titrated with aqueous iodine directly or the iodine can be obtained commonly be the redox reactions involving oxidation of potassium iodide by the reducing agents to iodine shown below:

(i) Reaction between potassium manganate(VII) in acidic medium with excess potassium iodide.

$$2MnO_4^-(aq) + 16H^+(aq) + 10I^-(aq) \longrightarrow 2Mn^{2+}(aq) + 5I_2(aq) + 8H_2O(l)$$

(ii) Reaction between potassium dichromate(VI) in acidic medium with excess potassium iodide.

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) \longrightarrow 2Cr^{3+}(aq) + 3I_2(aq) + 7H_2O(l)$$

(iii) Reaction between potassium iodate(V) in acidic medium with excess potassium iodide.

$$IO_3^-(aq) + 6H^+(aq) + 5I^-(aq) \longrightarrow 3I_2(aq) + 3H_2O(l)$$

(iv) Reaction between sodium chlorate(I) (usually from domestic bleach or Jik) in acidic medium with excess potassium iodide solution.

$$ClO^-(aq) + 2H^+(aq) + 2I^-(aq) \longrightarrow Cl^-(aq) + I_2(aq) + H_2O(l)$$

During this process, a dilute acid is added to Jik. Jik is a mixture of sodium hypochlorite and sodium chloride. When a dilute acid is added to jik, chlorine is given off.

$$ClO^-(aq) + Cl^-(aq) + 2H^+(aq) \longrightarrow Cl_2(g) + H_2O(l) \dots\dots\dots\dots\dots (i)$$

The chlorine can then oxidise the iodide ions in potassium iodide to iodine as it is reduced to chloride ions.

$$Cl_2(aq) + 2I^-(aq) \longrightarrow 2Cl^-(aq) + I_2(aq) \dots\dots\dots\dots\dots (ii)$$

The two equations (i) and (ii) when combined give the overall equation above.

Chlorine can also be obtained by adding a dilute acid to bleaching powder (calcium hypochlorite)

$$CaOCl_2(s) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + Cl_2(g) + H_2O(l)$$

(v) Addition of copper(II) ions to excess potassium iodide solution.

$$2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow Cu_2I_2(s) + I_2(aq)$$

Examples

1. **1.185g of potassium dichromate(VI) was dissolved in water to make 250cm^3 of solution. 25.0cm^3 of this solution was acidified and added to excess potassium iodide solution. The resultant solution was titrated against sodium thiosulphate and 17.50cm^3 of the thiosulphate was required. Find the concentration of the thiosulphate solution in grams per litre**.

$$Molar\ mass\ of\ K_2Cr_2O_7 = (39\times 2)+(52\times 2)+(7\times 16) = 294g$$

$$moles\ of\ K_2Cr_2O_7\ in\ 250cm^3 = \frac{1.185}{294}$$

$$250cm^3\ \ of\ solution\ \ contain\ \left(\frac{1.185}{294}\right)moles\ of\ K_2Cr_2O_7$$

$$25.0cm^3\ \ of\ solution\ \ contain\ \left(\frac{1.185\times 25.0}{294\times 250}\right)moles\ of\ K_2Cr_2O_7$$

~~$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$~~

~~$(2I^-(aq) \longrightarrow I_2(aq) + 2e)\times 3$~~

$$\boldsymbol{Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) \longrightarrow 2Cr^{3+}(aq) + 3I_2(aq) + 7H_2O(l)}$$

$$1\ mole\ of\ Cr_2O_7^{2-}\ reacts\ liberates\ \ 3\ moles\ of\ I_2$$

$$\left(\frac{1.185\times 25.0}{294\times 250}\right)moles\ will\ liberate\ \left(\frac{1.185\times 25.0\times 3}{294\times 250}\right)moles\ of\ I_2$$

$$\boldsymbol{2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)}$$

$$1\ mole\ of\ I_2\ reacts\ with\ 2\ moles\ of\ S_2O_3^{2-}$$

$$\left(\frac{1.185\times 25.0\times 3}{294\times 250}\right)moles\ \ will\ react\ with\ \left(\frac{1.185\times 25.0\times 3\times 2}{294\times 250}\right)moles\ of\ S_2O_3^{2-}$$

$$= 2.418\times 10^{-3} moles\ of\ S_2O_3^{2-}$$

$$17.50\ cm^3\ of\ solution\ contain\ 2.418\times 10^{-3} moles\ of\ S_2O_3^{2-}$$

$$1000\ cm^3\ of\ solution\ contain\ \left(\frac{2.418\times 10^{-3}\times 1000}{17.50}\right)moles\ of\ S_2O_3^{2-}$$

$$= 0.138\ moldm^{-3}$$

$$Molar\ mass\ of\ Na_2S_2O_3.5H_2O\ = (23\times 2)+(32\times 2)+(3\times 16)+(5\times 18)$$

$$= 248g$$

$$mass\ of\ Na_2S_2O_3.5H_2O = (0.138\times 248) = \boldsymbol{34.224gdm^{-3}}$$

2. **(a) A solution of potassium iodate was prepared by dissolving 1.0g of potassium iodate in 250cm^3 of distilled water. 10.0cm^3 of this solution was pipetted into a conical flask and to it was added 10.0cm^3 of 1.0M sulphuric acid followed by 10.0cm^3 of 0.5M potassium iodide solution. The iodine liberated required 11.10cm^3 of sodium thiosulphate solution using starch indicator. Calculate the molar concentration of sodium thiosulphate solution.**

$$Molar\ mass\ of\ KIO_3 = (39 \times 1) + (127 \times 1) + (3 \times 16) = 214g$$

$$moles\ of KIO_3\ in\ 250cm^3 of\ solution = \frac{1.0}{214}$$

$$250cm^3\ \ of\ solution\ \ contain\ \left(\frac{1.0}{214}\right) moles\ of\ KIO_3$$

$$10.0cm^3\ \ of\ solution\ \ contain\ \left(\frac{1.0 \times 10.0}{214 \times 250}\right) moles\ of\ KIO_3$$

~~$IO_3^-(aq) + 6H^+(aq) + 6e \longrightarrow I^-(aq) + 3H_2O(l)$~~

~~$(2I^-(aq) \longrightarrow I_2(aq) + 2e) \times 3$~~

$$\boldsymbol{IO_3^-(aq) + 6H^+(aq) + 5I^-(aq) \longrightarrow 3I_2(aq) + 3H_2O(l)}$$

$$1\ mole\ of\ IO_3^-\ reacts\ liberates\ \ 3\ moles\ of\ I_2$$

$$\left(\frac{1.0 \times 10.0}{214 \times 250}\right) moles\ will\ liberate\ \left(\frac{1.0 \times 10.0 \times 3}{214 \times 250}\right) moles\ of\ I_2$$

$$\boldsymbol{2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)}$$

$$1\ mole\ of\ I_2\ reacts\ with\ 2\ moles\ of\ S_2O_3^{2-}$$

$$\left(\frac{1.0 \times 10.0 \times 3}{214 \times 250}\right) moles\ \ will\ react\ with\ \left(\frac{1.0 \times 10.0 \times 3 \times 2}{214 \times 250}\right) moles\ of\ S_2O_3^{2-}$$

$$= 1.121 \times 10^{-3} moles\ of\ S_2O_3^{2-}$$

$$11.10\ cm^3\ of\ solution\ contain\ 1.121 \times 10^{-3} moles\ of\ S_2O_3^{2-}$$

$$1000\ cm^3\ of\ solution\ contain\ \left(\frac{1.121 \times 10^{-3} \times 1000}{11.10}\right) moles\ of\ S_2O_3^{2-}$$

$$= \mathbf{0.101\ M}$$

(b) **30.0cm^3 of a liquid bleach containing sodium hypochlorite was diluted to 250cm^3 of solution using distilled water. 10.0cm^3 of this solution was pipetted into a conical flask and to it was added 10.0cm^3 of 1.0M sulphuric acid followed by 10.0cm^3 of 0.5M potassium iodide solution. The iodine liberated required 10.20cm^3 of the same sodium thiosulphate solution in (a) above using starch indicator. Calculate the percentage by mass of aqueous chlorine in the 30.0cm^3 of liquid bleach**.

Part (a) was to standardise sodium thiosulphate which is now to be used in this part and should be the beginning point of our calculation.

$$1000\ cm^3\ of\ solution\ contain\ 0.101\ moles\ of\ of\ S_2O_3^{2-}$$

$$10.20\ cm^3\ of\ solution\ contain\ \left(\frac{0.101 \times 10.20}{1000}\right)\ moles\ of\ of\ S_2O_3^{2-}$$

$$=\ 1.03 \times 10^{-3}\ moles\ of\ of\ S_2O_3^{2-}$$

$$\boldsymbol{2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)}$$

$$2\ moles\ of\ S_2O_3^{2-} react\ with\ 1\ mole\ of\ I_2$$

$$1.03 \times 10^{-3}\ moles\ of\ of\ S_2O_3^{2-} react\ with\ \left(\frac{1.03 \times 10^{-3} \times 1}{2}\right) moles\ of I_2$$

$$= 5.15 \times 10^{-4}\ moles\ of\ I_2$$

$$\boldsymbol{Cl_2(aq) + 2I^-(aq) \longrightarrow 2Cl^-(aq) + I_2(aq)}$$

$$1\ mole\ of\ I_2\ is\ liberated\ by\ 1\ mole\ of\ Cl_2(aq)\ in\ liquid\ bleach$$

$$5.15 \times 10^{-4}\ moles\ of\ I_2\ are\ liberated\ by\ 5.15 \times 10^{-4}\ moles\ of\ Cl_2(aq)$$

$$10.0\ cm^3\ of\ liquid\ bleach\ solution\ contain\ \ 5.15 \times 10^{-4}\ moles\ of\ Cl_2$$

$$250\ cm^3\ of\ liquid\ bleach\ solution\ contain\ \left(\frac{5.15 \times 10^{-4} \times 250}{10.0}\right) moles\ of\ Cl_2$$

$$= 0.012875\ \ moles\ of\ \ Cl_2$$

Since dilution does not change number moles in the original volume, the 30cm3 of liquid bleach also contain 0.012875 moles of Cl_2

$$Molar\ mass\ of\ \ Cl_2 = (35.5 \times 2) = 71g$$

$$1\ mole\ \ of\ \ Cl_2 weighs\ 71g$$

$$0.012875\ \ moles\ of\ \ Cl_2\ weigh\ \left(\frac{0.012875\ \times 71}{1}\right) g$$

$$= 0.9141\ \ g$$

$$Assuming\ density\ of\ solution\ is\ 1gcm^{-3};$$

$$mass\ of\ liquid\ bleach\ used = 30 \times 1 = 30g$$

$$Percentage\ by\ mass\ of\ chlorine\ in\ liquid\ bleach = \frac{0.9141}{30} \times 100 = \mathbf{3.047}$$

Note that the values of volume and molarity of sulphuric acid and potassium iodide are not used in the calculation. The acid is just to provide acidic medium.

3. **A copper coin of mass 2.00g consists of copper alloyed with small quantities of tin and zinc. The coin was dissolved in moderately concentrated nitric acid and the resultant solution was made up to 250cm^3. 25.0cm^3 of this solution was pipetted , neutralised and added to an excess potassium iodide solution. The iodine liberated required 30.0cm^3 of 0.1M sodium thiosulphate solution using starch indicator in a titration. Calculate the percentage of copper in the coin.**

Copper reacts with moderately concentrated nitric acid to form copper(II) nitrate solution. the copper(II) ions then react with potassium iodide to liberate iodine by the reaction already stated before.

$$3Cu(s) + 8H^+(aq) + 2NO_3^-(aq) \longrightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l)$$

$$1000\ cm^3\ of\ solution\ contain\ 0.1 moles\ of\ of\ S_2O_3^{2-}$$

$$30.0\ cm^3\ of\ solution\ contain\ \left(\frac{0.1 \times 30.0}{1000}\right) moles\ of\ of\ S_2O_3^{2-}$$

$$= 0.003\ moles\ of\ of\ S_2O_3^{2-}$$

$$\boldsymbol{2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)}$$

$$2\ moles\ of\ S_2O_3^{2-} react\ with\ 1\ mole\ of\ I_2$$

$$0.003\ moles\ of\ of\ S_2O_3^{2-} react\ with\ \left(\frac{0.003 \times 1}{2}\right) moles\ of I_2$$

$$= 0.0015\ moles\ of\ I_2$$

$$\boldsymbol{2Cu^{2+}(aq) + 4I^{-}(aq) \longrightarrow Cu_2I_2(s) + I_2(aq)}$$

$$1\ mole\ of\ I_2\ is\ liberated\ by\ 2\ moles\ of\ Cu^{2+}$$

$$0.0015\ moles\ of\ I_2\ are\ liberated\ by\ \left(\frac{0.0015 \times 2}{1}\right)\ moles\ of\ Cu^{2+}$$

$$= 0.003\ moles\ of\ Cu^{2+}$$

$$25.0\ cm^3\ of\ \ solution\ contain\ \ 0.003\ moles\ of\ Cu^{2+}$$

$$250\ cm^3\ of\ solution\ contain\ \left(\frac{0.003 \times 250}{25.0}\right)\ moles\ of\ Cu^{2+}$$

$$= 0.03\ \ moles\ of\ Cu^{2+}$$

$$Molar\ mass\ of\ Cu = (63.5 \times 1) = 63.5g$$

$$1\ mole\ \ of\ Cu^{2+}\ weighs\ 63.5g$$

$$0.03\ \ moles\ of\ Cu^{2+}\ weigh\ \left(\frac{0.03\ \times 63.5}{1}\right)g$$

$$= 1.905g$$

$$Percentage\ of\ copper\ in\ the\ coin = \frac{1.905}{2.00} \times 100 = \mathbf{95.25}$$

Questions

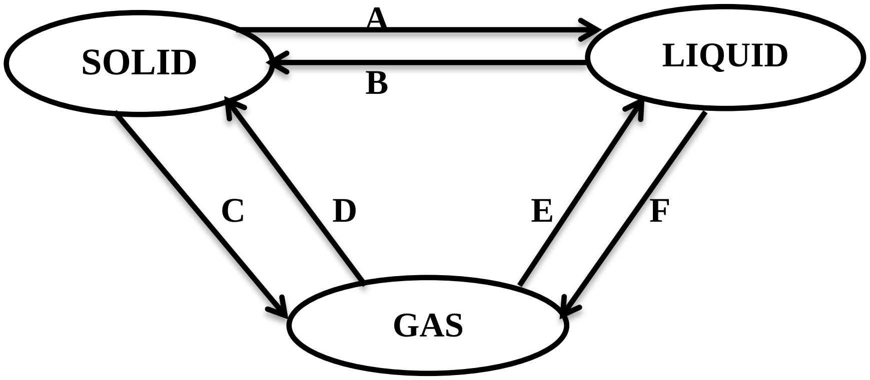
1. 0.89g of potassium iodate were weighed accurately and transferred into a clean 250cm^3 volumetric flask. About 100cm^3 of distilled water was added to dissolve the iodate and the solution was further diluted to the mark with more distilled water. 25.0cm^3 of the solution formed was pipetted into a clean conical flask, 1.0g of potassium iodide was added followed by 3.0 cm^3 of 1.0M sulphuric acid solution. The iodine liberated required 20.0cm^3 of sodium thiosulphate solution. calculate the concentration of the sodium thiosulphate in grams per litre
2. 10.0cm^3 of Jik was measured and then diluted to 250cm^3 of solution in a volumetric flask. 25.0cm^3 of this solution was pipetted and added to an excess of potassium iodide acidified with ethanoic acid. The resultant solution required 20.4cm^3 of 0.1M sodium thiosulphate for complete reaction. Calculate the percentage of available chlorine in the Jik
3. 1.2g of bleaching powder were dissolved in water to make 250cm^3 of solution. 25.0cm^3 of this solution were added to an excess of potassium iodide solution acidified with ethanoic acid and the iodine liberated required 22.3cm^3 of 0.05M sodium thiosulphate solution for complete reaction. Calculate the percentage by mass of available chlorine in the bleaching powder.
4. 8.0g of a copper ore was leached with dilute nitric acid and the resulting solution diluted to 250cm^3. 30.0cm^3 of this solution was accurately measured and added to excess 10% potassium iodide solution. The liberated iodine required 20.0cm^3 of a 0.05M solution of sodium thiosuphate for complete reaction. Calculate the percentage of copper in the ore.

5. 2.4g of brass was dissolved in dilute nitric acid to make 250cm^3 of solution. To 10.0cm^3 of the resultant solution was added excess potassium iodide solution. The iodine liberated required 9.60cm^3 of 0.1M sodium thiosulphate for complete oxidation using starch as indicator. Calculate the percentage of copper in the sample of brass.
6. The formula of double salt of copper; $Cu_w(NH_4)_x(SO_4)_y.zH_2O$, can be determined from the following data.
   (a) When 2g of the salt was boiled with excess sodium hydroxide, the ammonia evolved was absorbed in 40cm^3 of 0.5M hydrochloric acid in a conical flask. The resultant solution required 20cm^3 of 0.5M sodium hydroxide for neutralisation. Calculate the mass of ammonium ions in 2 g of the salt.
   (b) Another 2g of the salt was dissolved in water and treated with an excess of barium chloride solution. The mass of the dried precipitate formed was 2.33g. Calculate the mass of sulphate ions in 2g of the double salt.
   (c) 10g of the salt was dissolved to form 250cm^3 of solution. 25.0cm^3 of this solution was treated with excess potassium iodide and the resultant solution required 25cm^3 of 0.1M sodium thiosulphate solution for complete reaction.Calculate the mass of copper(II) ions in 2g of the salt.
   (d) Hence determine the mass of water of crystallisation in 2g of the salt.
   (e) Deduce the formula of the double salt of copper.

PHYSICAL STATES OF MATTER

There are three states of matter, i.e. solids, liquids and gases. The states can also be referred to as **phases**. However, at very high temperatures, matter exists as **plasma** which has its own strange characteristics.

Inter-conversion between the states



A. Melting
B. Freezing or solidification
C. Sublimation
D. Deposition
E. Condensation
F. Evaporation or vapourisation

Plasma

As a gas is heated to about 10,000K, the intermolecular and interatomic collisions become more and more violent until the molecules disintegrate into electrons and positively charged particles. A mixture of these is what is called plasma. Plasmas are neutral overall but the strong forces between charged particles are different from those between the neutral molecules or atoms in a gas. This makes plasmas very different from gases. External magnetic and electric fields affect the charged particles in plasma but have little or no effect on neutral particles in a gas. Plasmas also emit a lot of light and other electromagnetic radiation at such high temperatures. More modern research is taking place to fully understand the characteristics of plasmas in detail.

The kinetic theory of matter

The kinetic theory was developed between 1860 and 1890, mainly by R.J. Clausius, J.C. Maxwell and Boltzmann. It accounts for the known properties of gases, but it also clarifies many problems concerned with liquids and solids.

The theory can be summarized as follows;

(a) Matter is made up of particles which may be small groups of atoms (molecules) or single atoms in monoatomic gases.
(b) The particles in a gas are in continual, rapid, random motion in straight lines in every direction and collide with each and with the walls of the container in which they are. The pressure exerted by the gas on the walls of the container is due to bombardment by the moving particles. The random motion also applies to liquids but greatly decreased and also further decreased in a solid.
(c) The particles in a gas are separated from each other by distances which are large compared to the size of the particles. In a liquid, the particles are closer together, and they are still closer in a solid.
(d) The particles are regarded as being perfectly elastic so that the collisions they undergo in a gas do not result in any change in the total amount of kinetic energy of the gas.
(e) Increase in temperature causes the motion of the particles to increase, the average kinetic energy of the particles in a gas being proportional to the absolute temperature of the gas.

Differences in the states of matter

Parameter	State of matter		
	Gas	**Liquid**	**Solid**
Particle arrangement	*The particles are far apart and are not orderly arranged*	*The particles are closer to each other and are not orderly arranged*	*The particles are closely packed and orderly arranged, fixed in three dimensional structures.*
Forces of attraction	*Forces of attraction between the molecules are negligible*	*Intermolecular forces of attraction are weaker than those in solids*	*Attraction between the molecules is even more dominant*
Movement	*The particles are mobile with different speeds in various directions*	*Particles randomly move, as in a gas, but not as fast as in gases*	*Movement of the particles is restricted to vibration about mean/fixed positions*

Comparison of physical properties

Physical property	State of matter		
	Gas	**Liquid**	**Solid**
Compressibility	*Gases are highly compressible. Increasing the pressure on a gas decreases its volume and decreasing the pressure will increase its volume*	*Liquids are only slightly compressed*	*Solids are incompressible.*
Density	*Gases have low densities. When a gas is cooled, its density increases.*	*Densities of liquids are higher than gases but lower than those of solids*	*Solids have very high densities.*
Volume	*Gases have no definite volume. They take up volume of containers they occupy.*	*Liquids have definite volumes*	*Solids have definite volumes.*

Shape	*Gases have no definite shape. They take up shape of the container they occupy.*	*Liquids have no shape, they take up shape of the containers they occupy.*	*Solids have definite shapes.*

GASEOUS STATE OF MATTER

A gas is predicted as a random movement of atoms or molecules, not closely packed, with very weak forces between them so that they can move about quite freely.

That is why gases have low densities, they expand to occupy any container and are easily compressed.

The gaseous state in terms of kinetic theory of matter

According to the kinetic theory;

1. The gas molecules occupy only a tiny fraction of the volume of the container in which they are contained. The intermolecular distance is many times larger than the diameter of the molecules. A sample of a gas is nearly empty space and the molecules are scattered throughout this space.
2. The gas molecules are constantly moving in straight lines until they collide with each other and with the walls of the container, exerting no force upon one another. The collisions made are perfectly elastic, meaning that the molecules bounce apart with no loss of energy.
3. The average kinetic energy of the molecules is proportional to absolute temperature, therefore at a certain temperature; all gases have the same average kinetic energy.

AN IDEAL GAS

An ideal gas is also called a **perfect gas**.

An ideal gas is a gas that obeys all gas laws accurately at all temperatures and pressures, has no intermolecular forces of attraction and occupies a negligible volume. However there are known examples of ideal gases and the concept is just a theoretical one.

Gas pressure

This is the pressure exerted by a gas per unit area. The main unit of pressure is $newtons\ per\ unit\ metre\ (Nm^{-1})$.

1 $newton\ per\ unit\ metre\ (Nm^{-1})$ is called a $pascal\ (Pa)$.

$$Pressure\ (p) = \frac{Force}{Area}$$

Other units of pressure are $atmospheric\ pressure\ (atm)$ and $millimetres\ of\ mercury\ (mmHg)$.

$$1\ Nm^{-2} = 1\ Pa$$
$$1\ atm = 101325\ Pa$$
$$1\ atm = 760\ mmHg$$
$$760\ mmHg = 101325 Pa$$
$$1\ kNm^{-2} = 1\ kPa = 1000\ Nm^{-2}$$

Gas laws

Boyle's law

Boyle's law states that; ***at a constant temperature, the volume of a given mass of a gas is inversely proportional to the pressure.***

Or ***at a constant temperature, the pressure of a given mass of a gas is inversely proportional to the volume.***

$$V \propto \frac{1}{p}$$
$$V = k\frac{1}{p}$$
$$pV = k(\ where\ k\ is\ a\ \boldsymbol{constant})$$

Therefore if a gas has a volume V_1 at a pressure $P_1$and the pressure is changed to P_2, the new volume , V_2, at a constant temperature is given by the equation;

$$\boldsymbol{p_1V_1 = p_2V_2}$$

Real gases do not fully obey Boyle's law. The deviations from the law particularly occur at **high pressures** and **low temperatures**, and for gases which are easily liquefied.

The deviations from the law occur due to interactions between the molecules in a gas. If such interactions did not exist, then a gas would obey Boyle's law (would be *ideal* or *perfect*)

Real gases approach the ideal or perfect behaviour at **low pressures** and **high temperatures**.

Charles' law

Charles' law states that; ***at a constant pressure, the volume of a given mass of a gas is directly proportional to the temperature in Kelvin.***

Or ***at a constant pressure, the volume of a given mass of a gas is directly proportional to the absolute temperature.***

$$V \propto T$$
$$V = kT$$
$$\frac{V}{T} = k(\ where\ k\ is\ a\ \boldsymbol{constant})$$

Therefore if a gas has a volume V_1 at a temperature $T_1$and the temperature is changed to T_2, the new volume , V_2, at a constant pressure is given by the equation;

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

$$\boldsymbol{V_1T_2 = V_2T_1}$$

Real gases also deviate from Charles' law as they do for Boyle's law.

Combined gas laws

When Boyle's law and Charles' law are combined, one equation is obtained. This is called the **equation of state for an ideal gas**. The equation relates pressure, volume and the temperature of a gas.

From Boyle's law; $pV = k(\,where\ k\ is\ a\ \boldsymbol{constant})$

If a given mass of a gas has a volume of V_1 at a pressure of p_1, it will a volume V_y at a pressure p_2 at a **constant temperature**.

$$p_1V_1 = p_2V_y$$

$$V_y = \frac{p_1V_1}{p_2} \dots\dots\dots\dots\dots\dots\dots\dots\dots.(i)$$

From Charles' law; $\frac{V}{T} = k(\,where\ k\ is\ a\ \boldsymbol{constant})$

If now the temperature at which the volume of the gas, V_y is measured is changed from $T_1\ K$ to $T_2\ K$, the new volume V_2 will be given by;

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

$$V_yT_2 = V_2T_1$$

$$V_y = \frac{V_2T_1}{T_2} \dots\dots\dots\dots\dots\dots\dots\dots\dots.(ii)$$

Equating equations (i) and (ii) yields;

$$\frac{p_1V_1}{p_2} = \frac{V_2T_1}{T_2}$$

Multiplying through by $\frac{p_2}{T_1}$ yields;

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

and in a more general form, this can be expressed as $\boldsymbol{\frac{pV}{T} = k}$ $(\boldsymbol{where\ k\ is\ a\ numerical\ constant})$ and the temperature expressed in Kelvin.

The equation of state of an ideal gas helps us to calculate the effect of a change in temperature and pressure on the volume of a gas. We cannot compare gas volumes unless they are stated at the same temperature and pressure. Gas volumes are usually compared at 273K and 101325Pa (standard temperature and pressure).

Examples on calculations involving gas laws

In these calculations, it is very crucial to remember to change the temperature to the Kelvin scale. The pressure may be left in its units so long as they are the same on both sides throughout the calculation.

1. **If the volume of a gas at standard temperature and pressure is 51 cm^3, calculate the volume of the gas if it is collected at 60°C and 105 kPa.**

$$V_1 = 51\ cm^3 \qquad V_2 = ?$$
$$p_1 = standard\ pressure = 101325\ Pa \qquad p_2 = 105 \times 1000Pa$$
$$T_1 = standard\ temperature = 273K \qquad T_2 = (60 + 273)K$$
$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$
$$\frac{101325 \times 51}{273} = \frac{105 \times 1000 \times V_2}{(60 + 273)}$$
$$V_2 = \left(\frac{101325 \times 51 \times 333}{105 \times 1000 \times 273}\right) cm^3$$
$$\boldsymbol{V_2 = 60\ cm^3}$$

2. **A closed bulb contains a certain volume of a gas at 21°C and 755mmHg. Calculate the pressure of the gas if the temperature is raised to 51°C.**

$$V_1 = \mathrm{V} \qquad V_2 = V$$
$$p_1 = 755\ mmHg \qquad p_2 = ?$$
$$T_1 = (21 + 273) = 294K \qquad T_2 = (51 + 273) = 324K$$
$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$
$$\frac{755 \times V}{294} = \frac{p_2 \times V}{324}$$
$$p_2 = \left(\frac{755 \times 324}{294}\right) mmHg$$
$$\boldsymbol{p_2 = 832\ mmHg}$$

Ideal gas law

Boyle's law and Charles' law can be combined to form a single equation which represents the relationship between pressure, volume and kelvin temperature of a given mass of a gas under different conditions.

$$V \propto \frac{1}{p}(at\ constant\ temperature)\ by\ Boyle's\ law$$
$$V \propto T(at\ constant\ pressure)\ by\ Charles'\ law$$

By combining the two gas laws;

$$V \propto \frac{T}{p}$$
$$V = \frac{T}{p} \times \ constant$$
$$pV = constant \times T$$

When the quantity of gas is one mole, the constant in this equation is called the molar gas constant, represented by R.
Therefore for 1 mole of a gas; $pV = RT$
And for n moles of a gas;

$$\boldsymbol{pV = nRT}$$

The above equation is known as the **ideal gas equation** because it only holds when gases behave as **ideal** or **perfect** gases.

The molar gas constant is commonly used as $8.31JK^{-1}mol^{-1}$ when the units of pressure, volume and temperature are $pascals(Pa)/Nm^{-2}, m^3$ and Kelvin respectively.

Recall that;

$$1\ Nm^{-2} = 1\ Pa$$
$$1\ atm = 101325\ Pa$$
$$therefore\ 2\ atm = (2 \times 101325)Pa$$

$$760\ mmHg = 101325Pa$$
$$therefore\ 720\ mmHg = \left(\frac{720}{760} \times 101325\right) Pa$$

$$1\ kNm^{-2} = 1\ kPa = 1000\ Nm^{-2}$$
$$therefore\ 20.2\ kNm^{-2} = 20.2\ kPa = 20.2 \times 1000\ Nm^{-2}$$

$$1\ cm^3 = 10^{-6}m^3$$
$$56\ cm^3 = (56 \times 10^{-6})m^3$$

$$1\ litre/dm^3 = 1000\ cm^3 = 10^{-3}m^3$$
$$15\ litre/dm^3 = 15000\ cm^3 = 15 \times 10^{-3}m^3$$

$$The\ formula;\ \boldsymbol{pV = nRT}\ \ can\ be\ written\ as\ \boldsymbol{pV = \frac{m}{M_r}RT}\ since\ \boldsymbol{n = \frac{m}{M_r}}.$$
$$\boldsymbol{M_r}\ can\ therefore\ be\ obtained\ from\ the\ expression;$$
$$\boldsymbol{M_r = \frac{mRT}{pV}}$$

Examples

1. **Calculate the volume occupied by 200g of carbon dioxide gas at a temperature 30°C and a pressure of 98.65 kPa**.

$$m = 200g$$
$$T = (30 + 273) = 303\ K$$
$$p = (98.65 \times 1000)Pa$$
$$V = ?$$
$$M_r\ of\ CO_2 = (12 \times 1) + (16 \times 2) = 44g$$

$$pV = nRT$$
$$pV = \frac{m}{M_r}RT$$
$$V = \frac{mRT}{pM_r} = \frac{200 \times 8.31 \times 303}{98.65 \times 1000 \times 44}$$
$$V = 0.116m^3$$

2. **0.539g of a vapourised sample of gas X occupies 200 cm^3 at a temperature of 373K and a pressure of 0.938 atm. Calculate the relative molecular mass of X**.

$$m = 0.539g \quad T = 373\ K$$
$$p = (0.938 \times 101325)Pa$$
$$V = (200 \times 10^{-6})m^3$$
$$RFM = ?$$
$$pV = nRT$$

$$pV = \frac{m}{M_r}RT$$
$$M_r = \frac{mRT}{pV} = \frac{0.539 \times 8.31 \times 373}{(0.938 \times 101325) \times (200 \times 10^{-6})}$$
$$M_r = 87.89g$$
$$Relative\ molecular\ mass\ of\ X\ is\ 87.89$$

Questions

1. A certain mass of a gas has a volume of 241m^3 at 18°C and a pressure of 100400 Pa. determine its volume at s.t.p.
2. A gas occupies a volume of 1500 m^3 at 27°C and 102,700 Nm^{-2} pressure. What would be its volume at s.t.p?
3. A certain gas has a volume of 75 m^3 at 15°C and 104 kPa. What would be its volume at 27°C and 740 $mmHg$?
4. A sealed flask contains oxygen at 17°C and 99.3 kNm^{-2}. What would be the pressure of the oxygen if the temperature was lowered to -23 °C ?
5. At s.t.p, a certain mass of a gas has a volume of 1 litre. At 30 atm, the volume is 31.2 cm^3 and at 60 atm, the volume is 14.9 cm^3. Explain whether the gas shows ideal behaviour.
6. (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 decomposed into hydrogen and iodine. Calculate the pressure of the equilibrium mixture at 300°C assuming no change in volume.

7. Calculate the volume occupied by 200g of chlorine gas at a temperature 15 $°C$ and a pressure of 54.71 kPa.
8. 1212.5 cm^3 of a gas J has a mass of 0.88g at 50$°C$ and a pressure of 115000Nm^{-2}. Calculate the relative molecular mass of the gas.
9. A gas Q contains 30.43% nitrogen and the rest being oxygen. 0.23g of Q occupied 154.11cm^3 at 150$°C$ and 840mmHg. Determine the;
   (i) Empirical formula of Q
   (ii) Molecular formula of Q.

More of the application of this concept is covered in empirical and molecular formula.

Graham's law of gaseous diffusion

The concept of diffusion is not a new one to us at this level since you already have an idea from Ordinary level.

The rates at which different gases diffuse are not equal. A lighter gas diffuses more rapidly than a heavier one. After carrying out a number of experiments on the rates at which gases mix together, Graham(1832) came up with Graham's law which states that;

At constant temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its density.

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

Consider two gases X and Y which diffuse at rates R_X and R_Y respectively. If the densities of the gases are ρ_X and ρ_Y respectively;

$$R_X \propto \frac{1}{\sqrt{\rho_X}}\ and\ \ R_Y \propto \frac{1}{\sqrt{\rho_Y}}$$

$$R_X = k\frac{1}{\sqrt{\rho_X}} \ldots\ldots\ldots\ldots(i) \quad and \quad R_Y = k\frac{1}{\sqrt{\rho_Y}} \ldots\ldots\ldots\ldots\ldots(ii)$$

Dividing equation (i) by equation (ii) yields;

$$\boldsymbol{\frac{R_X}{R_Y} = \frac{k\frac{1}{\sqrt{\rho_X}}}{k\frac{1}{\sqrt{\rho_Y}}}}$$

$$\boldsymbol{\frac{R_X}{R_Y} = \frac{\frac{1}{\sqrt{\rho_X}}}{\frac{1}{\sqrt{\rho_Y}}}}$$

$$\boldsymbol{\frac{R_X}{R_Y} = \frac{\sqrt{\rho_Y}}{\sqrt{\rho_X}}}$$

$$\boldsymbol{\frac{Rate\ of\ diffusion\ of\ X}{Rate\ of\ diffusion\ of\ Y} = \frac{\sqrt{density\ of\ Y}}{\sqrt{density\ of\ X}}}$$

$But\ density = \frac{mass}{volume}$. If the volume is kept constant, then density is directly proportional to the relative molecular mass of the gas. We then have;

$$R_X \propto \frac{1}{\sqrt{\rho_X}} \; and \;\; R_Y \propto \frac{1}{\sqrt{\rho_Y}}$$

$$R_X = k\,\frac{1}{\sqrt{M_r of\ X}} \ldots\ldots\ldots\ldots.(i) \quad and \quad R_Y = k\,\frac{1}{\sqrt{M_r of\ Y}} \ldots\ldots\ldots\ldots\ldots(ii)$$

Dividing equation (i) by equation (ii) yields;

$$\boldsymbol{\frac{R_X}{R_Y} = \frac{k\,\frac{1}{\sqrt{M_r of\ X}}}{k\,\frac{1}{\sqrt{M_r of\ Y}}}}$$

$$\boldsymbol{\frac{R_X}{R_Y} = \frac{\sqrt{M_r of\ Y}}{\sqrt{M_r of\ X}}}$$

$$\boldsymbol{\frac{Rate\ of\ diffusion\ of\ X}{Rate\ of\ diffusion\ of\ Y} = \frac{\sqrt{M_r of\ Y}}{\sqrt{M_r of\ X}}}$$

Graham’s law can therefore also be stated as; ***at constant temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its relative molecular mass.***

Rate of diffusion of a gas can also be expressed as a reciprocal of the time taken for the gas to diffuse. Therefore;

$$\boldsymbol{R_X = \frac{1}{t_X} \; and \;\; R_Y = \frac{1}{t_Y}}$$

$$\boldsymbol{from;\ \frac{R_X}{R_Y} = \frac{\sqrt{\rho_Y}}{\sqrt{\rho_X}}}$$

$$\boldsymbol{{}^{\frac{1}{t_X}}\Big/_{\frac{1}{t_Y}} = \frac{\sqrt{\rho_Y}}{\sqrt{\rho_X}}}$$

$$\boldsymbol{\frac{t_Y}{t_X} = \frac{\sqrt{\rho_Y}}{\sqrt{\rho_X}}}$$

Similarly;

$$\boldsymbol{\frac{t_Y}{t_X} = \frac{\sqrt{M_r of\ Y}}{\sqrt{M_r of\ X}}}$$

Rate of diffusion of a gas can also be expressed in terms of volume of the gas and time taken by the gas to diffuse.

$$Rate\ of\ diffusion\ of\ a\ gas = \frac{volume\ of\ the\ gas}{time\ taken}$$

Avoid the common mistake done by students during most of these calculations by forgetting that most gases are diatomic. This should be observed when calculating molar masses of gases.

Examples

1. A given volume of gas ***W*** diffuses through a hole in 14.1 seconds while the same volume of carbon dioxide diffuses through the same hole in 10 seconds. Calculate the molecular mass of gas ***W***.

$V_w = V\ cm^3$ $V_{CO_2} = V\ cm^3$ $t_w = 14.1\ s$ $t_{CO_2} = 10\ s$ $M_r of\ w = ?$ $M_r of\ CO_2 = (12 \times 1) + (16 \times 2)$ $= 44g$ $R_W = \frac{V}{14.1}\ cm^3 s^{-1}$ $R_{CO_2} = \frac{V}{10}\ cm^3 s^{-1}$	$\frac{R_W}{R_{CO_2}} = \frac{\sqrt{M_r of\ CO_2}}{\sqrt{M_r of\ w}}$ $\frac{\left(\frac{V}{14.1}\right)}{\left(\frac{V}{10}\right)} = \frac{\sqrt{44}}{\sqrt{M_r of\ w}}$ $\left(\frac{10}{14.1}\right)^2 = \frac{44}{M_r of\ w}$ $M_r of\ w = 87.5g$

2. **A given volume of a gas X diffuses in two thirds of the time taken by an equal volume of hydrogen chloride under the same physical conditions. Calculate the relative molecular mass of the X.**

$V_X = V\ cm^3$ $V_{HCl} = V\ cm^3$ $t_X = \frac{2t}{3} s$ t_{HCl} $= t\ s$ $M_r of\ X = ?$ $M_r of\ HCl = (1 \times 1) + (35.5 \times 1) = 36.5g$ $R_X = \left(\frac{V}{\frac{2t}{3}}\right) = \left(\frac{3V}{2t}\right)\ cm^3 s^{-1}$ R_{HCl} $= \frac{V}{t}\ cm^3 s^{-1}$ $\frac{R_X}{R_{HCl}} = \frac{\sqrt{M_r of\ HCl}}{\sqrt{M_r of\ X}}$	$\left(\frac{3V}{2t}\right) \Big/ \left(\frac{V}{t}\right) = \frac{\sqrt{36.5}}{\sqrt{M_r of\ X}}$ $\left(\frac{3V}{2t} \times \frac{t}{V}\right) = \frac{\sqrt{36.5}}{\sqrt{M_r of\ X}}$ $\left(\frac{3}{2}\right)^2 = \frac{36.5}{M_r of\ X}$ $M_r of\ X = 16.22g$ $The\ relative\ molecular\ mass\ of\ X\ is\ 16.22$

3. **Oxygen diffuses 0.9 times faster than a hydrocarbon Y. Calculate the relative molecular mass of Y**.

$M_r of\ O_2 = (16 \times 2) = 32g$ $M_r of\ Y$ $= ?$ $R_{O_2} = 0.9\ R_Y$ R_Y $= rate\ of\ diffusion\ of\ Y$ $\frac{R_{O_2}}{R_Y} = \frac{\sqrt{M_r of\ Y}}{\sqrt{M_r of\ O_2}}$	$\frac{0.9\ R_Y}{R_Y} = \frac{\sqrt{M_r of\ Y}}{\sqrt{32}}$ $\left(\frac{0.9}{1}\right)^2 = \frac{M_r of\ Y}{32}$ $M_r of\ Y = 25.92$ $The\ relative\ molecular\ mass\ of\ Y\ is\ 25.92$

4. **The time taken for $0.06\ cm^3$ of oxygen to diffuse through a porous partition is 10 seconds. Another gas Z at the same conditions of temperature and pressure**

diffuses through the partition at the rate of $0.1cm^3$ in 20s. Determine the relative molecular mass of gas Z.

$$M_r of\ O_2 = (16 \times 2) = 32g \qquad M_r of\ Z = ?$$

$$R_{O_2} = \left(\frac{0.06}{10}\right) cm^3s^{-1} \quad R_Z = \left(\frac{0.1}{20}\right) cm^3s^{-1}$$

$$\frac{R_{O_2}}{R_Z} = \frac{\sqrt{M_r of\ Z}}{\sqrt{M_r of\ O_2}}$$

$$\left(\frac{0.06}{10}\right) \Big/ \left(\frac{0.1}{20}\right) = \frac{\sqrt{M_r of\ Z}}{\sqrt{32}}$$

$$\left(\frac{0.006}{0.005}\right)^2 = \frac{M_r of\ Z}{32}$$

$$M_r of\ Z = 46.08g$$

$The\ relative\ molecular\ mass\ of\ Z\ is\ 46.08$

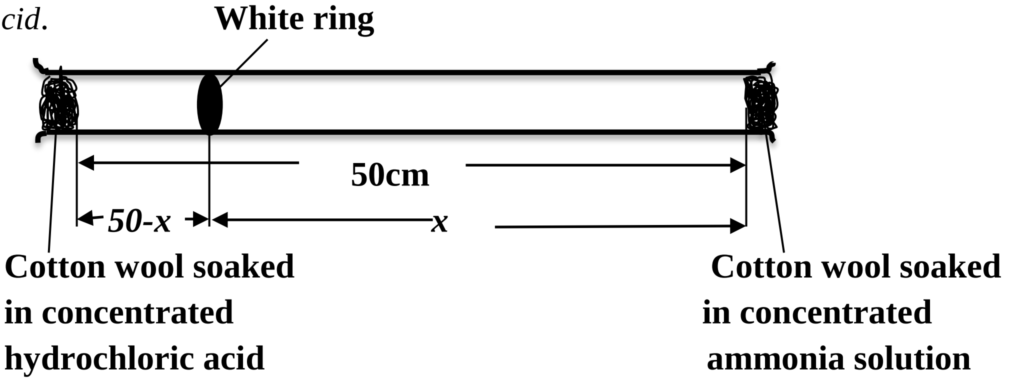
5. **Two pieces of cotton wool were each soaked separately in concentrated ammonia solution and concentrated hydrochloric acid respectively and simultaneously inserted into opposite ends of a horizontal wide glass tube. After a short time a white ring was across the tube. If the distance between the inner surfaces of the cotton wool plugs is 50cm.**
   - **(i) Name the white ring**
   - **(ii) Write the equation leading to formation of the white ring.**
   - **(iii) Determine how far from the ammonia plug the white ring is formed.**

(i) Ammonium chloride

(ii) $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

(iii) $let\ the\ distance\ of\ the\ white\ ring\ from\ the\ cotton\ wool\ soaked\ in\ ammonia\ be\ x\ cm$

Since ammonia gas from concentrated ammonia solution diffuses faster than hydrogen chloride gas from hydrochloric acid, the white ring is formed nearer the cotton wool soaked in hydrochloric acid.



$$M_r\ of\ HCl = (1 \times 1) + (35.5 \times 1) = 36.5g$$

$$M_r\ of\ NH_3 = (1 \times 14) + (3 \times 1) = 17g$$

$$R_{HCl} = \left(\frac{50 - x}{50}\right) \qquad R_{NH_3} = \left(\frac{x}{50}\right)$$

$$\left(\frac{50 - x}{50}\right) \Big/ \left(\frac{x}{50}\right) = \frac{\sqrt{17}}{\sqrt{36.5}}$$

$$\frac{R_{HCl}}{R_{NH_3}} = \frac{\sqrt{M_r of\ NH_3}}{\sqrt{M_r of\ HCl}}$$

$$\frac{50 - x}{x} = \sqrt{\left(\frac{17}{36.5}\right)}$$

$$50 - x = 0.6825x$$

$$x = 29.72$$

$$\boxed{\boldsymbol{The\ distance\ of\ the\ white\ ring\ from\ the\ ammonia\ plug\ is\ 29.72cm}}$$

6. **Oxygen diffuses 2.3 times as fast as a compound Z with the formula; $Ni(CO)_n$. Determine the molecular formula of Z.**

$M_r of\ O_2 = (16 \times 2) = 32g$ $\quad$ $M_r of\ Z = ?$

$R_{O_2} = 2.3\ R_Z$ $\quad$ $R_Z = rate\ of\ diffusion\ of\ Z$

$$\frac{R_{O_2}}{R_Z} = \frac{\sqrt{M_r of\ Z}}{\sqrt{M_r of\ O_2}}$$

$$\frac{2.3\ R_Z}{R_Z} = \frac{\sqrt{M_r of\ Z}}{\sqrt{32}}$$

$$\left(\frac{2.3}{1}\right)^2 = \frac{M_r of\ Z}{32}$$

$$M_r of\ Z = 169.28g$$

$$Ni(CO)_n = 169.28$$

$$58.7 + 12n + 16n = 169.28$$

$$28n = 110.58$$

$$n = 4$$

$$\boldsymbol{Molecular\ formula\ of\ Z\ is\ Ni(CO)_4}$$

Questions

1. Calculate the ratio of diffusion of a gas at 91°C and 0°C at a constant pressure.
2. A gas $\boldsymbol{Q}$ diffuses 4 times as rapidly as sulphur dioxide under the same conditions. If the density of sulphur dioxide under the same conditions of temperature and pressure is $2.88 \times 10^3 gm^{-3}$, calculate the density of $\boldsymbol{Q}$.
3. 100cm^3 of oxygen diffused through a membrane in 5 minutes. 120 cm^3 of an unknown gas under the same conditions, diffused through the membrane in 10 minutes. Calculate the molecular mass of the unknown gas.
4. Oxygen diffuses 1.19 times faster than an amine, $C_nH_{2n+1}NH_2$.
   (i) Determine the molecular formula of the amine.
   (ii) Deduce the structural formulae and names of all possible isomers of the amine.
5. 250 cm^3 of an alkene diffuse through a porous medium in 10 seconds and 716 cm^3 of oxygen diffuse through the same medium in 25 seconds under the same conditions. Calculate the molecular mass of the alkene and deduce its structural formula.
6. Oxygen diffused through a porous partition in 1.87 minutes. Under similar conditions, the same volume of an alkene, $\boldsymbol{T}$ diffused in 2.15 minutes.
   (a) Determine the formula of $\boldsymbol{T}$
   (b) Write equation and outline mechanism for the reaction between T and benzene. Indicate the conditions for the reaction.

7. 141.4 cm^3 of an inert gas diffused through a porous plug in the same time as it took 50cm^3oxygen to diffuse through the same plug under the same conditions. Calculate the relative atomic mass of the inert gas.
8. Two pieces of cotton wool were each soaked separately in concentrated amine ***Q*** and concentrated hydrochloric acid respectively and placed at opposite ends of a 2m long glass tube. After some time a white ring was formed at 0.96m from the end containing concentrated hydrochloric acid. Determine the relative molecular mass of amine ***Q***.
9. Two pieces of cotton wool were each soaked separately in concentrated amine ***Y*** and concentrated hydrochloric acid respectively and placed at opposite ends of a 1m long glass tube. After some time a white ring was formed at 0.52m from the end containing the concentrated ammine. Determine the relative molecular mass of amine ***Y***.
10. 6.3 cm^3 of gas L diffuses through a porous partition in 5s. 7.4 $cm^3$of oxygen diffuses through the same partition in the same time. Calculate the molecular mass of ***L***.
11. Nitrogen gas diffuses 1.25times faster than gas ***X***. calculate the relative molecular mass of gas ***X***.
12. 25 cm^3 of gas ***Q*** diffuse through a small aperture in 48 seconds while 25 cm^3 of an alkane diffuse through the same aperture in 40 seconds.
    - (i) Deduce the molecular formula of the alkane.
    - (ii) Write equations to show how the alkane can be synthesized from Pent-2-yne.
13. Gas ***X*** diffuses through a membrane in 20.5 minutes and under the same conditions, an equal volume of hydrogen diffuses through the same membrane in 3 minutes. Calculate the molecular mass of ***X***.
14. 141.4 cm^3 of gas ***X*** diffused through a porous plug in the same time it took 50 cm^3 of oxygen to diffuse through the same plug under identical conditions. Calculate the relative molecular mass of ***X***.

15. State Graham's law of gaseous diffusion.

    (b) Nickel forms a gaseous carbonyl; $Ni(CO)_n$. Deduce the value of n if carbon monoxide diffuses 2.46 times faster than the carbonyl compound.

    (c) State the ;

    (i) name of the nickel carbonyl

    (ii) coordination number of nickel in the compound.

16. (a) State Graham's law of gaseous diffusion.

    (b) A hydride of silicon contains 9.65% by mass of hydrogen and was found to diffuse through a porous plug at two thirds of the rate of diffusion of nitrogen. Determine the molecular formula of the hydride.
17. A gaseous compound ***X*** contained 46.1% carbon and 53.9% nitrogen. In 20 seconds, $50cm^3$of ***X*** diffused through a porous plug and the same volume of oxygen diffused in 15.7 seconds.
    - (i) Determine the molecular formula of ***X***.
    - (ii) Calculate the volume of carbon dioxide that diffuses in 20 seconds under the same conditions.
18. A compound, ***B*** has an empirical formula of C_3H_6O. Oxygen gas diffuses 1.345 times faster than ***B***.
    - (a) (i) Determine the molecular formula of ***B***
      - (ii) Write the structural formulae of all the possible isomers of ***B***.
    - (b) (i) ***B*** does not Fehling's solution. Using equations, show how ***B*** can be formed from propene
      - (ii) Write an equation for the reaction of ***B*** with sodium hydrogen sulphite and write the mechanism.
19. A gaseous oxide of sulphur, SO_n diffused through a porous partition in 2.68 minutes while equal volume methane at the same temperature diffused in 1.1985 minutes.
    - (a) Determine the value of n in the oxide SO_n
    - (b) The oxide in (a) above reacts with benzene via an electrophilic substitution mechanism.
      - (i) State whether the oxide in (a) above acts as an electrophile or nucleophile. Give a reason for your answer.
      - (ii) Write equation for the reaction with benzene and outline the mechanism.

$(H = 1; C = 12;\ N = 14; O = 16;\ Si = 28.1;\ S = 32;\ Cl = 35.5; Ni = 58.7)$

Mole fraction of a gas, (x)

Mole fraction <u>of a gas</u> is the ratio of the number of moles of the gas present to the total number of moles of all the gases in the mixture.

$$x = \frac{n_i}{n_{total}}$$

Therefore for a mixture of two gases A and . The mole fractions of gases A and B are given respectively as

$$x_A = \frac{n_A}{n_A + n_B}\ \ and\ x_B = \frac{n_B}{n_A + n_B}$$

$$x_A = \frac{n_A}{n_{total}}\ \ and\ x_B = \frac{n_B}{n_{total}}$$

$$we\ should\ also\ note\ that\ the\ total\ mole\ fraction\ should\ always\ be\ one$$

$$x_A + x_B = 1$$

$$Therefore\ \ x_A = 1 - x_B$$

Also from Avogadro's hypothesis, it follows that;

$$x_A = \frac{n_A}{n_A + n_B} = \frac{volume\ of\ gas\ A}{Total\ volume}$$

$$x_B = \frac{n_B}{n_A + n_B} = \frac{volume\ of\ gas\ B}{Total\ volume}$$

Dalton's law of partial pressure

In a mixture of gases, each gas behaves as if it was the only gas present assuming there are no chemical interactions between the gases. In a container in which a mixture of gases, that not react are enclosed, the total pressure exerted is a result of the individual pressures of each of the gases. Each of these pressures is called **partial pressure**.

Partial pressure of a gas is the pressure which that gas exerts if it occupies a vessel alone which was initially occupied by a mixture of gases.

In 1801, Dalton came up with Dalton's law of partial pressure which states that; in ***a mixture of gases which do not react chemically, the total pressure is the sum of the partial pressures of the components***.

$$p_{total} = p_1 + p_2 + p_3 + \ldots + p_n$$

Let us now consider a mixture of three gases A and B and C placed in a vessel each having partial pressures p_A , p_B and p_C respectively.

According to Dalton's law of partial pressures; the total pressure exerted by the gases is;

$$p_{total} = p_A + p_B + p_C$$

and if each of the gases has the number of moles as n_A and n_B and n_C respectively,

Then the mole fractions of the gases A and B and C are given by;

$$x_A = \frac{n_A}{n_A + n_B + n_c}, \quad x_B = \frac{n_B}{n_A + n_B + n_c}\ and\ x_c = \frac{n_c}{n_A + n_B + n_c}$$

$$x_A = \frac{n_A}{n_{total}}\ , \quad x_B = \frac{n_B}{n_{total}}\ and\ x_c = \frac{n_c}{n_{total}}$$

The partial pressures of each of the gases $p_A,\ p_B\ and\ p_C$ respectively are given as a product of their respective mole fractions and the total pressure, p_{total}.

$$p_A = x_A p_{total} = \left(\frac{n_A}{n_{total}}\right) p_{total}$$

$$p_B = x_B p_{total} = \left(\frac{n_B}{n_{total}}\right) p_{total}$$

$$p_C = x_c p_{total} = \left(\frac{n_c}{n_{total}}\right) p_{total}$$

Dalton came with his law experimentally but it can be deduced from the ideal gas equation. Therefore if each of the gases has the number of moles as n_A and n_B and

n_C respectively and occupy a volume V, then, the pressures of each of the gases p_A, p_B and p_C respectively are given as;

$$p_A V = n_A RT$$
$$p_B V = n_B RT$$
$$p_C V = n_C RT$$

The total pressure can then be expressed as

$$p_{total} V = (n_A + n_B + n_C)RT$$
$$p_{total} = (n_A + n_B + n_C)\frac{RT}{V}$$
$$p_{total} = p_A + p_B + p_C$$

Examples

1. **(a) State Dalton's law of partial pressures.**

   (b) Explain why a mixture of ammonia and hydrogen chloride does not hold for Dalton's law of partial pressures.

   (c) A mixture of 20% ammonia, 55% hydrogen and 25% nitrogen by volume has a pressure of $\mathbf{9.80 \times 10^4\ Nm^{-2}}$. Calculate the partial pressure of each gas.

(b) *Ammonia reacts with hydrogen chloride to form ammonium chloride. For Dalton's law to hold, there should be no chemical interactions between the gases.*

(c) According to Avogadro's hypothesis;

$$x_A = \frac{n_A}{n_A + n_B} = \frac{volume\ of\ gas\ A}{Total\ volume}$$

$$p_{NH_3} = x_{NH_3} p_{total}$$
$$= \frac{20}{100} \times 9.80 \times 10^4\ Nm^{-2}$$
$$= \mathbf{1.96 \times 10^4\ Nm^{-2}}$$

$$p_{H_2} = x_{H_2} p_{total}$$
$$= \frac{55}{100} \times 9.80 \times 10^4\ Nm^{-2}$$
$$= \mathbf{5.39 \times 10^4\ Nm^{-2}}$$

$$\boxed{p_{N_2} = x_{N_2} p_{total} = \frac{25}{100} \times 9.80 \times 10^4 = \mathbf{2.45 \times 10^4\ Nm^{-2}}}$$

2. **1.3g of carbon dioxide and 2.4g of oxygen were mixed in a 1 litre vessel. If the total pressure of the mixture is 100 atmospheres, calculate the partial pressure of each gas present in the container.**

$$molar\ mass\ of\ CO_2 = (1 \times 12) + (2 \times 16) = 44g$$
$$number\ of\ moles\ of\ CO_2, n_{CO_2} = \frac{1.3}{44} = 0.0295$$
$$total\ number\ of\ moles, n_{total} = 0.0295 + 0.075$$
$$= 0.1045$$
$$x_{CO_2} = \frac{n_{CO_2}}{n_{total}} = \frac{0.0295}{0.1045}$$

$$molar\ mass\ of\ O_2 = (2 \times 16) = 32g$$
$$number\ of\ moles\ of\ O_2, n_{O_2} = \frac{2.4}{32} = 0.075$$
$$x_{O_2} = \frac{n_{O_2}}{n_{total}} = \frac{0.075}{0.1045}$$

$$p_{CO_2} = x_{CO_2}p_{total}$$
$$= \left(\frac{0.0295}{0.1045}\right) \times 100$$
$$= 28.2297atm$$

$$p_{O_2} = x_{O_2}p_{total} = \left(\frac{0.075}{0.1045}\right) \times 100$$
$$= \mathbf{71.7703\ atm}$$

3. 50.0 cm^3 of carbon dioxide at $1 \times 10^5 Nm^{-2}$ are mixed with 150 $cm^3$of hydrogen at the same pressure. If the pressure of the mixture is $1.00 \times 10^5 Nm^{-2}$. Calculate the partial pressure of carbon dioxide.

$$total\ volume = (50.0 + 150)\ \ cm^3$$
$$= 200\ \ cm^3$$
$$x_A = \frac{volume\ of\ gas\ CO_2}{Total\ volume} = \frac{50}{200}$$

$$p_{CO_2} = x_{CO_2}p_{total}$$
$$= \left(\frac{50}{200}\right) \times 1.00 \times 10^5 Nm^{-2}$$
$$= \mathbf{2.5 \times 10^4 Nm^{-2}}$$

4. In a vessel of volume 10.0 dm^3 are introduced 4.00 $dm^3$of methane at a pressure of $2.02 \times 10^5 Nm^{-2}$, 12.5 $dm^3$of ethane at a pressure of $3.50 \times 10^5 Nm^{-2}$ and 1.50 $dm^3$of propane at a pressure of $1.01 \times 10^5 Nm^{-2}$. Calculate the pressure of the resulting gas mixture.

$$p_{CH_4} = \left(\frac{4}{10} \times 2.02 \times 10^5\right) Nm^{-2}$$
$$\mathbf{p_{CH_4} = 8.08 \times 10^4 Nm^{-2}}$$

$$p_{CH_3CH_3} = \left(\frac{12.5}{10} \times 3.50 \times 10^5\right) Nm^{-2}$$
$$\mathbf{p_{CH_3CH_3} = 4.375 \times 10^5 Nm^{-2}}$$

$$p_{CH_3CH_2CH_3} = \left(\frac{1.5}{10} \times 1.01 \times 10^5\right) Nm^{-2}$$
$$\mathbf{p_{CH_3CH_2CH_3} = 1.515 \times 10^4 Nm^{-2}}$$
$$\mathbf{p_{total} = p_{CH_4} + p_{CH_3CH_3} + p_{CH_3CH_2CH_3}}$$
$$p_{total} = (8.08 \times 10^4 + 4.375 \times 10^5 + 1.515 \times 10^4) Nm^{-2}$$
$$\mathbf{p_{total} = 5.3345 \times 10^5 Nm^{-2}}$$

5. A 2 dm^3 sample of air at 27°C contains 0.62 g of oxygen gas, 1.34g of carbon dioxide gas and 0.06g of nitrogen gas. Calculate;

(i) the partial pressures of each gaseous component in the mixture

(ii) the total pressure of the mixture of gases.

(i)

$$molar\ mass\ of\ O_2 = (2 \times 16) = 32g$$
$$molar\ mass\ of\ CO_2 = (1 \times 12) + (2 \times 16)$$
$$= 44g$$
$$molar\ mass\ of\ N_2 = (2 \times 14) = 28g$$
$$V = (2 \times 10^{-3})\ m^3, T = (27 + 273) = 300K$$

$$p_{O_2}V = n_{O_2}RT$$
$$p_{O_2} = \frac{\frac{0.62}{32} \times 8.31 \times 300}{2 \times 10^{-3}}$$
$$\mathbf{p_{O_2} = 24,150.938\ Nm^{-2}}$$

$p_{CO_2}V = n_{CO_2}RT$ $p_{CO_2} = \frac{\frac{1.34}{44} \times 8.31 \times 300}{2 \times 10^{-3}}$ $\boldsymbol{p_{CO_2} = 37,961.590\ Nm^{-2}}$	$p_{N_2}V = n_{N_2}RT$ $p_{N_2} = \frac{\frac{0.06}{28} \times 8.31 \times 300}{2 \times 10^{-3}}$ $\boldsymbol{p_{N_2} = 2,671.071\ Nm^{-2}}$

(ii) $p_{total} = p_{O_2} + p_{CO_2} + p_{N_2}$

$$= (24{,}150.938 + 37{,}961.590 + 2{,}671.071\ )Nm^{-2}$$

$$p_{total} = 64{,}783.599Nm^{-2}$$

Alternatively;

$$p_{total}V = \left(n_{O_2} + n_{CO_2} + n_{N_2}\right)RT$$

$$p_{total} = \left(n_{O_2} + n_{CO_2} + n_{N_2}\right)\frac{RT}{V}$$

$$p_{total} = \left(\frac{0.62}{32} + \frac{1.34}{44} + \frac{0.06}{28}\right) \times \frac{8.31 \times 300}{2 \times 10^{-3}}$$

$$p_{total} = 0.051972 \times \frac{8.31 \times 300}{2 \times 10^{-3}}$$

$$\boldsymbol{p_{total} = 64,783.098\ Nm^{-2}}$$

6. **At constant temperature, a vessel contains two gases, X and Y. The partial pressure of X is $5 \times 10^{-6}\ mmHg$ and its mole fraction is 0.85. Calculate the;**
   (i) total pressure exerted by the mixture of gases.
   (ii) partial pressure of gas Y .

(i) $p_X = x_X p_{total}$ $5 \times 10^{-6} = 0.85 \times p_{total}$ $p_{total} = \frac{5 \times 10^{-6}}{0.85}$ $\boldsymbol{p_{total} = 5.882 \times 10^{-6} mmHg}$	(ii) $x_X + x_Y = 1$ $x_Y = 1 - 0.85 = 0.15$ $p_Y = x_Y p_{total}$ $p_Y = 0.15 \times 5.882 \times 10^{-6}$ $\boldsymbol{p_Y = 8.823 \times 10^{-7} mm}Hg$

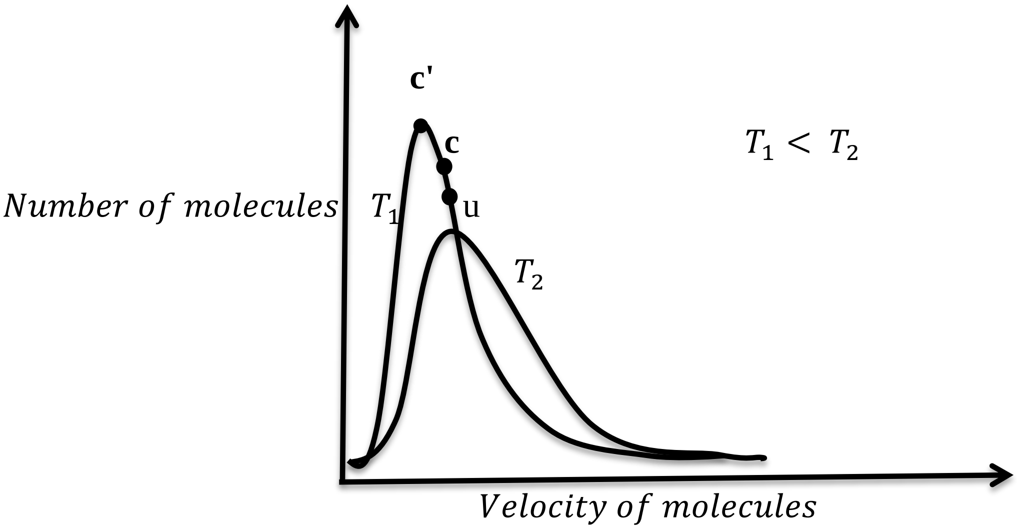
Questions

1. A mixture of gases, at a pressure of $1.01 \times 10^5 Nm^{-2}$ has the volume composition of 30% carbon monoxide , 50% oxygen and 20% carbon dioxide. Calculate the partial pressure of each gas.
2. A mixture of gases at s.t.p contains 65% nitrogen, 15% of carbon dioxide and 20% of oxygen by volume. Calculate the partial pressure of each gas in kPa.
3. 12g of nitrogen, 0.4g of hydrogen and 9g of Oxygen are put in a 1 dm^3 vessel at a pressure of 17.02mmHg. Calculate the partial pressure of each of the gases.

4. The partial pressures of the components of a mixture of gases are 26.64 kPa oxygen 34 kPa nitrogen and 42.66 kPa hydrogen. What is the percentage by volume of oxygen in the mixture?
5. 400 cm^3 of gas A at 2 atmospheres and 200cm^3 of gas B at 1 atmosphere are put in a 500 cm^3 container at the same time. Calculate the total pressure in the container.

Maxwell-Boltzmann distribution

According to the kinetic theory, the gas molecules are constantly moving in straight lines until they collide with each other and with the walls of the container. As a result of these numerous collisions within the gas, the velocities of the individual molecules vary enormously. Most molecules within the gas have velocity close to the mean, but some may acquire higher or lower values as a result of a series of favourable or unfavourable collisions. The distribution of velocities amongst molecules was calculated by Maxwell and Boltzmann, from the laws of probability and some typical results are shown below graphically.



The graph shows the distribution of molecular velocities in a gas a temperature , T_1 , and a higher temperature, T_2 .

At both temperatures, the number of molecules with very high or very low speeds is small, the bulk of the molecules having intermediate speeds. The peaks of the curves represent the most probable velocities possessed by an individual molecule at the given temperature. The most probable velocity(**c'**) is not the same as either the mean/ average velocity(c) or the root mean square velocity (u). At T_1 , the most probable velocity (**c'**), the mean velocity (c) and the root mean square velocity(u) are all shown.

It is noted that the distribution curve for the higher temperature, T_1, has a lower peak. It also more spread out although the total number of molecules (*represented by areas under the curves*) remain the same. The most probable velocity, the mean/ average velocity and the root mean square velocity are all higher, but the proportions of the molecules with these speeds are lower. This is because at higher temperature, there a greater range of possible velocities.

The distribution of kinetic energy amongst the molecules follows a similar pattern. It can be expressed as

$$n = n_o e^{-E/RT}$$

Where n_o is the total number of molecules and n is the number having an energy greater than the value E.

Deviation from Ideal behaviour

Previously, we discussed that Boyle's law is not valid over a wide range of pressures. Deviations from the law occur at **low temperatures** and **high pressures.**

Such deviations are due to the fact that **real gases are not ideal**.

A real gas is a gas that does not obey gas laws accurately at all temperatures and pressures, has intermolecular forces of attraction and occupies an appreciable volume.

Differences between a real gas and ideal gas

Real gas	Ideal gas
Possesses intermolecular forces	Has no intermolecular forces
Occupies an appreciable volume	Volume occupied is negligible
Collisions between particles are inelastic. (particles lose kinetic energy on collision)	Collisions are perfectly elastic (particles do not lose any kinetic energy on collision)

Conditions under which real gases behave like ideal gases

1. **Low pressure**. At low pressures, molecules of a gas are far away from each other, neither repulsive nor attractive forces are significant and the volume occupied by the real gas becomes negligible, behaving as an ideal gas.
2. **High temperature**. At high temperatures, the kinetic energy of the molecules increases, intermolecular collisions are high and are perfectly elastic, intermolecular forces of attraction become insignificant, molecules become far away from each other and the volume occupied by the real gas becomes negligible, behaving as an ideal gas.

Real gases are not ideal because the intermolecular forces of attraction have a significant effect on their pressure and their volume is not negligible. At low temperatures and high pressures, the molecules of a gas are close together and forces operate between them. At sufficiently low temperature and high pressure, a gas liquefies. Some of the ideas of the kinetic theory have to be modified to account for non-ideal behaviour of gases.

An ideal gas would obey Boyle's law such that $\frac{pV}{RT}$, known as compression or **compressibility factor**(Z).

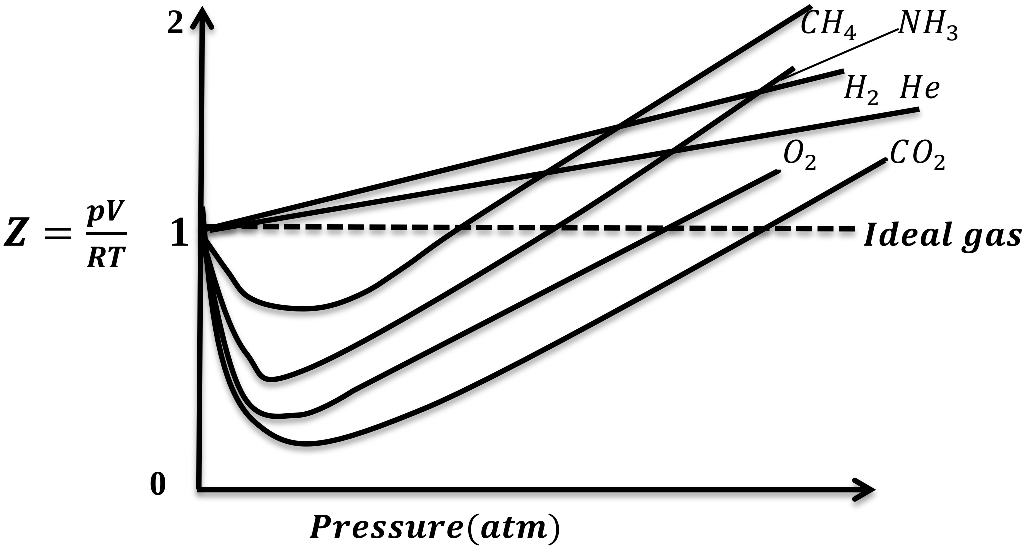
Compressibility factor is a measure of deviation real gas from ideal gas behaviour.

For any ideal gas the compressibility factor is equal to one.

$$Z = \frac{pV}{RT} = 1$$

However, for real gases, Z only approaches a value of one at very low pressures as shown in the figure below. At other pressures, Z may be greater than one (meaning the gas is more difficult to compress than an ideal gas) or less than one.

The graph below shows a plot of $\frac{pV}{RT}$ against pressure for some gases at the same temperature.



Explanations

At high pressures, the molecules of a gas are close to each other, there are strong repulsive forces between the molecules, and these hinder compression.

At moderate pressures, the forces between the molecules are attractive and favour compression.

At very low pressures, neither repulsive nor attractive forces are significant and that is why real gases approach ideal behaviour at low pressures.

Deviation for hydrogen and helium

For hydrogen and helium, there is a small deviation from ideal behaviour. This is because the gases have small molecules, with small molecular masses and held by weak van der Waals forces of attraction. The value of the compressibility factor $Z = \frac{pV}{RT}$ is greater than 1 and continuously increases with increase in pressure. This is because deviation due to molecular volume is greater than the deviation due to molecular attraction at all pressures. The molecules of hydrogen repel each other strongly thus this repulsion increases the volume of a gas.

Deviation for methane, ammonia, oxygen and carbon dioxide

For methane, ammonia, oxygen and carbon dioxide, the deviation from ideal behaviour increases in the order $CH_4 < NH_3 < O_2 < CO_2$. This is because the gases have larger molecules, with larger molecular masses that increase in the same order. The strength in the van der Waals forces of attraction between the molecules increase with the increase in molecular weight and reducing the volume occupied by the gases. For each of the gases, the value of the compressibility factor $Z = \frac{pV}{RT}$ initially decreases to a minimum. This is because the deviation due to molecular attraction is greater than the deviation due to molecular volume. The value of Z thereafter increases with increase in pressure because the effect of molecular volume overcomes that of molecular attraction.

Questions

1. (a) What is meant by the term compressibility factor?

   (b) On the same axes, draw a graph to show the variation of pressure with the compressibility factor for each of the gases; hydrogen, ammonia, propane and an ideal gas.

   (c) Explain the shape of the curve for;

   (i) hydrogen

   (ii) ammonia

   (iii) propane

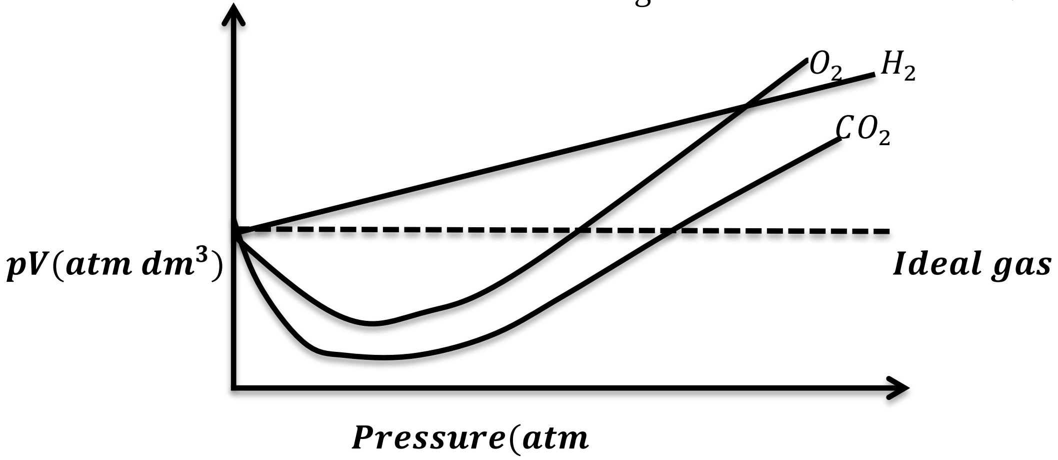
2. (a) State what is meant by an ideal gas

   (b) Explain how liquefaction of a gas can be affected by;

   (i) pressure

   (ii) temperature

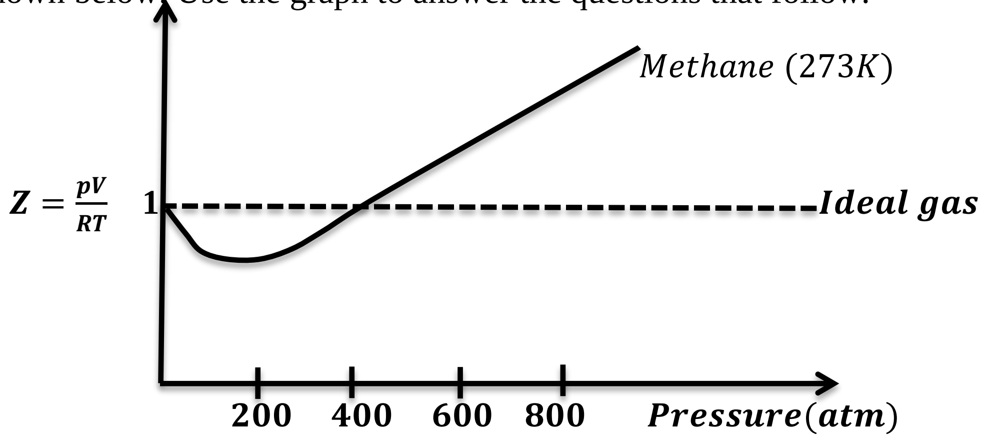
   (c) The curves below show the deviation of some gases from ideal behaviour.



(i) Explain why hydrogen shows a small deviation from ideal behaviour compared to other gases.

(ii) Compare the deviation of oxygen and carbon dioxide from ideal gas behaviour
(*Hint; the idea of compressibility factor should not be incorporated in your answer in this question*)

3. A plot of the compressibility factor, Z, against pressure for one mole of methane at 273K is as shown below. Use the graph to answer the questions that follow.



(a) Give reasons for the behavior of methane at 273K when the pressure is:
 (i) lower than 200 atmospheres
 (ii) higher than 200 atmospheres

(b) On the same graph, sketch graphs for ethane and nitrogen at 273K and give reasons for your sketches.

Correction of real gas behaviour by using van der Waals' equation

In 1873, Van der Waals replaced the simple gas equation by the equation;

$$\left(p + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

Where a and b are numerical constants.

Van der Waals argued that the actual size of the gas molecules means that the volume in which they are free to move is less than the total volume which a gas occupies. He replaced V by $(V - nb)$

He also argued that the attractive forces between the gas molecules lower the pressure that they can exert by lowering the frequency of impact with the walls of the containing vessel. This also lowers the force of impact of the gas with the walls of the vessel.

Since both these effects are proportional to gas density and inversely proportional to volume, Van der Waals replaced p by $\left(p+\frac{n^2a}{V^2}\right)$

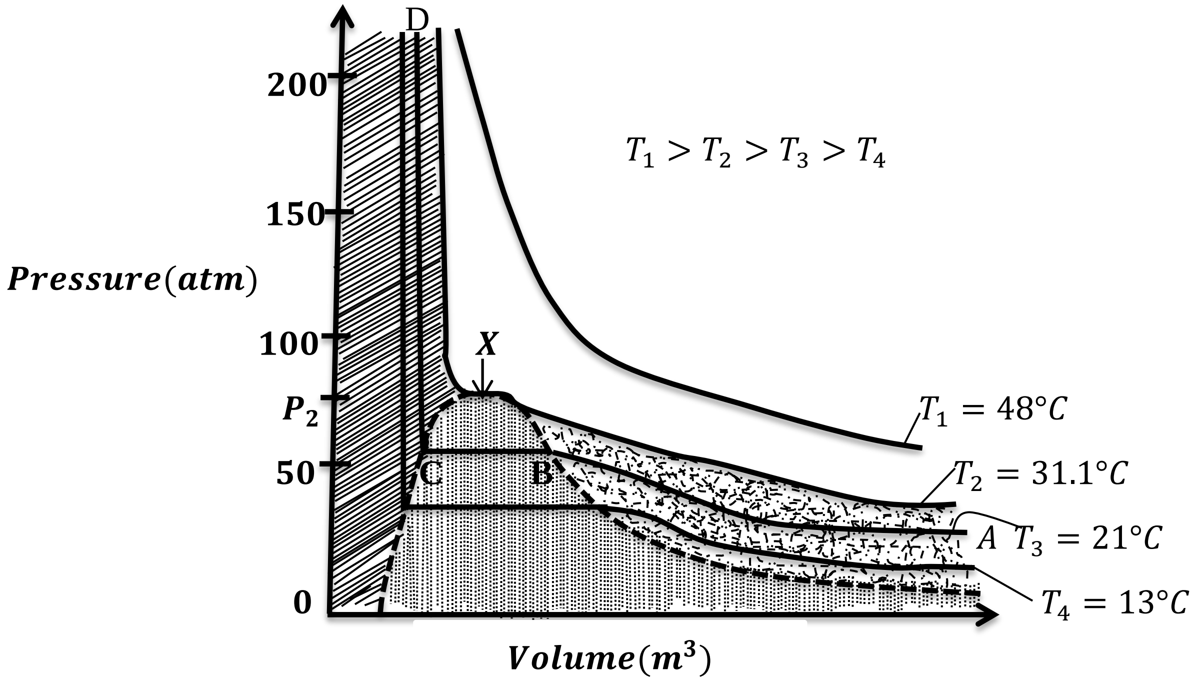
The Van der Waals' equation fits the experimental data better than the simple gas equation, and the values of a and b for different gases can be obtained by fitting the equation to known values of p , V and T.

Liquefaction of gases

If a gas is cooled sufficiently at atmospheric pressure, it can be liquefied. The conditions of temperature and pressure under which gases liquefy were first investigated by Andrews in 1869.

Andrews subjected carbon dioxide to various pressures at different temperatures and plotted the effect of pressure on the volume.

The isothermals for carbon dioxide ***which are defined as curves for variation of pressure with volume of the gas at particular temperatures*** were obtained as shown below.



KEY	
	Permanent gas
▨	**Liquid**
▒	**Vapour**
░	**Liquid and vapour**

The isothermal at $T_1 = 48°C$ shows that the volume of the gas (carbon dioxide) decreased with increase in pressure. This isothermal is in accordance with Boyle's law.

At a lower temperature $T_3 = 21°C$, the volume of the gas first decreased in accordance to Boyle's law along AB until the pressure increased to about 60 atm. At this pressure, there is a sudden break in the curve and liquid carbon dioxide forms. The pressure remains constant along BC until all the carbon dioxide is converted into liquid form. At C, liquefaction of the gas is complete. Any further increase in pressure causes no change in volume of the liquid carbon dioxide along CD. (*This is in accordance with the fact the extremely high pressures are required to compress a liquid appreciably*).

Similar changes take place in the effect of change in pressure on the volume of carbon dioxide at temperatures below $T_3 = 21°C$, although the pressure required to liquefy the gas becomes smaller as the temperature decreases.

Liquefaction of the gas can be brought about at all temperatures below $T_2 = 31.1°C$ but above this temperature, no liquefaction occurs no matter how much pressure is increased. This temperature is called the **critical temperature** of carbon dioxide. The pressure $P_2 = 75\ atm$ required to liquefy the gas at the critical temperature is called the **critical pressure** and the volume of 1 mole of the substance at the critical temperature and pressure is called the **critical volume**. Point X is called the **critical point**.

Definitions;

Critical temperature is the temperature above which a gas cannot be liquefied however much pressure is exerted on it.

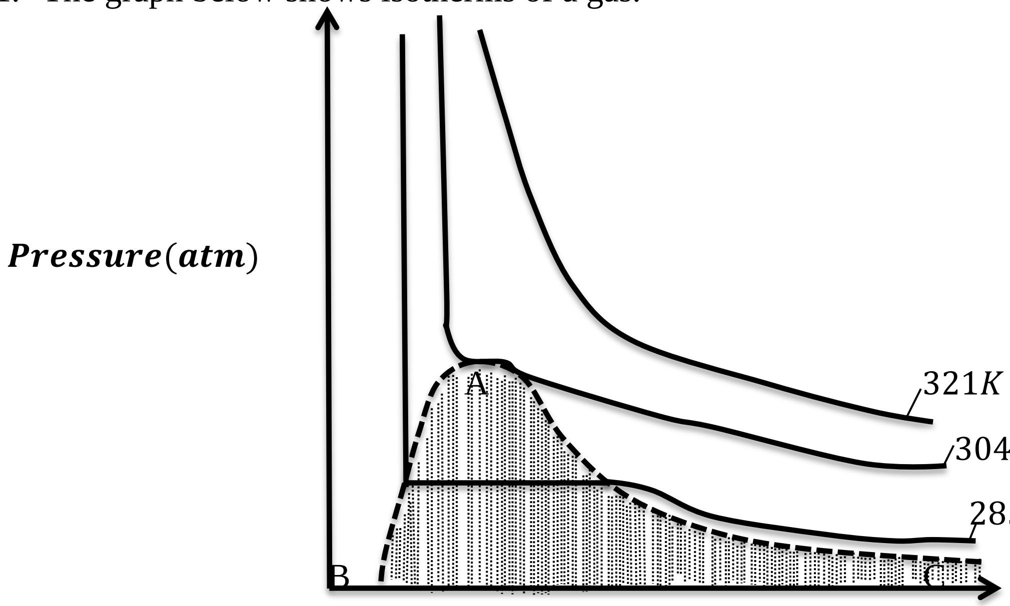
Critical pressure is the minimum pressure required to liquefy the gas at critical temperature.

The conditions for liquefaction of a gas are therefore; **low temperature below critical temperature** and **high pressure**.

Above critical temperature, a gas is regarded as a **permanent gas** since it cannot be liquefied.

Question

1. The graph below shows isotherms of a gas.



(a) Explain what is meant by the terms
   (i) Isothermal of a gas
   (ii) Critical temperature
(b) What is the critical temperature of the gas?
(c) Which isothermal represents the behaviour of an ideal gas?
(d) What does the region ABC represent.
(e) Explain the shape of the isothermal at 285K
(f) On the sketch graph, show the regions under which the gas exists as;
   (i) Vapour
   (ii) Liquid
   (iii) Permanent gas
(g) State the conditions for liquefaction of a gas to occur.

LIQUID STATE OF MATTER

The liquid state in terms of kinetic theory of matter

Most liquids are miscible like all gases. Liquids can be compressed although to a smaller extent than gases.

According to the kinetic theory, molecules in a liquid are in a state of random motion, as in a gas, but the motion is very much less than it is in a gas and the molecules in a liquid are very much closer.

Liquids actually lie midway between the disorderly, scattered distribution found in a gas and the orderly compact arrangement found in a crystalline solid.

The random distribution of molecules found in a liquid is shown by a phenomenon of Brownian motion. **Brownian motion** was first observed by a botanist Robert Brown in 1827, who found out that very small pollen grains immersed in water undergo an irregular motion when observed under a microscope. Such motion is due to bombardment of the pollen grains by molecules of the liquid in which the grains are suspended.

Properties of a liquid

1. Compressibility

Compressibility of a liquid (k)is the fractional change in its volume per unit increase in pressure. Liquids have low compressibility because the particles are closer to each other and the intermolecular forces of attraction are weaker than those in solids hence the particles can randomly move although not as fast as in gases.
The property of compressibility of liquids is applied in;

(i) ***Hydraulic breaks***. In a hydraulic break, there is a brake fluid whose compressibility is affected by temperature and the presence of trapped air and moisture. When the brake pedal is pressed, force is exerted on the pistons causing the brake fluid to flow into a pressure chamber. This increases the pressure in the entire hydraulic system. This pressure effect is also exerted on the brake pads to reduce the vehicle speed.

(ii) ***Hydraulic car jack***. The car jack is used to lift even the heaviest cars using a small force that is applied to a fluid from one piston of the car jack. This force builds up pressure in the fluid that then forces another piston to rise. This generated pressure lifts the car up.

2. Viscosity

The viscosity of a liquid is the resistance to flow of a liquid. Edible oil has a greater viscosity than water. Viscosity may be thought of as internal friction between the molecules. Viscosity is a major factor in determining the forces that must be overcome when fluids are used in lubrication and transported in pipelines. It controls the liquid flow in processes like spraying, injection moulding and surface coating. The viscosity of liquids decreases rapidly with an increase in temperature. That is why upon heating, liquids flow more easily. The viscosities of water at 27℃ and 77℃ are $8.5 \times 10^{-4} Pa\ s^{-1}$ and $3.6 \times 10^{-4} Pa\ s^{-1}$ respectively.

3. Surface tension

Molecules in the interior of a liquid are attracted equally on all sides by the molecules around them. Molecules on the surface are only attracted inwards and sideways. As a result, the liquid surface is always under tension and tends to contract so as to reduce the surface area to a minimum. The mutual attraction of the molecules in the liquid surface produces a resistance to penetration since work has to be done to force the molecules apart. The surface has a certain amount of "hardness" which is basically similar to the hardness of a solid metal surface. Therefore small metal objects such as a greased steel needle can float on water and certain insects can move freely on a water surface without getting wet. The values of surface tension decrease with increase in temperature.

Surface tension of a liquid, γ, is the force in newtons acting parallel to the surface along a line of one metre in length in the surface and at right angles to the line.

4. Diffusion

Like gases, liquids also diffuse since their molecules are also moving. The diffusion in liquids is however slower than in gases because the molecules are more closer together than in gases. When two miscible liquids are added together, they diffuse throughout the whole mixture until it is homogeneous. Solids can also diffuse in liquids to form solutions. For example copper(II) sulphate and potassium manganate(VII) crystals can diffuse in water.

5. Vapourisation/ Evaporation

Evaporation is the change of state from liquid to gas (or vapour) at a temperature below the boiling point of the liquid. Evaporation can take place at any temperature, the rate increasing with increase in temperature. Some molecules in the liquid have enough energy to escape into the gas phase (if they are near the surface and moving in the right direction). Because these are the molecules with higher kinetic energies, evaporation results in a cooling of the liquid. Evaporation is an endothermic process.

The rate of evaporation of a liquid depends on a number of factors which include its vapour pressure(which is most important), molar heat of vapourisation, molar heat capacity and other factors. Liquids with a high vapour pressure evaporate easily than those with a lower vapour pressure

6. Condensation

The change of a vapour or gas into a liquid. The change of phase is accompanied by the evolution of heat i.e. it is exothermic.

The evaporation of a liquid seen above can continue until no liquid remains. However, if the liquid is in a closed container, the molecules in the vapour state collide with the walls of the container and some fall back into the liquid(condense). Equilibrium will be reached when the rate at which molecules condense is equal to the rate at which molecules of vapour condense.

7. Boiling

When a liquid is heated, its temperature increases until there are molecules with sufficient energy to escape from the liquid surface. The temperature reaches a high enough value and the saturated vapour pressure becomes equal to the external pressure. At this point the liquid changes rapidly and completely into vapour. This process is called boiling and the temperature at which it occurs is the boiling point. The boiling point of a liquid depends on the cohesive forces in the liquid. If the cohesive forces are weak, the boiling point is low. When the cohesive forces increase in strength, the boiling point increases.

Boiling therefore occurs when the vapour pressure is equal to the external pressure exerted on the liquid.

Boiling point of a liquid is the constant temperature at which its saturated vapour pressure becomes equal to the external pressure on the liquid.

8. Vapour pressure

Vapour pressure of a pure liquid is the pressure exerted by the vapour over the liquid surface. The vapour pressure of a liquid depends on;

(i) ***The temperature of the liquid***

When the temperature of a liquid is raised, its molecules move more rapidly. This results into an increase in the average kinetic energies of the molecules. At higher temperatures, a greater number of molecules possess energy greater than the escape energy and therefore a greater number of molecules escape as vapour. This increases the vapour pressure of the liquid.

(ii) ***External pressure***

The boiling point of a liquid depends on the external pressure. At a given temperature, vapour pressure of a liquid is equal to the external pressure. Therefore the vapour pressure of the liquid at a given temperature increases with increase in external pressure. A liquid therefore boils at a higher temperature than its normal boiling point when the external pressure is increased.

(iii) ***Intermolecular forces***

The vapour pressure of a liquid depends on the strength of its intermolecular forces. A liquid with weak intermolecular forces acting between its molecules has a higher tendency to escape as a vapour hence a higher vapour pressure, said to be volatile. A liquid with stronger intermolecular forces acting between its molecules has a lower tendency to escape as a vapour hence a lower vapour pressure, said to be less volatile or non-volatile.

Question;

The table below shows the boiling points of different pure liquids.

Compound	**Boiling point($°C$)**
CH_3CH_2OH	78
H_2O	100
H_2	-253
N_2	-195
$CH_3CH_2OCH_2CH_3$	35

(a) Arrange the compound in order of increasing vapour pressure.

(b) Explain your answer in (a) above.

(a) Vapour pressure increases in the order;

$$H_2O < CH_3CH_2OH < CH_3CH_2OCH_2CH_3 < N_2 < H_2$$

(b) The vapour pressure increases from water to ethanol to ethoxyethane to nitrogen to hydrogen, since boiling point decreases in the same order.

The vapour pressure of a liquid depends on the strength of its intermolecular forces. Water molecules interact through strong intermolecular hydrogen bonds which require a high amount of energy to break. This reduces escaping tendency of water molecules into the vapour phase hence a low vapour pressure. Ethanol has a higher vapour pressure than water because the intermolecular hydrogen bonds in it are weaker than in water. This is because each ethanol molecule has only one hydrogen atom that is sufficiently partial positive hence forms only two hydrogen bonds unlike each water molecule that forms four hydrogen bonds. Ethanol molecules therefore have a higher escaping tendency than water molecules. Ethoxyethane molecules, liquid nitrogen molecules and liquid hydrogen molecules all interact through weak van der Waals forces of attraction whose strength decrease with decrease in molecular size and molecular weight and can easily be broken. Since molecular mass and molecular size decreases from ethoxyethane to nitrogen to hydrogen, strength of van der Waals forces decreases in the same order, amount of energy required to break the forces decreases in the same order, escaping tendency of the molecules into vapour phase increases in the same order, hence increasing the vapour pressure.

(also refer to the topic; bonding and structure)

SOLID STATE OF MATTER

A solid is a substance of definite shape, high density and with strong intermolecular forces of attraction between its molecules.

The solid state in terms of kinetic theory of matter

According to the kinetic theory, the molecules, atoms or ions in a solid are closely packed and orderly arranged. Movement of the particles is restricted to vibration or oscillation about mean/fixed positions. This makes solids incompressible. Attraction between the particles is even more dominant.

The slight motion observed in a solid at ordinary temperatures is shown by the fact that two solids when placed in close contact may diffuse very slightly into each other and also by the fact that solids can exert a vapour pressure. The vapour pressure of a solid at normal temperature is so small to be negligible but some solids like iodine and naphthalene exert considerable vapour pressures at temperatures below their melting points. On heating, they sublime (change directly to gas) and on cooling, the vapour formed condenses into a solid.

Majority of solids melt into liquid when heated because the cohesive forces between their molecules are broken and can no longer hold them together.

Phase changes in solids

1. Melting point

Melting point of a solid is the constant temperature at which the solid and liquid phases are in equilibrium at a given external pressure.

In a solid, the particles are in a constant state of vibration. When a solid is heated, energy is absorbed and the amplitude of vibration increases. The solid melts and the heat energy of its particles increases sufficiently to overcome the cohesive forces which hold them together. The process is a gradual one and the temperature remains constant even though heat is being supplied. Solids which have covalent and ionic bonds usually require a higher amount of energy to melt than those held by hydrogen bonds or van der Waals forces.

2. Freezing point

Freezing point is the constant temperature at which the liquid and solid phases are in equilibrium at a given external pressure.

The freezing point of a substance in its liquid form is the same as the melting point of its solid form and depends on factors such as purity of the substance and its external pressure.

3. Sublimation

A solid which when heated changes directly into vapours without an intermediate liquid stage, is said to have undergone sublimation. Every solid exerts a vapour pressure although it is usually very small. The vapour pressure of solids increases with increase in temperature. When the vapour pressure of a solid reaches the external pressure before it melts, then the solid will vapourise before it melts (it sublimes). Such substances include iodine, solid carbon dioxide (dry ice), naphthalene, camphor, etc.

4. Deposition

Under certain conditions, a gas can transform directly into a solid without passing through the liquid phase by a process called deposition. Examples are conversion of water vapour to ice and soot deposition on the walls of chimneys

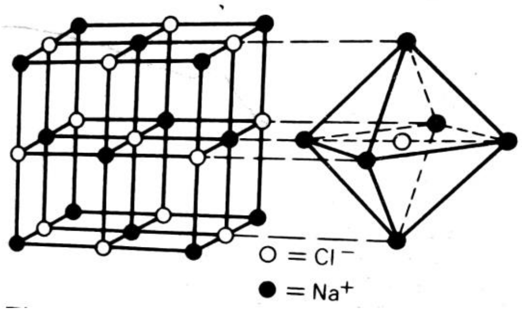
Types of solids

Giant ionic solids

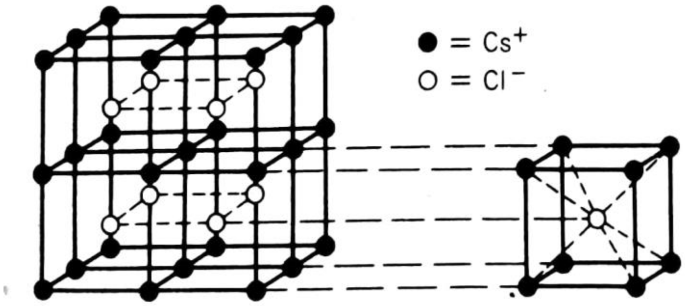
Ionic compounds are formed when metallic elements combine with non-metallic elements. The ionic bonds formed in these compounds are strong electrostatic attractions between the ions of opposite charges (cations and anions).

Each ion is surrounded by the greatest number of oppositely charged ions called the coordination number. Examples of giant ionic solids include ***sodium chloride***, ***caesium chloride*** and ***zinc blende***.

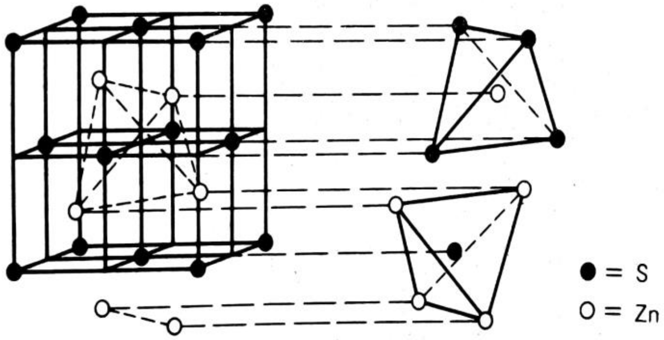
In **sodium chloride**, each sodium ion is surrounded *octahedrally* by six chloride ions, and each chloride ion is surrounded by six sodium ions.



In **caesium chloride**, each caesium ion is surrounded by eight chloride ions, and each chloride ion is surrounded by eight caesium ions.



In **zinc blende**, each zinc atom is surrounded *tetrahedrally* by four Sulphur atoms, and each Sulphur atom is surrounded by four zinc atoms. The structure is similar to that of diamond



Giant ionic solids have the following properties;

(a) They have high melting and high boiling points due to the strong electrostatic attractions between the ions that require a high amount of energy to break.

(b) They are strong electrolytes in molten state or when dissolved in solution because ions become free to move.

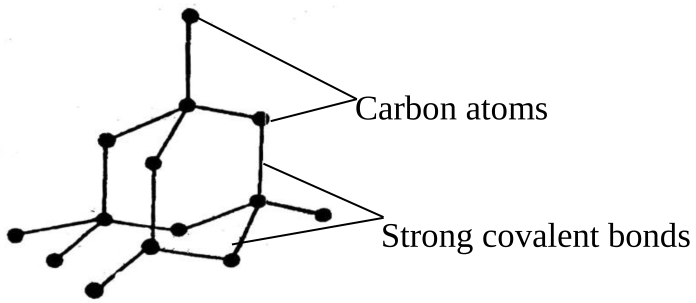
(c) Soluble in polar solvents like water because they consist of oppositely charged ions but insoluble in organic solvents like ether and benzene.
(d) Very hard and brittle.

Giant covalent solids

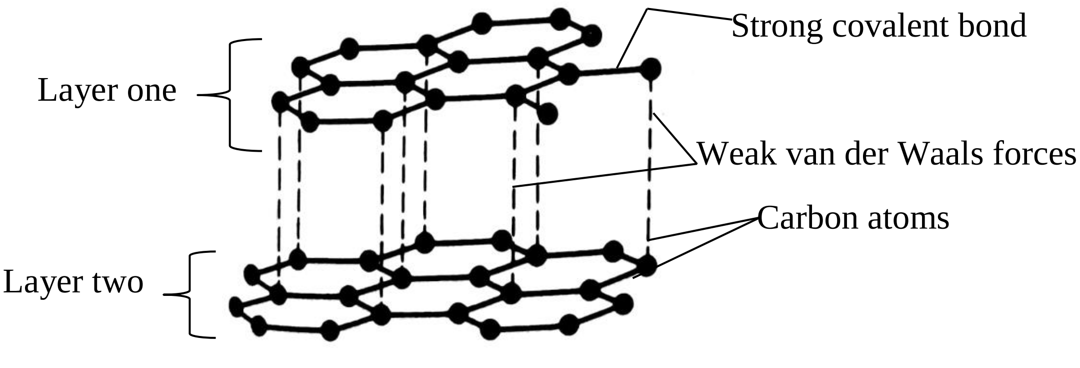
Covalent bonds are formed between atoms of non-metallic elements. When many very strong covalent bonds link one atom to another to form an extensive three dimensional lattice, a giant covalent structure is formed.

Examples of giant covalent solids include ***diamond, graphite***, ***silicon*** and ***fullerene***.

In **diamond**, each carbon atom is covalently bonded to four other carbon atoms to form a tetrahedral structure which is continuous to form a 3-dimensional giant covalent structure. The giant covalent structure has very many strong covalent bonds between carbon atoms which require a high amount of energy to break. This is why diamond is very hard and strong. All the four valence electrons of each carbon atom are used for bonding and none is delocalized. This makes diamond a non-conductor.



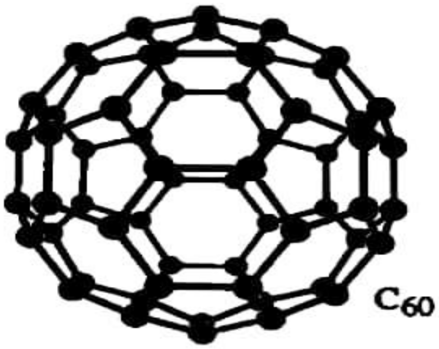
In **graphite**, each carbon atom is covalently bonded to three other carbon atoms to form two dimensional layers of hexagonal rings of carbon atoms. The hexagonal layers held together by weak Van-der-Waals' forces of attraction which allow the layers to slide over each other, a reason as to why graphite is soft and slippery, hence acts as a solid lubricant. For each carbon atom, one electron is not used for bonding. These electrons, one per carbon atom, are delocalized and used by graphite to conduct electricity.



Silicon also has a giant covalent diamond like structure. Each silicon atom is covalently bonded to four other silicon atoms to form a tetrahedral structure which is continuous to form a giant covalent structure.

Fullerene

Fullerene is an allotrope of carbon whose molecule contains a range of 30-70 carbon atoms. The carbon atoms are joined by single and double covalent bonds to form a closed mesh like structure, which is also a giant covalent structure with fused rings of five to seven carbon atoms each. The molecule can be a hollow sphere or in form of many other shapes and sizes. The most common fullerene is C_{60}.

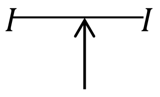


Giant covalent solids have high melting points and are non-volatile due to the strong covalent bonds holding the atoms together.

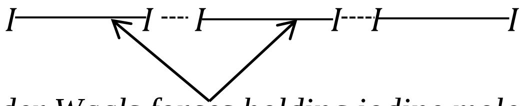
Molecular covalent solids

Iodine and phosphorus are molecular covalent solids.

Iodine is a diatomic molecule (I_2) in which the iodine atoms are held by strong covalent bonds. However, the diatomic iodine molecules interact through weak van der Waals forces of attraction. When iodine is heated, the weak van der Waals forces are broken and the molecules are set free, making iodine to sublime.

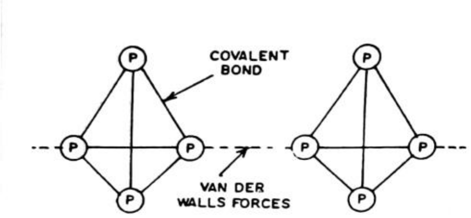


Covalent bond between two iodine atoms in the iodine molecule

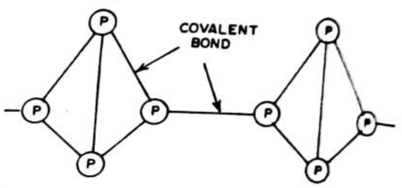


Van der Waals forces holding iodine molecules

Both white phosphorus and red phosphorus exist a tetratomic molecule (P_4). They are molecular covalent solids. White phosphorus has the four phosphorus atoms joined by covalent bonds but the tetratomic molecules are held by weak van der Waals forces which require a low amount of energy to break. This is why white phosphorus has a low melting point. Red phosphorus has the four phosphorus atoms joined by covalent bonds and the tetratomic molecules are also held by strong covalent bonds which require a low amount of energy to break. This is why red phosphorus has a high melting point



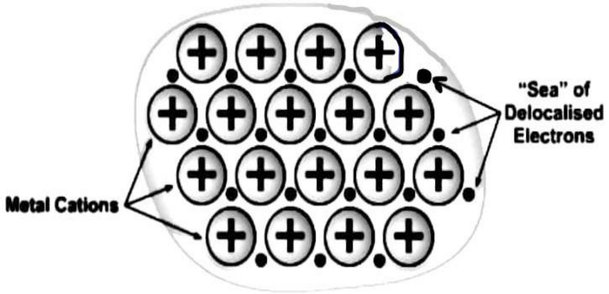
White phosphorus



Red phosphorus

Giant metallic solids

A metallic solid consists of a lattice of 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. The giant metallic structures occur in metals such as iron, copper, titanium, etc.



Solid copper has a giant metallic structure which consists of a lattice of copper ions surrounded by a sea of delocalized electrons moving randomly throughout the lattice of regularly spaced positive ions. Strong metallic bonds hold the crystal together. Copper has a face centred cubic close packed structure. Iron has a body centred cubic structure and titanium has a hexagonal close packed structure.

Giant metallic solids have the following properties;

1. High melting and boiling points because 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.
2. Good conductors of electricity and heat due to presence of free mobile electrons throughout the lattice. They conduct heat due to exchange of kinetic energy between free mobile electrons in the lattice.
3. Strong but malleable and ductile.

4. 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.

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.

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

$$where\ n = number\ of\ atoms\ of\ an\ element$$

Examples

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

$$molar\ mass\ of\ Ca(H_2PO_4)_2 = (40 \times 1) + (1 \times 4) + (30 \times 2) + (16 \times 8)$$
$$= 232g$$

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

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

$$molar\ \ mass\ of\ CuSO_4.5H_2O = (63.5 \times 1) + (32 \times 1) + (16 \times 4) + (18 \times 5) \quad = 249.5g$$

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

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

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

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

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, $(NH_4)_2SO_4.FeSO_4.6H_2O$.**

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

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

$$Let\ the\ number\ of\ moles\ of\ water\ of\ crystallisation\ be\ x$$
$$Formula\ is\ Al_2(SO_4)_3.XH_2O$$
$$molar\ mass\ of\ Al_2(SO_4)_3.XH_2O = (27 \times 2) + (32 \times 3) + (16 \times 12) + (18X)$$
$$= 54 + 96 + 192 + 18X$$
$$molar\ mass = (342 + 18X)g$$
$$Percentage\ by\ mass\ of\ \boldsymbol{Al}\ = \frac{(27 \times 2)}{(342 + 18X)} \times 100$$
$$8.1\ = \frac{(27 \times 2)}{(342 + 18X)} \times 100$$
$$\frac{8.1}{100} = \frac{(27 \times 2)}{(342 + 18X)}$$
$$2770.2 + 145.8X\ = 5400$$
$$145.8X\ = 2629.8$$
$$X\ = 18$$
$$molar\ mass = (342 + 18X) = (342 + 18 \times 18) = 666g$$
$$Percentage\ by\ mass\ of\ \boldsymbol{H_2O}\ = \frac{18 \times 18}{666} \times 100 = 48.65\%$$

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, $Fe_2(SO_4)_3.YH_2O$ 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) $Molecular\ mass = \ vapour\ density \times 2$

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

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

$V\ is\ volume\ in\ m^3$

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

$T\ is\ temperature\ in\ Kelvin$

$m\ is\ mass\ given\ and\ M_r\ is\ molecular\ mass$

(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.**

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

$Elements$	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

$$\boldsymbol{Empirical\ formula\ is\ C_4H_8O}$$

$$(C_4H_8O)_n = 36 \times 2$$
$$(48 + 8 + 16)_n = 36 \times 2$$
$$72n = 72$$
$$n = 1$$
$$\boldsymbol{Molecular\ \ formula\ is\ C_4H_8O}$$

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 148cm^3 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

$$\boldsymbol{Empirical\ formula\ is\ C_2H_4O}$$

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

$$\boldsymbol{M_r = 90.38}$$
$$\boldsymbol{molar\ mass\ of\ Q\ \approx 90}$$
$$\boldsymbol{(C_2H_4O)_n = 90}$$
$$\boldsymbol{(24 + 4 + 16)_n = 90}$$
$$\boldsymbol{44n = 90}$$
$$\boldsymbol{n = 2}$$
$$\boldsymbol{Molecular\ \ formula\ is\ C_4H_8O_2}$$

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

$$\boldsymbol{Q\ is\ CH_3CH_2CH_2COOH}$$

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

$$\boldsymbol{Empirical\ formula\ is\ C_3H_6O}$$

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

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

$$M_r \approx 58$$

$$molar\ mass\ of\ Q = 58g$$

$$(C_3H_6O)_n = 58$$

$$(36 + 6 + 16)_n = 58$$

$$58n = 58$$

$$n = 1$$

$$\boldsymbol{Molecular\ formula\ is\ C_3H_6O}$$

(b) From combustion data

4. When a hydrocarbon L was burnt in excess air, 14.4g of water and 13.44dm^3 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) $From\ 14.4g\ of\ H_2O;$

$$molar\ mass\ of H_2O = 2 + 16 = 18g$$

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

$$From\ 13.44dm^3\ of\ CO_2;$$

$$22.4\ dm^3\ of\ CO_2\ at\ stp\ contain\ 1\ mole$$

$$13.44\ dm^3\ of\ CO_2\ at\ stp\ contain\ \left(\frac{13.44 \times 1}{22.4}\right) mole$$

$$= 0.6\ moles$$

$$molar\ mass\ of CO_2\ = 12 + 32 = 44g$$

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

$Elements$	C	H
$mass(g)$	7.2	1.6
$moles$	$\frac{7.2}{12}$	$\frac{1.6}{1}$
$simplest\ ratio$	$\frac{0.6}{0.6}$:	$\frac{1.6}{0.6}$
	$\mathbf{1\ \times 3}$:	$\mathbf{2.6667\ \ \times 3}$
	$\mathbf{3}$:	$\mathbf{8}$

$$\boldsymbol{Empirical\ formula\ is\ C_3H_8}$$

(b)

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

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

$$44n = 44$$

$$n = 1$$

$$\boldsymbol{Molecular\ \ formula\ is\ C_3H_8}$$

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 44.8cm^3 of nitrogen gas, determine the molecular formula of Q if its relative molecular mass is 59.**

$$\boldsymbol{From\ 0.528g\ of\ CO_2;}$$

$$\boldsymbol{molar\ mass\ of CO_2\ = 12 + 32 = 44g}$$

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

$$\boldsymbol{From\ 0.324g\ of\ H_2O;}$$

$$\boldsymbol{molar\ mass\ of H_2O = 2 + 16 = 18g}$$

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

$$\boldsymbol{molar\ mass\ \ of N_2 = (2 \times 14) = 28g}$$

$$\boldsymbol{22400\ cm^3\ at\ stp\ contain\ 1\ mole\ \ of N_2}$$

$$\boldsymbol{22400\ cm^3\ at\ stp\ contain\ 28g\ \ of N_2}$$

$$\boldsymbol{44.8\ cm^3\ at\ stp\ contain\ \left(\frac{44.8 \times 28}{22400}\right) g\ \ of}$$

$$\boldsymbol{=\ 0.056g\ \ of N_2}$$

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

$$simplest\ ratio \qquad \frac{0.012}{0.004} : \frac{0.036}{0.004} : \frac{0.004}{0.004}$$

$$3 : 9 : 1$$

$$\boldsymbol{Empirical\ formula\ is\ C_3H_9N}$$

$$(C_3H_9N)_n = 59$$

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

$$59n = 59$$

$$n = 1$$

$$\boldsymbol{Molecular\ \ formula\ is\ C_3H_9N}$$

(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.

$$C_xH_y(g) + \left(x + \frac{y}{4}\right) O_2(g) \longrightarrow x\, CO_2(g) + \frac{y}{2} H_2O(l)$$

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

Volume of carbon dioxide formed is $(V - W)cm^3$

Volume of oxygen that reacts is $(Q - W)cm^3$

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

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

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

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

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

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

6. **20 cm^3 of a hydrocarbon Z was exploded with 200 cm^3 of oxygen. On cooling to room temperature, the residual gases occupied 160 cm^3. When the residual gases were passed through sodium hydroxide solution, the volume reduced to 20 cm^3.**
   - **(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.

(a) $C_xH_y(g) + \left(x + \frac{y}{4}\right) O_2(g) \longrightarrow x\,CO_2(g) + \frac{y}{2} H_2O(l)$

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

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

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

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

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

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

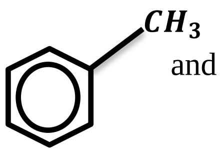
$$140 + 5y = 180$$

$$y = 8$$

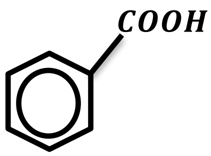
$$\boldsymbol{Molecular\ formula\ of\ Z\ is\ C_7H_8}$$

(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



and T is



(ii) *Try this on your own (convert ethyne to methylbenzene)*

7. 15 dm^3 of gaseous hydrocarbon X was exploded with 105dm^3 of excess oxygen. The residual gas occupied 75dm^3. On addition of concentrated potassium hydroxide, the volume reduced by 45dm^3. Determine the molecular formula of X.

$$C_xH_y(g) + \left(x + \tfrac{y}{4}\right) O_2(g) \longrightarrow x\, CO_2(g) + \tfrac{y}{2} H_2O(l)$$

Volume of carbon dioxide formed $= 45\ dm^3$

Volume of unreacted oxygen $= (75 - 45) = 30\ dm^3$

Volume of oxygen that reacted $= (105 - 30) = 75\ dm^3$

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

$$15\ dm^3\ of\ \ C_xH_y\ forms\ 45\ dm^3 of CO_2$$
$$15x = 45$$
$$x = 3$$

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

$$15\ dm^3\ of\ \ C_xH_y\ reacts\ with\ \ 75\ dm^3 of O_2$$
$$15\left(x + \frac{y}{4}\right) = 75$$
$$15\left(3 + \frac{y}{4}\right) = 75$$
$$y = \left(\frac{75}{15} - 3\right)4$$
$$y = 8$$

$$\boldsymbol{Molecular\ formula\ of\ X\ is\ C_3H_8}$$

8. When 142cm^3 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.

(i) Determine the molecular formula of Y.

(ii) Write the structural formula and IUPAC name of all possible isomers of Y.

$$C_xH_y(g) + \left(x + \tfrac{y}{4}\right) O_2(g) \longrightarrow x\, CO_2(g) + \tfrac{y}{2} H_2O(l)$$

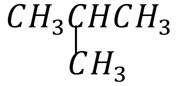
(i) *Volume of carbon dioxide formed is* $(694 - 126) = 568\ cm^3$

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

$$142\ cm^3\ of\ \ C_xH_y\ forms\ 568\ cm^3 of CO_2$$
$$142x = 568$$
$$x = 4$$
$$C_xH_y = 58$$
$$C_4H_y = 58$$
$$(4 \times 12) + y = 58$$

$$y = 10$$
$$\boldsymbol{Molecular\ formula\ of\ Z\ is\ C_4H_{10}}$$

(ii)

Structural formula of isomer	**Name of isomer**
$CH_3CH_2CH_2CH_3$	Butane
 $CH_3CH(CH_3)CH_3$	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.

1. Compound ***G***, with molecular mass 237.9g, contains 24.8% cobalt, 29.8% chlorine, the rest being water of crystallisation.
    (a) Calculate the empirical formula
    (b) Determine the molecular formula of ***G***.
2. 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.
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 $1.785 \times 10^{-3} gcm^{-3}$ 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 $2.0536 gl^{-1}$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.
        (i) Deduce the chemical formula of ***Z***.
        (ii) Identify ***X*** and ***Y***.
    (c) Write equation for the reaction that;
        (i) takes place when ***Z*** is heated.
        (ii) 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;
        (i) the mechanism for the reaction in (c)(i)
        (ii) 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.
    (a) Determine the empirical formula of the compound.
    (b) Hence determine the molecular formula of the compound (the molecular mass of compound is 245)
    (c) 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 ***Y*** consists of 48.6% carbon, 8.1% hydrogen and the rest being oxygen.
    (a) Determine the empirical formula of ***Y***.
    (b) 0.453g of a vapourised sample of ***Y*** occupied 200cm^3 at 100℃ and 95.0kPa pressure.
        (i) Calculate the molecular mass of ***Y***.
        (ii) Determine the molecular formula of ***Y***.
    (c) Y reacts with magnesium metal with evolution of a gas. Write;
        (i) the structural formula of ***Y***
        (ii) 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℃ and 760mmHg occupies $72.30cm^3$. Determine the:
        (i) molecular mass of ***Z***
        (ii) 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.
        (i) Identify ***Z***
        (ii) 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.
        (iii) Calculate the empirical formula of ***Y***.
        (iv) When 0.3g of ***Y*** was vapourised at 80℃ 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.
    - (i) Calculate the empirical formula of ***P***.
    - (ii) When 0.14g of ***P*** was vapourised at 20℃ 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.
    - (i) Write the name and formula of ***Q***.
    - (ii) 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.

    (a) Determine the empirical formula of ***P***

    (b) When vapourised, 0.1g of ***P*** occupied 78.8 cm^3 at 157℃ 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℃ and 98.3 kPa. 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, $MgCl_x.nH_2O$, was dissolved in water an 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^{o}C. Calculate the molecular formula of ***Z*** (k_f for water is $1.86°Cmol^{-1}kg^{-1}$)

(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

23. (a)When 0.1g of aluminium was vapourised at 350 ^{o}C and a pressure of 1 atmosphere, 19.2 cm^3 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 ^{o}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 cm^3 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 ^{o}C depression in freezing point of the solution. (K_f *of the solvent = 1.63*^{0}*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.
    (e) 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.

(f) 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℃ while pure benzene freezes at 5.50℃.
    (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℃ and a pressure of 700mmHg, it occupied a volume of 136 cm^3. 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℃. 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 $2.63gdm^{-3}$ 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***.

$(H = 1;\ O = 16;\ C = 12;\ Mg = 12;\ N = 14;\ Al = 27; Si = 28.1;\ Cl = 35.5;$
$Fe = 56;\ Co = 58.9; Br = 79.9)$

Questions 22, 26 and 27 will be simpler after covering colligative properties in Phase equilibria and gaining more knowledge of organic chemistry.

CHAPTER TWO

ATOMIC STRUCTURE AND THE PERIODIC TABLE

Fundamental particles of the atoms and radioactivity

Historical development of the atomic theory

It was the Greek philosophers Democritus and Leucippus who first considered the idea that matter is made up of particles in about 400BC. This was later supported by Boyle and Newton. The idea was however not accepted because there was no experimental evidence for it.

In 1808, a Manchester school teacher, John Dalton restated and extended the older concepts. He gathered experimental evidence with which people were convinced. In his Atomic Theory, Dalton said that "*matter is made up of atoms*". Dalton, however never dreamt that anyone would be able to see an atom.

Modern instruments like X-ray diffraction and advanced microscopes have provided direct evidence for existence of atoms

Modern theory of the atom

(a) John Dalton's atomic theory

The main points in Dalton's Atomic theory can be summarized as follows;

- ***All matter is made up of tiny particles called atoms.***
- ***The atoms are chemically indivisible, indestructible and cannot be created.***
- ***All the atoms of any one element are identical i.e. they have the same mass, same volume and the same chemical properties.***
- ***Atoms of different elements have different mass, volume and chemical properties.***
- ***Chemical combination occurs between elements by atoms joining in small whole numbers to form a small group of atoms chemically combined together. Dalton called such a group "a compound atom". It is now called a molecule.***

By using Dalton's theory, we can clearly understand that;

When a reaction occurs in a closed vessel, all the atoms present before the reaction are still present after the reaction. They just merely become rearranged. Since the masses of the atoms are constant, the total masses of the substances before and after the reaction should be the same.

> ***Point of thought; What can make us disagree with Dalton on the question whether atoms can be created or destroyed or split?***

(b) The J.J Thomson model of an atom

Although John Dalton had thought that the atom could not be broken down into anything simpler, physicists further investigated whether atoms could be made of smaller particles. In 1895, Crookes, through his experiments on the discharge of electricity through gases at low pressure, he discovered that a beam of rays was given off by the cathode (the negative electrode). He called them cathode rays. He also showed that cathode rays behave like negatively charged particles.

In 1897, Sir Joseph John Thomson, as a result of experimental work still on the conduction of electricity through gases at low pressure, measured the velocity of cathode rays and the value of charge to mass ratio of the cathode rays. He obtained the same value of ${}^{charge}/{}_{mass}$ regardless of which gas he used.

- ***J.J. Thomson therefore deduced that negatively charged particles were present in all matter.***
- ***The negatively charged particles were named electrons and were recognized as particles of which an electric current is composed***
- ***He described an atom as a sphere of positive electricity in which negative electrons are embedded***

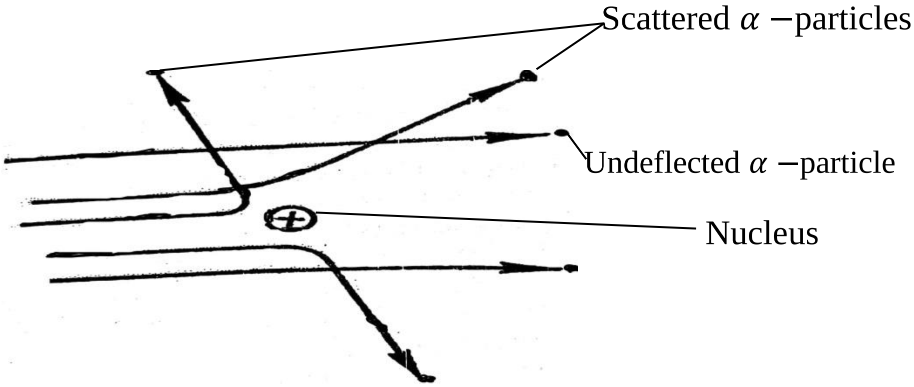
> ***Point of thought; What is the main difference between this J.J.Thomson's model and Dalton's model?***

J.J. Thomson's atomic model is popularly known as the plum pudding model. However, it had to be abandoned in 1911 on both theoretical and experimental grounds in favour of Rutherford's atomic model.

(c) Ernest Rutherford's atomic model

In 1909, Rutherford and colleagues found out that when α −particles from a Radium source were directed to a very thin sheet of gold or platinum foil;

- ***The α −particles penetrated the gold foil***
- ***A great majority of the α −particles passed through the foil without change in direction.***
- ***A small fraction (about 1 in 20,000) of the α −particles were scattered/deflected through large angles(as high as $90°$ or more)***



To explain the above facts; Rutherford deduced that;

- ***Since α −particles are positively charged, the few deflections that occurred were because the protons of the atom are collected in a heavy, small positively charged central nucleus which makes up just a tiny fraction of the atom.***
- ***Since most of the α −particles passed through the gold foil undeflected, most of the atom is empty space and the electrons rotate in this space around the nucleus in the in the same way planets rotate around the sun***

The analysis led Rutherford to propose a model in which an atom consists of a very small positively charged nucleus, in which most of the mass of the atom is concentrated, surrounded by negatively charged electrons, so that the atom is electrically neutral.

Fundamental particles of the atom

The fundamental particles of an atom include the; protons, neutrons and electrons.

The discovery of the fundamental particles of the atom

The existence of **electrons** in atoms was first suggested by **J.J.Thomson**, as a result of experimental work on the conduction of electricity through gases at low pressures which produces cathode rays and X-rays, and a study of radioactivity.

An atom is electrically neutral. This means that if it contains negatively charged electrons, it must also contain some positively charged particles. These positively charged particles are the **protons** and they were discovered after **Rutherford**'s experiments after bombardment of elements with $\propto -$ and $\beta -$ rays given off by radioactive elements.

The **neutron** was discovered by **Sir James Chadwick** in 1932, by bombarding beryllium with $\propto -$ rays. Chadwick found out that particles which had properties quite different from those of protons and electrons were given off. They were not deflected at all by electric and magnetic fields and therefore possessed no charge. The particles had almost the same mass as a proton. Since they were neutral particles, they were called neutrons. Later experiments showed that all atoms contain neutrons apart from that of hydrogen.

Properties of the fundamental particles of the atom

Property	**Electron**	**Proton**	**Neutron**
Approximate relative charge	-1	$+1$	$Not\ charged$
	Have equal but opposite charges		
Approximate relative mass	$^{1}/_{1836}$	1	1
Actual mass (kg)	9.1095×10^{-31}	1.6726×10^{-27}	1.6750×10^{-27}
		Have almost equal masses	
Charge (C)	-1.6022×10^{-19}	$+1.6022 \times 10^{-19}$	0

RADIOACTIVITY

Discovery

The discovery of radioactivity took place over several years beginning with the discovery of X-rays in 1895 by Wilhelm Conrad Roentgen. The work continued with Henri Becquerel who had learnt of Roentgen's discovery of X-rays through the fluorescence of some materials.

In 1896, a year following the discovery of X-rays, A.H. Becquerel found out that Uranium and Uranium compounds would also emit a penetrating radiation capable of affecting wrapped photographic plates. He was experimenting on salts which fluoresced(glowed in the dark). One day he developed a photographic plate which had been left wrapped in a drawer of his working table to be used the next day. To his surprise, he found that the plate had been exposed. Since he knew that no light could penetrate the wrapping, he perhaps thought the plate was penetrated by some rays coming from the Uranium salts. He though it wise to investigate this mysterious radiation and gave the problem to a young research worker called Marie Curie.

Marie Curie later found out that this strange effect happened with all Uranium salts and it depended on the amount of Uranium present in the compound. She realized that the ability to give off the radiation was a property of the atoms of uranium and that it was a completely new type of property quite different from a chemical reaction. Marie Curie called this property of the Uranium atom **radioactivity**.

In 1898, Marie Curie's husband left his own research work and joined her with this exciting discovery. They discovered two new radioactive elements. They called one **Polonium**, after Marie's native country Poland and the other as **Radium.**

The naturally occurring elements now known to be radioactive are polonium, radon, radium, actinium, thorium, protactinium, francium and uranium. Elements that are not naturally radioactive can also be induced to undergo artificial radioactivity.

In 1903, Rutherford put forward the theory that radioactivity was caused by **disintegration** or **decay** of the large heavy atoms of Radium, Uranium etc., into simpler atoms of other elements.

Definition;

Radioactivity is the spontaneous disintegration of heavier unstable nuclei to form lighter stable nuclei with emission of radioactive particles such as alpha particles, beta particles and gamma rays.

Types of radiations and their discovery

When an atom splits, the nucleus divides and the protons and neutrons in it form two new nuclei. The electrons divide themselves between the two. Radioactive substances therefore have unstable nuclei.

Three types of radiation are given off by radioactive substances. They include the beta rays ($\beta - rays$), gamma rays ($\gamma - rays$) and alpha rays ($\alpha - rays$). All these radiations cause certain substances such as zinc sulphide to luminesce. They also ionize gases through which they pass.

Radiation	Symbol	Nature
*Beta(**β**) rays*	$_{-1}^{0}e$	*Beta rays are streams of **high speed electrons** emitted by unstable nuclei* ***N.B. These electrons do not come from the extra-nuclear part of the atom. Beta particles are distinguished from electrons by their source and high energy**.*

Alpha(α) rays	${}_{2}^{4}He$	*Alpha rays are a stream of* ***helium nuclei*** *called* ***alpha particles*** *and are emitted with high energies from radioactive nuclei.* ***An alpha particle is a positively charged particle consisting of two neutrons and two protons and is identical to the nucleus of a helium atom.***
Gamma (γ)rays	${}_{0}^{0}\gamma$	*Gamma rays are* ***light rays(electromagnetic radiations)*** *of* ***extremely high energy*** *therefore* ***very short wave lengths***

A comparison between the characteristics of the different types of radiations

Property	**Radiation**		
	Beta rays (β − rays)	**Alpha rays**(α − rays)	**Gamma rays**(γ − rays)
Make up	*High speed electrons*	*Helium nuclei*	*Electromagnetic radiations*
Mass number	$9.11 \times 10^{-28} g$	$6.67 \times 10^{-24} g$	*Negligible*
Charge	$-1\ unit$	$+2\ units$	0
Velocity	$3 - 99\%$ *that of light*	*About* $\frac{1}{20}$ *th of that of light*	*Same as that of light*
Effect of electric field	*Deflected towards the positive pole*	*Deflected towards the negative pole*	*Not deflected*
Effect of magnetic field	*Deflected much more readily and in an opposite direction to that of alpha particles*	*Deflected in a direction that shows that they consisted of positively charged particles*	*Not deflected*
Tissue penetration	*1*	*0.01*	*100*
Penetrating power	*Higher penetrating power than alpha particles (can pass through 0.01m of a metal)*	*very low penetrating power (cannot penetrate more than through 0.01mm of a metal)*	*Very high penetrating power (can pass through 0.1m of a metal)*
Ionizing power	*Lower ionizing power than beta particles*	*Have high ionizing power*	*A very low ionizing power*

Some other important particles involved in radioactivity

Particle	**Symbol**
Neutron	${}_{0}^{1}n$
Proton	${}_{1}^{1}H$
Deuterium	${}_{1}^{2}H$
Tritium	${}_{1}^{3}H$
Positron	${}_{+1}^{0}e$

Radioisotopes

From their name, they are isotopes which are radioactive. They can also be called radioactive isotopes.

Radioisotopes are heavier unstable atoms of the same element with the same number of protons but different number of neutrons that undergo spontaneous disintegration to form lighter stable atoms with emission of radioactive particles such as alpha particles, beta particles and gamma rays.

Very many radioactive isotopes have been artificially made and are very useful.*(check under applications of radioactivity.*

Nuclear reactions

In a chemical reaction, the nature of the elements does not change. For example sodium reacts with chlorine to form sodium chloride. When molten sodium chloride is electrolyzed, sodium and chlorine can be got again. This means the nature of sodium and chlorine has not changed. The sodium atom changes to sodium ion and the chlorine atom changes to chloride ion. The number of protons and neutrons in the nuclei of the elements does not change in a chemical reaction. It is only the number of electrons in the extra-nuclear part that are transferred or shared. In a nuclear reaction however, both the nucleus and electrons are involved.

***Therefore in a chemical reaction, there is no change in the atomic nuclei of the combining elements whereas in a nuclear reaction, there is a change in the number of protons in the atomic nucleus of the element*.**

Differences between chemical and nuclear reactions

Chemical reaction	Nuclear reaction
Only the valence (outermost)electrons are involved	There is a change in the composition of the nucleus.
Elements do not lose their identities	New elements are formed
The number of protons and neutrons in the atomic nucleus does not change.	The number of protons in the atomic nucleus changes
A small amount of energy is evolved or absorbed	A very large amount of energy is given out
It's rate is affected by external factors like temperature, catalysts or pressure	Not affected by temperature, catalyst or pressure changes
Can be reversed by changing the reaction conditions	It cannot be reversed(irreversible)
All isotopes of an element undergo the same reactions	Isotopes of an element give different products in nuclear reactions
Mass is conserved	Some of the mass is converted into energy ($E = mc^2$)

Balancing nuclear reaction equations

When balancing nuclear reaction equations, the **sum of nucleon numbers** (mass numbers) should be the same on both sides. The **sum of the proton numbers** (atomic numbers) should also be the same.

Examples

1. ***Reactions involving emission of the, alpha particles, beta particles ,gamma rays and some other particles***

(i) **Emission of an alpha particle$\left({}^{4}_{2}He\right)$**

Consider the reaction;

$$^{a}_{b}X \longrightarrow {}^{4}_{2}He + {}^{c}_{d}Y$$

To balance the equation;

$$a = 4 + c \qquad\qquad b = 2 + d$$
$$c = a - 4 \qquad\qquad d = b - 2$$

The equation becomes; $\boldsymbol{^{a}_{b}X \longrightarrow {}^{4}_{2}He + {}^{a-4}_{b-2}Y}$

Emission of an alpha particle therefore reduces proton number(atomic number) by 2 units and reduces the mass number by 4 units

(ii) **Emission of a beta particle$\left({}^{0}_{-1}e\right)$**

Consider the reaction;

$$^{a}_{b}X \longrightarrow {}^{0}_{-1}e + {}^{c}_{d}Y$$

To balance the equation;

$$a = 0 + c \qquad\qquad b = -1 + d$$
$$c = a \qquad\qquad d = b + 1$$

The equation becomes; $\boldsymbol{^{a}_{b}X \longrightarrow {}^{0}_{-1}e + {}^{a}_{b+1}Y}$

Emission of a beta particle therefore has no effect the mass number on and increases proton number(atomic number)by 1 unit

(iii) **Emission of gamma rays$\left({}^{0}_{0}\gamma\right)$**

Consider the reaction;

$$^{a}_{b}X \longrightarrow {}^{0}_{0}\gamma + {}^{c}_{d}Y$$

To balance the equation;

$$a = 0 + c \qquad\qquad b = 0 + d$$
$$c = a \qquad\qquad d = b$$

The equation becomes; $\boldsymbol{^{a}_{b}X \longrightarrow {}^{0}_{0}\gamma + {}^{a}_{b}Y}$

Emission of a gamma ray therefore has no effect on both proton number(atomic number) and mass number

(iv) **Emission of a neutron $\left({}_{0}^{1}n\right)$**

Consider the reaction;

$${}_{b}^{a}X \longrightarrow {}_{0}^{1}n + {}_{d}^{c}Y$$

To balance the equation;

$$a = 1 + c \qquad b = 0 + d$$
$$c = a - 1 \qquad d = b$$

The equation becomes; $\boldsymbol{{}_{b}^{a}X \longrightarrow {}_{0}^{1}n + {}_{b}^{a-1}Y}$

Emission of a neutron therefore has no effect on the proton number(atomic number) and reduces mass number by 1 unit

(v) **Emission of a positron $\left({}_{+1}^{0}e\right)$**

Consider the reaction;

$${}_{b}^{a}X \longrightarrow {}_{+1}^{0}e + {}_{d}^{c}Y$$

To balance the equation;

$$a = 0 + c \qquad b = 1 + d$$
$$c = a \qquad d = b - 1$$

The equation becomes; $\boldsymbol{{}_{b}^{a}X \longrightarrow {}_{+1}^{0}e + {}_{b-1}^{a}Y}$

Emission of a positron therefore reduces the proton number(atomic number) by 1 unit and has no effect on mass number.

2. Bombardment by particles

(i) Bombardment of nitrogen-14 by an alpha particle to form oxygen-17

$${}_{7}^{14}N + {}_{2}^{4}He \longrightarrow \ldots\ldots\ldots. + {}_{8}^{17}O$$

Let the other particle emitted be ${}_{y}^{x}Q$

To balance the equation;

$$14 + 4 = x + 17 \qquad 7 + 2 = y + 8$$
$$x = 18 - 17 \qquad y = 9 - 8$$
$$x = 1 \qquad y = 1$$

The particle with atomic number 1 and mass number 1 is a proton.

The equation becomes; $\boldsymbol{{}_{7}^{14}N + {}_{2}^{4}He \longrightarrow {}_{1}^{1}H + {}_{8}^{17}O}$

(ii) Name the particle that must bombard with Cadmium-113 to convert it to Cadmium-114 with expulsion of a gamma ray

Let the bombarding particle be ${}_{b}^{a}X$

$${}_{48}^{113}Cd + {}_{b}^{a}X \longrightarrow {}_{48}^{114}Cd + {}_{0}^{0}\gamma$$

To balance the equation;

$$113 + a = 114 + 0 \qquad 48 + b = 48$$

$$a = 1 \qquad\qquad b = 0$$

The particle with atomic number 0 and mass number 1 is a neutron.

The equation becomes; $\mathbf{{}^{113}_{48}Cd + {}^{1}_{0}n \longrightarrow {}^{114}_{48}Cd + {}^{0}_{0}\gamma}$

(iii) Alpha bombardment of element Y produces two neutrons and astatine-211. Identify Y.

$${}^{m}_{q}Y + {}^{4}_{2}He \longrightarrow 2{}^{1}_{0}n + {}^{211}_{85}At$$

To balance the equation;

$$m + 4 = (2 \times 1) + 211 \qquad q + 2 = (2 \times 0) + 85$$
$$m = 213 - 4 \qquad q = 85 - 2$$
$$m = 209 \qquad q = 83$$

N.B. Strictly use the atomic number and not the mass number to identify the element from the Periodic Table

The element with atomic number 83 is $\mathbf{{}^{209}_{83}Bi}$***.***

3. A nuclear reaction can be written in the form;

$$\mathbf{{}^{a}_{b}X(w, z)\,{}^{c}_{d}Y}$$

This in detail means

$\mathbf{initial\ nuclide(bombarding\ particle, expelled\ particle)nuclide\ formed}$

The reactions shown in the bombardments above can therefore be represented as;

(i) $\mathbf{{}^{14}_{7}N(\alpha, p){}^{17}_{8}O}$

(ii) $\mathbf{{}^{113}_{48}Cd(n, \gamma){}^{114}_{48}Cd}$

(iii) $\mathbf{{}^{209}_{83}Bi(\alpha, 2n){}^{211}_{85}At}$

4. Other problems

(i) Complete the equation

$$\mathbf{{}^{250}_{98}Cf + {}^{11}_{5}B \longrightarrow {}^{257}_{103}Lw\ + ...}$$

Let the mass number and atomic number of the other product be x and y respectively.

$$250 + 11 = 257 + x \qquad 98 + 5 = 108 + y$$
$$x = 261 - 257 \qquad y = 103 - 103$$
$$x = 4 \qquad y = 0$$

Note that the atomic number got is 0. But there is no element in the Periodic table with atomic number 0. Therefore this should be the particle ${}^{1}_{0}n$ *but multiplied by 4*

The equation therefore becomes;

$$\mathbf{{}^{250}_{98}Cf + {}^{11}_{5}B \longrightarrow {}^{257}_{103}Lw\ + 4{}^{1}_{0}n}$$

(ii) Balance the equation

$$^{235}_{92}\boldsymbol{U} + {}^{1}_{0}\boldsymbol{n} \longrightarrow {}^{144}_{56}\boldsymbol{Ba} + \ldots + 2{}^{1}_{0}\boldsymbol{n}$$

Let the mass number and atomic number of the other product be x and y respectively.

$$\begin{aligned} 235 + 1 &= 144 + x + 2 \\ x &= 236 - 146 \\ x &= 90 \end{aligned}$$

$$\begin{aligned} 92 + 0 &= 56 + y + 0 \\ y &= 92 - 56 \\ y &= 36 \end{aligned}$$

The element with atomic number 36 is $^{90}_{36}\boldsymbol{Kr}$

The equation therefore becomes;

$$^{235}_{92}\boldsymbol{U} + {}^{1}_{0}\boldsymbol{n} \longrightarrow {}^{144}_{56}\boldsymbol{Ba} + {}^{90}_{36}\boldsymbol{Kr} + 2{}^{1}_{0}\boldsymbol{n}$$

(iii) Determine the number of alpha particles and beta particles that must be emitted for $\boldsymbol{Bi-214}$ to transform to$\boldsymbol{Pb-206}$.

Let the number of alpha particles and beta particles emitted be x and y respectively
Note that atomic numbers of the elements can be obtained from the Periodic Table

$$^{214}_{83}\boldsymbol{Bi} \longrightarrow {}^{206}_{82}\boldsymbol{Pb} + \boldsymbol{x}{}^{4}_{2}\boldsymbol{He} + \boldsymbol{y}{}^{0}_{-1}\boldsymbol{e}$$

$$\begin{aligned} 214 &= 206 + 4x \\ 4x &= 8 \\ x &= 2 \end{aligned}$$

$$\begin{aligned} 83 &= 82 + 2x - y \\ y &= 86 - 83 \\ y &= 3 \end{aligned}$$

Therefore 2 alpha particles and 3 beta particles must be emitted

(iv) A series of radioactive decays can be represented as;

$$^{212}_{82}\boldsymbol{Pb} \xrightarrow{(\mathbf{1})} {}^{212}_{83}\boldsymbol{X} \xrightarrow{(\mathbf{2})} {}^{208}_{81}\boldsymbol{Y} \xrightarrow{\boldsymbol{\beta-particle}} \boldsymbol{Z}$$

(a) Name the particles 1 and 2
(b) Identify elements X , Y and Z.
(c) State the groups to which X, Y and Z belong.

Equations;

$$^{212}_{82}Pb \longrightarrow {}^{212}_{83}X + {}^{0}_{-1}e$$

$$^{212}_{83}X \longrightarrow {}^{208}_{81}Y + {}^{4}_{2}He$$

$$^{208}_{81}Y \longrightarrow {}^{0}_{-1}e + {}^{208}_{82}Z$$

(a) 1 is ***beta particle***
2 is ***alpha particle***
(b) X; $^{212}_{83}\boldsymbol{Bi}$
Y; $^{208}_{81}\boldsymbol{Tl}$
Z; $^{208}_{82}\boldsymbol{Pb}$
(c) X; ***Group V***
Y; ***Group III***
Z; ***Group IV***

Questions

1. Explain with use of suitable examples; the terms;
   (i) Atom
   (ii) Ion
   (iii) molecule

2. (a) Explain what is meant by each of the following terms;
   (i) Radioactivity
   (ii) Radioactive isotopes
   (iii) Nuclear reaction
   (iv) nucleons

(b) State the differences between a nuclear reaction and a chemical reaction.

3. (a) Explain the difference between;
   (i) a $\beta - particle$ and an $\alpha - particle$
   (ii) a proton and a deuteron
   (iii) $\alpha - particle$ and a helium atom

   (b) Explain why when alpha particles are directed to thin metal foils, most of them pass through and a few are scattered backwards.

   (c) State the effect of emission of each of the following on the nucleus of an atom;
   (i) a positron
   (ii) a neutron
   (iii) an alpha particle
   (iv) a beta particle
   (v) a gamma ray

4. Identify the unknown elements $E, G, J, Q, R, T, W, X, Y\ and\ Z$ in each of the following equations using the Periodic Table. Add mass numbers and atomic numbers wherever they are missing.
   (i) $E + {}_{2}^{4}He \longrightarrow {}_{7}^{13}N + {}_{0}^{1}n$
   (ii) ${}_{11}^{24}Na + {}_{0}^{1}n \longrightarrow G + {}_{-1}^{0}e$
   (iii) ${}_{\dots}^{\dots}Si \longrightarrow {}_{\dots}^{\dots}J + {}_{+1}^{0}e$
   (iv) ${}_{7}^{14}N + {}_{0}^{1}n \longrightarrow {}_{\dots}^{14}Q + {}_{1}^{\dots}R$
   (v) ${}_{7}^{14}N + {}_{2}^{4}T \longrightarrow {}_{\dots}^{17}W + {}_{1}^{\dots}X$
   (vi) ${}_{82}^{207}Pb \longrightarrow {}_{83}^{\dots}Y + {}_{-1}^{0}e$
   (vii) ${}_{3}^{7}Li + {}_{1}^{2}H \longrightarrow 2{}_{\dots}^{\dots}Z + {}_{0}^{1}n$

5. Complete each of the following equations
   (i) ${}_{88}^{226}Ra \longrightarrow {}_{2}^{4}He + \dots..$
   (ii) ${}_{7}^{16}N \longrightarrow \dots.. + {}_{-1}^{0}e$
   (iii) ${}_{6}^{14}C \longrightarrow \beta + \dots..$
   (iv) ${}_{33}^{73}As + \dots. \longrightarrow {}_{32}^{73}Ge$
   (v) ${}_{27}^{60}Co \longrightarrow \beta + \dots\dots..$
   (vi) ${}_{92}^{238}U \longrightarrow \dots\dots + {}_{2}^{4}He$
   (vii) ${}_{92}^{238}U \longrightarrow \dots.. + {}_{-1}^{0}e$
   (viii) ${}_{42}^{96}Mo + {}_{1}^{2}H \longrightarrow \dots.. + {}_{0}^{1}n$

(ix) $^{25}_{12}Mg + ^{4}_{2}He \longrightarrow ..... + ^{1}_{1}H$

(x) $^{238}_{92}U + ^{1}_{0}n \longrightarrow ...... + ^{0}_{-1}e$

(xi) $^{109}_{47}Ag + ^{1}_{0}n \longrightarrow ..... + \gamma$

(xii) $...... + \alpha \longrightarrow ^{13}_{7}N + ^{1}_{0}n$

(xiii) $^{223}_{91}Pa \longrightarrow \beta + ... \longrightarrow ^{4}_{2}He + ..$

(xiv) $^{223}_{88}Ra \longrightarrow .... + ^{219}_{86}Rn \longrightarrow .... + ^{215}_{84}Po$

(xv) $^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{95}_{42}Mo + ... + 2\,^{1}_{0}n + 7\beta$

6. Naming the particle involved in each case, complete each of the equations.
   (i) $^{99}_{46}Pd \longrightarrow ^{99}_{45}Rh + ...$
   (ii) $^{226}_{88}Ra \longrightarrow ..... + ^{222}_{86}Ra$
   (iii) $^{24}_{11}Na + ... \longrightarrow ^{23}_{12}Mg + ^{1}_{0}n$
   (iv) $^{10}_{5}B + ... \longrightarrow ^{7}_{3}Li + ^{4}_{2}He$
   (v) $^{238}_{92}U \longrightarrow ^{206}_{82}Pb + 8\,^{4}_{2}He + ...$
   (vi) $^{7}_{3}Li + ... \longrightarrow ^{8}_{3}Li + ^{1}_{1}H$
7. State the atomic number and mass number of the new element formed when;
   (i) $^{224}_{88}Ra$ emits a neutron
   (ii) $^{19}_{10}Ne$ emits a positron
   (iii) $^{228}_{89}Ac$ emits a beta particle
   (iv) $^{212}_{82}Pb$ emits gamma rays
   (v) $^{216}_{84}Po$ emits an alpha particle
   (vi) $^{235}_{92}U$emits 3 alpha particles and 4 beta particles
   (vii) $^{230}_{90}Th$ emits 4 alpha particles and 2 beta particles
8. Write well balanced equations for the following nuclear reactions;
   (i) $^{31}_{15}P(n,\gamma)^{32}_{15}P$
   (ii) $^{14}_{7}N(n,p)^{14}_{6}C$
   (iii) $^{14}_{7}N(n, ...)^{14}_{6}C$
   (iv) $^{14}_{7}N(\alpha, ...)^{17}_{8}O$
   (v) $^{27}_{13}Al(\alpha, n)$ ....
   (vi) $^{96}_{42}Mo(....., n)^{97}_{43}Te$
   (vii) $....(\alpha, 2n)^{211}_{85}At$

9. Write well balanced equations for the following nuclear reactions;
   (i) Decay of radioactive phosphorus-30 to form silicon-30 with emission of a positron.
   (ii) Proton bombardment of lithium-7 to form alpha particles
   (iii) Fusion of deuterium and tritium to form an alpha particle and a neutron
   (iv) Bombardment of nitrogen with and alpha particle to form a proton and oxygen-12
   (v) Uranium loses first one and then a second $\beta - particle$.

(vi) Uranium loses first one and then a second $\alpha - particle$.

(vii) $^{234}_{92}U$ loses five $\alpha - particles$.

(viii) $^{226}_{88}Ra$ loses two $\beta - particles$.

10. Find the;
    (i) the number beta particles and alpha particles that must be emitted for $lead - 211$ to transform to $lead - 207$.
    (ii) the number beta particles and alpha particles that must be emitted for $^{241}_{95}Am$ to decay to $^{237}_{95}Am$.
    (iii) the number beta particles and alpha particles that must be emitted for $^{234}_{90}Th$ to decay to $^{206}_{82}Pb$.
    (iv) the number beta particles and alpha particles that must be emitted for $^{232}_{90}Th$ to transform to $^{208}_{82}Pb$.
    (v) the number beta particles and alpha particles that must be emitted for $^{238}_{92}U$ to transform to $^{230}_{90}Th$.
    (vi) the number beta particles and alpha particles that must be emitted for $^{234}_{90}Th$ to transform to $^{218}_{84}Po$.
11. (a)A series of radioactive decays can be represented as;

$$^{212}_{82}Pb \xrightarrow{\alpha-emission} X \xrightarrow{\beta-emission} Y \xrightarrow{\beta-emisssion} Z$$

State the mass number and atomic number of element Z. Show your working

(b) In a radioactive emission, actinium $^{227}_{89}Am$ loses an alpha particle and the product loses another alpha particle. The product also loses one beta particle. Calculate the mass number and atomic number of the element that is finally formed.

RADIOACTIVE DECAY

The rate at which a radioactive isotope decays cannot be speeded up or slowed down by any physical or chemical means. The rate depends on the identity of the isotope and the amount of isotope present. Radioactive isotopes do not decay at the same rate. Some decay very rapidly in a few millionths of a second and others can even take billions of years to decay.

All radioactive decay processes follow first order kinetics.

The rate of radioactive decay at time t is directly proportional to the number of radioactive atoms present. The rate of decay therefore decreases and continues to decrease as more and more atoms break up.

Therefore if N represent number of atoms, then;

$$Rate\ of\ decay \propto N$$

$$Since\ N\ decreases\ as\ t\ increases, the\ the\ rate\ of\ decay\ decreases(\ it\ is\ negative)$$

$$-\frac{dN}{dt} \propto N$$

$$-\frac{dN}{dt} = \lambda N$$

$$where\ \lambda\ is\ the\ \boldsymbol{decay\ constant}\ or\ radioactive\ decay\ constant$$

$$or\ disintegration\ constant\ of\ the\ isotope$$

$$On\ separating\ variables;$$

$$-\frac{dN}{N} = \lambda dt$$

$$If\ N_0\ is\ the\ number\ of\ atoms\ present\ at\ t = 0$$

$$and\ N_t\ is\ the\ number\ of\ atoms\ present\ at\ t = t,$$

$$Integrating\ using\ the\ above\ limits\ yields;$$

$$-\int_{N_0}^{N_t} \frac{dN}{N} = \lambda \int_0^t dt$$

$$-[lnN]_{N_0}^{N_t} = \lambda[t]_0^t$$

$$-(lnN_t - lnN_0) = \lambda t$$

$$lnN_0 - lnN_t = \lambda t$$

$$\boldsymbol{ln\left(\frac{N_0}{N_t}\right) = \lambda t} \ldots\ldots\ldots\ldots\ldots(\boldsymbol{i})$$

Equation ($\boldsymbol{i}$) *can also be written in the form shown below*

$$\boldsymbol{ln}\left(\frac{N_0}{N_t}\right) = \lambda t$$

$$\boldsymbol{2.303log\left(\frac{N_0}{N_t}\right) = \lambda t} \ldots\ldots\ldots\ldots(\boldsymbol{ii})$$

Any of the equations (i) or (ii) can be used any of the unknown values it by substitution so long as all the others are known.

Since Activity is proportional to number of radioactive atoms present, we can also have the equations in the form;		***We can also express the equations in terms of counts per unit time***	
$\boldsymbol{ln\left(\frac{A_0}{A_t}\right) = \lambda t}$	$\boldsymbol{2.303log\left(\frac{A_0}{A_t}\right) = \lambda t}$	$\boldsymbol{ln\left(\frac{C_0}{C_t}\right) = \lambda t}$	$\boldsymbol{2.303log\left(\frac{C_0}{C_t}\right) = \lambda t}$
We can also express the equations in terms of mass			
$\boldsymbol{ln\left(\frac{M_0}{M_t}\right) = \lambda t}$		$\boldsymbol{2.303log\left(\frac{M_0}{M_t}\right) = \lambda t}$	

Activity of a radioactive sample is the number of disintegrations per second of a radioactive sample.

The decay constant is the proportionality between the number of radioactive atoms and the rate at which the radioactive atoms decay.

Half life

The time taken for a number N_0 of radioactive atoms to decay to ${}^{N_0}/_{2}$ atoms is called the half-life. The half-life of Radium is about 1600 years. This means that 1g of Radium decays to 0.5g in 1600 years. 0.5g decay to 0.25g in a further 1600 years, and so on.

Half-life is the time taken for the amount of a radioactive sample to decay to half its original value.

Derivation of expression for half life

It can be derived using any of the equations (i) or (ii) above

$\boldsymbol{From\ \ ln\left(\frac{N_0}{N_t}\right) = \lambda t}$	$\boldsymbol{From\ 2.303log\left(\frac{N_0}{N_t}\right) = \lambda t}$
when $\boldsymbol{N_0}$ decays to half its original value, then at $\boldsymbol{t = t_{1/2}}$ and $\boldsymbol{N_t = \frac{1}{2}N_0}$ $\boldsymbol{ln\left(\frac{N_0}{\frac{1}{2}N_0}\right) = \lambda t_{1/2}}$ $\boldsymbol{ln2 = \lambda t_{1/2}}$ $\boldsymbol{t_{1/2} = \frac{ln2}{\lambda}}$ $\boldsymbol{t_{1/2} = \frac{0.693}{\lambda}}$	when $\boldsymbol{N_0}$ decays to half its original value, then at $\boldsymbol{t = t_{1/2}}$ and $\boldsymbol{N_t = \frac{1}{2}N_0}$ $\boldsymbol{2.303log\left(\frac{N_0}{\frac{1}{2}N_0}\right) = \lambda t_{1/2}}$ $\boldsymbol{2.303\log 2 = \lambda t_{1/2}}$ $\boldsymbol{t_{1/2} = \frac{2.303\log 2}{\lambda}}$ $\boldsymbol{t_{1/2} = \frac{0.693}{\lambda}}$
The equation $\boldsymbol{t_{1/2} = \frac{0.693}{\lambda}}$ *can be used to find half life when the decay constant is known or the decay constant when the half life is known.*	

Examples

1. **A radioactive isotope decays from an initial count of 160 counts per minute to 20 counts per minute in 27 days. Calculate its half-life.**

$C_0 = 160\ min^{-1}$ $C_t = 20\ min^{-1}$ $t = 27\ days$	$ln\left(\frac{C_0}{C_t}\right) = \lambda t$ $\lambda = \frac{1}{t}ln\left(\frac{C_0}{C_t}\right)$ $\lambda = \frac{1}{27}ln\left(\frac{160}{20}\right)$ $\boldsymbol{\lambda = 0.077016\ day^{-1}}$	$t_{1/2} = \frac{0.693}{\lambda}$ $t_{1/2} = \frac{0.693}{0.077016}$ $t_{1/2} = \frac{0.693}{0.077016}$ $t_{1/2} = 8.99813$ $\boldsymbol{t_{1/2} \approx 9\ days}$

2. **The nuclide of carbon-14 has a half-life of 5600 years. Calculate the age of a wood from an ancient tomb, if this wood gave 10 counts per minute per gram of carbon compared with the 15 counts that are given by the carbon from new wood.**

   N.B. This is a process of carbon dating that will be seen later. The counts per minute tend to reduce after the tree is cut and wood begins to decay. This helps us interpreted the values of C_0 and C_t. Mistaking them will yield a negative value of time. Time cannot be negative!!!

$C_0 = 15\,min^{-1}g^{-1}$ $C_t = 10\,min^{-1}g^{-1}$ $t_{1/2} = 5600\,years$ $t = ?$	$t_{1/2} = \frac{0.693}{\lambda}$ $\lambda = \frac{0.693}{t_{1/2}}$ $\lambda = \frac{0.693}{5600\,years}$ $\lambda = \mathbf{0.000124\,year^{-1}}$	$ln\left(\frac{C_0}{C_t}\right) = \lambda t$ $t = \frac{1}{\lambda} ln\left(\frac{C_0}{C_t}\right)$ $t = \frac{1}{0.000124} ln\left(\frac{15}{10}\right)$ $\mathbf{t = 3270\,years}$

3. **If the decay constant for radium is $\mathbf{1.356 \times 10^{-11} s^{-1}}$. Calculate the time required for 90% of a sample of radium to disintegrate.**

$\lambda = 1.356 \times 10^{-11} s^{-1}$ $N_0 = 100\%$ $After\ a\ 90\%\ decay, amount\ present$ $after\ time\ t\ is\ \mathbf{N_t} = (\mathbf{100 - 90}) = \mathbf{10}\%$ $t = ?$	$ln\left(\frac{N_0}{N_t}\right) = \lambda t$ $t = \frac{1}{\lambda} ln\left(\frac{N_0}{N_t}\right)$ $t = \frac{1}{1.356 \times 10^{-11}} ln\left(\frac{100}{10}\right)$ $\mathbf{t = 1.698 \times 10^{11} seconds}$

4. **The half-life of Radium is 1590 years. How long will it take for a sample of Radium to decay to 25% of its original amount?**

$t_{1/2} = 1590\,years$ $N_0 = 100\%$ $N_t = 25\%$ $t = ?$	$t_{1/2} = \frac{0.693}{\lambda}$ $\lambda = \frac{0.693}{t_{1/2}}$ $\lambda = \frac{0.693}{1590\,years}$ $\lambda = \mathbf{0.000436\,year^{-1}}$	$ln\left(\frac{N_0}{N_t}\right) = \lambda t$ $t = \frac{1}{\lambda} ln\left(\frac{N_0}{N_t}\right)$ $t = \frac{1}{0.000436} ln\left(\frac{100}{25}\right)$ $\mathbf{t = 3180\,years}$

5. **The half-life of radioisotope bromine-82 is 36 hours. Calculate the fraction of a sample of the isotope will remain after one day.**

   NB. In our previous calculations, you note that units for the decay constant, counts or amount and time were not consistent but we did not change them. This is because the ratio $\frac{N_0}{N_t}$ cancels the units out. In this question however, half-life and time should have consistent units.

$t_{1/2} = 36\ hours$

$t = (1 \times 24) = 24\ hours$

$N_0 = 1 (Total\ fraction\ should\ be\ 1)$

$N_t = ?$

$t_{1/2} = \frac{0.693}{\lambda}$

$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{36\ hours}$

$\lambda = \mathbf{0.01925\ hour^{-1}}$

$ln\left(\frac{N_0}{N_t}\right) = \lambda t$

$ln\left(\frac{1}{N_t}\right) = 0.01925 \times 24$

$ln1 - \ln(N_t) = 0.462$

$\ln(N_t) = -0.462$

$N_t = 0.63$

$\frac{\mathbf{N_t}}{\mathbf{N_0}} = \frac{\mathbf{0.63}}{\mathbf{1}} = \mathbf{0.63}$

6. **The half-life of a radioactive element is 150 seconds. What percentage of the isotope will remain after 600 seconds?**

$t_{1/2} = 150\ seconds$

$t = 600\ seconds$

$N_0 = 100\%$

$N_t = ?$

$t_{1/2} = \frac{0.693}{\lambda}$

$\lambda = \frac{0.693}{t_{1/2}}$

$\lambda = \frac{0.693}{150\ s}$

$\lambda = \mathbf{0.00462\ s^{-1}}$

$ln\left(\frac{N_0}{N_t}\right) = \lambda t$

$ln\left(\frac{100}{N_t}\right) = 0.00462 \times 600$

$ln100 - \ln(N_t) = 2.772$

$\ln(N_t) = 4.60517 - 2.772$

$ln(N_t) = 1.83317$

$N_t = \mathbf{6.25}$

$\boldsymbol{The\ percentage\ that\ remains\ is\ 6.25\%}$

7. **If a sample of a radioactive isotope has a half-life of 3.11 hours and an activity of $\mathbf{1000 s^{-1}}$ at a certain time, calculate the activity one hour later.**

$t_{1/2} = 3.11\ hours$

$A_0 = 1000\ s^{-1}$

$t = 1\ hour$

$A_t = ?$

$t_{1/2} = \frac{0.693}{\lambda}$

$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{3.11\ hours}$

$\lambda = \mathbf{0.22283\ hour^{-1}}$

$ln\left(\frac{A_0}{A_t}\right) = \lambda t$

$ln\left(\frac{1000}{A_t}\right) = 0.22283 \times 1$

$ln1000 - \ln(A_t) = 0.22283$

$\ln(A_t) = 6.907755 - 0.22283$

$ln(A_t) = 6.684925$

$\mathbf{A_t = 800 s^{-1}}$

8. **It takes 1620 years for 0.03 moles of Radium-226 to decay to 0.015 moles. Calculate the number of moles of Radium-226 left when 26g decayed for 6 years?**

$since\ 0.015 = \left(\frac{0.03}{2}\right),$

$then\ t_{1/2} = 1620\ years$

$t = 6\ years$

$M_0 = 26\ g$

$M_t = ?$

$t_{1/2} = \frac{0.693}{\lambda}$

$\lambda = \frac{0.693}{t_{1/2}}$

$\lambda = \frac{0.693}{1620\ years}$

$\lambda = \mathbf{0.000428\ year^{-1}}$

$ln\left(\frac{M_0}{M_t}\right) = \lambda t$

$ln\left(\frac{26}{M_t}\right) = 0.000428 \times 6$

$ln26 - \ln(M_t) = 0.002567$

$ln(M_t) = 3.25553$

$M_t = 25.9333g$

$\boldsymbol{The\ number\ of\ moles\ left}$

$= \left(\frac{\mathbf{25.9333}}{\mathbf{226}}\right) = \mathbf{0.1147\ moles}$

Questions

1. A radioactive sample of caesium-136 decays from 480 counts per minute to 60 counts per minute in 42 days. Calculate its half-life.
2. The half-life of strontium-90 is 29 years. Calculate its decay constant.
3. The disintegration constant of lead-199 is $0.0077 min^{-1}$. Determine its half-life.
4. A sample of wood has an activity of $8\ min^{-1}g^{-1}$. A freshly cut wooden tree has an activity of $15.3\ min^{-1}g^{-1}$. Calculate the age of the wood sample. The half-life of carbon-14 is 5600 years.
5. A radioactive isotope decays at such a rate that after 68 minutes, only one fourth of its original amount remains. Calculate its half-life.
6. The half-life of Bismuth is 19.7 minutes. Determine the time taken for 43% by mass of Bismuth to decay.
7. A radioactive element to a count rate of 120 counts per minute. After 3 hours, it dropped to 15 counts per minute. Determine the half-life of the isotope.
8. The half-life of Sulphur-31 is 2.54 seconds. How long will it take for 99% of Sulphur-31 to get converted to phosphorus?
9. 1.0g of strontium-90 was reduced to 0.953g after 2 years. Calculate the half-life of strontium-90.
10. Radium undergoes radioactive decay according to the following equation forming relatively stable nuclides X, Y and Z.

$$^{226}_{88}Ra \xrightarrow{\beta} X \xrightarrow{\alpha} Y \xrightarrow{\alpha} Z$$

(a) Identify the particles X, Y and Z.

(b) 0.02 moles of $^{226}_{88}Ra$ were allowed to decay for 2.40×10^4 years. The half life of Radium-226 is 1600 years. Calculate the number of atoms of Radium-226 left at the end of 2.40×10^4 years.
($Avogadro's\ constant\ = 6.02 \times 10^{23}\ atoms\ per\ mole$)

(c) State any two practical applications of radioactive isotopes.

11. (a) (i) The decay law is given in the expression below $-\frac{dN}{dt} = \lambda N$. State what the symbols represent.

(ii) Using the above expression derive the expression for relating the half-life ($t_{1/2}$) and the decay constant.

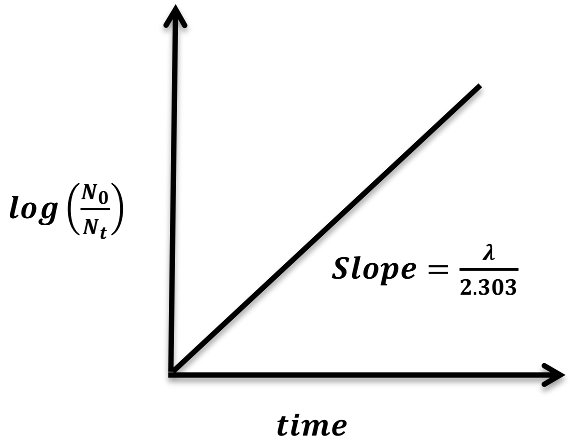
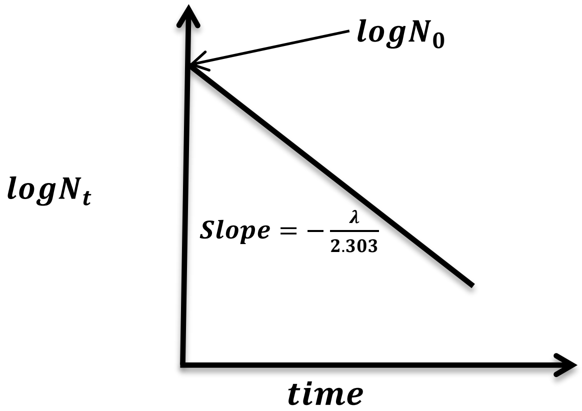
(b) (i) Nickel (^{63}Ni) decays to copper (^{63}Cu). Name the particle emitted and write the equation for the reaction.

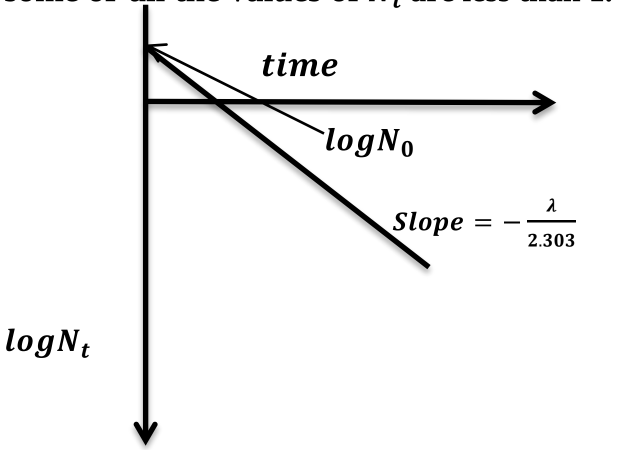
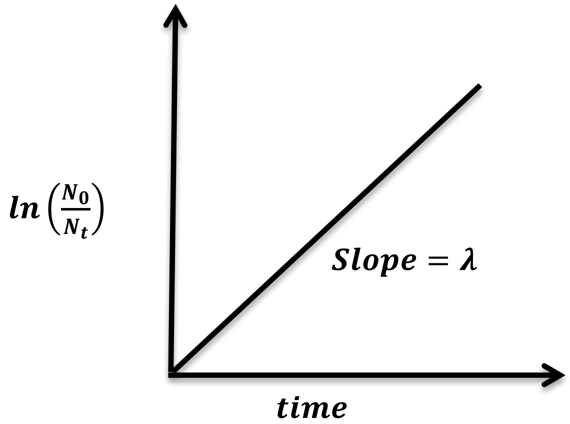
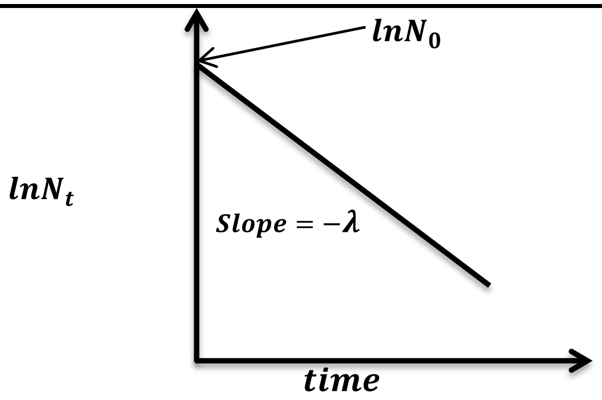
(ii) Calculate the time taken for $\frac{15}{16}$ of nickel to change to copper. (The half-life of nickel is 120 years)

Graphical representation of radioactive decay

The decay of a radioactive substance can be represented graphically by plotting various kinds of graphs depending on data experimental data provided.

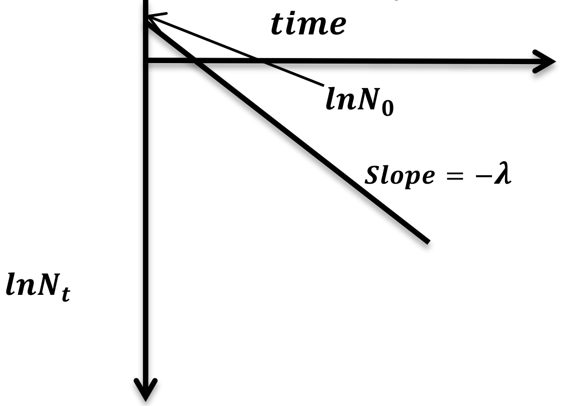
Note that in each of these graphs N can be substituted with Activity (A), amount, Number of moles, mass or counts

$From\ 2.303log\left(\frac{N_0}{N_t}\right)=\lambda t$ $log\left(\frac{N_0}{N_t}\right)=\frac{\lambda}{2.303}t$ $compare\ with\quad y\ =mx\ +c$ **A graph of $log\left(\frac{N_0}{N_t}\right)$ agaist time(t) is a straight line through the origin and its slope is $\frac{\lambda}{2.303}$ from which λ can be obtained and used to find $t_{1/2}$ from the expression $t_{1/2}=\frac{0.693}{\lambda}$**	
$From\ 2.303log\left(\frac{N_0}{N_t}\right)=\lambda t$ $log\left(\frac{N_0}{N_t}\right)=\frac{\lambda}{2.303}t$ $logN_0-logN_t=\frac{\lambda}{2.303}t$ $logN_t=-\frac{\lambda}{2.303}t+logN_0$ $compare\ with\ y\ =mx\ +c$	

A graph of $logN_t$ agaist time(t) is a straight line with an intercept on the $logN_t$ axis. This intercept = $logN_0$ and can be used to find the initial amount, N_0. The graph has a negative slope = $-\frac{\lambda}{2.303}$ from which λ can be obtained and used to find $t_{1/2}$ from the expression $t_{1/2} = \frac{0.693}{\lambda}$	**The graph has a slightly different look if some or all the values of N_t are less than 1.** 
$From\ ln\left(\frac{N_0}{N_t}\right) = \lambda$ $compare\ with\ \ y = mx + c$ **A graph of $ln\left(\frac{N_0}{N_t}\right)$ agaist time(t) is a straight line through the origin and its slope λ can be obtained and used to find $t_{1/2}$ from the expression $t_{1/2} = \frac{0.693}{\lambda}$**	
$From\ ln\left(\frac{N_0}{N_t}\right) = \lambda t$ $lnN_0 - lnN_t = \lambda t$ $lnN_t = -\lambda t + lnN_0$ $compare\ with\ y = mx + c$	

A graph of lnN_t agaist time(t) is a straight line with an intercept on the lnN_t axis. This intercept = lnN_0 and can be used to find the initial amount, N_0. The graph has a negative slope = $-\lambda$ from which λ can be obtained and used to find $t_{1/2}$ from the expression $t_{1/2} = \frac{0.693}{\lambda}$

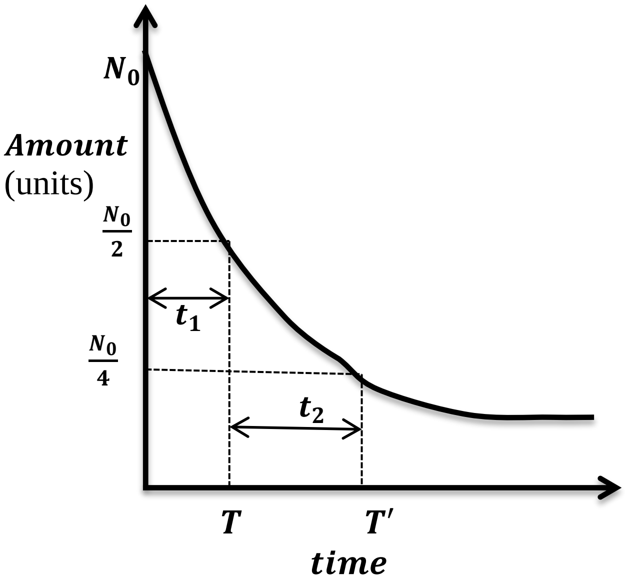
The graph has a slightly different look if some or all the values of N_t are less than 1.



The commonest graph is that of *Activity* or *mass* or *amount* or *number of atoms* plotted against time. The uniqueness with this graph is that it is a curve with a negative slope. From this graph half-life can be got directly from the graph and can be used to find the decay constant λ using the expression $t_{1/2} = \frac{0.693}{\lambda}$.

Half-life is got by getting the time that corresponds to $\frac{N_0}{2}$ and then $\frac{N_0}{4}$. The half-life can then be got by the expression $t_{1/2} = \frac{t_1+t_2}{2}$. The values t_1 and t_2 are got from the graph by $t_1 = T - 0$ and

$$t_2 = T' - T$$



It is advisable that when plotting graphs on radioactivity, the axes begin from the origin.

Questions

1. (a) State what is meant by the terms
   (i) Radioactivity
   (ii) Half-life

   (b) The table below shows data for radioactive decay of element W.

Time (hours)	0.0	5.0	10.0	15.0	20.0	25.0	30.0
Activity (counts per minute)	25.00	23.00	21.25	19.50	18.00	16.50	15.25

   (i) Plot a graph of activity against time
   (ii) Determine the half-life of element W.

(iii) Determine the decay constant and state its units.

2. A sample of bromine was irradiated in a nuclear reactor. The table below shows the radioactivity count rates at various times

Time(hours)	0	1.0	2.0	5.0	10	25	50	75	100
Count rate	500	268	242	225	204	154	95	55	35

(a) Plot a graph of count rate against time

(b) Use your graph to determine;

  (i) half life

  (ii) the rate constant in s^{-1}

  (iii) order of the reaction

3. The table below shows the results of radioactive decay of ${}^{234}_{91}Pa$

Time(seconds)	20	40	60	80	100	120
Mass of $\mathbf{{}^{234}_{91}Pa}$(g)	48.2	38.5	31.5	26.0	21.0	17.2

(a) Plot a graph of $\boldsymbol{log_{10}(\ mass \ )}$against **time**

(b) Use your graph to determine;

  (i) initial mass of ${}^{234}_{91}Pa$

  (ii) slope and hence the decay constant of ${}^{234}_{91}Pa$

  (iii) half-life of ${}^{234}_{91}Pa$

Nuclear energy

Nuclear energy is energy released during **nuclear fission** or **nuclear fusion**. Nuclear energy has been increasingly used to provide electricity and to drive large ships.

Discovery

In 1935, Enrico Fermi discovered that when a radioactive substance such as Uranium was bombarded by neutrons, it produced by-products that were not Uranium and were lighter than the original sample.

In 1938, Otto Hahn, Fritz Strassman, Lise Meitner and Otto Frisch discovered fission. They found out that the lighter by-products of neutron bombardment on Uranium-235 also released energy. This proved Albert Einstein's theory put forth 33 years earlier that $E = mc^2$. This was the first time that all the components of fission were known. This discovery resulted into making of the **atomic bomb** and **nuclear power plants**.

Nuclear fission

A very large amount of energy is released in splitting heavy atomic nuclei. Uranium-235 nuclei can be split into smaller elements when a controlled nuclear reaction is carried out.

Nuclear fission is the process by which a nucleus of a heavier atom is split into nuclei of lighter atoms, by bombardment with neutrons, with release of a large amount of energy.

When Uranium-235 is bombarded with neutrons, it undergoes fission to form lighter elements. The lighter elements include barium (Ba), lanthanum (La), rubidium (Rb), krypton (Kr), strontium (Sr), and others. Three neutrons are released per Uranium-235 fission. These neutrons produced induce three more fission reactions which release 9 neutrons. The 9 neutrons will also induce nine fission reactions and so on. Therefore a **chain reaction** occurs and a large amount of energy is liberated.

$$\boldsymbol{{}^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{139}_{56}Ba + {}^{94}_{36}Kr + 3\,{}^{1}_{0}n + 175\ MeV}$$

The fission products ${}^{139}_{56}Ba$ and ${}^{94}_{36}Kr$ are unstable too and emit radiations until stable isotopes are formed.

The energy released in accordance with Einstein's law

Nuclear fusion

Nuclear fusion is a process of combining nuclei of lighter atoms to form heavier nuclei at very high temperature, liberating a very large amount of energy.

The lighter elements include **hydrogen, helium and lithium**. The energy produced comes from decrease in mass of the nuclides.

The fusion reactions only take place at **extremely high temperature** more than $2 \times 10^{8}\ °C$. This is because a very large amount of energy is required for the positively charged nuclei to overcome strong repulsion between them. The nuclear fusion reactions are therefore also known as **thermonuclear reactions**.

Energy from nuclear fusion is used in the **hydrogen bomb**

Some examples of nuclear fusion reactions include;

$$\boldsymbol{4\,{}^{1}_{1}H \longrightarrow {}^{4}_{2}He + 2\,{}^{0}_{+1}e + Energy}$$

$$\boldsymbol{\underset{Deuterium}{{}^{2}_{1}H} + {}^{2}_{1}H \longrightarrow {}^{4}_{2}He + Energy}$$

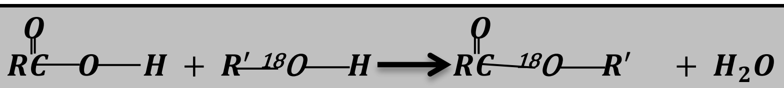
$$\boldsymbol{\underset{tritium}{{}^{3}_{1}H} + {}^{2}_{1}H \longrightarrow {}^{4}_{2}He + 2\,{}^{1}_{0}n + Energy}$$

Nuclear power

Nuclear power is electricity created from a nuclear power plant. The heat produced during fission of Uranium-235 is used to convert water into steam. This steam is used to drive turbines that generate electricity.

Applications of radioactivity

Radioactive isotope or radiation	Use/ application
Radium-226	*In radiotherapy for treatment of cancer*
$\gamma - rays$**(from Radium or Radon)**	*Taking radiographs in radiotherapy instead of X-rays*
Phosphorus-32	*In radioactive tracing for the uptake of phosphorus by a plant from a phosphate fertilizer*
Carbon-14	*To elucidate the nature of photosynthesis*
	In carbon dating, to estimate the age of old objects. Living plants and animals take in carbon which includes a small proportion of carbon-14. When a plant or animal dies, the carbon-14 present in it starts to decay. The amount of carbon-14 in the dead object after t *years is determined as* N_t*. The amount of carbon-14 in the similar live object is also determined as* N_0*. Using a known half-life of carbon-14,* $t_{1/2}$*, the decay constant (*λ*) is determined using the equation* $t_{1/2} = \frac{0.693}{\lambda}$*. The value of* λ *is then substituted in the rate equation* $ln\left(\frac{N_0}{N_t}\right) = \lambda t$ *to determine the age of the object (*t*) in years.*
Iron-59	*To study the role of iron in blood formation*
Iodine-131	*Diagnosis of thyroid diseases and in research on the functioning of the thyroid gland and the kidneys*
$\beta - rays\ or\ \gamma - rays$	*Measure thicknesses in materials. The amount of radiation passing through a material decreases as the material gets thicker. A source of* $\beta - rays\ or\ \gamma - rays$ *is placed on one side of the material and a detector on the other side. The scale reading on the detector will give a measure of the thickness.*
Cobalt-60	*It gives out* $\gamma - rays$ *which are used to kill cancerous cells*
Plutonium-239	*Plutonium-239 which is produced from Uranium-238 in chain reacting units is used as a fuel in some nuclear reactors.*
Oxygen-18	*To determine the mechanism of esterification of monocarboxylic acids with primary alcohols. An alcohol with oxygen atom labeled with oxygen-18 is reacted with the carboxylic acid in presence of concentrated sulphuric acid to form an ester and water. On analysis of the ester and water formed using a mass spectrometer, it is found that the oxygen-18 is present in the ester and not in water. This proves that the* O—H *bond in the alcohol and* C—O *bond in the acid cleaved.*

	 $RC(=O)—O—H + R'\,^{18}O—H \longrightarrow RC(=O)—^{18}O—R' + H_2O$ ***The reverse of esterification is acid alkaline ester hydrolysis. An ester containing a labeled radioactive oxygen-18 atom is heated with sodium hydroxide solution. Analysis of the products using a mass spectrometer shows that the oxygen-18 is not in the carboxylic acid formed. This means that the $RCO—OR'$ bond cleaved.***  $RC(=O)—^{18}O—R' + \bar{O}H \longrightarrow RC(=O)—O—H + R'\,^{18}O^-$

NUCLEAR STABILITY

Many atomic nuclei are stable but others decay by giving out radiations. All nuclei with atomic numbers greater than 83 are unstable and therefore radioactive.

Nuclear stability is the ability of the nucleus of an atom to resist spontaneous decay that would result into formation of other nuclei and emission of radiations.

A summarized comparison between stable and unstable nuclei

Stable nucleus	Unstable nucleus
Number of protons is approximately equal to the number of neutrons	The number of neutrons is much greater than the number of protons or has a high number of protons than neutrons
Does not undergo radioactive disintegration.	Undergoes radioactive decay emitting alpha and beta particles to attain stability
Those with odd numbers of both protons and neutrons are least stable	Those with even numbers of both protons and neutrons are most stable.

The stability of a nucleus is related to the ratio of the number of neutrons to the number of protons. This ratio is represented as $\left({}^{n}/_{p}\right)$.

Lighter elements with **mass number** up to 20 have the ${}^{n}/_{p}$ approximately equal to one. After atomic number 20, addition of protons is not favoured because of the creation of more repulsive forces in the nucleus. Addition of neutrons is favoured up to ${}^{n}/_{p} = 1.6$.

Beyond this value, atomic nuclei become unstable due an increased number of protons that lead to increased repulsive forces within the nuclei. The nuclei therefore emit radiations to become stable and get converted to new nuclei.

Factors affecting nuclear stability

1. $\boldsymbol{n}:\boldsymbol{p\ ratio}$.

Nuclear stability depends on the ${}^{n}/_{p}$ value. Nuclei that have ${}^{n}/_{p}$ value equal to one are stable. Those with ${}^{n}/_{p} > 1$ have more neutrons than protons and those with ${}^{n}/_{p} < 1$ have more protons than neutrons hence unstable.

2. Atomic number

Stability of the nucleus decreases as the atomic number increases. Atoms with atomic number 83 are have unstable nuclei.

3. Mass number

As mass number increases, the number of protons in the nucleus also increases, repulsive forces increase much more rapidly than the attractive forces making the nucleus unstable.

4. Half-life

The higher half-life of a radioactive isotope, the slower the decay rate and the nucleus becomes more stable and the lower the half-life, the higher the decay rate and the nucleus is less stable. For example iodine-131 with half-life about 8 days is less stable than Uranium-238 with half-life of about 4.5 billion years.

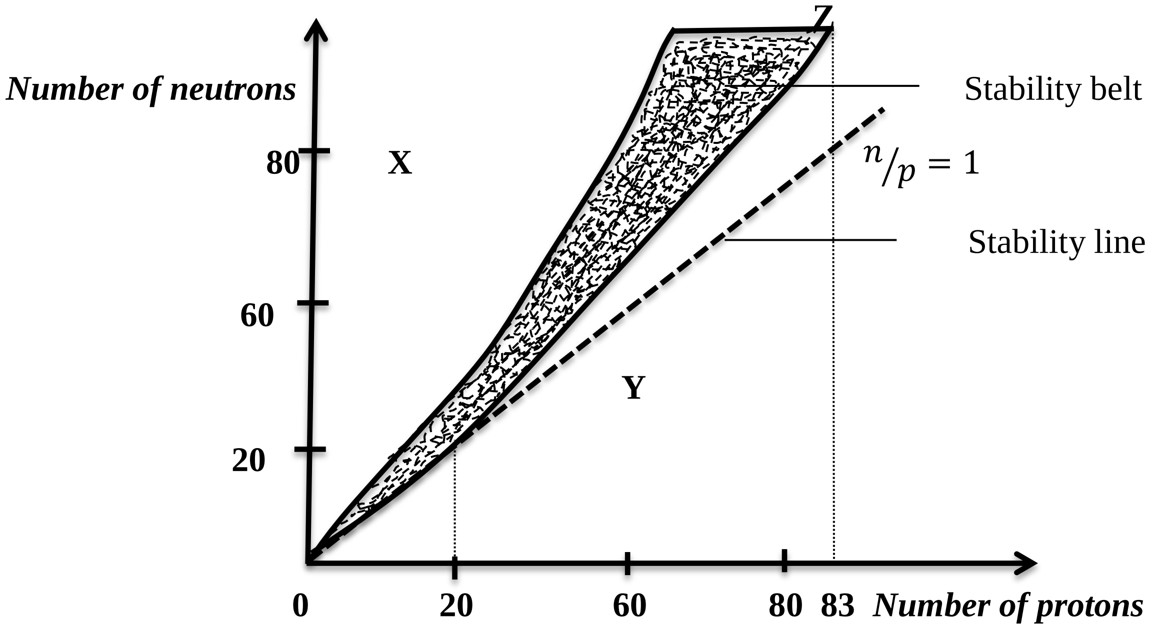
5. Binding energy

This is the energy given out when a nucleus is formed from its constituent neutrons and protons

or ***The energy required to separate the nucleus into its constituent neutrons and protons***.

The greater the binding energy, the more stable the nucleus and the lower the binding energy, the less stable the nucleus.

Variation in number of neutrons and protons



The dotted line is a line along which number or protons is equal to number of neutrons. It is called the **stability line** and along this line $^n/_p = 1$

The **stability belt** or **stability region** or **band of nuclear stability** is the area on the graph where all stable nuclei lie. Any nuclei out of this band are unstable and undergo radioactivity to achieve stability.

The **band of nuclear stability** starts to deviate from the **line of stability**$(^n/_p = 1)$ at atomic number 20. This is because as **atomic number** or **number of protons increases**, there is a strong repulsive force that develops in the nucleus. More neutrons are needed to counterbalance the repulsive forces. This increases the neutron- proton ratio.

The stability belt stops abruptly at atomic number 83 because no stable isotope exists beyond atomic number 83.

The nuclei in regions X, Y and Z outside the stability zone are unstable and therefore undergo radioactive decay to form isotopes which lie in the stability zone. This can occur by **electron capture**(or **positron emission**), **beta emission** and **alpha emission**.

Region X

In this region, **number of neutrons is greater than number of protons**. The neutron-proton ratio is greater than one. To stabilize the nucleus, the neutron–proton ratio can be reduced by **reducing the number of neutrons** and **increasing the number of protons**. This happens by **beta emission** which reduces the number of neutrons by one and increases the number of protons by one.

$$\boldsymbol{{}^{a}_{b}X \longrightarrow {}^{0}_{-1}e + {}^{a}_{b+1}Q}$$

Region Y

In this region, **number of protons is greater than number of neutrons**. The neutron-proton ratio is less than one. To stabilize the nucleus, the neutron–proton ratio can be increased by **reducing the number of protons** and **increasing the number of neutrons**. This happens by **electron capture** or **positron emission**. Both electron capture and positron emission reduces number of protons by one and increases number of neutrons by one.

$$^{a}_{b}Y + {}^{0}_{-1}e \longrightarrow {}^{a}_{b-1}R$$

$$^{a}_{b}Y \longrightarrow {}^{a}_{b-1}R + {}^{0}_{+1}e$$

Region Z

In this region, **the nuclides have atomic number greater than 83 and are heavy**. To stabilize the nucleus, both **the number of protons** and **the number of neutrons must be reduced**. This happens by a **series of** alpha **emissions**. Alpha emission reduces both the number of protons and the number of neutrons. There must be a series of alpha emissions until a very stable nuclide is formed because stability cannot be gained by one alpha emission.

$$^{a}_{b}Z \longrightarrow {}^{a-4}_{b-2}W + {}^{4}_{2}He$$

ELECTRONIC STRUCTURE OF ATOMS

Electronic structure is the state of motion of electrons in an electrostatic field created by stationary nuclei. The term encompasses both the wave functions of the electrons and the energies associated with them. In Rutherford's "planetary" model, it was proposed that electrons rotated around the nucleus and could not fall into the nucleus by centrifugal force. However, it was found out that a charged particle like the electron should radiate energy, causing a decrease in its velocity and would fall into the nucleus. For this reason, the electron part of Rutherford's model was soon rejected but his concept of the nucleus remained.

The modern ideas on electronic distribution in atoms originated from the model of the hydrogen atom by Bohr. Bohr's theory was based on the spectrum of the hydrogen atom.

Electromagnetic radiation

Electromagnetic radiation is the energy resulting from the acceleration of electric charge and the associated electric fields and magnetic fields. The energy can be regarded as waves propagated through space involving oscillating electric and magnetic fields at right angles to each other and to the direction of propagation.

Alternatively, the energy can be regarded as a stream of photons (which are bundles of light energy) travelling at the speed of light as quantized harmonic waves.

Electromagnetic radiation as quanta

Planck, in his quantum theory of absorption and emission of radiation, proposed that all material systems can absorb or give off electromagnetic radiation only in "chunks" of energy called quanta , E. Quanta are described as discrete packets of energy because it requires a certain amount of energy to be released by an atom when an electron goes from a higher energy level to a lower energy level.

The quanta are proportional to the frequency of the radiation, v.

$$E \propto v$$
$$E = hv$$
$$(The\ constant\ of\ proportinality, h\ is\ the\ Planck's\ constant)$$

Relationship between wavelength , λ, frequency, v, and energy, E.

The energy of an electromagnetic radiation is directly proportional to its frequency but inversely proportional to its wave length.

$$E = hv \quad or \quad E = \frac{hc}{\lambda}$$
$$where\ E\ is\ the\ value\ of\ the\ quantum (J)$$
$$h\ is\ the\ Planck's\ constant (6.6256 \times 10^{-34} Js)$$
$$v\ is\ the\ frequency (s^{-1} or\ Hz)$$
$$\lambda\ is\ the\ wavelength\ (m)$$
$$c\ is\ the\ velocity\ of\ light (3 \times 10^{8} ms^{-1})$$

Using the equation in calculations

Examples

1. Find the energy of a photon with wavelength 415nm.

$$E = \frac{hc}{\lambda}$$
$$E = \frac{6.6256 \times 10^{-34} \times 3 \times 10^{8}}{415 \times 10^{-9}}$$
$$\boldsymbol{E = 4.79 \times 10^{-19} J}$$

2. Calculate the energy of a photon with frequency$275 \times 10^{9} Hz$.

$$E = hv$$
$$E = 6.6256 \times 10^{-34} \times 275 \times 10^{9}$$
$$\boldsymbol{E = 1.822 \times 10^{-22} J}$$

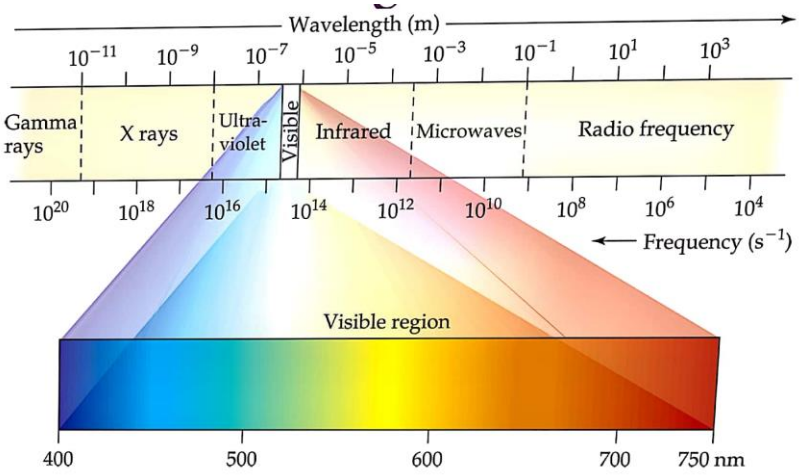
Atomic spectra

Atoms of different elements can be made to absorb or emit energy when they are excited. The emission spectra from the vapours of the elements are known as **atomic or line spectra**. They consist of a series of lines, each corresponding to a particular wavelength, and indicating that the number of possible energy changes that can take place within the atom of the element is in some way limited. Each element produces a unique set of spectral lines and no two elements can emit the same series of spectral lines. This means that an element can be identified by its line spectrum.

The word **spectrum** was first used in optics to describe the rainbow of colours in visible light after passing through a prism. After advancement in the understanding of light, the concept came to apply to the entire **electromagnetic spectrum**.

A spectrum can be defined as a range of electromagnetic energies arranged in order of increasing or decreasing wavelength or frequency of electromagnetic radiation emitted or absorbed by an atom or molecule.

An electromagnetic spectrum is the entire range of wave length or frequency of electromagnetic radiation extending from gamma rays to the longest radio waves and including visible light.



The emission of radiation may be induced by a variety of methods; for example, by high temperature, bombardment by electrons, absorption of higher-frequency radiation, etc.

Types of spectra

Emission spectrum

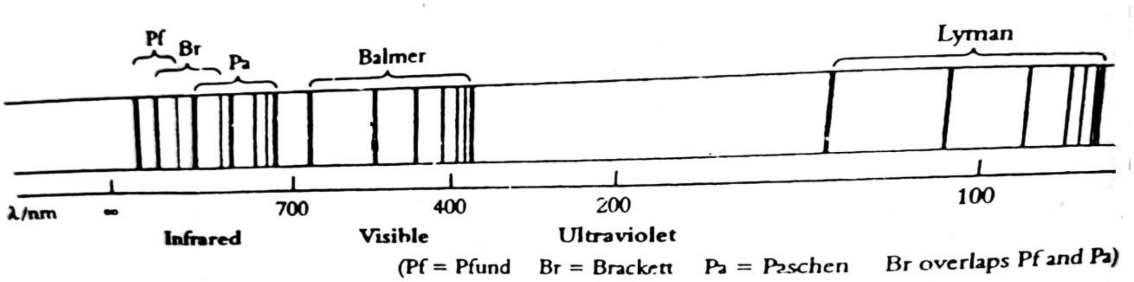
If atoms are heated to sufficiently high temperatures, they emit light of certain wave lengths. The emission of energy occurs as a result of electrons moving from higher energy levels to lower energy levels. The observed spectrum consists of a number of coloured lines on a black background. The spectrum is called an **atomic emission**

spectrum. The emission spectra of atoms provide evidence that the electrons are distributed around the nucleus in various energy levels.

Absorption spectrum

If atoms absorb light of a certain wave length, black lines appear in the spectrum where light of some wave length has been absorbed. The absorbed energy by the atoms causes energy changes from lower to higher energy levels. The observed spectrum is called an **absorption spectrum**.

A description of the hydrogen emission spectrum



When electricity is passed through a **discharge tube containing hydrogen** at **low pressure**, the **hydrogen molecules break up** to form **single hydrogen atoms**. The hydrogen atoms **emit radiations** in the and **ultraviolet**, **visible** and **infrared** part of the spectrum. When the radiations are analysed by a spectrograph, a **line spectrum** is formed. **Each line in the spectrum represents a definite wavelength** of a radiation.

The wave length is given by the Rydberg equation, $\frac{1}{\lambda} = R_H\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right)$ where R_H is Rydberg constant, n_1 and n_2 being simple whole numbers and λ is the wavelength.

A series of lines in the ultra violet region is called the **Lyman series**. The series of lines in the visible region is the **Balmer series** and there is a series of lines in the infra-red region. The series in the infra-red region consist of the **Paschen**, **Brackett** and **Pfund series**.

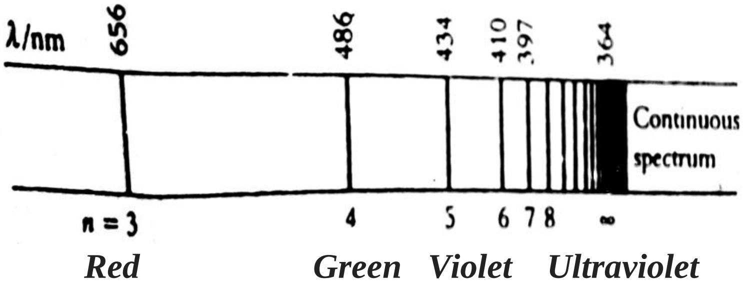
In each series, the intervals between the **frequencies of the lines become smaller and smaller** towards the **low wave length or high frequency end of the spectrum** until the lines run together or **converge** to form a **continuum of light**.

An explanation of the hydrogen spectrum

When the hydrogen atom **absorbs energy**, it causes the electron to experience a transition from a **lower to a higher energy level**. The observed lines in the spectrum are due to electronic transitions from the **higher energy levels to the lower energy levels** in the atom with **emission of energy**. When an electron from jumps from a higher energy level to a lower energy level, it **emits energy equal to the difference between the**

energy of the two energy levels in the form of small packets of light known as photons. For every transition of the electron, there is a line in the spectrum and there are different types of spectral series formed.

The **Lyman Series** is formed when the electron jumps from any higher energy level to first energy level ; $\boldsymbol{n = 1}$.
The **Balmer Series** is formed when the electron jumps from any higher energy level to the second energy level; $\boldsymbol{n = 2.}$
The **Paschen Series** is formed when the electron jumps from any higher energy level to the third energy level; $\boldsymbol{n = 3}$.
The **Brackett series** is formed when the electron jumps from any higher energy level to the fourth energy level ; $\boldsymbol{n = 4}$.
The **Pfund** series is formed when the electron jumps from any higher energy level to the fifth energy level ; $\boldsymbol{n = 5}$.
The observed convergence between the lines towards the high frequency end in each series is because **the differences in energy between successive energy levels in atoms become smaller and smaller with increasing distance of the energy levels from the nucleus** until they **finally merge to form a continuum of light** (continuous band of radiation)



The Balmer series of hydrogen

The application of the Rydberg equation

The Rydberg equation is the equation ;

$$\frac{1}{\lambda} = R_H\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right)$$

where $R_H = 109678\ cm^{-1} or\ 1.097 \times 10^7 m^{-1}$ is Rydberg constant,
n_1 and n_2 being simple whole numbers and
λ is the wavelength.

For the **Lyman Series**, the electron jumps to ; $n_1 = 1$ from $n_2 = 2, 3, 4, \ldots$
For the **Balmer Series,** the electron jumps from; $n_1 = 2$ from $n_2 = 3, 4, 5, \ldots$

For the **Paschen Series,** the electron jumps to; $\boldsymbol{n_1 = 3}$ from $\boldsymbol{n_2 = 4, 5, 6}$, ...
For the **Brackett series,** the electron jumps to; $\boldsymbol{n_1 = 4}$ from $\boldsymbol{n_2 = 5, 6, 7}$ ...
For the **Pfund series**, the electron jumps to ; $\boldsymbol{n_1 = 5}$ from $\boldsymbol{n_2 = 6, 7, 8}$, ...

Examples

1. **If an electron falls from an energy level $n = 5$ to an energy level $n = 3$. Calculate the;**
   - **(i) wavelength in nanometers of the emitted radiation.**
   - **(ii) the frequency**
   - **(iii) change in energy of the radiation .**

($\boldsymbol{Rydberg\ constant = 109678\ cm^{-1}, velocity\ of\ light = 3 \times 10^8 ms^{-1}\ and\ Planck's\ constant = 6.6256 \times 10^{-34} Js}$)

$$n_1 = 3, n_2 = 5,$$
$$R_H = 109678\ cm^{-1}$$

(i)
$$\frac{1}{\lambda} = R_H\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right)$$
$$\frac{1}{\lambda} = 109678\left(\frac{1}{3^2} - \frac{1}{5^2}\right)$$
$$\frac{1}{\lambda} = 7799.32444$$
$$\lambda = 0.000128\ cm$$
$$\lambda = 0.000128 \times 10^{-2}\ m$$
$$\lambda = 1.28 \times 10^{-6}\ m$$
$$\lambda = 1.28 \times 10^{-6} \times 10^9 nm$$
$$\lambda = 1.28 \times 10^{-6} \times 10^9 nm$$
$$\boldsymbol{\lambda = 1280\ nm}$$

(ii)
$$v = \frac{c}{\lambda}$$
$$v = \frac{3 \times 10^8 ms^{-1}}{1.28 \times 10^{-6}\ m}$$
$$\boldsymbol{v = 2.344 \times 10^7 Hz}$$

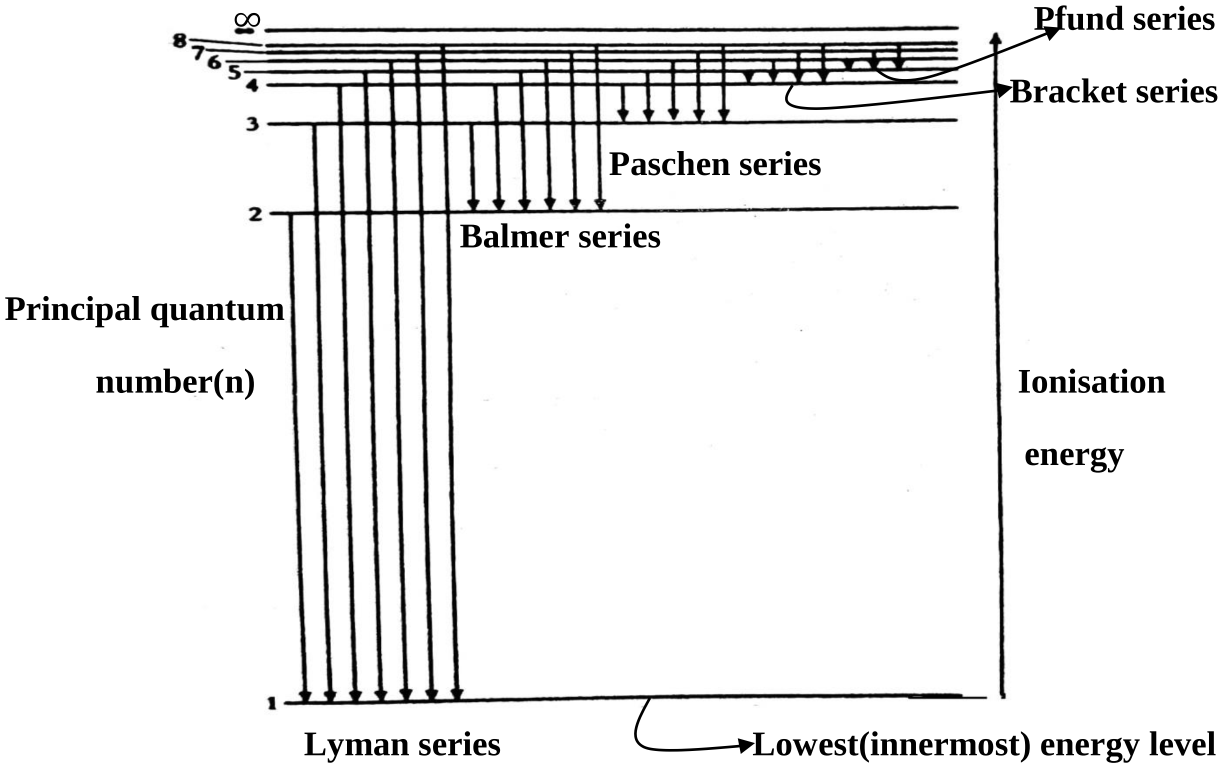
(iii)
$$E = \frac{hc}{\lambda} = hv$$
$$E = 6.6256 \times 10^{-34} \times 2.344 \times 10^7$$
$$\boldsymbol{E = 1.553 \times 10^{-26} J}$$

2. **Use the Rydberg equation to calculate the wavelength in nm of the light emitted when the electron in a hydrogen atom undergoes a transition from $n = 9$ to $n = 6$. Determine the region of light emitted.**

$$n_1 = 6, n_2 = 9,$$
$$R_H = 1.097 \times 10^7\ m^{-1}$$
$$\frac{1}{\lambda} = R_H\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right)$$
$$\frac{1}{\lambda} = 1.097 \times 10^7\left(\frac{1}{6^2} - \frac{1}{9^2}\right)$$
$$\frac{1}{\lambda} = 169290.1235$$
$$\lambda = 5.907 \times 10^{-6}\ m$$
$$\lambda = 5.907 \times 10^{-6} \times 10^9 nm$$
$$\boldsymbol{\lambda = 5907\ nm}$$

Note; The units in which the Rydberg constant is given determine the way in which you carry out the calculation. Also note that to convert from m to nm, a multiplication factor of $\boldsymbol{10^9}$ is used.

Energy level diagram for the hydrogen atom



The principle quantum number (n) only takes on integral values from 1 to infinity(∞).

As **frequency increases** in each of the series of lines, **each line becomes closer to the previous line** until the lines **converge** and the spectrum becomes **continuous**. The **Lyman series** arises from electron transition **to the ground state from higher energy levels**. The ground state occurs when the electron is at the lowest energy level $n = 1$, and the atom is most stable in this state. The electron normally occupies this energy level unless given sufficient energy to move up to a higher energy level.

The highest frequency lines relate to the highest energy levels. The limit of the Lyman series(the convergence of the lines) corresponds to a transition from the $n = \infty$ to the $n = 1$ energy level. The $n = \infty$ is the energy level where the electron has escaped from the atom and the atom has ionised.

The atom is said to be in an excited state when the electron is found in the higher energy levels. When an electron is excited from the ground state to a higher energy, it becomes unstable and falls back to one of the lower energy levels by emitting photon(s)/electromagnetic radiation

By convention, the $n = \infty$ energy level is usually assigned an energy value of $0\ eV$.

The lower the energy level, the more negative the energy value associated with that level. Thus, the more negative energy states correspond to more stable states. Negative value of energy indicates that the electron is bound to the nucleus and there exists an attractive force between the electron and the nucleus. Also, since the potential at infinity is defined as zero, energy levels at a distance below infinity are negative.

The energy difference between any two adjacent levels gets smaller as n increases, which results in the higher energy levels getting very close and crowded together just below $n = \infty$.

The ionization energy of an atom is the energy required to remove the electron completely from the atom (transition from ground state $n = 0$ to infinity $n = \infty$). For hydrogen, the ionization energy $= 13.6eV \ or \ 2.18 \times 10^{-18}J$

The significance of lines in the hydrogen spectrum

Explain the significance of lines in the hydrogen spectrum

The spectrum consists of a series of lines, each corresponding to a particular wavelength, and indicating that the number of possible energy changes that can take place within the atom of the element is in some way limited. The observed lines in the spectrum are due to electrons making transitions from the higher energy levels to the lower energy levels in the atom with emission of energy.

The importance of the Convergence limit

State the importance of the Convergence limit

The convergence limit is reached when the electron is completely removed from the atom and corresponds to a transition from the $n = \infty$ to the $n = 1$ energy level. The transition happens when an electron collides with an ion and returns to the ground state. The convergence frequency can be used to calculate the ionisation energy.

The Bohr's model of the hydrogen atom

Rutherford's model of an atom could not explain that facts as to **why the atomic spectra consisted of separate lines**. The model did not explain **why atoms absorb or emit light of certain frequencies**. In his model too, Rutherford could not explain **why the spectral lines converge to form a continuum**.

In 1913, Niels Bohr put forward his theory that explained these facts. He based on Planck's quantum theory which fundamentally proposed that matter cannot absorb or emit energy in continuous amounts, but only in small discrete units called quanta.

According to Bohr's theory;

- ***The single hydrogen electron could travel around the nucleus in various possible orbits but only certain orbits in which the electron possessed a whole number of quanta of energy were permissible.***
- ***No energy was radiated while the electron was rotating in a permissible orbit.***

- ***The permissible orbits were called stationary states or energy levels.***
- ***The atom could be excited by an electric discharge or strong heat.***
- ***The electron could absorb energy and jump to one of the higher energy levels.***
- ***The excited state was however unstable and the electron could fall back to the ground state.***
- ***As the electron falls back to the lower energy level, it gives out some of its energy in the form of radiation. The wavelength of the radiation emitted was determined by the energy difference of the electron in the two energy levels.***

Bohr deduced that if $\boldsymbol{E_1}$ was the energy of the electron in the higher energy level and that $\boldsymbol{E_2}$ is that in the lower energy level, then $E_1 - E_2$ is the energy difference for an electron falling from the higher energy level to a lower energy level and was proportional to wavelength, λ. If v is the frequency, then;

$$\boldsymbol{E_1 - E_2 = hv = \frac{hc}{\lambda}}$$

Bohr assigned quantum numbers to the orbits or energy levels . He gave the orbit of lowest energy(nearest to the nucleus) the quantum number 1. The next energy levels quantum numbers 2,3,4,... and so on.

The weaknesses of Bohr's atomic model

- ***Bohr's theory cannot explain the atomic spectra of atoms with more than one electron.***
- ***Bohr's model could not explain the hydrogen atomic spectrum under the influence of external magnetic field i.e. the Zeeman effect, when the spectral line is split into several components in the presence of a magnetic field.***
- ***It could not explain the hydrogen spectrum under the influence of an external electric field. i.e. the Stark effect, when the spectral line gets split into fine lines in the presence of an electric field.***

Ionisation energy

Energy is required to remove an electron from a free gaseous atom against the attraction of the nucleus. For a single atom, the energy required to remove one electron from the atom in its ground state is called the **first ionisation energy**.

$$\boldsymbol{X(g) \longrightarrow X^+(g) + e \qquad \Delta U = first\ ionisation\ energy}$$

The first ionisation energy results into formation of a free gaseous ion from a free gaseous atom and not formation of an ion of an element in its normal state. Successive ionisation energies refer to the loss of a second, third,...... n th electron.

Ionisation energy is quoted in units $kJmol^{-1}$ as ionisation potentials in $eVmol^{-1}$

The value of first ionisation energy for hydrogen can be found by the formula relating the wavelengths of the lines in the various spectral lines; $\boldsymbol{\frac{1}{\lambda} = R_H\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right)}$.

When an electron is removed from the Lyman series($n = 1$) to $n = \infty$,

$$n_1 = 1, n_2 = \infty,$$
$$R_H = 1.097 \times 10^7\ m^{-1}$$
$$\frac{1}{\lambda} = R_H\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right)$$
$$\frac{1}{\lambda} = 1.097 \times 10^7\left(\frac{1}{1^2} - 0\right)$$
$$\frac{1}{\lambda} = 1.097 \times 10^7$$
$$\lambda = 9.11577 \times 10^{-8}\ m$$

$$E = \frac{hc}{\lambda}$$
$$E = \frac{6.6256 \times 10^{-34} \times 3 \times 10^8}{9.11577 \times 10^{-8}}$$
$$\boldsymbol{E = 2.18 \times 10^{-18} J}$$

To convert this value to $kJmol^{-1}$, multiply the ionisation energy of one electron by Avogadro's number.

$$\Delta U = 2.18 \times 10^{-18} \times 6.02 \times 10^{23} = 1312360J$$
$$= \boldsymbol{1312.36 kJmol^{-1}}$$

Calculations involving ionisation energies

1. **The limits of the spectral lines formed by transitions from ground state occur at 229.9nm for lithium and 285.6nm for potassium. Calculate the molar ionisation energies of the two elements.**

For lithium;

$$E = \frac{hc}{\lambda}$$
$$E = \frac{6.6256 \times 10^{-34} \times 3 \times 10^8}{229.9\ \times 10^{-9}}$$
$$\boldsymbol{E = 8.646 \times 10^{-19} J}$$

$$\Delta U = 8.646 \times 10^{-19} \times 6.02 \times 10^{23}$$
$$= 520489.2J = \boldsymbol{520.5 kJmol^{-1}}$$

For Sodium;

$$E = \frac{hc}{\lambda}$$
$$E = \frac{6.6256 \times 10^{-34} \times 3 \times 10^8}{285.6 \times 10^{-9}}$$
$$\boldsymbol{E = 6.9596 \times 10^{-19} J}$$

$$\Delta U = 6.9596 \times 10^{-19} \times 6.02 \times 10^{23}$$
$$= 418967.92J = \boldsymbol{418.97 kJmol^{-1}}$$

If it's the frequency, v given, then use the formula $E = hv$. Your answer may be left in Joules.

2. **If the ionisation energy of sodium is 496 $kJmol^{-1}$. Calculate the wavelength of the convergence limit for sodium.**

From $E = \frac{hc}{\lambda}$, $\lambda = \frac{hc}{E} = \frac{6.6256 \times 10^{-34} \times 3 \times 10^8}{\left(\frac{496 \times 1000}{6.02 \times 10^{23}}\right)} = \boldsymbol{2.412 \times 10^{-10} m}$

Heisenberg's Uncertainty principle

According to De Broglie, moving electrons had waves of definite wavelength associated with them. Further experiments showed that a stream of electrons could be diffracted just as X-rays can. Since it is only possible to account for diffraction in terms of waves, it was necessary to assume that a stream of electrons behaves as a wave-like radiation.

As far as atomic structure is concerned, the idea of tiny, negatively charged particles existing in fixed orbits around the nucleus of an atom is replaced by the idea of charge clouds of varying charge density existing in a wave like pattern around the nucleus.

An electron can no longer be considered to occupy a specific, limited **orbit** but instead it exists in a much more diffuse region known as **atomic orbital**.

An electron is different from a larger particle in a way that its wave-like nature is of much greater significance than the wave-like nature of the larger particle.

The other difference is that both the **position and the velocity of a large particle** like a planet can be measured with reasonable accuracy. However, there is no way of measuring the velocity of an electron exactly and locating it exactly at any one time. This is because any method used affects the electron being measured.

The information which can be obtained about an individual electron is therefore far from precise. This an example of application of the **Heisenberg Uncertainty Principle in 1927** which states that;

The more accurately the position of a particle is defined, the less accurately is its velocity known, and the more accurately the velocity is defined, the less accurately is its position known.

The concept of quantum numbers

The term quantum number is used to label the various energy levels. A set of four quantum numbers are used to describe completely the movement and trajectories of each electron within an atom. Each electron in an atom has a unique set of quantum numbers and no two electrons can share the same combination of the four quantum numbers. Quantum numbers are important in determining the electronic configuration of an atom and the location of the electrons in the atom. They are also used to understand other characteristics of atoms such as ionisation energy and atomic radius.

Quantum numbers are a set of four integers which are necessary to locate the energy level or position of an electron and to specify the size, shape and orientation of orbital.

In atoms, there are a total of four quantum numbers. These include;

1. *The Principal quantum number* (n)
2. *The Azimuthal quantum number or angular momentum quantum number*(l)
3. *The magnetic quantum number*(m)
4. *The electron spin quantum number* (s)

Principal quantum number, n.

This specifies the energy level of an electron and its distance from the nucleus. The first orbital nearest to the nucleus has principal quantum number, $n = 1$ and is also called the ground state. The second principal quantum number, $n = 2$ and is called the excited state and so on. As n increases, the size of the orbit increases and the electron is far away from the nucleus. An increase in n also means that the electron has higher energy and is therefore less bound to the nucleus. Energy levels closer to the nucleus have lower energy. All the orbitals having the same value of n are said to be in the same level. The total number of electrons that can occupy any energy level is given by $2n^2$ where n principal quantum number.

Principal quantum number	***Maximum number of electrons***$(\mathbf{2n^2})$
$\mathbf{n = 1}$	2
$\mathbf{n = 2}$	8
$\mathbf{n = 3}$	18
$\mathbf{n = 4}$	32

Azimuthal quantum number (angular momentum quantum number), l.

This determines the shape of an orbital and the angular distribution. It represents the various sub energy levels within an energy level. Each value of l indicates a specific s, p, d, f or g subenergy level.

Azimuthal quantum number	***Sub energy level***
$\mathbf{l = 0}$	*s*
$\mathbf{l = 1}$	*p*
$\mathbf{l = 2}$	*d*
$\mathbf{l = 3}$	*f*
$\mathbf{l = 4}$	*g*

The values of $\boldsymbol{l}$ are in a range of 0 to $n - 1$ for each value of n. If an electron has a principal quantum number $n = \mathbf{3}$ and an angular momentum quantum number $\boldsymbol{l = 2}$**,** then it is said to be a $3d$ electron. The different combinations of the two quantum numbers n and l are shown in the table below.

Principal quantum number	*Azimuthal quantum number*	*Possible combination of n and l*
$\boldsymbol{n=1}$	$l=0$	$1s$
$\boldsymbol{n=2}$	$l=0,1$	$2s \quad 2p$
$\boldsymbol{n=3}$	$l=0,1,2$	$3s \quad 3p \quad 3d$
$\boldsymbol{n=4}$	$l=0,1,2,3$	$4s \quad 4p \quad 4d \quad 4f$

Magnetic quantum number, m

This gives the maximum number of orbitals for the different values of the azimuthal quantum number, l and their orientation in space within a sub energy level. This quantum number accounts for the ***splitting of the spectral lines in the line spectrum of elements***. For each value of l, there are $2l+1$ subdivisions. These ***m*** values range from $-l$ to $+l$.

Azimuthal quantum number	*Sub energy level*	*No. of subdivisions* $(\boldsymbol{2l+1})$	*Values of m*
$\boldsymbol{l=0}$	*s*	*1*	*0*
$\boldsymbol{l=1}$	*p*	*3*	*-1,0,+1*
$\boldsymbol{l=2}$	*d*	*5*	*-2,-1,0,+1,+2*
$\boldsymbol{l=3}$	*f*	*7*	*-3,-2,-1,0,+1,+2,+3*

Electron spin quantum number, s.

It represents the spin of an electron on its own axis, which can be clockwise or anticlockwise relative to the orbital of the electron. The electron spin quantum number does not depend on any other quantum number. It designates the direction of the electron spin. An electron may have a spin of $+\frac{1}{2}$ (represented as ↑) or $-\frac{1}{2}$ (represented as ↓). Because an electron spins, it creates a magnetic field which can be oriented in one of the two directions.

Differentiation between an orbit and an orbital

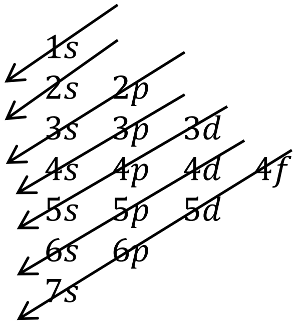
Orbit	Orbital
An orbit is a path traced by an electron revolving around the nucleus of an atom	An orbital is a region of space around the nucleus in which there is maximum probability of finding an electron of a particular energy level
The distance of the orbit from the nucleus for a given electron is fixed	It is impossible to know the exact trajectory of an electron in an atom
An orbit is a one dimensional path of an electron	An orbital is a three dimensional space around the nucleus
The movement of an electron in an orbit is known definitely which is against Heisenberg Uncertainty Principle	It is in accordance with Heisenberg Uncertainty Principle

The Aufbau principle

"*Aufbau*" is a German word meaning 'building up'. Aufbau principle is a principle that gives the order in which orbitals are filled in successive elements in the periodic table.

It states that electrons enter orbitals of lowest energy first. The electrons are added to atomic orbitals starting with the lowest energy orbitals and building up to higher energy orbitals

The order is as follows:



The filling proceeds as $1s\ 2s\ 2p\ 3s\ 3p\ 4s\ 3d\ 4p\ 5s\ 4d\ 5p\ 6s\ 4f\ 5d\ 6p\ 7s$ ...

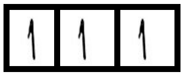
Pauli Exclusion principle

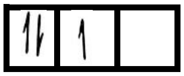
It states that ***all the electrons in any atom must be distinguishable*** or that no ***two electrons in a single atom can have all their quantum numbers alike***. It follows that if two electrons in an atom have the same values of n, l and m, they must have different values of s. Their spins must be opposed. One must spin up and the other spins down.

Hund's rule

It is also called **Hund's Multiplicity Rule**. According to the rule, ***when electrons occupy orbitals of equal energy, they do not pair up in an orbital until all the other orbitals in the sub energy level have been occupied by a single electron***.

The filling shown first is acceptable but not the second case





Electronic configuration of atoms

The Hund's rule, Pauli Exclusion principle and the Aufbau principle are all applied in writing of electronic configurations of atoms.

The $spdf$ notation is used and the subenergy levels contain a maximum number of electrons as shown. The atomic number is used to write the configuration.

s	**2**
p	6
d	10
f	14

The table below shows the first 20 elements with their electronic configurations. Some configurations are written and others are not. Complete the table

Element	*Symbol*	*Atomic number*	*Electronic configuration*
Hydrogen	*H*	1	$1s^1$
Helium	*He*	2	
Lithium	*Li*	3	
Beryllium	*Be*	4	$1s^2\ 2s^2$
Boron	*B*	5	
Carbon	*C*	6	$1s^2\ 2s^2 2p^2$
Nitrogen	*N*	7	
Oxygen	*O*	8	
Fluorine	*F*	9	$1s^2\ 2s^2\ 2p^5$
Neon	*Ne*	10	
Sodium	*Na*	11	$1s^2\ 2s^2\ 2p^6\ 3s^1$
Magnesium	*Mg*	12	
Aluminium	*Al*	13	$1s^2\ 2s^2\ 2p^6\ 3s^2 3p^1$
Silicon	*Si*	14	$1s^2\ 2s^2\ 2p^6\ 3s^2 3p^2$
Phosphorus	*P*	15	
Sulphur	*S*	16	
Chlorine	*Cl*	17	$1s^2\ 2s^2\ 2p^6\ 3s^2 3p^5$
Argon	*Ar*	18	$1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6$
Potassium	*K*	19	
Calcium	*Ca*	20	$1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6 4s^2$

Below is another table for the electronic configurations of the first transition series for elements scandium to zinc.

An atom of an element is only stable if its outermost sub energy level is either completely filled or half filled with electrons. In this series, this affects the electronic configuration of **chromium** and **copper**. An electron that would be in the 4s sub energy level is filled in the 3d sub energy level do make it half-filled for copper and completely filled for chromium. Complete the table too to show the electronic configurations of the other elements.

Scandium	$\boldsymbol{Sc}$	**21**		$\boldsymbol{1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6 4s^2 3d^1}$
Titanium	Ti	22		
Vanadium	V	23		$1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6 4s^2 3d^3$
Chromium	$\boldsymbol{Cr}$	**24**		$\boldsymbol{1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6 4s^1 3d^5}$
Manganese	Mn	25		
Iron	Fe	26		$1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6 4s^2 3d^6$
Cobalt	Co	27		
Nickel	Ni	28		
Copper	$\boldsymbol{Cu}$	**29**		$\boldsymbol{1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6 4s^1 3d^{10}}$
Zinc	Zn	30		$1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6 4s^2 3d^{10}$

More other elements with atomic numbers greater than 30 are shown below with some electronic configurations filled. Follow the same procedure to complete the electronic configurations for the other elements.

Germanium	**Ge**	**32**	$\boldsymbol{1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6 3d^{10} 4s^2 4p^2}$
Bromine	*Br*	35	
Strontium	*Sr*	38	$1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$
Silver	*Ag*	47	
Tin	*Sn*	*50*	$1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$
Iodine	*I*	53	
Barium	*Ba*	56	$1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$
Lead	*Pb*	82	

Electronic configuration of ions

Ions are formed by gaining electrons (anions) or losing electrons (cations). When writing their electronic configurations, electrons are either removed or added to the outer most sub energy levels depending on the charge on the ion. For cations of the elements in the first transition series (scandium to zinc), electrons in the 4s sub energy level are removed first before those in the 3d sub energy level. Similarly, we can subtract or add electrons to the atomic number of the neutral atom and use the remaining electrons to write the configuration. Write configurations for the following ions.

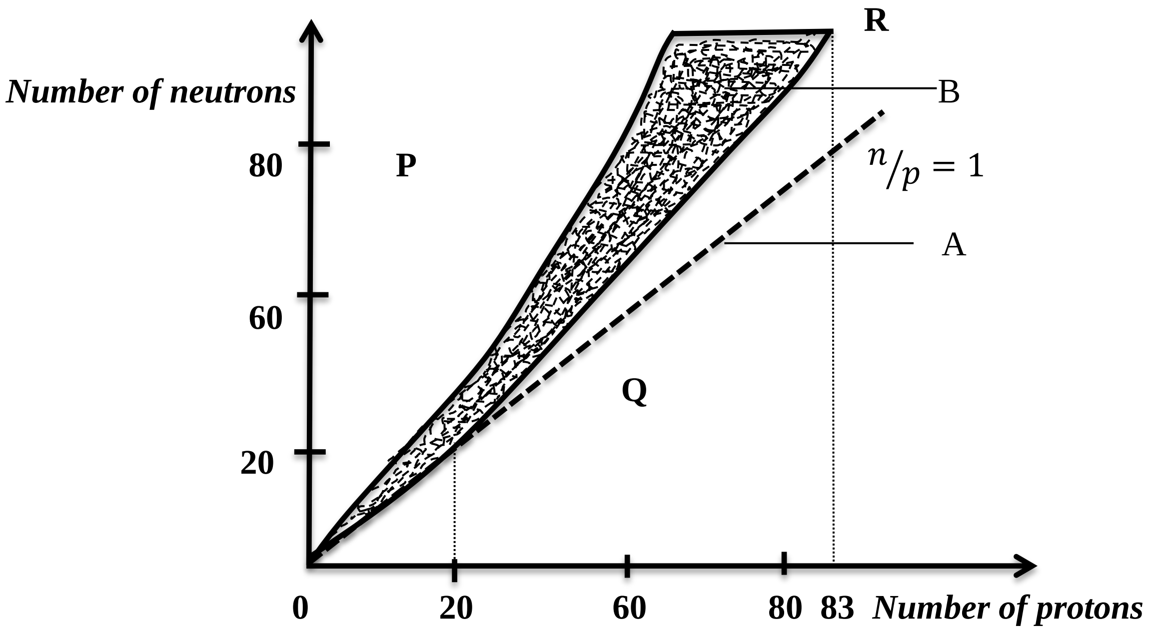
Ion	***Electronic configuration***
H^+	
H^-	
C^{4+}	
C^{4-}	
Na^+	
Al^{3+}	
P^{5-}	
Cl^-	
Ca^{2+}	
V^{5+}	
Cr^{3+}	
Mn^{2+}	
Fe^{2+}	
Co^{2+}	
Cu^+	
Cu^{2+}	
Br^-	

Questions

1. What is meant by the terms?
   - (i) Orbital
   - (ii) Pauli's exclusion principle
   - (iii) Ionisation energy

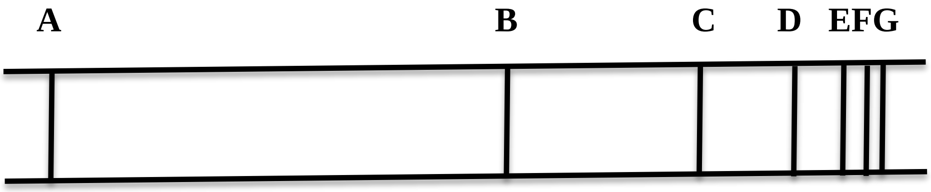
2. (a) Describe and explain the atomic spectrum of hydrogen
   (b) Explain how the hydrogen spectrum is related to the idea of quantized energy levels in atoms and ionisation energy.

3. (a) (i) What is meant by **stability of a nucleus**?
   (ii) State and explain the factors that affect stability of a nucleus.
   (b) The graph below shows how the number of neutrons varies with that of protons.



(i) State what line ***A*** and region ***B*** represent.
(ii) State why nuclei in the following regions ***P***, ***Q*** and ***R*** are unstable
(iii) Briefly explain how nuclei in the regions ***P*** and ***R*** can gain stability

4. The diagram below shows the Lyman series part of a hydrogen emission spectrum.



(a) State;
   (i) the information obtained from the separate lines about the electronic structure of hydrogen
   (ii) the direction in which energy increases
   (iii) the direction in which frequency increases
   (iv) the direction in which wavelength increases
   (v) how the emission spectrum arises

(b) Briefly explain why the lines get closer together from left to right

(c) State what is meant by the term "principal quantum number"

5. (a) What is meant by the term quantum number?

(b) State the significance each of these quantum numbers on information about an atom.

(i) the spin quantum number

(ii) the angular momentum quantum number
(iii) the magnetic quantum number
(iv) the principal quantum number

6. (a) Write the electronic configuration of:
    (i) nitrogen
    (ii) phosphorus
   (b) Explain why nitrogen only forms nitrogen trichloride while phosphorus forms both phosphorus trichloride and phosphorus pentachloride.

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 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	H													
2	Li	Be	B	C	N	O	F							
3	Na	Mg	Al	Si	P	S	Cl							
4	K	Ca	…	…	…	…	…	Ti	V	Cr	Mn	Fe	Co	Ni
5	Cu	Zn	…	…	As	Se	Br							

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 a 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, $\mathbf{1s^1}$, 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 ***Oganeson-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

PERIODS

	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VIIB	O
1	$^{1.0}_{1}\mathbf{H}$																$^{1.0}_{1}\mathbf{H}$	$^{4.0}_{2}\mathrm{He}$
2	$^{6.9}_{3}\mathrm{Li}$	$^{9.0}_{4}\mathrm{Be}$											$^{10.8}_{5}\mathrm{B}$	$^{12.0}_{6}\mathrm{C}$	$^{14.0}_{7}\mathrm{N}$	$^{16.0}_{8}\mathrm{O}$	$^{19.0}_{9}\mathrm{F}$	$^{20.2}_{10}\mathrm{Ne}$
3	$^{23}_{11}\mathrm{Na}$	$^{24.3}_{12}\mathrm{Mg}$											$^{27.0}_{13}\mathrm{Al}$	$^{28.1}_{14}\mathrm{Si}$	$^{31.0}_{15}\mathrm{P}$	$^{32.1}_{16}\mathrm{S}$	$^{35.4}_{17}Cl$	$^{40.0}_{18}\mathrm{Ar}$
4	$^{39.1}_{19}\mathrm{K}$	$^{40.1}_{20}\mathrm{Ca}$	$^{45}_{21}\mathrm{Sc}$	$^{47.9}_{22}\mathrm{Ti}$	$^{50.9}_{23}\mathrm{V}$	$^{52}_{24}\mathrm{Cr}$	$^{54.9}_{25}\mathrm{Mn}$	$^{55.8}_{26}\mathrm{Fe}$	$^{58.9}_{27}Co$	$^{58.7}_{28}Ni$	$^{63.5}_{29}Cu$	$^{65.7}_{30}Zn$	$^{69.7}_{31}Ga$	$^{72.6}_{32}Ge$	$^{74.9}_{33}As$	$^{79.0}_{34}Se$	$^{79.9}_{35}Br$	$^{83.8}_{36}Kr$
5	$^{85.5}_{37}Rb$	$^{87.6}_{38}Sr$	$^{88.9}_{39}Y$	$^{91.2}_{40}Zr$	$^{92.9}_{41}\mathrm{Nb}$	$^{95.9}_{42}\mathrm{Mo}$	$^{98.9}_{43}Tc$	$^{101}_{44}Ru$	$^{103}_{45}Rh$	$^{106}_{46}Pd$	$^{108}_{47}Ag$	$^{112}_{48}Cd$	$^{115}_{49}In$	$^{119}_{50}Sn$	$^{122}_{51}Sb$	$^{128}_{52}Te$	$^{127}_{53}I$	$^{131}_{54}Xe$
6	$^{133}_{55}\mathrm{Cs}$	$^{137}_{56}Ba$	$^{139}_{57}La$	$^{178}_{72}Hf$	$^{181}_{73}Ta$	$^{184}_{74}W$	$^{186}_{75}Re$	$^{190}_{76}Os$	$^{192}_{77}Ir$	$^{195}_{78}Pt$	$^{197}_{79}Au$	$^{201}_{80}Hg$	$^{204}_{81}Tl$	$^{207}_{82}Pb$	$^{209}_{83}Bi$	$^{210}_{84}Po$	$^{210}_{85}At$	$^{222}_{86}Rn$
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	$^{232}_{90}Th$	$^{231}_{91}Pa$	$^{238}_{92}U$	$^{237}_{93}Np$	$^{242}_{94}Pu$	$^{243}_{95}Am$	$^{247}_{96}Cm$	$^{245}_{97}Bk$	$^{251}_{98}Cf$	$^{254}_{99}Es$	$^{253}_{100}Fm$	$^{256}_{101}Md$	$^{254}_{102}No$	$^{257}_{103}Lr$

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

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.

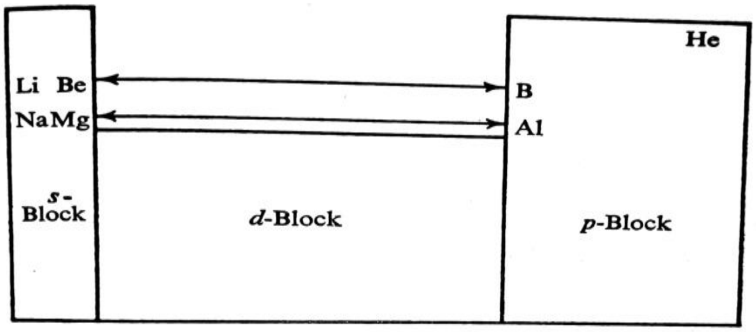
f-block elements

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 is $6s^2$.
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.

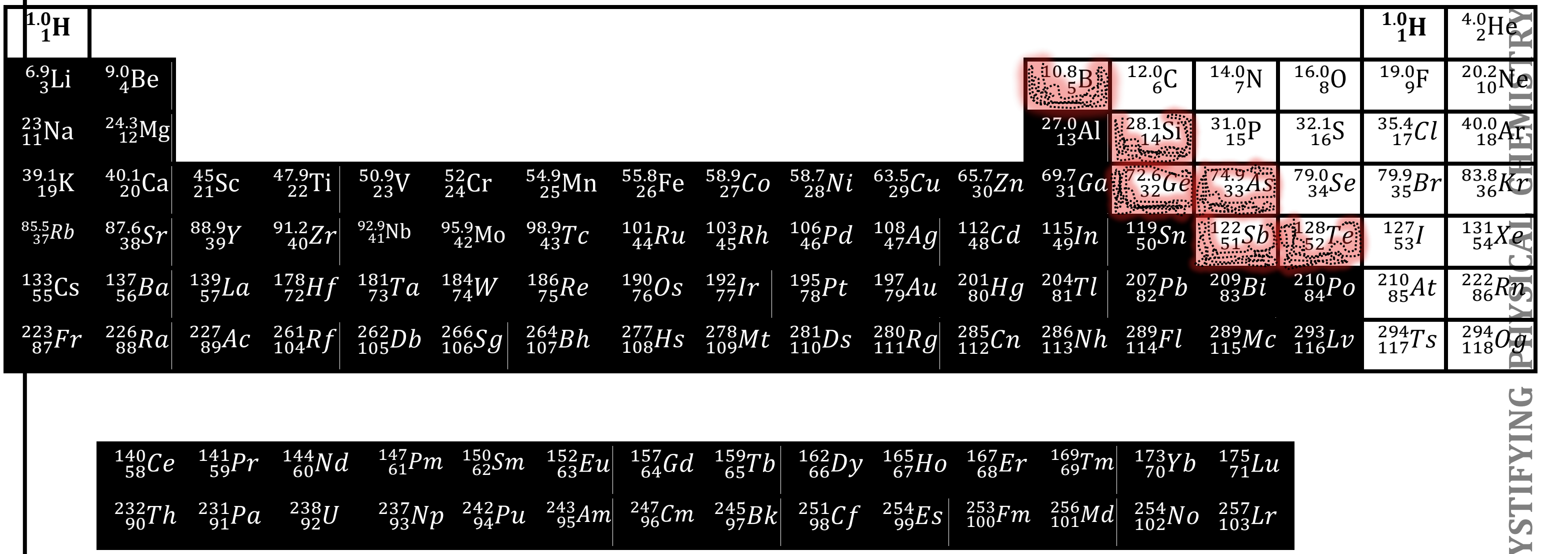


The table below shows the common elements. Use their electronic configurations to classify them into groups, periods and the s, p, d and f blocks

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

Ar	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



■	***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)

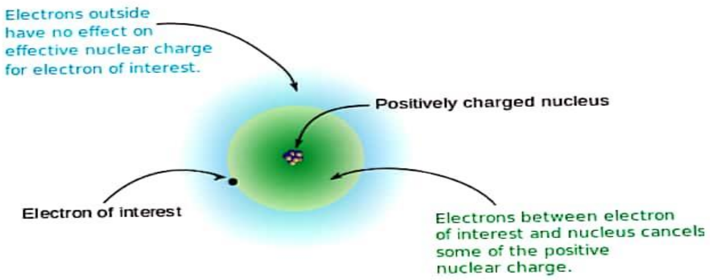
This is the repulsion of the outermost electrons by those in the innermost sub energy levels from nuclear attraction. Electrons in an atom shield each other from the pull of the nucleus. Shielding effect describes the decrease in attraction between an electron and the nucleus in any atom with more than 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 experienced by an electron in an atom. Effective nuclear charge is given by the equation;

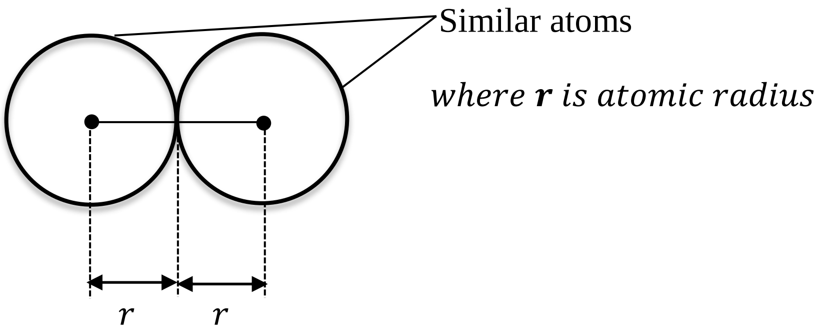
$$Z_{eff} = Z - S$$

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 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

$$X(g) \longrightarrow X^{+}(g) + e \qquad \Delta H = First\ ionisation\ energy$$
$$X^{+}(g) \longrightarrow X^{2+}(g) + e \qquad \Delta H = Second\ ionisation\ energy$$

First ionisation energy is the minimum amount of energy required to remove an electron from a gaseous atom to form a <u>unipositively</u> 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 from 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

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

Element	***Li***	***Be***	***B***	***C***	***N***	***O***	***F***	***Ne***
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)

$$\underline{Be - 1s^2\ 2s^2}$$
$$\underline{B - 1s^2\ 2s^2\ 2p^1}$$

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)

$$\underline{O - 1s^2\ 2s^2\ 2p^4}$$
$$\underline{N - 1s^2\ 2s^2\ 2p^3}$$

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)

$$\underline{Ne - 1s^2\ 2s^2\ 2p^6}$$

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

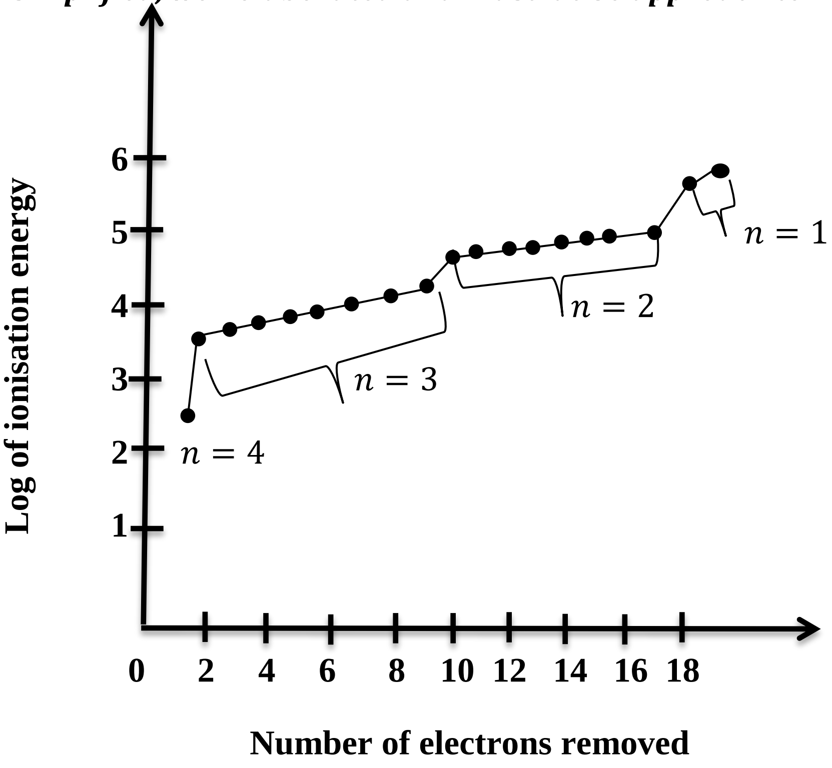
First ionization energy decreases from fluorine to iodine.

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) Valency

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})**			
	1st	**2nd**	**3rd**	**4th**
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.

$$\boldsymbol{X(g) + e \longrightarrow X^{-}(g) \qquad \Delta H = negative}$$

This enery is called first electron affinity.

First electron affinity *is the energy given out when* ***one mole*** *of electron*__*s*__ *combines with* ***one mole*** *of gaseous atom*__*s*__ *to form* ***one mole*** *of uninegatively charged gaseous ion*__*s*__

<u>or</u>

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)

$$\boldsymbol{X^{-}(g) + e \longrightarrow X^{2-}(g) \qquad \Delta H = positive}$$

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

$$O(g) + e \longrightarrow O^{-}(g) \qquad \Delta H = -142\ kJmol^{-1}$$
$$O^{-}(g) + e \longrightarrow O^{2-}(g) \qquad \Delta H = +702\ kJmol^{-1}$$

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.

$$\underline{Mg - 1s^2\ 2s^2\ 2p^6\ 3s^2}$$

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 higher than that of magnesium

$$\underline{Al - 1s^2\ 2s^2\ 2p^6\ 3s^2 3p^1}$$
$$\underline{Mg - 1s^2\ 2s^2\ 2p^6\ 3s^2}$$

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, hence giving off a higher amount of energy.

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, hence giving off a lower amount of energy.

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

$$\underline{P - 1s^2\ 2s^2\ 2p^6\ 3s^2 3p^3}$$
$$\underline{S - 1s^2\ 2s^2\ 2p^6\ 3s^2 3p^4}$$

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 unstable. The incoming electron experiences more nuclear attraction than repulsion by the existing electrons.

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

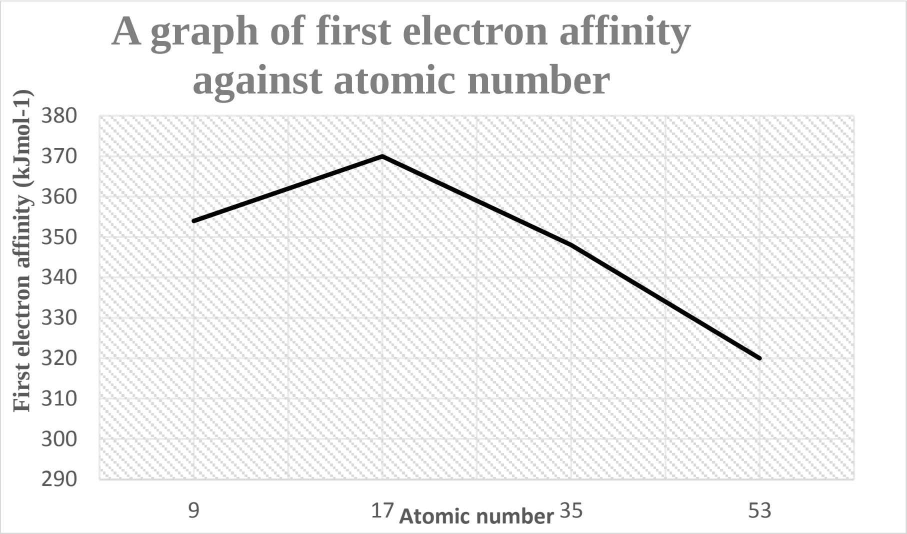
Element	***F***	***Cl***	***Br***	***I***
Atomic number	9	17	35	53
First electron affinity(kJmol^{-1})	-354	-370	-348	-320

(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 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.

$$H^{\delta+}\text{—}F^{\delta-}$$

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	***Be***	***Mg***	***Ca***	***Sr***	***Ba***
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 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	***Be***	***Mg***	***Ca***	***Sr***	***Ba***
First ionisation energy (kJmol^{-1})	899	738	589	549	502

(a) Define the term first ionisation energy.

(b) State and explain the trend in ionization energy of the elements

5. (a)(i) What is meant by the term ionisation energy of an element?

   (ii) Write an equation to show the first ionisation of magnesium

   (b) The second and third ionisation energies of magnesium are $1450\ kJmol^{-1}$ and $7730\ kJmol^{-1}$ respectively. Give a reason for the large difference between the second and the third ionisation energies of magnesium.

6. The table below shows the results obtained for the ionisation energies of element X.

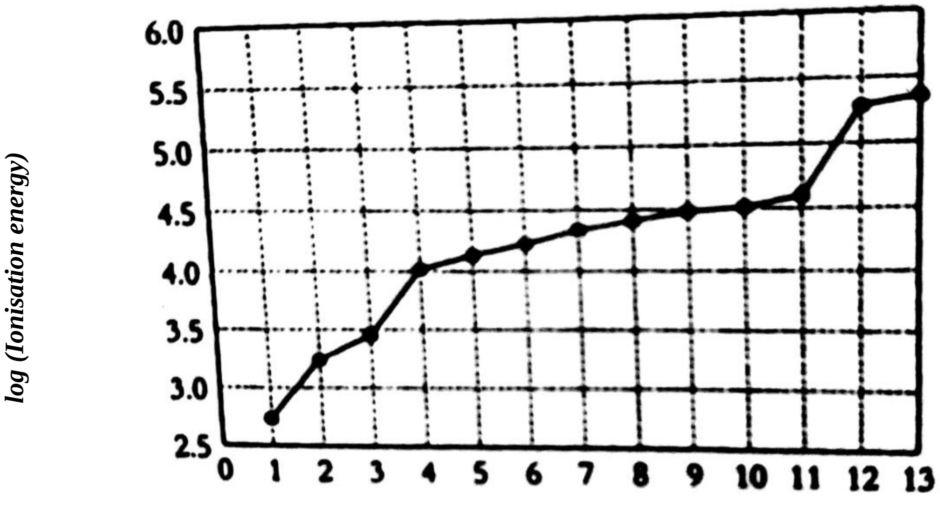
Electron number	1st	2nd	3rd	4th	5th
Ionisation energy (kJmol^{-1})	800	2400	3700	25000	32800

   (a) Plot a graph of $log_{10}\ (ionisation\ energy)$ against number of electron removed.

   (b) Explain the shape of your graph

   (c) Write the formula of the chloride of X.

7. The graph below shows a plot of the logarithm of all the successive ionisation energies against number of electrons removed for element Y.



Number of electrons removed.

   (a) Explain the shape of the graph

   (b) State the electronic configuration of element Y.

8. Successive ionisation energies(kJmol^{-1}) for some elements in Period 3 of the periodic Table are shown in the table below.

Element	**Ionisation energy**				
	1st	**2nd**	**3rd**	**4th**	**5th**
Silicon	787	1577	3230	4355	16090
Phosphorus	1060	1896	2908	4954	6272
Sulphur	1000	2258	3381	4565	6995

   (a) State and explain the trend in successive ionisation energies.
   (b) Explain why the;
      (i) First ionisation energy of sulphur is less than that of phosphorus
      (ii) third ionisation energy of phosphorus is less than that of silicon.
      (iii) the first ionisation energy of aluminium is less than that of magnesium.

9. The table below shows the first three successive ionisation energies of elements A, B, C, D, E and F.

Ionisation energy(kJmol^{-1})	**Element**					
	A	**B**	**C**	**D**	**E**	**F**
1st	1013	1000	1255	1519	418	590
2nd	1904	2255	2297	2665	3067	1146
3rd	2916	3389	3853	3933	4393	4916

With a reason in each case; state which element;

(i) is a noble gas
(ii) belongs to group I
(iii) belongs to group II

10. The table below shows the first five ionisation energies of elements W, X, Y and Z.

Element	**Ionisation energy(kJmol^{-1})**				
	1st	**2nd**	**3rd**	**4th**	**5th**
W	577	1816	2745	11575	13251
X	738	1450	7730	10550	12756
Y	495	4563	6912	9540	11936
Z	1255	2297	3849	5163	13989

   (a) Identify the group to which each of the elements belongs and give a reason for your answer.
   (b) Give a pair of elements which;
      (i) forms an ionic bond between them
      (ii) forms an ionic compound.

11. Explain what is meant by the term first electron affinity.

    (b) State three factors that can affect electron affinity.

    (c) The first electron affinities of some elements in Period 3 are given in the table below.

Element	*Al*	*Si*	*P*	*S*
First electron affinity	-44	-134	-71.7	-200

    (i) State the trend in variation in electron affinities

    (ii) Explain your answer in c(i) above.

12. The table below shows the electronegativity values of the elements in Group VII of the Periodic Table.

Element	***F***	***Cl***	***Br***	***I***
Electronegativity	4.10	2.83	2.74	2.21

State and explain the trend in electronegativity values of the elements

13. Explain the following observations;

    (a) The potassium ion is larger than the calcium ion yet the two ions have the same electronic configurations.

    (b) The ions Na^+ and Mg^{2+} have the same electronic configuration but the ionic radius of Mg^{2+} is lower than that of Na^+

    (c) The first electron affinities of the halogens generally decrease down the group. However, the first electron affinity of fluorine is abnormally high.

    (d) There are no compounds containing the O^- or S^- ions although the first electron affinities of oxygen and Sulphur are $-142\ kJmol^{-1}$ and $-200\ kJmol^{-1}$ respectively.

    (e) Oxygen is more electronegative than Sulphur although more energy is released when a Sulphur atom accepts an electron than when an oxygen atom accepts an electron.

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

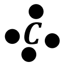
1. *Identify the number of valence electrons for the element. These are the total number of electrons in the outermost energy level. They can be known by the electronic configuration*
2. *Write the correct chemical symbol of the element*
3. *Put one dot in all directions; up, down, left and right of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

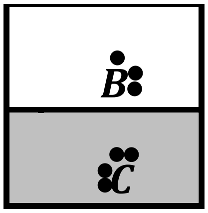
$$\begin{aligned}&Number\ of\ bonds\ formed\ by\ an\ element\\&= the\ number\ of\ unpaired\ electrons\ present\ in\ its\ Lewis\ Dot\ symbol\end{aligned}$$

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	$1s^2\ \mathbf{2s^1}$	1		Three bonds
C	6	$1s^2\ \mathbf{2s^2}\ \mathbf{2p^2}$	4		Four bonds
N	7	$1s^2\ \mathbf{2s^2}\ \mathbf{2p^3}$	5		Three bonds
O	8	$1s^2\ \mathbf{2s^2}\ \mathbf{2p^4}$	6		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

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

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;

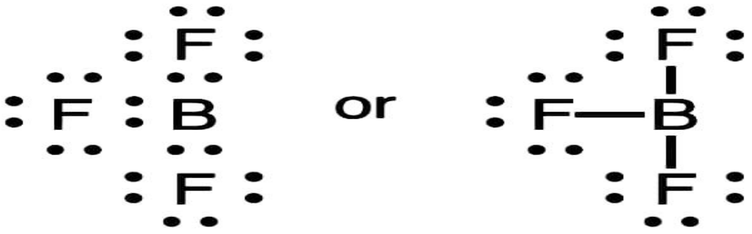
1. It explains the formation of chemical bonds in various compounds depending on the nature of the elements involved.
2. It is used to predict stability of atoms

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***.

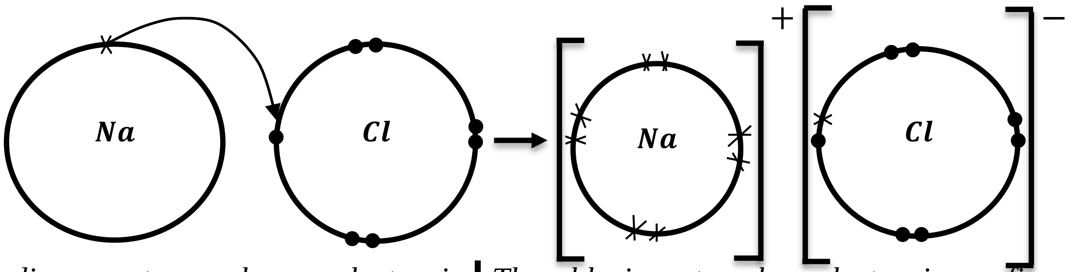
The electron or electrons are transferred from ***a metallic element*** to a ***nonmetallic element***.

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.*

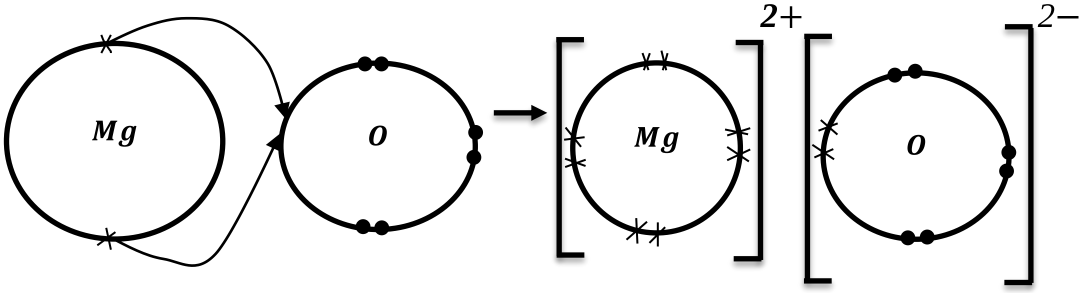
$$Na \longrightarrow Na^+ + e$$

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.*

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

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

(ii) Formation of magnesium oxide



The magnesium atom has electronic configuration, $1s^22s^22p^63s^2$. The two 3s electrons are transferred to the oxygen atom by magnesium to form noble gas configuration, $1s^22s^22p^6$. A magnesium ion is formed.

$$Mg \longrightarrow Mg^{2+} + 2e$$

The oxygen atom has electronic configuration, $1s^22s^22p^4$. The 2p sub energy level has four electrons and is unstable. The two electrons transferred from magnesium occupy this sub energy level form noble gas configuration, $1s^22s^22p^6$. An oxide ion is formed.

$$O + 2e \longrightarrow O^{2-}$$

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 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

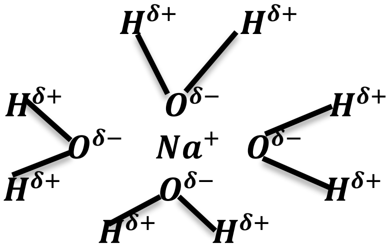
Compound	***Structure***
Sodium oxide	$(Na^+)_2O^{2-}$
Magnesium oxide	$Mg^{2+}O^{2-}$
Calcium chloride	$Ca^{2+}(Cl^-)_2$
Sodium hydride	Na^+H^-
Magnesium sulphate	$Mg^{2+}SO_4^{2-}$

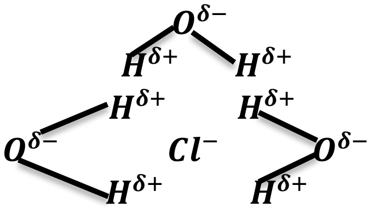
The properties of ionic compounds

Property	Explanation
1. High melting and boiling points.	*There are strong electrostatic forces of attraction between the oppositely charged ions that require a high amount of energy to break.*
2. They are strong electrolytes in molten state or aqueous state	*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.*
3. They readily dissolve polar solvents like water but insoluble in non-polar solvents like methylbenzene	*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.*
4. Exist as crystalline solids at room temperature	*There are strong electrostatic forces of attraction between the oppositely charged ions that require a high amount of energy to break at room temperature, keeping the molecules so closely packed together.*

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	$\frac{1}{0.095} = 10.53\ (nm)^{-1}$	$\frac{2}{0.065} = 30.77\ (nm)^{-1}$	$\frac{3}{0.050} = 60\ (nm)^{-1}$

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 covalent 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 choride (^oC)	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℃ whereas that of tin(II) chloride is 247℃. 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(IV) 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(^OC)	**1263**	**714**	**711**	**634**

Explain the general trend in melting points of the halides.

The melting points of the halides ***decrease 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 $1270°\mathrm{C}$ whereas aluminium chloride sublimes at $178°\mathrm{C}$
   - (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. 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;

$AlF_3 > AlCl_3 > AlBr_3 > AlI_3$

3. 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 (^{O}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***.

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.

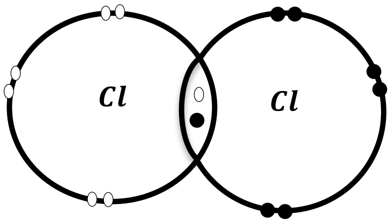
In double covalent bonds, two pairs of electrons are shared and in a triple covalent bond, three pairs of electrons are shared.

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

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

Examples

(i) Formation of chlorine molecule



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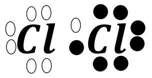
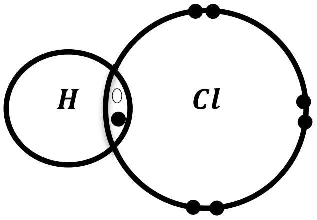


The chlorine atom has electronic configuration, $1s^2 2s^2 2p^6 3s^2 3p^5$. *The chlorine molecule is formed by each of the chlorine atom sharing one of its valence electrons with another atom. The two atoms approach each other closely for their atomic orbitals to overlap.*

(ii) Formation of hydrogen chloride molecule



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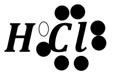
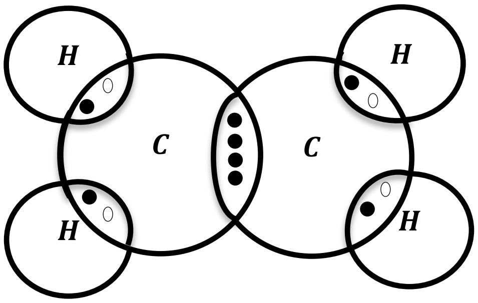


The hydrogen atom has electronic configuration $1s^1$ *and the chlorine atom has electronic configuration,* $1s^2 2s^2 2p^6 3s^2 3p^5$. *Hydrogen contributes its only electron and chlorine contributes one of its valence electrons. The electron pair is shared to make hydrogen have a full s sub energy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



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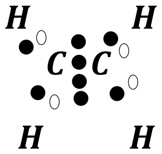


In a simple way, covalent bonds are usually represented by a line to indicate a pair of shared electrons, double lines to indicate two shared pairs and triple lines to indicate a three shared pairs.

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

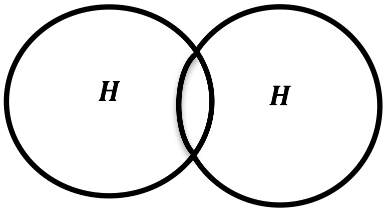
In a normal covalent bond, two atoms with very similar electronegativities or almost similar electronegativities are bonded together and the combined atoms contribute an equal number of electrons to be shared.

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

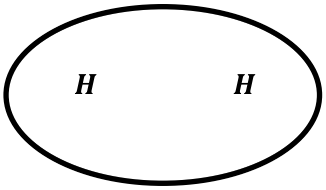
The two electrons that are shared between the atoms must be unpaired and the must also have opposite spins from the orbitals from which they are got.

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

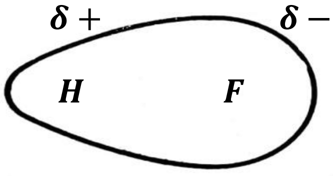


Resulting molecular orbital of hydrogen

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.

$$H^{\delta+}—F^{\delta-}$$



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 result of difference in electronegativity of the bonding atoms 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. This will be seen later under **polarity of molecules.**

3. Dative covalent bond

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

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

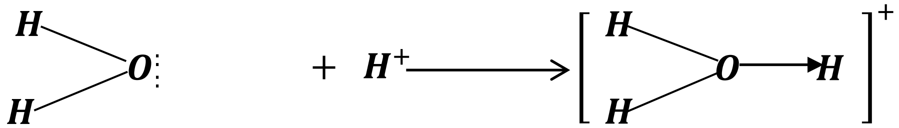
The atom that contributes the pair of the electrons is the **donor atom** and the other atom is called the **acceptor atom**. For an atom to act as a donor atom, it must have atleast one pair of unshared electrons, called a **lone pair**.

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 (⟶) is always drawn from the donor atom to the acceptor atom to show a dative bond.

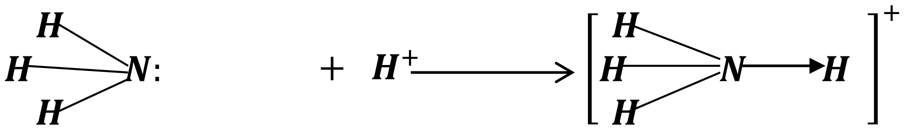
Examples

(i) Formation of hydroxonium ion.



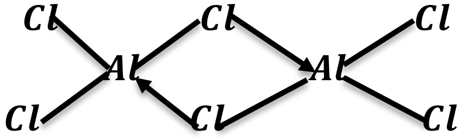
This ion is formed by coordination of water to a hydrogen ion. The oxygen atom in the water molecule has two lone pairs of electrons. The hydrogen ion has electronic configuration $1s^0$.The hydrogen ion therefore accepts one of the lone pairs of electrons from oxygen to have a full 1s sub energy level.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

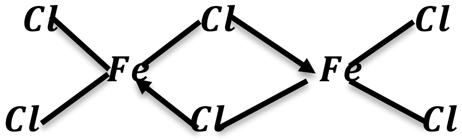
(ii) Formation of Ammonium ion

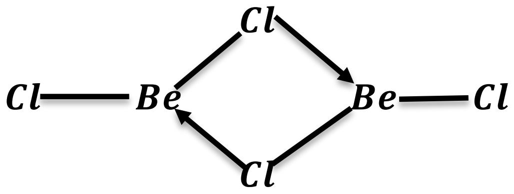


This ion is formed by coordination of ammonia to a hydrogen ion. The nitrogen atom in the ammonia molecule has a lone pair of electrons. The hydrogen ion has electronic configuration $1s^0$.The hydrogen ion therefore accepts the lone pair of electrons from nitrogen to have a full 1s subenergy level.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

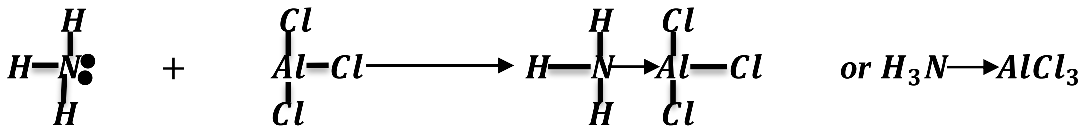
(iii) ***Formation of dimerised aluminium chloride(Al_2Cl_6), dimerised iron(III) chloride(Fe_2Cl_6) and dimerised beryllium chloride(Be_2Cl_4).***







(iv) Reaction between ammonia and anhydrous aluminium chloride

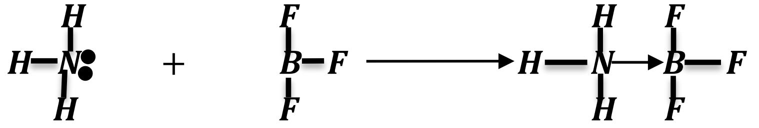


or $H_3N \rightarrow AlCl_3$

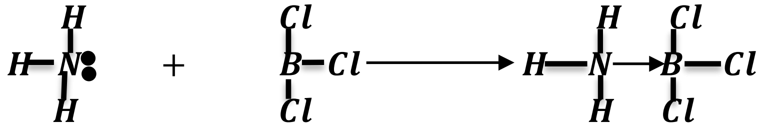
The nitrogen atom in the ammonia molecule has a lone pair of electrons. The aluminium atom has only three valence electrons. When aluminium covalently bonds with three chlorine atoms in aluminium chloride, it has six electrons in its outermost energy level, requiring two electrons to complete its octet.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



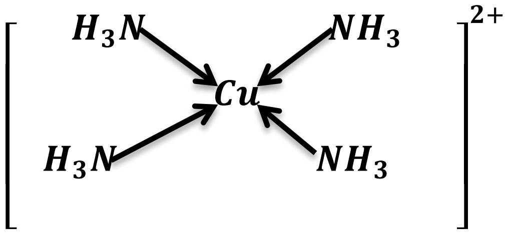
or $H_3N \rightarrow BF_3$



or $H_3N \rightarrow BCl_3$

(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

<table>
<tr><th>Normal covalent bond</th><th>Polar covalent bond</th><th>Dative or coordinate covalent bond</th></tr>
<tr><td>Can be formed between two similar atoms of the same element</td><td>The atoms involved must be different</td><td>A dative bond is formed between two different atoms</td></tr>
<tr><td>Can occur between atoms of the same electronegativity or almost similar electronegativities</td><td colspan="2">The bond occurs between atoms with different electronegativities</td></tr>
<tr><td colspan="2">Each atom contributes an equal number of electrons to be shared</td><td>The bonding electrons are contributed by only one of the involved atoms</td></tr>
</table>

Covalent bond strength

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

Bond dissociation energy is defined as the heat absorbed 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.

$$XY(g) \longrightarrow X(g) + Y(g)$$

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.

(i) 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.

(ii) 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

(iii) 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—I***
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.	*There are weak forces of attraction between the molecules thus a low amount of energy is required to break them.*
2. They do not conduct electricity except graphite	*They neither form free mobile ions nor have delocalized electrons to conduct electricity.*
3. Most covalent substances are insoluble in polar solvents like water but soluble in non-polar solvents like benzene, ethanol or propanone	*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.*

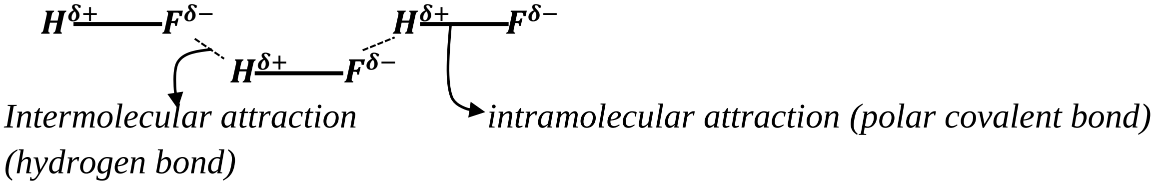
	Note that some covalent compounds containing polar bonds as O—H or N—H may dissolve in water due to interaction between the polar bond and the water.
4. Exist as gases or liquids at room temperature	*There are weak van der Waals' forces of attraction between the molecules that require a low amount of energy to break at room temperature, keeping the molecules far apart.*

Point of thought; Compare properties of ionic and covalent compounds.

Intermolecular forces

Intermolecular forces are forces that exist between **molecules**. There 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 i**ntramolecular** forces.

Intermolecular forces	Intramolecular forces
van der Waals forces	Covalent bond
Hydrogen bonds	Ionic bond
	Metallic bond



Van der Waals' forces

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 molecule 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 function when the molecules are very close to each other.

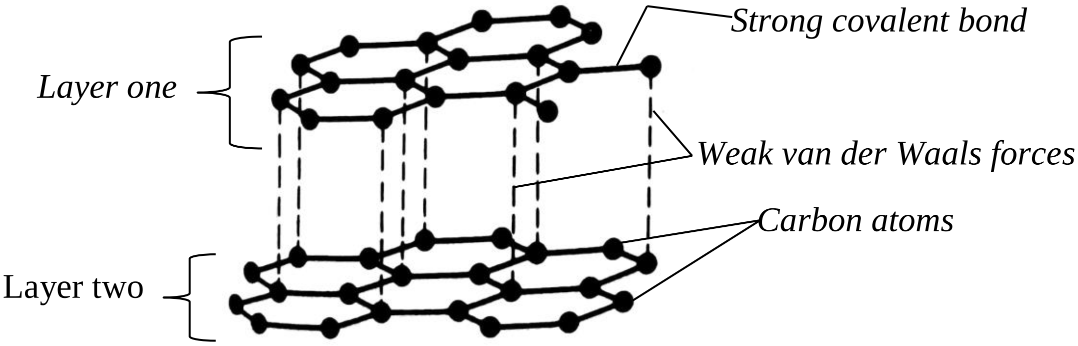
The size of the force however increases as the number of electrons in the molecules increase.

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(^{O}C)	44.2	115.2	-101.5	-189.4

Explain the trend in the melting points the elements

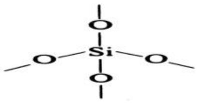
Phosphorus, Sulphur, chorine and argon have ***simple molecular structures*** *with* ***weak Van-der-Waal's forces of attraction*** *whose magnitude* ***increases in strength*** *with* ***increase in molecular weight****. Sulphur is octatomic (S_8) with a higher molecular weight hence stronger Van der 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 $SiO_2 > P_2O_5 > SO_3 > Cl_2O_7$. 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(^{0}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 increase in the order; $F_2 < Cl_2 < Br_2 < I_2$*. 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	CH_3CH_2Cl	$CH_3CH_2CH_2Cl$	$CH_3CH_2CH_2CH_2Cl$
Boiling point(^{O}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**

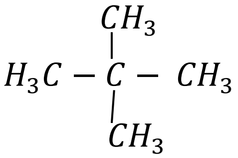
Element	CH_3F	CH_3Cl	CH_3Br	CH_3I
Boiling point(^{O}C)	-78.4	-24.0	5.0	43.0

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.**

$CH_3CH_2CH_2CH_2CH_3$ *and*



$$H_3C - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_3$$

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 commonly 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

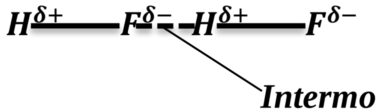
This is the type of hydrogen bond that occurs between two or more similar or different molecules.

Intermolecular hydrogen bonds occur in the following examples;

(a) Hydrogen fluoride , water and ammonia molecules

Hydrogen fluoride

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.



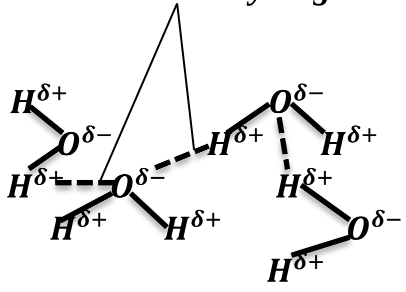
Intermolecular hydrogen bond

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.

Intermolecular hydrogen bonds



Ammonia

Both ammonia (NH_3)and phosphine(PH_3) are trigonal pyramidal but ammonia has a higher boiling point($-33.4°C$) than phosphine($-87.7°C$). 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

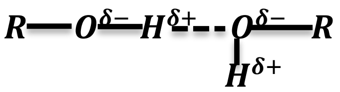
Molecule	*Boiling point*($°C$)
HF	19.9
H_2O	100
NH_3	−33.4

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

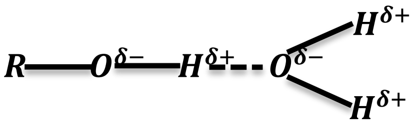
Alcohols associate in their liquid form due to intermolecular hydrogen bonding. The boiling points of alcohols are higher than boiling points of corresponding alkanes or alkyl halides with similar molar mass because of association through hydrogen bonding.

For example the boiling point of methanol is $64.6°C$ whereas that of methane is $-24.2°C$.



$$R-O^{\delta-}-H^{\delta+}\cdots\underset{H^{\delta+}}{\underset{|}{O^{\delta-}}}-R$$

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.



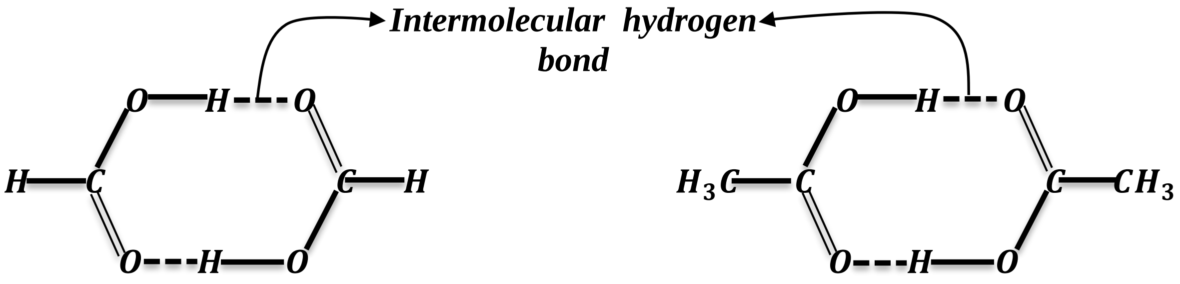
Alcohols with more hydroxyl groups have higher boiling points than alcohols with one hydroxyl group. Propane-1,2,3-triol, ethane-1,2-diol and ethanol have boiling points $290°C$, $197°C$ and $78.4°C$ respectively.

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.

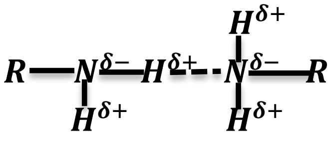
Association(dimerization of methanoic acid) ***Association(dimerization of ethanoic acid)***



In aqueous solution however, molecules of carboxylic acids do not dimerise but form intermolecular hydrogen bonds with water. This explains their solubility in water.

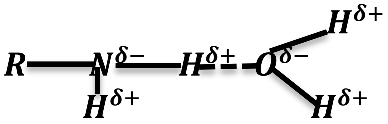
(d) Amines

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.



$$R-\underset{\displaystyle H^{\delta+}}{N^{\delta-}}-H^{\delta+}\cdots\overset{\displaystyle H^{\delta+}}{\underset{\displaystyle H^{\delta+}}{N^{\delta-}}}-R$$

Amines are also soluble in water because of the ability to form hydrogen bonds with water.

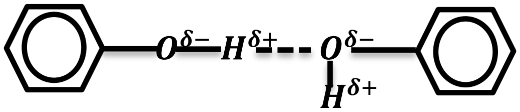


Amines have lower boiling points than corresponding alcohols or carboxylic acids because nitrogen is less electronegative than oxygen. The nitrogen-hydrogen bonds are less polar than oxygen- hydrogen bonds so the hydrogen bonds formed in amines are weaker than in alcohols.

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.

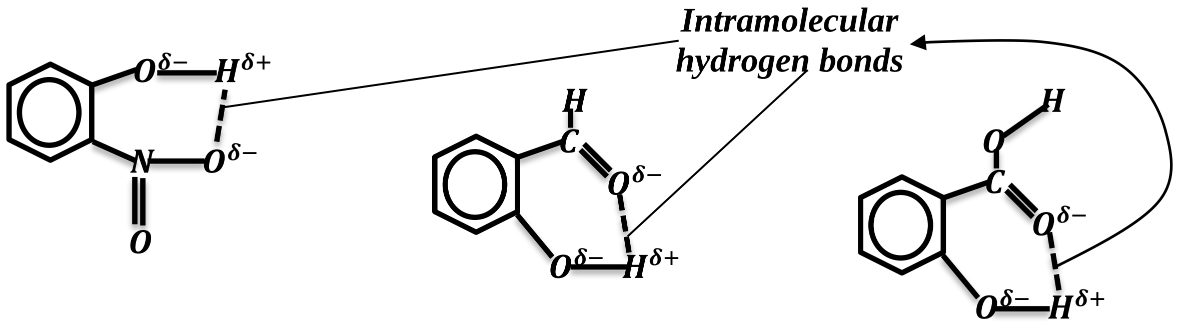


Phenols are more soluble in water than corresponding alkanes or alkyl halides because of the ability to form hydrogen bonds with water just like alcohols.

(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

2-nitrophenol **2-hydroxybenzaldehyde** **2-hydroxybenzoic acid**



Intramolecular hydrogen bonds

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 atom 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(^{O}C)	+19.9	-85.0	-66.7	-35.4

Explain the variation in boiling points, including any anomalies involved.

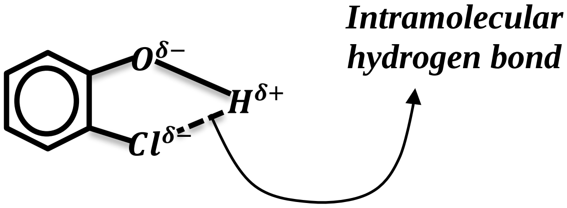
*Boiling points increases from **hydrogen chloride to hydrogen iodide**. However, **hydrogen fluoride has an abnormally high value of boiling point.***

*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**.*

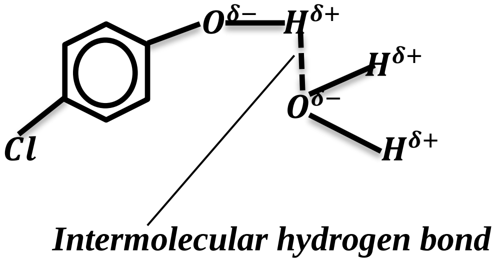
Hydrogen fluoride has an abnormally high melting point because the fluorine atom has the smallest atomic radius and the highest electronegativity, making the hydrogen-fluorine highly polar. The hydrogen fluoride molecules are therefore held by strong intermolecular hydrogen bonds which require a high amount of energy to break.

3. **Explain why;**

(i) 2-chlorophenol is less soluble in water than 4-chlorophenol.



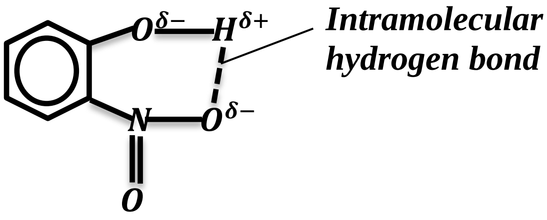
Intramolecular hydrogen bond



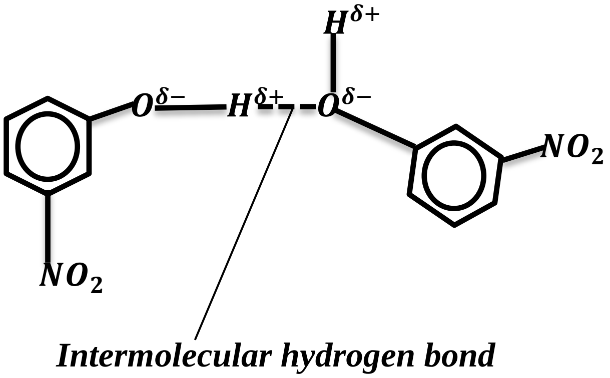
Intermolecular hydrogen bond

*Molecules of 2-chlorophenol form **intramolecular hydrogen bonds** because the choro 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 .



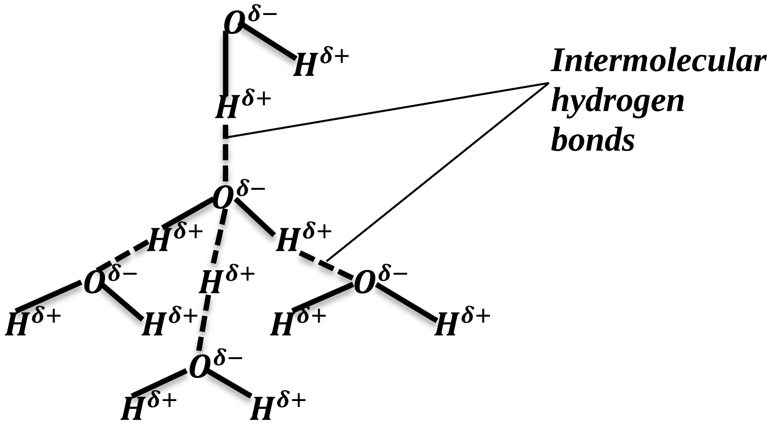
Intramolecular hydrogen bond



Intermolecular hydrogen bond

*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 hence only weak van der Waals' forces hold the molecules. However, molecules of 3-chlorophenol cannot form intramolecular hydrogen bonds because the nitro group is far from the hydroxyl group. Molecules of 3-nitrophenol* *therefore form* ***intermolecular hydrogen bonds*** *which are stronger hence not easily broken.*

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 break down*** *and the molecules* ***pack closely together*** *so that liquid water has a* ***lower volume*** *hence a higher density than ice.*

Questions

1. Explain why

(a) The melting of silicon is much higher than that of phosphorus yet both silicon and phosphorus are covalent substances.

(b) hydrogen and helium gases show a small deviation from ideal behaviour

(c) For gases methane, ammonia, oxygen and carbon dioxide, the deviation from ideal behaviour increases in the order $CH_4 < NH_3 < O_2 < CO_2$.

(d) The boiling point of the given arylhalides increases in the order

$C_6H_5I > C_6H_5Br > C_6H_5Cl > C_6H_5F$

(e) The boiling point of chlorobenzene is higher than benzene which is also higher than cyclohexane

(f) 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(°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(°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.

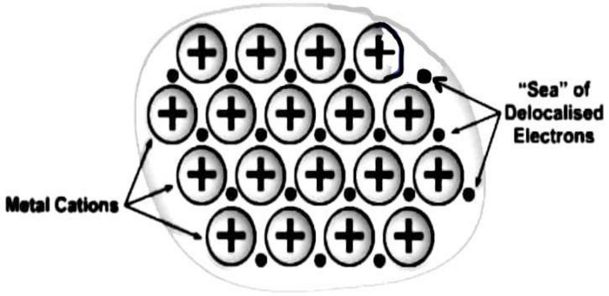
(h) ethane boils at lower temperature than butane.

(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 their atoms 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

$$Ca - 1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6\ 4s^2$$

$$Cr - 1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6 4s^1 3d^5$$

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 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 solvent-solvent 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.

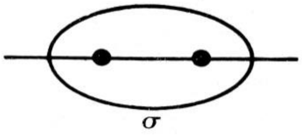
The shape of a molecule depends upon the shapes of the combining atomic orbitals. Only outer atomic orbitals for a valence energy level are involved in bonding. The number of covalent bonds formed is equal to half the number of combining atomic orbitals.

Sigma(σ) and pi (π)bonds

The nomenclature s and p used for atomic orbitals is replaced by σ and π for molecular orbitals.

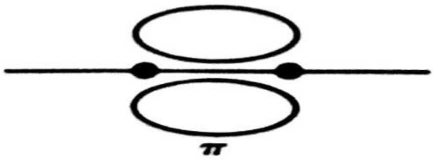
Sigma(σ) bond

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.

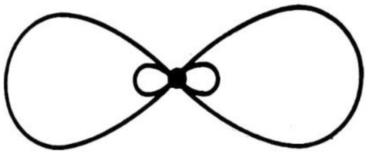
	$1s^2$	$2s^2$	$2p^0$
Be	↑↓	↑↓	
	$1s^2$	$2s^1$	$2p^1$
Be^*	↑↓	↑	↑

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.

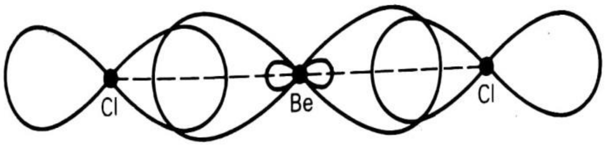
For beryllium to form compounds, one of the $2s$ electrons is promoted to the $2p$ subenergy level to form an excited beryllium atom, Be^*.

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

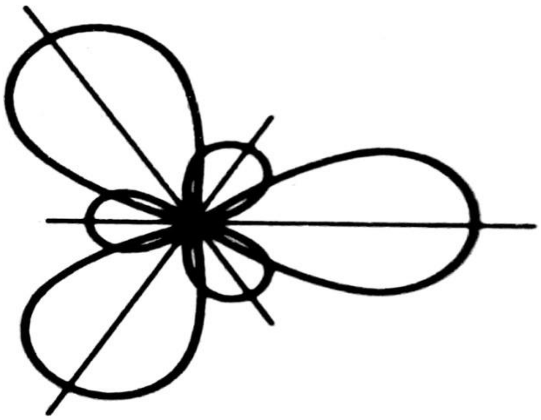
This occurs when one s and two p-orbitals of the same atom combine to form a set of three equivalent sp^2-hybrid orbitals which are **trigonal planar** with a bond angle 120°.

The boron atom with electronic configuration $1s^2\ 2s^2 2p^1$ has the $2p$ subenergy level having one unpaired electron.

$\mathbf{1s^2}$ $\mathbf{2s^2}$ $\mathbf{2p^1}$
$\mathbf{2p_x}$ $\mathbf{2p_y}$ $\mathbf{2p_z}$
$\boldsymbol{B}$ ⇅ ⇅ ↿
$\mathbf{1s^2}$ $\mathbf{2s^1}$ $\mathbf{2p^1}$
$\boldsymbol{B^*}$ ⇅ ↿ ↿ ↿

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.

	$\mathbf{1s^2}$	$\mathbf{2s^2}$		$\mathbf{2p^2}$	
			$\mathbf{2p_x}$	$\mathbf{2p_y}$	$\mathbf{2p_z}$
$\boldsymbol{C}$	↿⇂	↿⇂	↿	↿	
	$\mathbf{1s^2}$	$\mathbf{2s^1}$	$\mathbf{2p^1}$		
$\boldsymbol{C^*}$	↿⇂	↿	↿	↿	↿

From the configuration in the ground state of carbon, two of the three two p orbitals have one unpaired electron each.

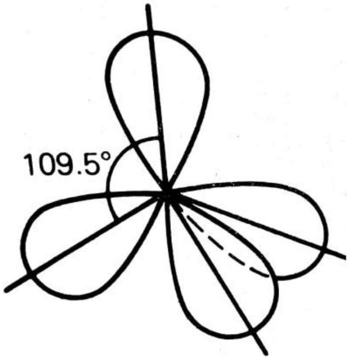
For carbon to form compounds, one of the $2s$ electrons is promoted to the empty $2p_z$ orbital to form an excited carbon atom, C^*. The excited carbon atom therefore has three p electrons.

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.

	$1s^2$	$2s^2$		$2p^2$	
			$2p_x$	$2p_y$	$2p_z$
C	⇅	⇅	↑	↑	
	$1s^2$	$2s^1$	$2p^1$		
C^*	⇅	↑	↑	↑	↑

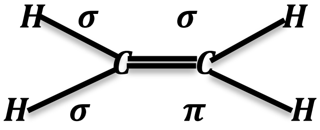
From the configuration in the ground state of carbon, two of the three two p orbitals have one unpaired electron each.

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

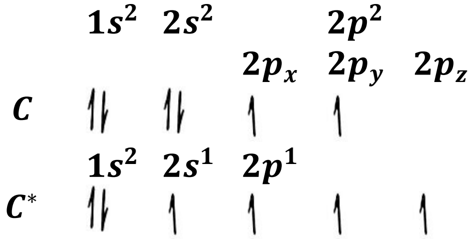
The unhybridised $2p_z$ orbital forms a π bond between the carbon atoms.

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.



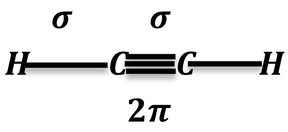
From the configuration in the ground state of carbon, two of the three two p orbitals have one unpaired electron each.

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.

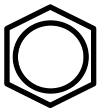
The two unhybridised $2p_y$ and $2p_z$ orbitals form two $\pi -$ bonds between the carbon atoms.

This gives ethyne a linear shape.

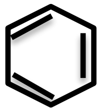


The double bond formation in benzene

Benzene has the structure as shown below;



or



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

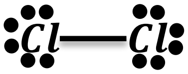
A Lewis structure is a simplified representation of the arrangement of the outermost electrons of each atom in a molecule and the lone pairs of electrons that may exist in the molecule or polyatomic ions.

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;

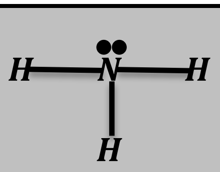
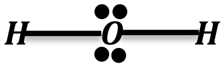
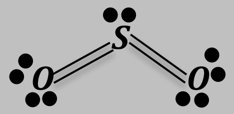
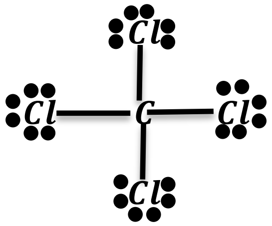
The Lewis structure of a chlorine molecule shows 3 unshared electron pairs for each atom (**lone pairs**) and one shared pair of electrons (**bonding pair**).

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)	*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***	
Water (H_2O)	*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***	
Sulphur dioxide (SO_2)	*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.*	
Carbon tetrachloride (CCl_4)	*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.*	

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*

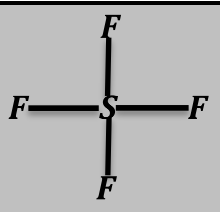
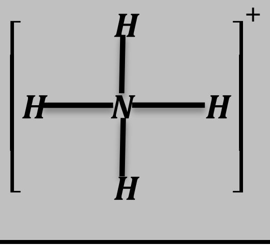
got from the Lewis Dot symbol of the atom or its electronic configuration. For a negatively charged ion, add one electron for each negative charge.

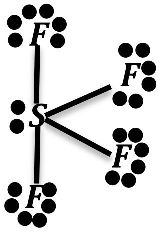
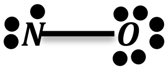
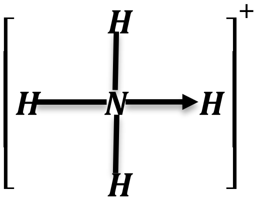
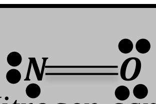
For a positively charged ion, subtract one electron for each positive charge.

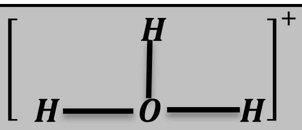
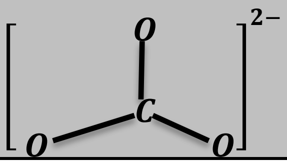
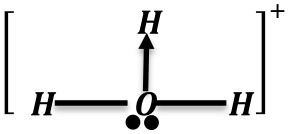
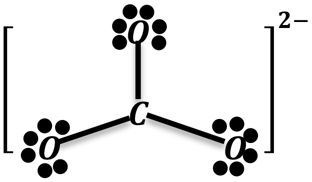
3. *Subtract two valence electrons for each bond formed in the skeleton structure.*
4. *Beginning with the terminal atoms, add enough electrons of the remaining electrons as valence electrons to satisfy the octets of the atoms (two for hydrogen). These electrons are the lone pairs.*
5. *The remaining 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*

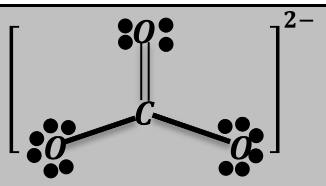
Examples

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	
2	*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* $= 6 + 28 = 34$	*Number of valence electrons for Nitrogen is* 5 *Number of valence electrons for oxygen* $= 6$ *Total number of valence electrons* $= 5 + 6 = 11$	*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*** $\mathbf{(9 - 1) = 8}$
3	*For each of the four bonds* $(4 \times 2) = 8$ *electrons are used* *Remaining electrons* $= 34 - 8 = 26$	*For the bond shown* $(2 \times 1) = 2$ *electrons are used* *Remaining electrons* $= 11 - 2 = 9$	*For each of the four bonds* $(4 \times 2) = 8$ *electrons are used* *Remaining electrons* $= 8 - 8 = 0$

4 5			
6	Not applicable	 *Nitrogen cannot get an octet for reasons explained later.*	

	H_3O^+	CO_3^{2-}
1		
2	*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** $(\mathbf{9 - 1}) = \mathbf{8}$	*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** $(\mathbf{22 + 2}) = \mathbf{24}$
3	*For each of the three bonds* $(3 \times= 6$ *electrons are used* *Remaining electrons* $= 8 - 6 = 2$	*For each of the three bonds* $(3 \times 2) = 6$ *electrons are used* *Remaining electrons* $= 24 - 6 = 18$
4 **5**		 ***All the remaining 18 electrons have been used but carbon doesn't have a full octet yet. Rule 6 must be satisfied.***

6	Not applicable	 ***More resonance structures can be made for this ion as we shall see later.***

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. In 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;

Molecule	*Total number of electrons*
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. NCl_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. NCl_3	14. PO_4^{3-}
7. CO_2	15. SO_3^{2-}
8. SCl_2	16. BH_2^-

Formal charges

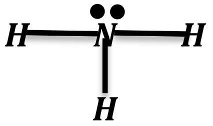
A formal charge compares the number of electrons around a neutral atom and the number of electrons around an atom in a molecule.

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.

$$\begin{matrix}\textit{Formal}\\ \textit{charge}\end{matrix} = \begin{pmatrix}\textit{number of valence}\\ \textit{electrons}\\ \textit{in free atom}\end{pmatrix} - \begin{pmatrix}\begin{matrix}\textit{number of}\\ \textit{nonbonding}\\ \textit{electrons}\end{matrix} + \frac{1}{2}\ \textit{number of bondingelectrons}\end{pmatrix}$$

Examples

1. ***Calculate the formal charges of the atoms in ammonia.***

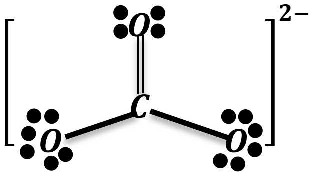


$$FC = V - (N + \frac{B}{2})$$

$$Formal\ charge\ of\ nitrogen = 5 - \left(2 + \frac{1}{2} \times 6\right) = 0$$

$$Formal\ charge\ of\ one\ hydrogen\ atom = 1 - \left(0 + \frac{1}{2} \times 2\right) = 0$$

2. ***Calculate the formal charges of the atoms in the carbonate ion***



$$FC = V - (N + \frac{B}{2})$$

$$Formal\ charge\ of\ carbon = 4 - \left(0 + \frac{1}{2} \times 8\right) = 0$$

$$Formal\ charge\ of\ one\ oxygen\ atom\ bonded\ with\ single\ bond = 6 - \left(6 + \frac{1}{2} \times 2\right) = -1$$

$$Formal\ charge\ of\ the\ oxygen\ atom\ bonded\ with\ a\ double\ bond = 6 - \left(4 + \frac{1}{2} \times 4\right) = 0$$

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.

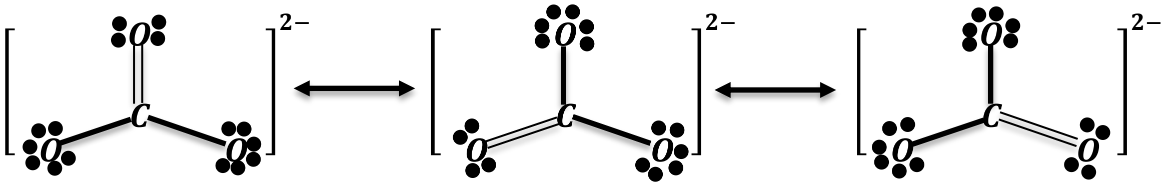
(c) In the case where there must be either positive or negative formal charges on various atoms, the most stable structures have negative formal charges on the more electronegative atoms and positive charges on the less electronegative atoms.

Resonance

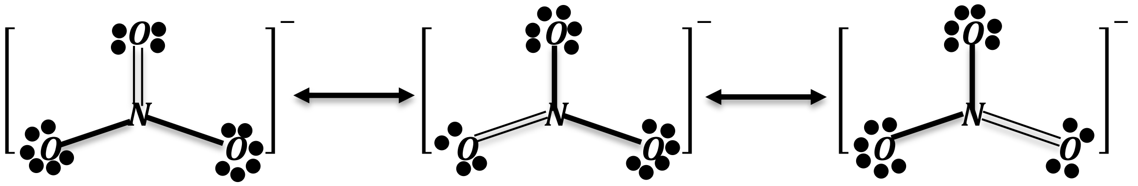
This is the situation in which two or more Lewis structures can be written. Resonance is used when a single Lewis structure cannot fully describe the bonding in a molecule or ion. Resonance structures arise when there are more than one way to draw a Lewis structure that satisfies the Octet rule. They 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.

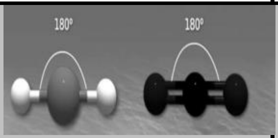
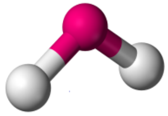
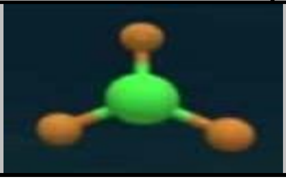
For the purpose of determining electron geometry, the VSEPR theory considers the electron pairs in a double bond or a triple bond are treated as one pair

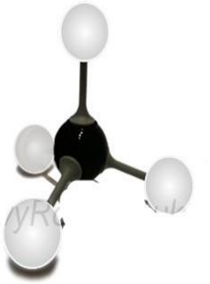
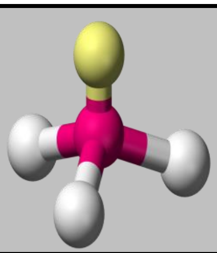
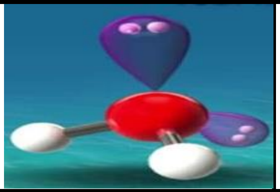
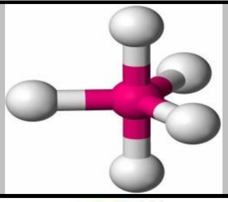
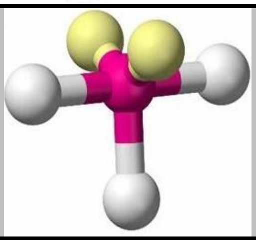
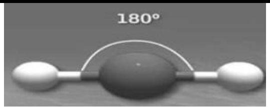
Since the lone pairs are closer the to the central atom, they cause greater repulsion than bonding pairs and the repulsions are in the order;

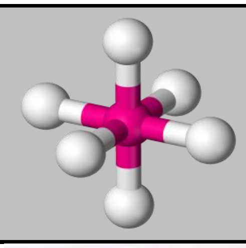
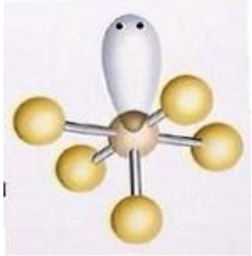
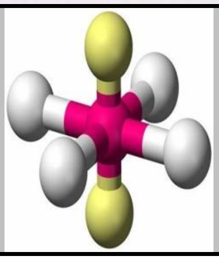
$$\textbf{Lone pair} - \textbf{lone pair repulsion} > \textbf{lone pair} - \textbf{Bonding pair repulsion} > \textbf{bonding pair} - \textbf{bonding pair repulsion.}$$

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^-

(a) Steps followed to draw the structure of molecules and cations

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 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	$2:8:\mathbf{5}$	5
NH_4^+	$2:\mathbf{5}$	$5-1=4$
SBr_6	$2:8:\mathbf{6}$	6
Cl_2O	$2:\mathbf{6}$	6

2. 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
$\mathbf{PBr_3}$	5	$5 + 3 = \mathbf{8}$
$\mathbf{NH_4^+}$	4	$4 + 4 = \mathbf{8}$
$\mathbf{SBr_6}$	6	$6 + 6 = \mathbf{12}$
$\mathbf{Cl_2O}$	6	$6 + 2 = \mathbf{8}$

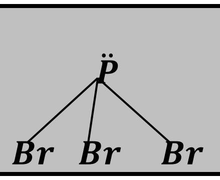
3. Divide the ***total number of valence electrons by two*** to get the ***total number of electron pairs***. This is because electrons bond in pairs

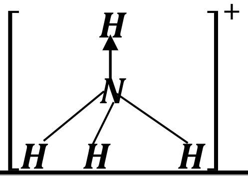
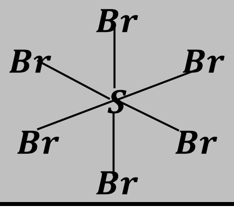
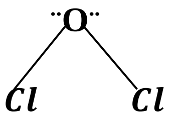
Molecule or ion	Total number of valence electrons	Total number of electron pairs
$\mathbf{PBr_3}$	8	$\frac{8}{2} = \mathbf{4}$
$\mathbf{NH_4^+}$	8	$\frac{8}{2} = \mathbf{4}$
$\mathbf{SBr_6}$	12	$\frac{12}{2} = \mathbf{6}$
$\mathbf{Cl_2O}$	8	$\frac{8}{2} = \mathbf{4}$

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
$\mathbf{PBr_3}$	4	3	$4 - 3 = \mathbf{1}$
$\mathbf{NH_4^+}$	4	4	$4 - 4 = \mathbf{0}$
$\mathbf{SBr_6}$	6	6	$6 - 6 = \mathbf{0}$
$\mathbf{Cl_2O}$	4	2	$4 - 2 = \mathbf{2}$

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
$\mathbf{PBr_3}$	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 , =O bonds and $-O^-$ 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	$2:8:\mathbf{6}$	6
H_2SO_3	$2:8:\mathbf{6}$	6
H_3PO_4	$2:8:\mathbf{5}$	5
NO_2^-	$2:\mathbf{5}$	5

SO_4^{2-}	$2:8:\mathbf{6}$	6
HCO_3^-	$2:\mathbf{4}$	4
MnO_4^{2-}	*Oxidation state of* **Mn** *is* +6	6

6. Deduce the nature of bonds in the ion or molecule. Begin with $-O^-$ bonds, followed by $O-H$ bonds and then $=O$ bonds.

- **(i)** For every negative charge in the anion, there is one $-O^-$ bond.
- **(ii)** For every hydrogen atom, there is one $O-H$ 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.

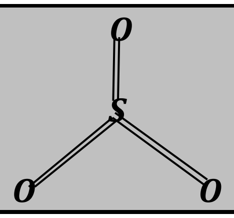
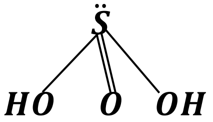
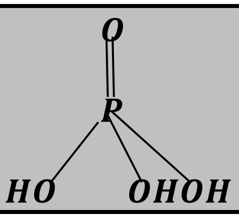
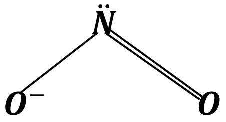
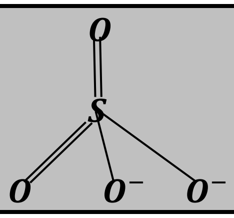
Molecule or ion	*Expected number of bonds formed by central atom*	*Nature of bonds*
SO_3	6	3 $S=O$ bonds
H_2SO_3	6	2 $O-H$ bonds *one* $S=O$ bond
H_3PO_4	5	3 $O-H$ bonds *one* $P=O$ bond
NO_2^-	5	*one* $N-O^-$bond *one* $N=O$ bond
SO_4^{2-}	6	2 $S-O^-$bonds 2 $S=O$ bonds
HCO_3^-	4	*one* $O-H$ bond *one* $C-O^-$bond *one* $C=O$ bond
MnO_4^{2-}	6	2 $Mn-O^-$bonds 2 $Mn=O$ bonds

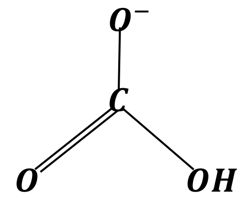
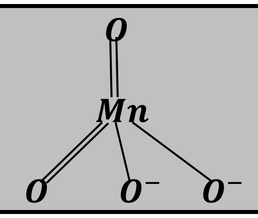
7. Since for each single bond, one electron of the valence electrons of the central atom is used, and two for a double bond, the unbounded electrons are the lone pairs. The lone pairs are obtained by subtracting the number of bonds formed from the number of valence electrons.

Molecule or ion	*Number of valence electrons of central atom*	*Nature of bonds*	*Number of valence electrons involved in bonds*	*Number of non-bonding electrons (lone pairs)*
SO_3	6	3 $S=O$ bonds	$(3\times 2)=\mathbf{6}$	$6-6=\mathbf{0}$
H_2SO_3	6	2 $O-H$ bonds *one* $S=O$ bond	$(2+2)=\mathbf{4}$	$6-4=\mathbf{2}$ **(1 lone pair)**

H_3PO_4	5	3 $O-H$ bonds one $P=O$ bond	$(3+2)=\mathbf{5}$	$5-5=\mathbf{0}$
NO_2^-	5	one $N-O^-$bond one $N=O$ bond	$(1+2)=\mathbf{3}$	$5-3=\mathbf{2}$ **(1 lone pair)**
SO_4^{2-}	6	2 $S-O^-$bonds 2 $S=O$ bonds	$2+(2\times 2)=\mathbf{6}$	$6-6=\mathbf{0}$
HCO_3^-	4	one $O-H$ bond one $C-O^-$bond one $C=O$ bond	$(1+1+2)=\mathbf{4}$	$4-4=\mathbf{0}$
MnO_4^{2-}	6	2 $Mn-O^-$bonds 2 $Mn=O$ bonds	$2+(2\times 2)=\mathbf{6}$	$6-6=\mathbf{0}$

8. Draw the structure of the molecule/ion using the nature of bonds and lone pairs. Where there are 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-}	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*
$BeCl_2$	$Cl{-}Be{-}Cl$	*Linear*
CO_2	$O{=}C{=}O$	
ICl_2^-	$[Cl{-}\ddot{\underset{..}{I}}{-}Cl]^-$	

(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.***

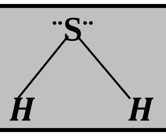
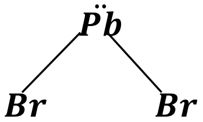
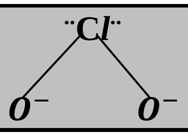
For example in $PbBr_2$,

- ***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

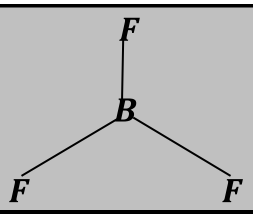
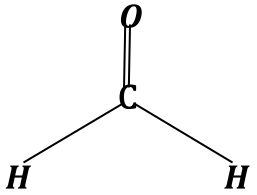
Trigonal planar molecules have ***three bonding pairs of electrons*** and ***no lone pairs***. The ***three bonding pairs lie in the same plane*** and the molecules have a ***bond angle of*** $120°$ because the ***bonding pairs greatly repel each other equally***.

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°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°28′making the molecule tetrahedral.***

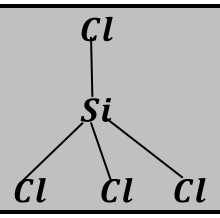
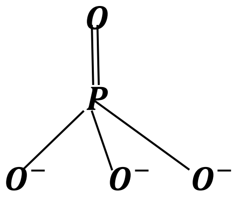
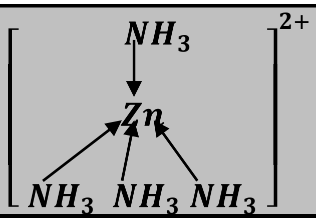
Some ions also form a tetrahedral structure.

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 $109°28'$making the molecule tetrahedral.***

Some complexes also form a tetrahedral structure.

For example in $Zn(NH_3)_4^{2+}$,

Molecule	*Structure*	*Shape*
$SiCl_4$		*Tetrahedral*
PO_4^{3-}		
$Zn(NH_3)_4^{2+}$		

(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 <u>smaller</u> than $109°28'$, 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 $93°20'$ making the molecule trigonal pyramidal.***

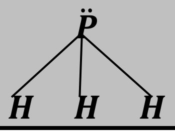
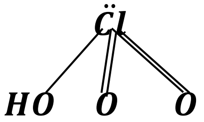
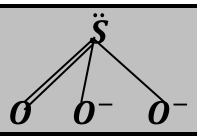
For example in $HClO_3$,

- ***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		*Trigonal pyramidal*
$HClO_3$		
SO_3^{2-}		

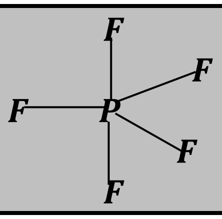
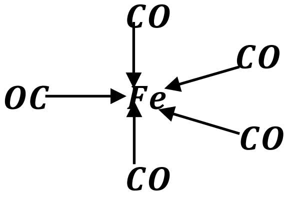
(f) Molecules or ions with a trigonal bipyramidal shape

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,

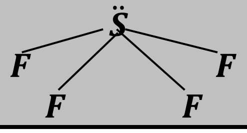
Molecule	*Structure*	*Shape*
PF_5		*Trigonal bipyramidal*
$Fe(CO)_5$		

(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***

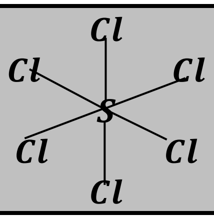
(h) Molecules or ions with an octahedral shape

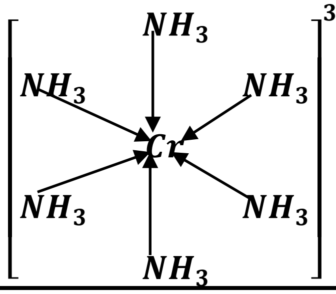
Octahedral molecules have ***six bonding pairs of electrons***.

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		***Octahedral***

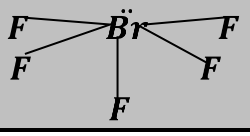
$Cr(NH_3)_6^{3+}$		*Octahedral*

(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.***

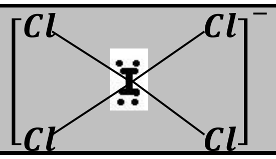
Molecule	*Structure*	*Shape*
BrF_5		*Square pyramidal*

(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		
$HOCl$		
$Ag(NH_3)_2^+$		
O_3		
$Co(NH_3)_6^{3+}$		
$POCl_3$		
ClO_3^-		
Cl_2O		
$Ag(CN)_2^-$		
$HClO_4$		
$GeCl_2$		

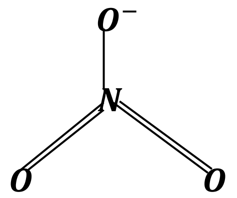
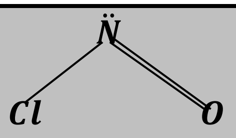
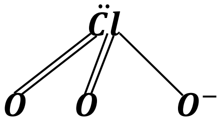
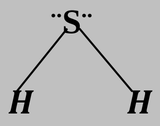
SO_2Cl_2		
CrO_4^{2-}		
$Al(H_2O)_6^{3+}$		
NH_2^-		
$S_2O_3^{2-}$		
NO_2^+		

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***

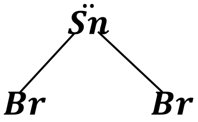
Molecule / ion	*Structure*	*Explanation*
$BeCl_2$	$Cl—Be—Cl$	*Beryllium chloride molecule has* ***two bonding pairs of electrons*** *and* ***no lone pair****. The two bonding pairs* ***repel each other greatly to form*** *a* ***linear molecule*** *with a* ***bond angle of*** **180°.**

NO_3^-		*The nitrite ion possesses* ***three bonding pairs of electrons*** *and* ***no lone pair****. The* ***three bonding pairs 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****.*
ClO_3^-		*The chlorate(V) 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.***
H_2S		*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.***

2. **Explain why;**

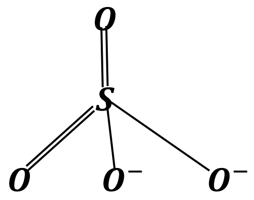
(i) **Beryllium bromide has a bond angle of 180° but tin(II) bromide has a bond angle less than 120°**

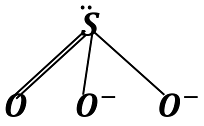
Br——Be——Br



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****.*

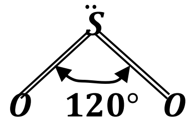
(ii) **The sulphate ion is tetrahedral but the sulphite ion is trigonal pyramidal**

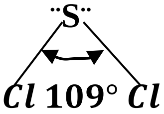




The sulphate ion has ***four bonding pairs*** *and* ***no lone pairs. The four bonding pairs of electrons mutually repel each other, resulting into a bond angle of*** $\mathbf{109°28'}$***making the molecule tetrahedral.*** *The sulphite ion possesses* ***three bonding pairs of electrons*** *and* ***one 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*** $\mathbf{120°}$ ***.****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**.

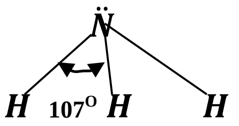
For two molecules or ions in which the central atoms are similar but the bonded atoms are the different, the **increase in electro negativity of the bonded atoms increases the attraction for the bonding electrons** by **the bonded atoms** in their molecules. This makes the **bonding pairs of electrons closer to the more electronegative atom than to**

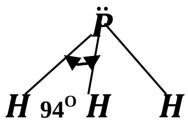
the less electronegative element. This implies that the **bonding pairs of electrons far apart** leading to a **decreased repulsion** between them, **which reduces the bond angle**.

Examples

Explain why;

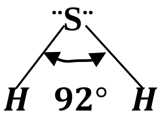
(i) the bond angle in ammonia is $107°$ while that in phosphine is $94°$.

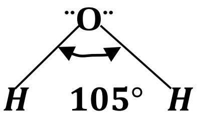




Both ammonia and phosphine molecules adopt a ***trigonal pyramidal shape****. However, the* ***nitrogen atom is more electronegative than the phosphorus atom****. The bonding pairs of electrons are* ***closer to the nitrogen atom in ammonia than they are to the phosphorus atom in phosphine****. This 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.*

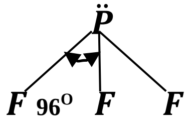
(ii) the bond angle in hydrogen sulphide is $92°$ while that in water is $105°$.

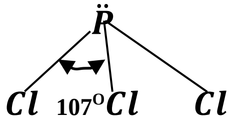




Both hydrogen sulphide and water molecules adopt a ***V- shaped structure****. However, the* ***oxygen atom is more electronegative than the sulphur atom****. The bonding pairs of electrons are* ***closer to the oxygen atom in water than they are to the sulphur atom in hydrogen sulphide****. This causes 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 atoms therefore* ***withdraw away the bonded pairs of electrons*** *from the phosphorus atom* ***more than the chlorine atoms do****. 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 symetrical 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;

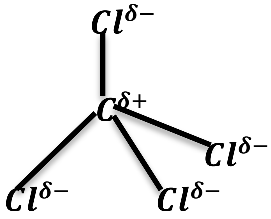
(i) ***linear molecules***
(ii) ***trigonal planar molecules***
(iii) ***square planar molecules***
(iv) ***tetrahedral molecules***
(v) ***trigonal bipyramidal molecules***
(vi) ***octahedral molecules***

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 ($\delta -$)*** *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*** **($\delta -$)** *and the carbon atom gains a* ***partial positive charge*** **($\delta+$).** *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****.*

$$O{=}C{=}O$$

Molecules in which the bonded atoms are not symetrically 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
(c) Which practical evidence is there for existence of hydrogen bonds in ice and ethanoic acid?

3. Explain the following observations;
   (i) Both graphite and copper conduct electricity
   (ii) Solid copper(II) sulphate is a non-conductor but aqueous copper(II) sulphate conducts electricity.
   (iii) Nitrogen is a gas at room temperature but phosphorus can exist in several solid forms at room temperature.
   (iv) Diamond is hard and an electrical insulator whereas graphite is soft and a good electrical conductor
   (v) Both diethyl ether and butan-1-ol have the same molecular mass but diethyl ether boils at $34°C$ whereas butan-1-ol boils at $118°C$.
   (vi) Magnesium has a higher melting point that sodium
   (vii) Sodium is softer than copper
   (viii) Both sodium and copper are good electrical conductors.
   (ix) Chlorine is a gas whereas iodine is a solid at room temperature.

4. Explain why;
    - (i) trichloromethane is deflected by a charged rod but tetrachloromethane is not.
    - (ii) Boron trichloride is non-polar whereas nitrogen trichloride is polar
    - (iii) A stream of chloroform is deflected by a charged rod but a stream of tetrachloromethane is not.
    - (iv) the bond angle in ammonium ion is $109°C$ whereas that in ammonia is $107°C$.
5. (a) State the type of hybridization expected in simple compounds of;
    - (i) Boron
    - (ii) Beryllium
    - (iii) carbon

   (b) state the effect of the type of hybridization stated in (a) above on the geometry of the following;
    - (i) boron trifluoride
    - (ii) beryllium chloride
    - (iii) carbon tetrafluoride

CHAPTER FOUR

THERMOCHEMISTRY (CHEMICAL ENERGETICS)

Thermochemistry is the study of energy changes that accompany chemical reactions. It is also called **chemical energetics** or **chemical thermodynamics**.

Thermochemistry investigates;

- ***the position of equilibrium in the reaction***
- ***the feasibility of the reaction***
- ***and how far the reaction can go.***

CHEMICAL ENERGY

Energy is the capacity to do work. There are many forms of energy among which **chemical energy** is one.

Chemical substances also have capacity to do work, thus possess chemical energy.

The chemical energy must be converted to another form of energy for chemical substances to do work. The form of energy to which chemical energy is converted is the **heat energy**.

Heat is a form of kinetic energy associated with motion of atoms and molecules. It is the transfer of energy from regions of high temperature to regions of low temperature.

The heat evolved by a chemical substance can be used as a measure of the chemical energy liberated. The change in chemical energy of a chemical substance is measured only if the substance is treated in a certain way, for example when it is burnt in oxygen.

During a chemical reaction, bonds between atoms of the reactants are broken and new bonds are formed in the products formed. Energy is absorbed to break the bonds between atoms and energy is given out when new bonds are formed.

Heat content of a substance

Every substance has some stored chemical energy. The heat content differs from one substance to another because the molecules of different substances differ in the number and type of atoms and the number and type of bonds between their atoms.

Enthalpy, H

Enthalpy is the total energy content of a substance.

It is denoted by the symbol, $\boldsymbol{H}$.

Enthalpy change, ΔH

Enthalpy change is the heat content of a substance measured at standard temperature and pressure during a chemical reaction.

Enthalpy change is called **heat of reaction** and is denoted as ΔH_{rxn}

Standard enthalpy change, ΔH^{θ}

This is the heat change when molar quantities of reactants shown in the balanced equation for the reaction in their standard states react completely at 1 atmosphere and 298K.

Standard state of the substance is the phase in which a pure substance exists at 1 atmosphere and 298K.

The units for standard enthalpy of reaction are $kJmol^{-1}$

TYPES OF HEAT OF REACTIONS

All chemical reactions are accompanied by evolution or absorption of heat. This results into two types of reactions namely;

- **(i)** **exothermic reaction**
- **(ii)** **endothermic reaction**

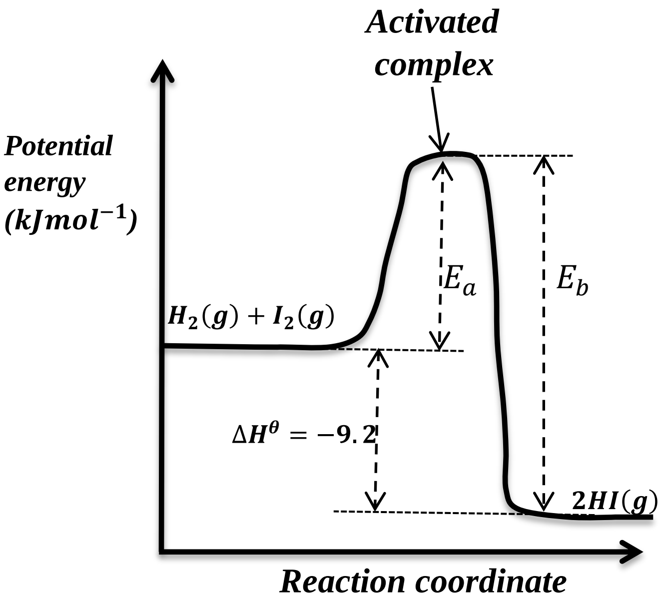
Exothermic reaction	**Endothermic reaction**
• Proceed with evolution of heat to the environment	• Proceed with absorption of heat from the environment
• Denoted by a negative sign	• Denoted by a positive sign
• The products are at a lower energy level than the reactants	• The products are at a higher energy level than the reactants
For example;	**For example;**
$H_2(g) + I_2(g) \longrightarrow 2HI(g)\ \ \Delta H^{\theta} = -9.2\ kJmol^{-1}$	$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)\ \Delta H^{\theta} = +131.4\ kJmol^{-1}$
The equation can be interpreted as;	The equation can be interpreted as
1 mole of hydrogen gas reacts with 1 mole of gaseous iodine to form 2 moles of hydrogen iodide gas with evolution of $9.2\ kJmol^{-1}$	***1 mole of carbon reacts with 1 mole of steam to form 1mole of carbon monoxide gas and 1 mole of hydrogen gas with absorption of*** $131.4kJmol^{-1}$

The sign of the enthalpy change for a reaction is an indicator of its feasibility. The more negative (exothermic) the value of ΔH , the more is the reaction likely to be feasible.

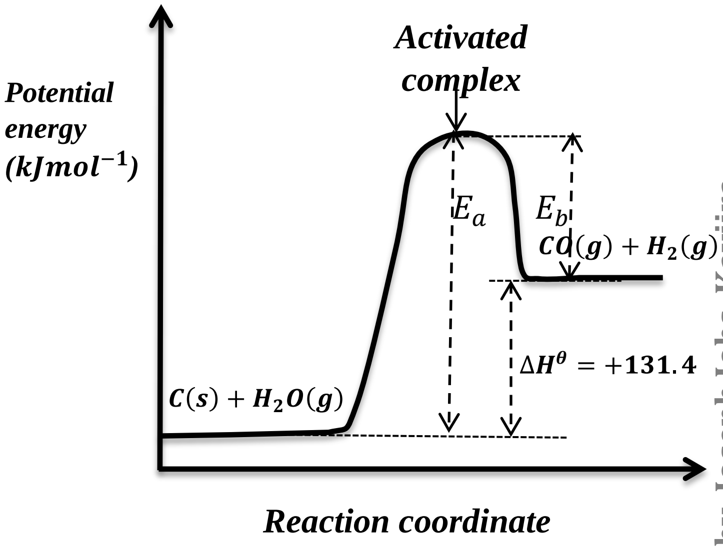
Energy level diagrams for exothermic and endothermic reactions

An energy level diagram is a graph of potential energy of a reaction against reaction path or reaction coordinate.

For the exothermic reaction shown above;



For the endothermic reaction shown above;



E_a is the ***activation energy for the reaction***.

It can also be called ***activation energy for forward reaction***.

E_b is ***activation energy for backward reaction***

ΔH^{θ} ***is the enthalpy of reaction***

Activation energy is the minimum energy which is required to be possessed by reactants in order to react and form products.

Activated complex is the intermediate unstable compound formed immediately once the reactants have absorbed the activation energy available.

This unstable compound undergoes bond re-organization by releasing some of the energy to form the final stable product. The activated complex can also be called a **transition state.**

The enthalpy of reaction can be got from the expression ;

$$\Delta H^{\theta} = E_a - E_b$$

Questions

1. For the reaction $CO(g) + NO_2(g) \rightleftharpoons CO_2(g) + NO(g) \quad \Delta H^{\theta} = negative$
   (a) Draw a well labeled energy level diagram for the reaction.
   (b) The activation energies for the forward and reverse reactions are known to be respectively $32kJmol^{-1}$ and $82.1\ kJmol^{-1}$. Calculate the heat of reaction.
2. (a) Define the term activation energy
   (b) X and Y react to form W and Z according to the following equation
   $$X(g) + Y(g) \rightleftharpoons W(g) + Z(g) \qquad \Delta H^{\theta} = +50\ kJmol^{-1}$$
   (i) Draw a fully labeled potential energy versus reaction coordinate diagram for the reaction of X and Y.
   (ii) Calculate the activation energy of the backward reaction. (the activation for forward reaction is $+200\ kJ$
3. Dinitrogen tetraoxide dissociates at 40 °C and 1 atm according to the following equation.
   $$N_2O_4 \rightleftharpoons 2\,NO_2(g) \qquad \Delta H = +57kJmol^{-1}$$

Draw a well labelled energy level diagram for the reaction above

Applications of exothermic reactions in everyday life

(i) In **hot packs** which are used to treat sports injuries and warming the body in case of coldness. The instant hot packs have separate compartments of water and anhydrous calcium chloride separated by a thin film placed in a plastic bag. When the bag is squeezed, the thin film breaks and the anhydrous calcium chloride dissolves in the water exothermically to release heat.

$$CaCl_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2Cl^-(aq) \qquad \Delta \boldsymbol{H^{\theta}} = -83\ kJmol^{-1}$$

There are other salts that dissolve exothermically and can be used in a hot pack for example ***anhydrous magnesium sulphate*** and ***anhydrous copper(II) sulphate***

(ii) **Combustion of fuels** to release energy during cooking of food
(iii) In **cellular respiration**, where energy is obtained from carbohydrates and used by living organisms. During the process carbohydrates react with oxygen to form carbon dioxide, water and energy.
(iv) **Condensation** during formation of rain from water vapour
(v) **Freezing** of water into ice

Applications of endothermic reactions in everyday life

(i) In **instant cold packs** which are used to treat sports injuries. The instant cold packs have separate compartments of water and solid ammonium nitrate separated by a thin film placed in a plastic bag. When the bag is squeezed, the thin film breaks and the solid ammonium nitrate dissolves in water endothermically to provide instant coldness. Heat is absorbed from the surrounding such as the injured area of the athlete's body.

$$NH_4NO_3(s) \xrightarrow{H_2O} NH_4NO_3(aq) \quad \Delta\boldsymbol{H^{\theta}} = +26\ kJmol^{-1}$$

There are other salts that dissolve endothermically and can be used in a cold pack for example ***ammonium chloride, potassium nitrate*** and ***sodium thiosulphate***.

(ii) **Photosynthesis**. Energy is absorbed to convert carbon dioxide and water to sugars in presence of chlorophyll.

(iii) Evaporation of liquid water

(iv) Melting of ice

Factors affecting enthalpy of reaction

1. **Temperature at which the reaction is carried out**
2. **Pressure of gaseous reactants or products**
3. **Amount of reactants used**
4. **Physical state of reactants and products**

   Latent heat is involved in changes of state so that the state of the reagents and products affect the enthalpy of a reaction

   Combination of hydrogen and oxygen to form liquid water at 25°C and atmospheric pressure evolves $286kJmol^{-1}$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(\boldsymbol{l}) \quad \Delta\boldsymbol{H^{\theta}} = -286\ kJmol^{-1}$$

   When 2g of hydrogen are burnt just above 100°C, less heat is given out.

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(\boldsymbol{g}) \quad \Delta\boldsymbol{H^{\theta}} = -245.4\ kJmol^{-1}$$

   The observed difference is due to heat of vapourisation of 1 mole of water.

$$H_2O(\boldsymbol{l}) \longrightarrow H_2O(\boldsymbol{g}) \quad \Delta\boldsymbol{H^{\theta}} = +40.6\ kJmol^{-1}$$

5. **Allotropic modifications**

There is an enthalpy change involved in conversion one allotrope to another. A particular allotrope of an element used in a reaction affects the enthalpy of reaction. For example;

$$S(rhombic) + O_2(g) \longrightarrow SO_2(g) \quad \Delta\boldsymbol{H^{\theta}}(\boldsymbol{298K}) = -297.0\ kJmol^{-1}$$

$$S(monoclinic) + O_2(g) \longrightarrow SO_2(g) \quad \Delta\boldsymbol{H^{\theta}}(\boldsymbol{298K}) = -297.3\ kJmol^{-1}$$

CALORIMETRY

Calorimetry is a technique used to measure amounts of heat transferred to or from a substance. A calorimeter is a container that is insulated against heat loss that is used to measure the amount of heat involved in a chemical or physical process.

The common calorimeters used in laboratory experiments include the **coffee cup calorimeter** and **the bomb calorimeter**.

The coffee cup calorimeter is used when measuring the heats of neutralisation, solution, precipitation. It is constructed from a polystyrene cup with a lid. A thermometer is usually inserted in it to measure heat changes.

The bomb calorimeter is mainly used to determine heat of combustion of a solid substance.

Heat capacity of a calorimeter

The heat capacity of a calorimeter is the quantity of heat absorbed by the calorimeter for each $\mathbf{1°C}$ rise in temperature. Its unit is $J°C^{-1}$

The heat capacity of a calorimeter must be determined experimentally.

Experiment to determine heat capacity of a simple calorimeter/ plastic cup calorimeter

Using a measuring cylinder, measure $100\ cm^3$of water into the calorimeter and record its temperature, $T_1°C$ using a thermometer.
Measure another $100\ cm^3$ of water into a beaker and heat it to $60°C$. Keep the temperature steady to for 2 to 3 minutes.
Then pour the hot water quickly into the calorimeter containing cold water and stir the mixture. Record the temperature, $T_2°C$.

Treatment of results

$$Initial\ temperature\ of\ \ cold\ water\ before\ mixing = T_1°C$$
$$Initial\ temperature\ of\ hot\ water\ before\ mixing\ = 60°C$$
$$Final\ temperature\ after\ mixing\ cold\ and\ hot\ water\ = T_2°C$$
$$Density\ of\ water = 1gcm^3$$
$$Specific\ heat\ capacity\ of\ water = 4.2Jg^{-1}°C^{-1}$$
$$Let\ heat\ capacity\ of\ the\ calorimeter = \boldsymbol{C}$$
$$Mass\ of\ water = density \times volume = (1 \times 100) = 100g$$

$$Heat\ gained\ by\ calorimeter\ and\ cold\ water = Heat\ lost\ by\ hot\ water$$

$$[\boldsymbol{C} \times (T_2 - T_1)] + \left[\left(100 \times 4.2 \times (T_2 - T_1)\right)\right] = \left(100 \times 4.2 \times (60 - T_2)\right)$$
$$[\boldsymbol{C} \times (T_2 - T_1)] = \left(100 \times 4.2 \times (60 - T_2)\right) - \left[\left(100 \times 4.2 \times (T_2 - T_1)\right)\right]$$

$$C = \frac{\left(100 \times 4.2 \times (60 - T_2)\right) - \left[\left(100 \times 4.2 \times (T_2 - T_1)\right)\right]}{(T_2 - T_1)}$$

$$\boldsymbol{C} = \left(\frac{[(\boldsymbol{60 - T_2}) - (\boldsymbol{T_2 - T_1})](\boldsymbol{100 \times 4.2})}{(\boldsymbol{T_2 - T_1})}\right)\boldsymbol{J°C^{-1}}$$

TYPES OF ENTHALPY CHANGES

Enthalpy of formation

Enthalpy of formation of a compound is the heat evolved or absorbed when one mole of a compound is formed from the constituent elements in their standard states.

When enthalpy of formation is determined under standard conditions, it is called **standard enthalpy of formation**.

Standard enthalpy of formation(ΔH_f^θ)

The standard enthalpy of formation of a compound, ΔH_f^θ ***, is the heat evolved or absorbed when one mole of the compound is formed from its elements in their normal states at 298K and 1 atmosphere***.

Enthalpy of formation can be **exothermic** or **endothermic**.

Prediction of relative stability of compounds from enthalpy of formation

- When a compound is formed with evolution of heat (exothermically), that compound is ***more stable and less reactive***.
- When a compound is formed with absorption of heat (endothermically), that compound is ***less stable and very reactive***.
- The standard enthalpy of formation of elements in their standard states is conventionally taken as zero. i.e. enthalpy of formation of Na, Mg, O_2, S_8, etc is $0.00kJmol^{-1}$

The table below shows some compounds, equations and their enthalpies of formation. Their stability can be predicted using values for enthalpy of formation. Also note that all the equations show one mole of compound being formed.

Compound	Equation for formation	$\boldsymbol{\Delta H_f^\theta(kJmol^{-1})}$
Sodium chloride	$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(\boldsymbol{s})$	-418
Water	$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\boldsymbol{l})$	-286
Hydrogen fluoride	$\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \longrightarrow HF(\boldsymbol{l})$	-271.1
Aluminium oxide	$2Al(s) + \frac{3}{2}O_2(g) \longrightarrow Al_2O_3(\boldsymbol{s})$	-1675.7

Ammonia	$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(\boldsymbol{g})$	-50.2
Ethyne	$2C(s) + H_2(g) \longrightarrow C_2H_2(\boldsymbol{g})$	$+211$
Nitrogen monoxide	$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(\boldsymbol{g})$	$+90$

The first equation means that 1 mole of solid sodium chloride is formed from 1 mole of solid sodium and 0.5 moles of chlorine gas with evolution of $418\ kJ$ of heat under standard conditions.

The last equation means that 1 mole of nitrogen monoxide gas is formed from 0.5 mole of nitrogen gas and 0.5 mole of oxygen gas with absorption of $90\ kJ$ of heat under standard conditions.

Determination of enthalpy of formation

Enthalpy of formation of compounds can be obtained directly by measuring the heat change in the combination of known masses of the elements.

It can also be obtained indirectly by use of Hess' law when values of other enthalpies for a given compound or components of the compound are known (this will be seen later).

Calculating $\Delta H^{\theta}_{reaction}$ using heats of formation

Enthalpy of reaction can be expressed as the difference between the sum of the standard enthalpies of formation of the products and the sum of the standard enthalpies of formation of the reactants when both reactants and products are in their standard states at 1 atmosphere and 298K

$$\Delta H^{\theta}_{reaction} = \sum \Delta H^{\theta}_{f\,products} - \sum \Delta H^{\theta}_{f\,reactants}$$

The standard enthalpy of formation of elements in their standard states is conventionally taken as zero whenever the above equation is used.

Reactions involving ions can similarly be treated using the same equation if the values of the standard molar enthalpies of formation of ions are known. The standard enthalpy of formation of the hydrogen ion is 0.00$kJmol^{-1}$.

Examples

1. **Calculate the enthalpy change for the reaction below using the information given;**

$$2NH_3(g) + 3Cl_2(g) \longrightarrow N_2(g) + 6HCl(g)$$
$$\Delta H^{\theta}_{f}, NH_3(g) = -46.19kJmol^{-1}$$
$$\Delta H^{\theta}_{f}, HCl(g) = -92.30kJmol^{-1}$$

$$\Delta H^{\theta}_{reaction} = \sum \Delta H^{\theta}_{f\,products} - \sum \Delta H^{\theta}_{f\,reactants}$$
$$= \left[\Delta H^{\theta}_{f} N_2 + (6\Delta H^{\theta}_{f} HCl)\right] - \left[(2\Delta H^{\theta}_{f} NH_3) + (3\Delta H^{\theta}_{f} Cl_2)\right]$$
$$= [0 + (6 \times -92.30)] - [(2 \times -46.19) + (3 \times 0)]$$
$$= (-553.8) - (-92.38)$$
$$= \boldsymbol{-461.42 kJmol^{-1}}$$

2. **The enthalpies of formation of some selected compounds are shown in the table below.**

Compound	$\boldsymbol{H_2O(g)}$	$\boldsymbol{CO(g)}$	$\boldsymbol{C_8H_{18}(g)}$
$\boldsymbol{\Delta H^{\theta}_{f}(kJmol^{-1})}$	$\boldsymbol{-242}$	$\boldsymbol{-111}$	$\boldsymbol{-169}$

Calculate the enthalpy change for the following reaction.

$$\boldsymbol{8CO(g) + 17H_2(g) \xrightarrow{Fe/CO\ catalyst} C_8H_{18}(g) + 8H_2O(g)}$$

$$\Delta H^{\theta}_{reaction} = \sum \Delta H^{\theta}_{f\,products} - \sum \Delta H^{\theta}_{f\,reactants}$$
$$= \left[\Delta H^{\theta}_{f} C_8H_{18} + (8\Delta H^{\theta}_{f} H_2O)\right] - \left[(8\Delta H^{\theta}_{f} CO) + (17\Delta H^{\theta}_{f} H_2)\right]$$
$$= [-169 + (8 \times -242)] - [(8 \times -111) + (17 \times 0)]$$
$$= (-2105) - (-888)$$
$$= \boldsymbol{-1217kJmol^{-1}}$$

3. **The standard enthalpies of formation of water, sodium ion and hydroxyl ion are given in the table below.**

Compound/ion	**Enthalpy of formation,** $\boldsymbol{\Delta H^{\theta}_{f}(kJmol^{-1})}$
$\boldsymbol{H_2O}$	$\boldsymbol{-286}$
$\boldsymbol{Na^{+}}$	$\boldsymbol{-239.7}$
$\boldsymbol{\bar{O}H}$	$\boldsymbol{-229.9}$

Calculate the enthalpy of the reaction between sodium and water.

$$Equation;\ 2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

$$\Delta H^{\theta}_{reaction} = \sum \Delta H^{\theta}_{f\,products} - \sum \Delta H^{\theta}_{f\,reactants}$$
$$= \left[2\Delta H^{\theta}_{f} NaOH(aq) + (\Delta H^{\theta}_{f} H_2)\right] - \left[(2\Delta H^{\theta}_{f} Na) + (2\Delta H^{\theta}_{f} H_2O)\right]$$
$$= \left[2\Delta H^{\theta}_{f} Na^{+}(aq) + 2\Delta H^{\theta}_{f} \bar{O}H(aq) + (\Delta H^{\theta}_{f} H_2)\right] - \left[(2\Delta H^{\theta}_{f} Na) + (2\Delta H^{\theta}_{f} H_2O)\right]$$
$$= [(2 \times -239.7) + (2 \times -229.9) + 0] - [(2 \times 0) + (2 \times -286)]$$
$$= (-939.2) - (-572)$$
$$= \boldsymbol{-367.2\ kJmol^{-1}}$$

Questions

1. The standard enthalpies of formation of different compounds are given in the table below.

Compound	**Enthalpy of formation, $\Delta H_f^\theta (kJmol^{-1})$**
H_2O	-285.9
H_2S	-20.15
SO_2	-296.9

Calculate the enthalpy of the reaction;

$$SO_2(g) + 2H_2S(g) \longrightarrow 3S(s) + 2H_2O(l)$$

2. Calculate the standard enthalpy change for the reaction below using the information given the table;

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2$$

Compound	**Enthalpy of formation, $\Delta H_f^\theta (kJmol^{-1})$**
$H_2O(g)$	-241.8
$CO(g)$	-110.5

3. The standard enthalpies of formation of different compounds are given in the table below.

Compound	**Enthalpy of formation, $\Delta H_f^\theta (kJmol^{-1})$**
$Fe_2O_3(s)$	-822.2
CO	-110.5
CO_2	-393.5

Calculate the enthalpy of the reaction;

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$$

4. The standard enthalpies of formation of different compounds are given in the table below.

Compound	**Enthalpy of formation, $\Delta H_f^\theta (kJmol^{-1})$**
Water	-250
Oxygen difluoride	$+20$
Hydrogen fluoride	-270

Calculate the enthalpy of the reaction;

$$OF_2(g) + H_2O(g) \longrightarrow 2HF(g) + O_2(g)$$

5. The standard enthalpies of hydrogen peroxide and water.

Compound	$H_2O_2(l)$	$H_2O(l)$
$\Delta \boldsymbol{H_f^\theta}(\boldsymbol{kJmol^{-1}})$	-188	-286

Calculate the enthalpy change for the following reaction.

$$2H_2O_2(l) \longrightarrow O_2(g) + 2H_2O(l)$$

Enthalpy of combustion

Enthalpy of combustion is the heat evolved when one mole of a substance is completely burnt in oxygen under specified conditions, when the reactants and products are in their standard states.

When enthalpy of combustion is determined under standard conditions ($298K\ and\ 1\ atm$), it is called **standard enthalpy of combustion**.

Standard enthalpy of combustion ($\Delta \boldsymbol{H_c^\theta}$)

Standard enthalpy of combustion, ΔH_c^θ, is the heat evolved when one mole of a substance is completely burnt in oxygen at 298K and 1 atmosphere.

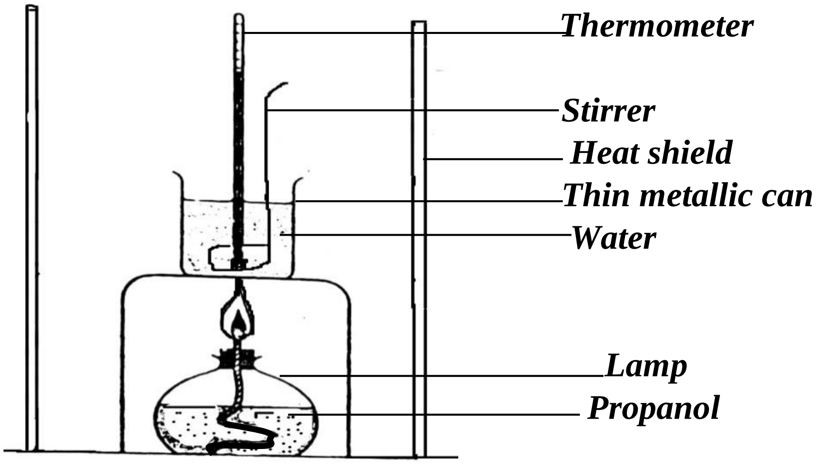
Enthalpy of combustion is always a **negative value** indicating that heat is evolved (reaction is **exothermic**)
The table below shows some compounds, equations and their standard enthalpies of combustion.

Compound	**Equation for combustion**	$\Delta \boldsymbol{H_f^\theta}(\boldsymbol{kJmol^{-1}})$
Carbon(graphite)	$C(s) + O_2(g) \longrightarrow CO_2(g)$	-393
Methane	$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$	-891
Ethyne	$C_2H_2(g) + 2\frac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$	-1310
Ethane	$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$	-1560
Ethanol	$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$	-1370.7

Experiment to determine enthalpy of combustion of low molecular mass alcohols (ethanol, propanol and butanol)

In this experiment we shall consider propanol but the same treatment can be done for ethanol and butanol. The same experiment can be used for any other liquid fuel for example liquid hexane.

Set up



A ***known volume of water***, $V\ cm^3$ is put in a ***thin metallic can***.
The can is fitted with a ***thermometer and a stirrer***
The ***initial temperature of the water*** is read and recorded from the thermometer as , T_1°C
A spirit lamp is ***filled halfway with propanol*** and the ***mass of the lamp and its contents is measured*** and recorded as $m_1 g$
The ***spirit lamp is lit*** and the ***flame adjusted to just touch the bottom of the metallic can***.
The ***water is heated while stirring*** until a ***reasonable rise in temperature*** is obtained.
The ***lamp is extinguished*** and ***the final temperature of the water recorded*** as T_2°C
The ***mass of the spirit lamp and its contents is measured*** and recorded as $m_2 g$

Treatment of results

Assuming no heat was lost to the surrounding;
Heat capacity of the can is negligible
Heat produced by combustion of propanol is equal to heat absorbed by water.

$$Density\ of\ water = 1gcm^3$$

$$Specific\ heat\ capacity\ of\ water = 4.2Jg^{-1}{}^\circ C^{-1}$$

$$Mass\ of\ water = density \times volume = 1 \times V = Vg$$

$$Temperature\ rise = \Delta T = (T_2 - T_1)^\circ C$$

$$Heat\ absorbed\ by\ H_2O = mass\ of\ water \times specific\ heat\ capacity\ \times temperature\ rise$$
$$= (V \times 4.2 \times \Delta T)J$$

$$Molar\ mass\ of propanol(CH_3CH_2CH_2OH) = 36 + 16 + 8 = 60g$$

$$Mass\ of propanol\ burnt = (m_1 - m_2)g$$

$$(m_1 - m_2)g\ of\ CH_3CH_2CH_2OH\ evolve\ (V \times 4.2 \times \Delta T)J$$

$$60g\ of\ CH_3CH_2CH_2OH\ evolve\ \left(\frac{60\ \times V \times 4.2 \times \Delta T}{(m_1 - m_2)}\right)J$$

$$Heat\ of\ combustion\ of\ propanol = -\left(\frac{60\ \times V \times 4.2 \times \Delta T}{(m_1 - m_2)}\right)Jmol^{-1}$$

$$\boldsymbol{Heat\ of\ combustion\ of\ propanol = -\left(\frac{60\ \times V \times 4.2 \times \Delta T}{1000(m_1 - m_2)}\right)kJmol^{-1}}$$

Question;

Describe an experiment to determine the enthalpy of combustion of;

- **(i) Ethanol**
- **(ii) Butanol**
- **(iii) Liquid hexane**

Use of experimental data

Example

When ethanol was burnt in a spirit lamp, the following results were obtained;

$$Mass\ of\ spirit\ lamp\ and\ ethanol\ before\ burning\ = 3.6g$$

$$Mass\ of\ spirit\ lamp\ and\ ethanol\ after\ burning\ = 2.1g$$

$$Volume\ of\ \ water\ heated\ = 500cm^3$$

$$Initial\ \ temperature\ of\ water = 25.20°C$$

$$Final\ \ temperature\ of\ water = 44.70°C$$

(a) Calculate the heat of combustion of ethanol.

$(Density\ of\ water\ 1gcm^{-3}\ and\ \ specific\ heat\ capacity\ of\ water\ is\ 4.18Jg^{-1}K^{-1})$

(b) State why the value obtained in (a) above is lower than the actual value obtained in books.

***(a) Heat produced by combustion of ethanol is equal to heat absorbed by water**.*

$$Mass\ of\ water = density \times volume = 1 \times 500 = 500g$$

$$Temperature\ rise = (44.70 - 25.20) = 19.5°C$$

$$Heat\ absorbed\ by\ water = (500 \times 4.18 \times 19.5)J$$

$$= 40755\ Joules$$

$$Molar\ mass\ of CH_3CH_2OH = 24 + 16 + 6 = 46g$$

$$Mass\ of propanol\ burnt = (3.6 - 2.1) = 1.5g$$

$$1.5g\ of\ CH_3CH_2OH\ evolve\ 40755\ J$$

$$46g\ of\ CH_3CH_2OH\ evolve\ \left(\frac{46\ \times 40755}{1.5}\right)J$$

$$Heat\ of\ combustion\ of\ ethanol = -1249820\ J$$

$$\boldsymbol{Heat\ of\ combustion\ of\ ethanol = -1249.82kJmol^{-1}}$$

(b) The calculated value is less than the theoretical value because some of the heat evolved is lost to the surroundings.

Questions

1. A spirit burner containing ethanol was weighed and then used to heat up a copper calorimeter containing $200cm^3$ of cold water and then reweighed. The results were recorded as shown below;

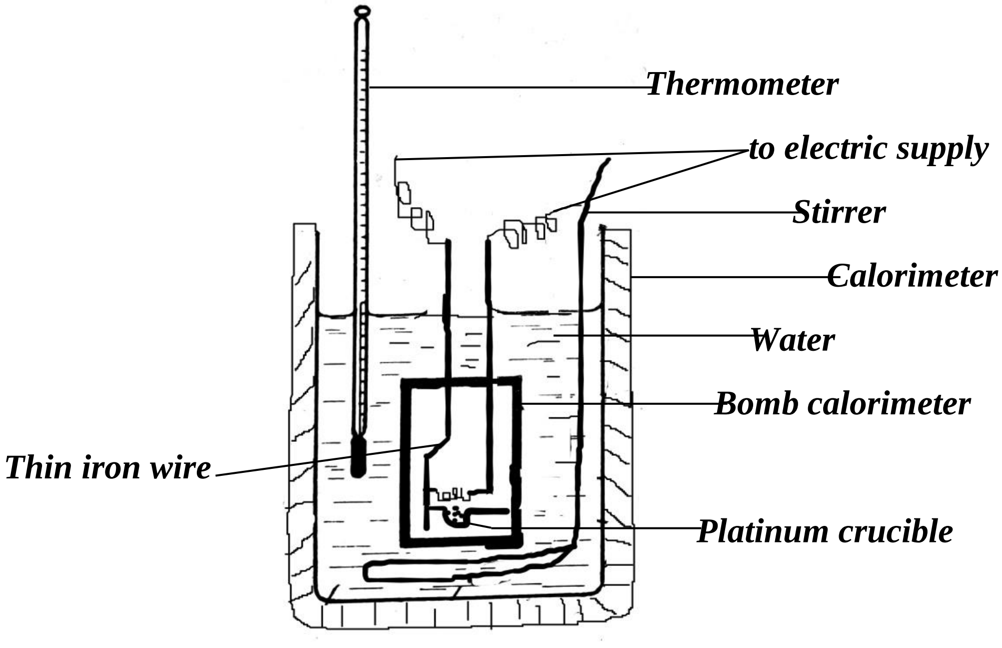
$$\textit{Decrease in mass of ethanol} = 0.4g$$
$$\textit{Rise in temperature of water} = 10°C$$
$$\textit{Decrease in mass of ethanol} = 0.4g$$
$$\textit{Specific heat capacity of water} = 4.2Jg^{-1}K^{-1}$$
$$\textit{Heat capacity of calorimeter is negligible}$$

   Use the results to calculate the enthalpy of combustion of ethanol
2. When 0.95g of ethanol was burnt, the heat produced raised the temperature of $400\ cm^3$ of water from $25°C$ to $37°C$. Calculate the heat of combustion of ethanol. $(Density\ of\ water\ 1gcm^{-3}\ and\ \ specific\ heat\ capacity\ of\ water\ is\ 4.18Jg^{-1}K^{-1}$

Experiment to determine enthalpy of combustion of a solid substance for example carbon (graphite) or coke

Enthalpy of combustion of a solid substance is determined using a bomb calorimeter.

Set up



A ***known mass of carbon***, $m\ g$, is placed in a ***small platinum crucible***
The crucible with its contents is placed in a ***bomb calorimeter***
The bomb calorimeter is ***filled with oxygen at a pressure of about 25 atmospheres*** to ***ensure rapid and complete combustion***
The bomb calorimeter is ***immersed a known volume of water,*** $\boldsymbol{V\ cm^3}$ placed in a ***calorimeter*** fitted with a ***thermometer and stirrer***
The ***initial temperature of the water is recorded as*** $\boldsymbol{T_1°C}$
The ***carbon is ignited*** by passing ***electric current through a small coil of iron wire touching the carbon***
The ***final temperature of the water is read from the thermometer as*** $\boldsymbol{T_2°C}$

Treatment of results

Heat evolved by combustion of carbon and the iron wire = heat absorbed by water+ heat gained by calorimeter

$$Let\ Q\ be\ heat\ produced\ by\ burning\ of\ the\ iron\ wire$$
$$Let\ C_B\ be\ heat\ capacity\ of\ the\ bomb\ calorimetr$$
$$Density\ of\ water = 1gcm^3$$
$$Specific\ heat\ capacity\ of\ water = 4.2Jg^{-1}°C^{-1}$$
$$Mass\ of\ water = density \times volume = 1 \times V = Vg$$
$$Temperature\ rise = \Delta T = (T_2 - T_1)°C$$
$$Heat\ absorbed\ by\ H_2O = mass\ of\ water \times specific\ heat\ capacity\ \times temperature\ rise$$
$$= (V \times 4.2 \times \Delta T)J$$
$$Heat\ gained\ by\ bomb\ calorimeter =\ heat\ capacity\ of\ calorimeter\ \times temperature\ rise$$
$$= (C_B \times \Delta T)J$$
$$Heat\ evolved\ by\ carbon\ alone =\ [(V \times 4.2 \times \Delta T) + (C_B \times \Delta T)] - Q$$
$$Heat\ evolved\ by\ carbon\ alone =\ [(V \times 4.2) + C_B]\Delta T - Q$$
$$Molar\ mass\ of\ carbon = 12g$$
$$mg\ of\ carbon\ evolve\ \left[\left((V \times 4.2) + C_B\right)\Delta T - Q\right] Joules$$
$$12g\ of\ carbon\ \ evolve\ \left(\frac{12\ \times \left[\left((V \times 4.2) + C_B\right)\Delta T - Q\right]}{m}\right)J$$
$$Heat\ of\ combustion\ of\ carbon = -\left(\frac{12\ \times \left[\left((V \times 4.2) + C_B\right)\Delta T - Q\right]}{m}\right)Jmol^{-1}$$
$$\boldsymbol{Heat\ of\ combustion\ of\ carbon = -\left(\frac{12\ \times \left[\left((V \times 4.2) + C_B\right)\Delta T - Q\right]}{1000m}\right)kJmol^{-1}}$$

Calculation of enthalpy of reaction and enthalpy of formation, using enthalpies of combustion

Examples

1. **If the heat of formation of carbon dioxide is $-393kJmol^{-1}$, heat of formation of water is $-286kJmol^{-1}$ and heat of combustion of butane is $-2877kJmol^{-1}$ Calculate the standard heat of formation of butane**.

Equation for the reaction required;

$$\boldsymbol{4C(s) + 5H_2(g) \longrightarrow C_4H_{10}(g)} \qquad \Delta H^{\theta}_{f,C_4H_{10}} = ?$$

Equations for reactions given;

(i) $C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_1 = -393kJmol^{-1}$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_2 = -286\ kJmol^{-1}$

(iii) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l) \quad \Delta H_3 = -2877\ kJmol^{-1}$

According to the required equation, the 4C is obtained by multiplying equation (i) by 4. The $5H_2$ obtained by multiplying equation (ii) by 5. Since C_4H_{10} is on right hand side of the required equation, the last equation is reversed. After this treatment and addition of the 3 resulting equations the required equation is generated. The same treatment is done to the ΔH values. Check through the working below and subsquent examples.

$$\boldsymbol{4C(s)} + \cancel{4O_2(g)} \longrightarrow \cancel{4CO_2(g)} \qquad \boldsymbol{4\Delta H_1}$$

$$\boldsymbol{5H_2(g)} + \cancel{\tfrac{5}{2}O_2(g)} \longrightarrow \cancel{5H_2O(l)} \qquad \boldsymbol{5\Delta H_2}$$

$$\cancel{4CO_2(g)} + \cancel{5H_2O(l)} \longrightarrow \boldsymbol{C_4H_{10}(g)} + \cancel{\tfrac{13}{2}O_2(g)} - \Delta H_3$$

$$\boldsymbol{\Delta H^{\theta}_{f,C_4H_{10}} = 4\Delta H_1 + 5\Delta H_2 - \Delta H_3}$$

$$= (4 \times -393) + (5 \times -286\ ) - (-2877)$$

$$= -3002 + 2877$$

$$= \boldsymbol{-125\ kJmol^{-1}}$$

2. **The table below shows the values of enthalpies of combustion of carbon, rhombic sulphur and carbon disulphide.**

Substance	Enthalpy of combustion($kJmol^{-1}$)
Carbon	$\boldsymbol{-393.30}$
Sulphur	$\boldsymbol{-293.72}$
Carbon disulphide	$\boldsymbol{-1108.76}$

Calculate the enthalpy of formation of carbon disulphide.

Equation for the reaction required;

$$\boldsymbol{C(s) + 2S(s) \longrightarrow CS_2(l)} \qquad \Delta H^{\theta}_{f,CS_2(l)} = ?$$

Equations for reactions given;

(i) $C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_1 = -393.30\ kJmol^{-1}$

(ii) $S(s) + O_2(g) \longrightarrow SO_2(g) \qquad \Delta H_2 = -293.72\ kJmol^{-1}$

(iii) $CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g) \quad \Delta H_3 = -1108.76\ kJmol^{-1}$

The required equation is obtained by adding all the three equations after equation (i) is unchanged, equation (ii) multiplied by 2 and a reversed equation (iii). The same treatment is done to the ΔH values.

$$\boldsymbol{C(s)} + \cancel{O_2(g)} \longrightarrow \cancel{CO_2(g)} \qquad \Delta H_1$$
$$\boldsymbol{2S(s)} + \cancel{2O_2(g)} \longrightarrow \cancel{2SO_2(g)} \qquad 2\Delta H_2$$
$$\cancel{CO_2(g)} + \cancel{2SO_2(g)} \rightarrow \boldsymbol{CS_2(l)} + \cancel{3O_2(g)} \quad -\Delta H_3$$

$$\Delta H^{\theta}_{f,CS_2(l)} = \Delta H_1 + 2\Delta H_2 - \Delta H_3$$
$$= -393.30 + (2 \times -293.72\ ) - (-1108.76)$$
$$= \boldsymbol{+128.02\ kJmol^{-1}}$$

3. **Given that the enthalpy of combustion of ethyne is $-1260\ kJmol^{-1}$ and the enthalpy of combustion of ethanal is $-1160 kJmol^{-1}$Calculate the heat change of the reaction;**

$$\boldsymbol{C_2H_2(g) + H_2O(l) \longrightarrow CH_3CHO(l)}$$

Equation for the reaction required;

$$\boldsymbol{C_2H_2(g) + H_2O(l) \longrightarrow CH_3CHO(l)} \qquad \Delta H^{\theta}_{rxn} = ?$$

Equations for reactions given;

(i) $C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l) \qquad \Delta H_1 = -1260\ kJmol^{-1}$

(ii) $CH_3CHO(l) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l) \quad \Delta H_2 = -1160\ kJmol^{-1}$

The required equation is obtained by simply adding equation (i) to a reversed equation (ii). The same treatment is done to the ΔH values.

$$\boldsymbol{C_2H_2(g)} + \cancel{\tfrac{5}{2}O_2(g)} \longrightarrow \cancel{2CO_2(g)} + \cancel{H_2O(l)} \quad \Delta H_1$$
$$\cancel{2CO_2(g)} + \cancel{2}\boldsymbol{H_2O(l)} \rightarrow \boldsymbol{CH_3CHO(l)} + \cancel{\tfrac{5}{2}O_2(g)} - \Delta H_2$$

$$\Delta H^{\theta}_{rxn} = \Delta H_1 - \Delta H_2$$
$$= -1260 - (-1160\ )$$
$$= \boldsymbol{-100\ kJmol^{-1}}$$

4. **Given that the ;**

Enthalpy of combustion of ethanol is $-1371\ kJmol^{-1}$

Enthalpy of formation of carbon dioxide gas is $-393\ kJmol^{-1}$

Enthalpy of formation of water is $-286\ kJmol^{-1}$.

Use the above information to calculate the heat of formation of ethanol

Equation for the reaction required;

$$\boldsymbol{2C(s) + 3H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow CH_3CH_2OH(l)} \quad \Delta H^{\theta}_{f,C_2H_5OH(l)} = ?$$

Equations for reactions given;

(i) $CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H_1 = -1371\ kJmol^{-1}$

(ii) $C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_2 = -393\ kJmol^{-1}$

(iii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_3 = -286\ kJmol^{-1}$

The required equation is obtained by adding all the three equations after equation (i) is reversed, equation (ii) multiplied by 2 and equation (iii) multiplied by 3. The same treatment is done to the ΔH values..

$$\cancel{2CO_2(g)} + \cancel{3H_2O(l)} \rightarrow \boldsymbol{CH_3CH_2OH(l)} + \cancel{3O_2(g)} - \Delta H_1$$
$$\boldsymbol{2C(s)} + \cancel{2O_2(g)} \longrightarrow \cancel{2CO_2(g)} \qquad 2\Delta H_2$$
$$\boldsymbol{3H_2(g)} + \cancel{\tfrac{1}{2}}\tfrac{3}{2}\boldsymbol{O_2(g)} \longrightarrow \cancel{3H_2O(l)} \qquad 3\Delta H_3$$

$$\Delta H^{\theta}_{f,C_2H_5OH(l)} = -\Delta H_1 + 2\Delta H_2 + 3\Delta H_3$$
$$= -(-1371) + (2 \times -393\ ) + (3 \times -286)$$
$$= +1371 - 1644 = \boldsymbol{-273\ kJmol^{-1}}$$

5. The standard enthalpies of combustion of some substances are given below.

Substance	$\Delta H_c^\theta\ (kJmol^{-1})$
Hydrogen	**-286**
Benzene	**-3268**
Cyclohexene	**-3752**
Cyclohexane	**-3920**

(a) **Calculate the enthalpy of hydrogenation of;**

(i) Cyclohexene

(ii) Benzene

(b) **Using the two values in a(i) and (ii) above , explain the relative stability of benzene**.

(a) (i) *Equation for the reaction required;*

$$\boldsymbol{C_6H_{10}(l) + H_2(g) \longrightarrow C_6H_{12}(l)} \qquad \Delta H^\theta_{\substack{hydration \\ C_6H_{10}}} = ?$$

Equations for reactions required;

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_1 = -286\ kJmol^{-1}$$

$$C_6H_{10}(l) + \tfrac{17}{2}O_2(g) \longrightarrow 6CO_2(g) + 5H_2O(l) \qquad \Delta H_2 = -3752\ kJmol^{-1}$$

$$C_6H_{12}(l) + 9O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta H_3 = -3920\ kJmol^{-1}$$

The required equation is obtained by simply adding equation (i), equation (ii) and a reversed equation (iii). The same treatment is done to the ΔH values.

$$\boldsymbol{H_2(g)} + \cancel{\tfrac{1}{2}O_2(g)} \longrightarrow \cancel{H_2O(l)} \qquad \boldsymbol{\Delta H_1}$$

$$\boldsymbol{C_6H_{10}(l)} + \cancel{\tfrac{17}{2}O_2(g)} \longrightarrow \cancel{6CO_2(g)} + \cancel{5H_2O(l)} \qquad \boldsymbol{\Delta H_2}$$

$$\cancel{6CO_2(g)} + \cancel{6H_2O(l)} \longrightarrow \boldsymbol{C_6H_{12}(l)} + \cancel{9O_2(g)} \qquad \boldsymbol{-\Delta H_3}$$

$$\boldsymbol{\Delta H^\theta_{\substack{hydration \\ C_6H_{10}}} = \Delta H_1 + \Delta H_2 - \Delta H_3}$$

$$= -286 - 3752 - (-3920\ )$$

$$\boldsymbol{= -118\ kJmol^{-1}}$$

(ii) *Equation for the reaction required;*

$$\boldsymbol{C_6H_6(l) + 3H_2(g) \longrightarrow C_6H_{12}(l)} \qquad \Delta H^\theta_{\substack{hydration \\ C_6H_6}} = ?$$

Equations for reactions required;

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_1 = -286\ kJmol^{-1}$$

$$C_6H_6(l) + \tfrac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l) \qquad \Delta H_2 = -3268\ kJmol^{-1}$$

$$C_6H_{12}(l) + 9O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta H_3 = -3920\ kJmol^{-1}$$

The required equation is obtained by adding equation (i) multiplied by 3 to equation (ii) and a reversed equation (iii). The same treatment is done to the ΔH values.

$$\boldsymbol{3H_2(g)} + \cancel{\tfrac{3}{2}O_2(g)} \longrightarrow \cancel{3H_2O(l)} \qquad \boldsymbol{3\Delta H_1}$$

$$\boldsymbol{C_6H_6(l)} + \cancel{\tfrac{15}{2}O_2(g)} \longrightarrow \cancel{6CO_2(g)} + \cancel{3H_2O(l)} \qquad \boldsymbol{\Delta H_2}$$

$$\cancel{6CO_2(g)} + 6\cancel{H_2O(l)} \longrightarrow \boldsymbol{C_6H_{12}(l)} + 9O_2\cancel{(g)} \qquad \boldsymbol{-\Delta H_3}$$

$$\boldsymbol{\Delta H^\theta_{\substack{hydration \\ C_6H_6}} = 3\Delta H_1 + \Delta H_2 - \Delta H_3}$$

$$= (3 \times -286) + (-3268) - (-3920\ )$$

$$\boldsymbol{= -206\ kJmol^{-1}}$$

(b) *Cyclohexene has* $\boldsymbol{one\ localized\ \pi - bond}$ *and its hydrogenation to form cyclohexane evolves* $-118\ kJmol^{-1}$*. If the* ***three double bonds in benzene where localized****, the enthalpy of hydrogenation of benzene would be* $(\mathbf{3 \times -118}) = \mathbf{-354\ kJmol^{-1}}$*. The enthalpy of hydrogenation of benzene is however* $-206\ kJmol^{-1}$*. The* ***difference of*** $\mathbf{148\ kJmol^{-1}}$ *is due to the* ***delocalization energy/ resonance energy*** *of benzene since it has* ***three delocalised*** $\boldsymbol{\pi - bonds}$*.*

Questions

1. Calculate the enthalpy of formation of methane given that its enthalpy of combustion is $-891\ kJmol^{-1}$ and the enthalpy of formation of carbon dioxide and water are $-286\ kJmol^{-1}$ and $-393\ kJmol^{-1}$respectively.
2. Calculate the enthalpy of formation of carbon monoxide given that the enthalpy of combustion of carbon is $-393\ kJmol^{-1}$, and the enthalpy of combustion of carbon monoxide is$-286\ kJmol^{-1}$.
3. Calculate the standard enthalpy of formation of propane if its standard enthalpy of combustion is $-2213\ kJmol^{-1}$ and the standard enthalpies of combustion of carbon and hydrogen are $-393 kJmol^{-1}$ and $-286 kJmol^{-1}$ respectively.
4. Use the data given below to find the standard enthalpy change for the reaction below at 298K;

$$\boldsymbol{CO(g) + 2H_2(g) \longrightarrow CH_3OH(l)}$$

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^{\theta} = -283.0\ kJmol^{-1}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^{\theta} = -285.8\ kJmol^{-1}$$

$$CH_3OH(l) + 1\tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \quad \Delta H^{\theta} = -715.0\ kJmol^{-1}$$

5. Given the following enthalpy values under standard conditions ;

Heat of combustion of hydrogen gas $= -285.8\ kJmol^{-1}$

Heat of combustion of carbon (graphite) $= -393.5\ kJmol^{-1}$

Heat of combustion of methane $= -890.0\ kJmol^{-1}$

Heat of combustion of ethane $= -1560.0\ kJmol^{-1}$

Heat of formation of propane $= -103.8\ kJmol^{-1}$

Determine the enthalpy of the reaction;

$$C_3H_8(g) + H_2(g) \longrightarrow C_2H_6(g) + CH_4(g)\ at\ 25°C$$

6. Calculate the standard enthalpy of formation of ethene using the following information.

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\theta = -286\ kJmol^{-1}$$
$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\theta = -384\ kJmol^{-1}$$
$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + H_2O(l) \quad \Delta H^\theta = -1411\ kJmol^{-1}$$

7. (a) The enthalpies of some reactions are given below;

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\theta = -393.5\ kJmol^{-1}$$
$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\theta = -285.9\ kJmol^{-1}$$
$$C_6H_5OH(g) + 7O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l) \quad \Delta H^\theta = -3009\ kJmol^{-1}$$

Calculate the standard enthalpy of formation of phenol from its elements.

(b)From your answer in (a) above, state whether phenol is a stable compound or not. Give a reason for your answer.

(c) Write equation(s) to show how phenol can be synthesised from chlorobenzene

8. If the enthalpies of combustion of ethane, ethene and hydrogen are $1323, 1429\ and\ 242\ kJmol^{-1}$. Calculate the enthalpy of hydrogenation of ethene.
9. (a) Define heat of reaction

   (b) Calculate the standard enthalpy of hydrogenation of ethene using the following information.

$$C_2H_6(g) + 3\tfrac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H^\theta = -1550\ kJmol^{-1}$$
$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + H_2O(l) \qquad \Delta H^\theta = -1390\ kJmol^{-1}$$
$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\theta = -285.8\ kJmol^{-1}$$

10. Calculate the standard enthalpy of hydrogenation of ethyne using the following thermochemical data.

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + H_2O(l) \qquad \Delta H^\theta = -1390\ kJmol^{-1}$$
$$C_2H_2(g) + 2\tfrac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l) \quad \Delta H^\theta = -1310\ kJmol^{-1}$$
$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\theta = -285\ kJmol^{-1}$$

11. Calculate the standard enthalpy of formation of ethene using the following information using the following information;

Enthalpy of combustion of ethane is $-1393\ kJmol^{-1}$
Enthalpy of combustion of hydrogen is $-286\ kJmol^{-1}$
Enthalpy of combustion of carbon is $-393\ kJmol^{-1}$

Calculating heats of combustion from other experimental data

Examples

1. **When 2 g of ethane is burnt in excess oxygen, $\mathbf{100\ kJ}$ of heat is liberated. Calculate the enthalpy of combustion of ethane**.

$$molar\ mass\ of\ CH_3CH_3 = 24 + 6 = 30g$$
$$2g\ of\ CH_3CH_3\ liberate\ 100\ kJ\ of\ heat$$
$$30g\ of\ CH_3CH_3\ liberate\ \left(\frac{30 \times 100}{2}\right)\ kJ\ of\ heat$$
$$=\ 1500\ kJ\ of\ heat$$
$$\boldsymbol{The\ enthalpy\ of\ combustion\ of\ ethane\ is - 1500\ kJ}$$

2. **The table below shows the values for standard enthalpies of formation of benzoic acid, carbon dioxide and water in $\boldsymbol{kJmol^{-1}}$. Use the data to calculate the enthalpy of combustion of benzoic acid.**

Compound	$\boldsymbol{C_6H_5COOH(s)}$	$\boldsymbol{CO_2(g)}$	$\boldsymbol{H_2O(l)}$
$\Delta \boldsymbol{H_f^{\theta}(kJmol^{-1})}$	$\mathbf{-408}$	$\mathbf{-393}$	$\mathbf{-286}$

$$\boldsymbol{C_6H_5COOH(s) + \frac{15}{2}O_2(g) \longrightarrow 7CO_2(g) +\ 3H_2O(l)}$$
$$\Delta H^{\theta}{}_{\underset{\boldsymbol{C_6H_5COOH}}{C}} = \sum \Delta H^{\theta}_{f\ products} - \sum \Delta H^{\theta}_{f\ reactants}$$
$$= \left[\left(7\Delta H_f^{\theta} CO_2\right) + (3\Delta H_f^{\theta} H_2O)\right] - \left[(\Delta H_f^{\theta} C_6H_5COOH) + (\frac{15}{2}\Delta H_f^{\theta} O_2)\right]$$
$$= [(7 \times -393) + (3 \times -286)] - \left[(-408) + (\frac{15}{2} \times 0)\right]$$
$$= (-3609) - (-408)$$
$$= \boldsymbol{-3201\ kJmol^{-1}}$$

3. **Calculate the enthalpy of combustion of benzene if the enthalpy of combustion of carbon is $\boldsymbol{-393\ kJmol^{-1}}$, enthalpy of formation of benzene is $\boldsymbol{+82.84\ kJmol^{-1}}$, and enthalpy of formation of water is $\boldsymbol{-285\ kJmol^{-1}}$.**

Equation for the reaction required;

$$\boldsymbol{C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)} \qquad \boldsymbol{\Delta H^{\theta}{}_{\underset{C_6H_6}{C}}} = ?$$

Equations for reactions required;

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_1 = -393\ kJmol^{-1}$$
$$6C(s) + 3H_2(g) \longrightarrow C_6H_6(l) \qquad \Delta H_2 = +82.84\ kJmol^{-1}$$
$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_3 = -285\ kJmol^{-1}$$

The required equation is obtained by adding equation (i) multiplied by 6 to a reversed equation (ii) and equation (iii) multiplied 3. The same treatment is done to the ΔH values.

$$\cancel{6C(s)} + 6O_2(g) \longrightarrow 6CO_2(g) \qquad 6\Delta H_1$$
$$C_6H_6(l) \longrightarrow \cancel{6C(s)} + \cancel{3H_2(g)} \qquad -\Delta H_2$$
$$\cancel{3H_2(g)} + \frac{3}{2}O_2(g) \longrightarrow 3H_2O(l) \qquad 3\Delta H_3$$

$$\Delta H^{\theta}{}_{C}{}_{C_6H_6} = 6\Delta H_1 - \Delta H_2 + 3\Delta H_3$$
$$= (6 \times -393) - (+82.84) + (3 \times -285\ )$$
$$= -3295.84\ kJmol^{-1}$$

Questions

1. When 1 g of graphite is burnt in excess oxygen, 32 kJ of heat is liberated. Calculate the enthalpy of combustion of graphite.
2. Calculate the standard enthalpy of combustion of propene using the following information.

(i) $C_3H_6(g) + H_2(g) \longrightarrow C_3H_8(g) \qquad \Delta H^{\theta} = -124\ kJmol^{-1}$

(ii) $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l) \qquad \Delta H^{\theta} = -2220\ kJmol^{-1}$

(iii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^{\theta} = -285.5\ kJmol^{-1}$

3. Calculate the standard enthalpy of combustion of ethene if the enthalpy of combustion of carbon is $-393\ kJmol^{-1}$, standard enthalpy of formation of ethene is $+52.3\ kJmol^{-1}$, and standard enthalpy of combustion of hydrogen is $-286\ kJmol^{-1}$.
4. The table below shows the values for standard enthalpies of formation of water, carbon dioxide and benzene in $kJmol^{-1}$. Use the data to calculate the enthalpy of combustion of benzene.

Compound	$H_2O(l)$	$CO_2(g)$	$C_6H_6(l)$
$\Delta H_f^{\theta}(kJmol^{-1})$	-285.9	-393.7	$+49$

5. (a) State what is meant by the terms;

(i) ***Standard enthalpy of formation of a substance***

(ii) ***Standard enthalpy of combustion of a substance***

(b) Use the data below to calculate the standard enthalpy of combustion of ethanol.

$$\Delta H_f^{\theta}\ for\ liquid\ ethanol = -277.0\ kJmol^{-1}$$
$$\Delta H_f^{\theta}\ for\ carbon\ dioxide\ gas = -393.7\ kJmol^{-1}$$
$$\Delta H_f^{\theta}\ for\ liquid\ water = -285.9\ kJmol^{-1}$$

Application of heat of combustion in real life situation

- Burning of wood or charcoal to release energy during cooking
- Petrol and diesel cars rely on combustion to release the engine driving energy
- Gas cookers use alkane gases for combustion

The fuel values of various fuels

The fuel value of a fuel is the amount of heat released during its combustion. It is also referred to as heat or energy or calorific value. The table below fuel values of various fuels in kilo Joules per kilogram.

Fuel	**Fuel value** $(\mathbf{kJkg^{-1}})$
Hydrogen	141,700
Methane	55,500
Natural gas	50,840
Propane	50,000
Butane	49,300
Petrol/ gasoline	46,940
Kerosene	46,200
Diesel	45,600
Crude oil	45,300
Butanol	37,300
Ethanol	29,700
Charcoal	29,600
Coke	28,400
Coal	27.05
Methanol	22,700
Wood	19,800

The higher the fuel value, the more valuable the fuel.

Enthalpy of neutralisation

Enthalpy of neutralisation is the heat evolved in the reaction between that mass of an acid which provides one mole of hydrogen ions and that mass of an alkali which provides one mole of hydroxyl ions.

When enthalpy of neutralisation is determined under standard conditions ($298K \ and \ 1 \ atm$), it is called **standard enthalpy of neutralisation**.

Standard enthalpy of neutralisation (ΔH_n^θ)

Standard enthalpy of neutralisation ΔH_n^θ, is the heat evolved when one mole of an acid reacts with one mole of a base to form one mole of water at 298K and 1 atmosphere.

Neutralisation is the formation of water from hydrogen ions and water.

$$H^+(aq) + \bar{O}H(aq) \longrightarrow H_2O(l)$$

The enthalpy of neutralisation is **exothermic**.

The enthalpies of nuetralisation of strong acids and strong alkalis are approximately constant about a value of $-57.3\ kJmol^{-1}$.

Experiment to determine enthalpy of neutralisation between a strong acid and strong alkali

(for example nitric acid and potassium hydroxide)

Describe an experiment to determine enthalpy of neutralisation of nitric acid by potassium hydroxide.

A ***known volume, $V\ cm^3$*** of ***nitric acid*** of ***known concentration, M*** is measured and placed in a ***plastic beaker***.

The ***initial temperature of the acid solution, T_1°C*** is noted from the ***thermometer***.

An ***equal volume, $V\ cm^3$*** of ***potassium hydroxide*** solution of the ***same concentration, M*** is also measured into another plastic beaker.

The ***initial temperature of potassium hydroxide solution, T_2°C*** is also noted from the clean and dried thermometer.

The ***two solutions are added together*** carefully, as fast as possible while ***stirring*** and the ***maximum temperature, T_3°C*** attained is noted.

Assumptions

The solution has the same specific heat capacity as water $= 4.2Jg^{-1}°C^{-1}$

Heat loss to the surroundings is negligible

Heat capacity of the beaker is negligible

Density of solution is $1gcm^{-3}$

Treatment of results

$$Initial\ temperature\ of\ nitric\ acid = T_1°C$$

$$Initial\ temperature\ of\ potassium\ hydroxide = T_2°C$$

$$Average\ initial\ temperature\ of\ solution = \left(\frac{T_1 + T_2}{2}\right)°C$$

$$Temperature\ rise = \Delta T = \left[T_3 - \left(\frac{T_1 + T_2}{2}\right)\right]°C$$

$$Total\ volume\ of\ solution = (V + V) = 2V\ cm^3$$

$$Total\ mass\ of\ solution = (volume \times density) = (2V \times 1) = 2V\ g$$

$$Heat\ change = mass\ of\ solution \times specific\ heat\ capacity \times temperature\ rise$$

$$Heat\ change = (2V \times 4.2 \times \Delta T)J$$

$$Moles\ of\ nitric\ acid\ nuetralised = \left(\frac{V \times M}{1000}\right)$$

$$\left(\frac{V \times M}{1000}\right) moles\ of nitric\ acid\ evolve (2V \times 4.2 \times \Delta T)$$

$$1\ mole\ of nitric\ acid\ evolves\ \left(\frac{1000 \times 2V \times 4.2 \times \Delta T}{V \times M}\right) J$$

$$Enthalpy\ of\ neutralisation = -\left(\frac{1000 \times 2V \times 4.2 \times \Delta T}{V \times M}\right) Jmol^{-1}$$

$$\boldsymbol{Enthalpy\ of\ neutralisation = -\left(\frac{2V \times 4.2 \times \Delta T}{V \times M}\right) kJmol^{-1}}$$

Describe an experiment to determine enthalpy of neutralisation of sulphuric acid by sodium hydroxide.

A ***known volume, V*** $\boldsymbol{cm^3}$ of ***sulphuric acid*** of ***known concentration, M*** is measured and placed in a ***plastic beaker***.
The ***initial temperature of the solution,*** $\boldsymbol{T_1 °C}$ is noted from the ***thermometer***.
$\boldsymbol{2V\ cm^3}$ of ***sodium hydroxide*** solution of the ***same concentration, M*** is also measured into another plastic beaker.
The ***initial temperature of sodium hydroxide solution,*** $\boldsymbol{T_2 °C}$ is also noted from the clean and dried thermometer.
The ***two solutions are added together*** carefully, as fast as possible while ***stirring*** and the ***maximum temperature,*** $\boldsymbol{T_3 °C}$ attained is noted.

Assumptions

The solution has the same specific heat capacity as water $\boldsymbol{= 4.2 Jg^{-1} °C^{-1}}$
Heat loss to the surroundings is negligible
Heat capacity of the beaker is negligible
Density of solution is $\boldsymbol{1gcm^{-3}}$

Treatment of results

$$Initial\ temperature\ of\ \ sulphuric\ acid = T_1 °C$$

$$Initial\ temperature\ of\ sodium\ hydroxide\ \ = T_2 °C$$

$$Average\ initial\ temperature\ of\ solution = \left(\frac{T_1 + T_2}{2}\right) °C$$

$$Temperature\ rise = \Delta T = \left[T_3 - \left(\frac{T_1 + T_2}{2}\right)\right] °C$$

$$Total\ volume\ of\ solution = (V + 2V) = 3V\ cm^3$$

$$Total\ mass\ of\ solution = (volume\ \times density) = (3V \times 1) = 3V\ g$$

$$Heat\ change = mass\ of\ solution \times specific\ heat\ capacity \times temperature\ rise$$

$$Heat\ change = (3V \times 4.2 \times \Delta T) J$$

$$Moles\ of\ sulphuric\ acid\ neutralised = \left(\frac{V \times M}{1000}\right)$$

$$\left(\frac{V \times M}{1000}\right) moles\ of sulphuric\ acid\ evolve (3V \times 4.2 \times \Delta T)$$

$$1\ mole\ of sulphuric\ acid\ evolves\ \left(\frac{1000 \times 3V \times 4.2 \times \Delta T}{V \times M}\right) J$$

$$Enthalpy\ of\ neutralisation = -\left(\frac{1000 \times 3V \times 4.2 \times \Delta T}{V \times M}\right) Jmol^{-1}$$

$$\boldsymbol{Enthalpy\ of\ neutralisation = -\left(\frac{3V \times 4.2 \times \Delta T}{V \times M}\right) kJmol^{-1}}$$

Calculations on enthalpy of neutralisation

Example

1. **$250\ cm^3$ of $0.5M$ potassium hydroxide at 12℃ were mixed in a plastic beaker of negligible heat capacity with an equal volume of $0.5M$ hydrochloric acid at the same temperature. If the final temperature was 15.4℃ . Calculate the enthalpy of neutralization of potassium hydroxide and hydrochloric acid from the following data.**
   ($\boldsymbol{Assume\ the\ density\ of\ the\ solution\ is\ 1.00gcm^{-3}\ and\ its\ specific\ heat\ capacity\ is\ 4.2\ JK^{-1}g^{-1}}$)

$$Initial\ temperature\ of\ \ KOH\ solution = 12°C$$

$$Initial\ temperature\ of\ HCl\ solution\ = 12°C$$

$$Average\ initial\ temperature\ of\ solution = \left(\frac{12 + 12}{2}\right) = 12°C$$

$$Temperature\ rise = (15.4 - 12) = 3.4°C$$

$$Total\ volume\ of\ solution = (250 + 250) = 500\ cm^3$$

$$Total\ mass\ of\ solution = (volume\ \times density) = (500 \times 1.00) = 500\ g$$

$$Heat\ change = mass\ of\ solution \times specific\ heat\ capacity \times temperature\ rise$$

$$Heat\ change = (500 \times 4.2 \times 3.4) = 7140\ Joules$$

$$Moles\ of\ base\ neutralised = \left(\frac{250 \times 0.5}{1000}\right) = 0.125$$

$$0.125\ moles\ of KOH\ evolve\ \ 7140\ J\ of\ heat$$

$$1\ mole\ of KOH\ evolves\ \left(\frac{1 \times 7140}{0.125}\right) J$$

$$Enthalpy\ of\ neutralisation = -57120\ J$$

$$\boldsymbol{Enthalpy\ of\ neutralisation = -57.12\ kJmol^{-1}}$$

Questions

1. 25.0 cm^3 of 1.0M hydrochloric acid at 25.1°C were placed in a plastic cup. 25.0 cm^3 of 1.0M sodium hydroxide at 25.1°C were added, the mixture stirred and the temperature rose to 28.2°C. Calculate the enthalpy of neutralisation.
   ($Assume\ the\ density\ of\ each\ solution\ is\ 1.00gcm^{-3}\ and\ the\ specific\ heat\ capacity\ of\ each\ solution\ is\ 4.18JK^{-1}g^{-1}$)

2. $50.0\,cm^3$ of $0.500\,moldm^{-3}$ sodium hydroxide solution and $50.0\,cm^3$ of $0.500\,moldm^{-3}$ nitric acid, both at $20.0°C$ were mixed and stirred in a calorimeter with negligible heat capacity. The temperature of the mixture rose to $23.2°C$. Calculate the enthalpy of neutralisation.
   $(Assume\ the\ density\ of\ the\ solution\ is\ 1.00gcm^{-3}\ and\ the\ specific\ heat\ capacity\ of\ the\ solution\ is\ 4.2JK^{-1}g^{-1})$
3. (a) $50.0\,cm^3$ of $0.2\,M$ potassium hydroxide solution required $20.0\,cm^3$ of $0.25\,M$ sulphuric acid for neutralisation in a calorimeter with negligible heat capacity.. If the temperature rise was $2.0°C$. Calculate the standard enthalpy of neutralisation of potassium hydroxide by sulphuric acid.
   $(Assume\ the\ density\ of\ the\ solution\ is\ 1.0gcm^{-3}\ and\ the\ specific\ heat\ capacity\ of\ the\ solution\ is\ 4.18JK^{-1}g^{-1})$

The difference between heat of neutralisation between strong acid and strong alkali and weak acid and strong alkali

Strong acid and strong alkali

The enthalpy of neutralisation of any strong acid and any strong alkali is ***approximately constant at about*** $\boldsymbol{-57\,kJmol^{-1}}$. This is because strong acids and strong alkalis and the salts they form, are ***completely ionised in dilute solution***. The ***only reaction that takes place is that between hydrogen ions and hydroxyl ions to form water***.

$$H^+(aq) + \bar{O}H(aq) \longrightarrow H_2O(l)$$

Weak acid and strong alkali

The enthalpy of neutralisation of any weak acid and strong alkali is ***lower than*** $\boldsymbol{-57\,kJmol^{-1}}$. This is because for a weak acid and weak alkali, ***some of the heat produced due to neutralisation*** is ***used for further ionisation of the weak acid***. This further ionisation is ***endothermic***.

The table below shows enthalpies of neutralisation between different acids and alkalis

Acid	Alkali	$\Delta H_n^\theta(kJmol^{-1})$
$\boldsymbol{HF}$	$NaOH$	-68.6
$\boldsymbol{HCl}$	$NaOH$	-57.3
$\boldsymbol{HCl}$	KOH	-57.3
$\boldsymbol{HNO_3}$	$NaOH$	-57.1
$\boldsymbol{HNO_3}$	KOH	-57.3
$\boldsymbol{HNO_3}$	$\frac{1}{2}Ca(OH)_2$	-58.4

$\frac{1}{2}H_2SO_4$	$NaOH$	-57.1
HCl	$NH_3(aq)$	-51.5
HCN	$NaOH$	-12.0

The enthalpy of neutralisation of sodium hydroxide by nitric acid is $-57.1\ kJmol^{-1}$ whereas the enthalpy of neutralisation of sodium hydroxide by hydrocyanic acid is $-12.0\ kJmol^{-1}$.

*Sodium hydroxide is a **strong base** and nitric acid is a **strong acid** hence completely ionise in dilute solution. The sodium chloride formed is also **completely ionised** in dilute solution. The **only reaction involved is between hydrogen ions and hydroxyl ions** to form water.*

$$H^+(aq) + \bar{O}H(aq) \longrightarrow H_2O(l)$$

*Hydrocyanic acid is a **weak acid**. Some of the heat is used for **further ionisation** of the weak acid which is **endothermic**.*

$$HCN(aq) \rightleftharpoons H^+(aq) + \bar{C}N(aq) \qquad \Delta H = +Q\ kJmol^{-1}$$

Enthalpy of displacement

This is the heat evolved when one mole of ions of a less electropositive element is displaced from its solution by a more electropositive element.

When enthalpy of displacement is determined under standard conditions ($298K$ and 1 atm), it is called **standard enthalpy of displacement**.

Standard enthalpy of displacement

Standard enthalpy of displacement is the heat evolved when one mole of ions of a less electropositive element is displaced from its solution by a more electropositive element at 298K and 1 atmosphere.

A displacement reaction is a **redox reaction**.
The enthalpy of displacement is **exothermic**.

Determination of enthalpy of displacement between zinc powder and copper(II) sulphate solution

A ***known volume*** (***$V\ cm^3$***) of ***copper(II) sulphate solution*** of a ***known concentration***(***$C\ moldm^{-3}$***) is put in a ***plastic beaker***
The ***initial temperature, T_1°C of the solution*** is measured and recorded from the ***thermometer***
An ***excess of zinc powder*** is added quickly and carefully to the solution while ***stirring***
The ***final steady temperature, T_2°C*** is read and recorded from the thermometer.

Assumptions:

Density of solution is equal to density of water $= \mathbf{1.0gcm^{-3}}$

Specific heat capacity of solution is equal to specific heat capacity of water

$$= \mathbf{4.2Jg^{-1}K^{-1}}$$

No heat is lost to the surroundings

Heat capacity of beaker is negligible

Treatment of results

$$Temperature\ rise = \Delta T = (T_2 - T_1)°C$$
$$Mass\ of\ solution = (volume\ \times density) = (V \times 1) = V\ g$$
$$Heat\ change = mass\ of\ solution \times specific\ heat\ capacity \times temperature\ rise$$
$$Heat\ change = \left(V \times 4.2 \times (T_2 - T_1)\right)J$$
$$Moles\ of\ copper(II)\ ions\ displaced = \left(\frac{V \times C}{1000}\right)$$
$$Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$$
$$\left(\frac{V \times C}{1000}\right)\ moles\ of\ Cu^{2+}\ are\ displaced\ with\ evolution\ of\ (V \times 4.2 \times \Delta T)J$$
$$1\ mole\ of\ Cu^{2+}\ is\ displaced\ with\ evolution\ of\ \left(\frac{1000 \times (V \times 4.2 \times \Delta T)}{V \times C}\right)J$$
$$Enthalpy\ of\ displacement\ of\ Cu^{2+} = -\left(\frac{1000 \times (V \times 4.2 \times \Delta T)}{V \times C}\right)Jmol^{-1}$$
$$\boldsymbol{Enthalpy\ of\ displacement\ of\ Cu^{2+} = -\left(\frac{(V \times 4.2 \times \Delta T)}{V \times C}\right)kJmol^{-1}}$$

Calculations involving heat of displacement

Example

1. **$50\ cm^3$ of $1.0M$ copper(II) chloride solution is poured in a polystyrene cup and the initial temperature of the solution is recorded as $28\ °C$. 4g of zinc powder is added to the solution and the mixture stirred. The highest temperature of the mixture was recorded as $69\ °C$. Calculate the heat of displacement of copper by zinc.**

$$(\boldsymbol{Density\ of\ the\ solution\ is\ 1.0gcm^{-3}\ and\ the\ specific\ heat\ capacity\ of\ the\ solution\ is\ 4.2J°C^{-1}g^{-1}})$$

$$Temperature\ rise = (69 - 28) = 41°C$$
$$Mass\ of\ solution = (volume\ \times density) = (50 \times 1) = 50\ g$$
$$Heat\ change = mass\ of\ solution \times specific\ heat\ capacity \times temperature\ rise$$
$$Heat\ change = (50 \times 4.2 \times 41) = 8610\ Joules$$
$$Moles\ of\ copper(II)\ ions\ displaced = \left(\frac{50 \times 1.0}{1000}\right) = 0.05$$
$$Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

$$0.05\ moles\ of\ Cu^{2+}\ are\ displaced\ with\ evolution\ of\ 8610\ J$$

$$1\ mole\ of\ Cu^{2+}\ is\ displaced\ with\ evolution\ of\ \left(\frac{1 \times 8610}{0.05}\right) J$$

$$Enthalpy\ of\ displacement\ of\ Cu^{2+}\ by\ zinc = -172{,}200 Jmol^{-1}$$

$$\boldsymbol{Enthalpy\ of\ displacement\ of\ Cu^{2+}\ = -172.2\ kJmol^{-1}}$$

Note; The zinc added is excess so that all the copper is displaced. So its mass is not involved in the calculation

Questions

1. Excess iron powder is added to $50\ cm^3$ copper(II) chloride solution of concentration $1.0\ moldm^{-3}$ at an initial temperature of $28.0\ °C$. If the temperature of the mixture rose to a maximum temperature of $57.0\ °C$.
   (i) State what was observed
   (ii) Calculate the heat of displacement of copper by iron. $(Density\ of\ the\ solution\ is\ 1.0gcm^{-3}\ and\ the\ specific\ heat\ capacity\ of\ the\ solution\ is\ 4.2J°C^{-1}g^{-1})$
2. In an experiment to determine heat of displacement of iron by magnesium, excess magnesium powder is added to $50\ cm^3$ of $0.2M$ iron(II) sulphate solution at an initial temperature of $30.5\ °C$. If the temperature of the mixture rose to a maximum temperature of $40.0\ °C$. Calculate the heat of displacement of iron by magnesium. $(Density\ of\ the\ solution\ is\ 1.0gcm^{-3}\ and\ the\ specific\ heat\ capacity\ of\ the\ solution\ is\ 4.2J°C^{-1}g^{-1})$

Atomisation energy

This is the heat absorbed when an element in its normal physical state is converted into one mole of free gaseous atoms.

Standard enthalpy of atomisation (ΔH_a^θ)

This is the heat absorbed when an element in its normal physical state is converted into one mole free gaseous atoms at 1 atmosphere and 298K.

Or ***This is the heat absorbed when a compound in its normal physical state is converted into free gaseous atoms at 1 atmosphere and 298K.***

The table below shows values of standard enthalpies of atomization for some elements.

Element	$\Delta H_a^\theta (kJmol^{-1})$
$Na(s) \longrightarrow Na(g)$	+109
$C(graphite) \longrightarrow C(g)$	+715
$\frac{1}{2}H_2(g) \longrightarrow H(g)$	+218
$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$	+121

The values shown above show the enthalpy of formation of one mole of the gaseous monoatomic element in its standard state.

For a compound, for example butanol, atomization can be shown as below;

$$C_4H_9OH(l) \longrightarrow 4C(g) + 10H(g) + O(g) \qquad \Delta H_a^\theta(positive)$$

Standard enthalpy of sublimation

The standard enthalpy of sublimation is the heat absorbed when one mole of an element in its <u>solid state</u> is converted to <u>one mole free gaseous atoms</u> at 1 atmosphere and 298K.

Enthalpy of sublimation is equal to enthalpy of atomization but only for solid elements.

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.

$$X(g) \longrightarrow X^+(g) + e \qquad \Delta H = First\ ionisation\ energy$$
$$X^+(g) \longrightarrow X^{2+}(g) + e \qquad \Delta H = Second\ ionisation\ energy$$

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

For example formation of a free gaseous sodium ion from a free gaseous sodium atom involves removal of one electron against the nuclear attraction.

$$Na(g) \longrightarrow Na^+(g) + e \qquad \Delta H = 502\ kJmol^{-1}$$

Electron affinity

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

$$X(g) + e \longrightarrow X^-(g) \qquad \Delta H = negative$$

This enery is called **first electron affinity**.

First electron affinity *is the energy given out when* ***one mole*** *of electron<u>s</u> combines with* ***one mole*** *of gaseous atom<u>s</u> to form* ***one mole*** *of uninegatively charged gaseous ion<u>s</u>*

<u>or</u>

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)

For chlorine, it can be represented as;

$$Cl(g) + e \longrightarrow Cl^-(g) \qquad \Delta H = -365\ kJmol^{-1}$$

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)

$$X^-(g) + e \longrightarrow X^{2-}(g) \qquad \Delta H = positive$$

For the case of Sulphur the values of first and second electron affinities are given below

$$S(g) + e \longrightarrow S^-(g) \qquad \Delta H = -200\ kJmol^{-1}$$

$$S^-(g) + e \longrightarrow S^{2-}(g) \qquad \Delta H = +848\ kJmol^{-1}$$

The reasons for second electron affinity being endothermic are explained in the topic: Atomic structure and the Periodic Table **(Page 195)**

Lattice energy

This is the heat given out when one mole of an ionic solid is formed from its component gaseous ions under standard conditions.

For example solid sodium is formed from gaseous sodium ions and gaseous chloride ion

$$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s) \qquad \Delta H = -788\ kJmol^{-1}$$

Lattice energy can also be defined as the heat absorbed when one mole of an ionic solid is broken down into its component gaseous ions.

$$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g) \qquad \Delta H = +788\ kJmol^{-1}$$

Factors affecting lattice energy

(i) Ionic charges.

The higher the product of ionic charges, the higher the lattice energy because of the strong electrostatic forces of attraction between the oppositely charged ions. ***This explains why magnesium oxide has a higher (more exothermic) lattice enthalpy than sodium chloride yet both compounds have the same molecular structure.***

(ii) Ionic radius.

The smaller the ***cationic radius***, the higher the lattice energy because the cations will strongly attract the anions because of the increased effective nuclear charge .

The smaller the ***anionic radius***, the higher the lattice energy because the cations will strongly attract the anions.

In summary, lattice enthalpy is directly proportional to the product of ionic charges but inversely proportional to the sum of ionic radii.

$$lattice\ enthalpy \propto \frac{(charge\ of\ cation) \times (charge\ of\ anion)}{sum\ of\ ionic\ radii}$$

Examples

1. **The values of lattice energies of potassium halides are given below.**

Formula of halide	KF	KCl	KBr	KI
Lattice energy(kJmol^{-1})	-813	-710	-671	-643

Explain the trend in these values for the potassium halides.

*The lattice energies of the halides **decrease (become less exothermic) from potassium fluoride to potassium iodide**. This is because the **anionic radius increases** from the **fluoride ion to the iodide ion**. The halide anions therefore **become less attracted by the potassium ion**. Thus a **decreasing amount of energy is evolved** when the **potassium halides are formed from the free gaseous ions**.*

2. **The values of lattice energies of sodium chloride and magnesium chloride are given below.**

Formula of chloride	$NaCl$	$MgCl_2$
Lattice energy(kJmol^{-1})	-788	-2525

Explain the difference in the two values.

*Magnesium chloride has a **higher (more exothermic)** lattice energy than sodium chloride.*

*This is because the magnesium ion has a **higher ionic charge** and **smaller ionic radius**, than the sodium ion. The magnesium ion therefore **strongly attracts the chloride ion more than the sodium ion does**. Therefore greater amount energy is evolved when solid magnesium chloride is formed into gaseous ions than sodium chloride.*

Standard enthalpy of hydration

When an ionic solid is dissolved in water, the ions are first separated from the ionic lattice. The energy involved in this process is called the ***lattice dissociation enthalpy***.

The separate ions then interact with water molecules. The positive ions are attracted to the negative end of the water molecules and the negative ions are attracted to the positive end of the water molecules. Energy is released during this process and is called the **enthalpy of hydration or solvation**.

$$NaCl(s) \xrightarrow{\Delta H_{lattice}} Na^+(g) + Cl^-(g) \xrightarrow{\Delta H_{hydration}} Na^+(aq) + Cl^-(aq)$$

Enthalpy of hydration is the heat given out when one mole of gaseous ions is completely surrounded by water molecules to form an infinitely dilute solution with no change in pH.

Enthalpy of hydration is **exothermic** hence always a **negative value**.

Factors affecting enthalpy of hydration

(i) Ionic radius

The smaller the ionic radius, the higher the hydration energy because the forces of attraction between ions for water molecules are strong.

(ii) Ionic charge

The higher the ionic charge , the higher the hydration energy because the forces of attraction for water molecules is strong.

Which of the metal ions Na^{+}, Mg^{2+} and $Al^{3+}$is likely to have the highest hydration energy? Give a reason.

The aluminium ion has the highest hydration energy because it has the highest ionic charge, smallest ionic radius, highest charge density and highest polarizing power. The ion is easily hydrated and therefore strongly attracts very many water molecules hence giving off the highest amount of energy.

Calculations involving enthalpy of hydration

The table below shows the enthalpies of hydration of some ions

Ion	Enthalpy of hydration ($kJmol^{-1}$)
K^{+}	305
Ca^{2+}	1545
F^{-}	530
Cl^{-}	394

(a) State whether the values of enthalpies of hydration given in the table should be positive or negative. Give reasons for your answer.

The values should be negative

Reason

Hydration of the ions involves attraction of water molecules releasing a lot of heat

(b) Explain the differences in the enthalpies of hydration of;

(i) Potassium ion and calcium ion

The potassium ion has a ***larger ionic radius*** *and* ***smaller ionic charge*** *than the calcium ion. The potassium ion therefore has a* ***lower charge density*** *thus* ***a lower attraction for water molecules*** *than* ***the calcium ion****, giving* ***off a lower amount of heat*** *than the calcium ion.*

(ii) Fluoride ion and chloride ion

The fluoride ion has a ***smaller ionic radius*** *than the chloride ion. The fluoride ion therefore has a* ***higher attraction for water molecules*** *than* ***the chloride ion****, giving* ***off a higher amount of heat*** *than the chloride ion.*

(c) Calculate the enthalpy of hydration of;

(i) Calcium fluoride

$$CaF_2(aq) \longrightarrow Ca^{2+}(aq) + 2F^-(aq)$$

$$\Delta \boldsymbol{H}_{\underset{CaF_2}{\boldsymbol{hydration}}} = \Delta \boldsymbol{H}_{\underset{Ca^{2+}}{\boldsymbol{hydration}}} + \left(2\Delta \boldsymbol{H}_{\underset{F^-}{\boldsymbol{hydration}}}\right)$$

$$\Delta \boldsymbol{H}_{\underset{CaF_2}{\boldsymbol{hydration}}} = \mathbf{-1545} + (\mathbf{2} \times \mathbf{-530})$$

$$= \mathbf{-2605}\ \boldsymbol{kJmol^{-1}}$$

(ii) Potassium chloride

$$\Delta \boldsymbol{H}_{\underset{KCl}{\boldsymbol{hydration}}} = \Delta \boldsymbol{H}_{\underset{K^{+}}{\boldsymbol{hydration}}} + \Delta \boldsymbol{H}_{\underset{Cl^-}{\boldsymbol{hydration}}}$$

$$\Delta \boldsymbol{H}_{\underset{CaF_2}{\boldsymbol{hydration}}} = \mathbf{-305} + (\mathbf{-394})$$

$$= \mathbf{-699}\ \boldsymbol{kJmol^{-1}}$$

Standard enthalpy of solution

The standard enthalpy of solution is the heat evolved or absorbed when one mole of a substance is dissolved in a specified number of moles of water under standard conditions.

$$MX(s) \longrightarrow M^+(aq) + X^-(aq) \quad \Delta \boldsymbol{H} = \boldsymbol{Enthalpy\ of\ solution}$$

Enthalpy of solution can be either **positive (endothermic)** or **negative (exothermic).**
The enthalpy of solution of an ionic solid involves two energy terms:

- ***(i) Lattice enthalpy***
- ***(ii) Enthalpy of hydration***

In this case the lattice enthalpy required is lattice dissociation enthalpy and is endothermic.

$$MX(s) \longrightarrow M^+(g) + X^-(g) \quad \Delta \boldsymbol{H} = +\boldsymbol{lattice\ enthalpy}$$

The enthalpy of solution of an ionic compound is therefore the sum of lattice dissociation enthalpy and enthalpy of hydration.

$$\Delta \boldsymbol{H}^{\boldsymbol{\theta}}_{\boldsymbol{solution}} = \Delta \boldsymbol{H}^{\boldsymbol{\theta}}_{\boldsymbol{lattice\ dissociation}} + \Delta \boldsymbol{H}^{\boldsymbol{\theta}}_{\boldsymbol{hydration}}$$

A high (more positive)lattice enthalpy and a low(less negative) makes the enthalpy of solution more positive.
Ionic salts that dissolve endothermically include ***ammonium nitrate, ammonium chloride, potassium nitrate, potassium chloride, sodium chloride, sodium thiosulphate and sodium hydrogencarbonate.***

A low (less positive)lattice enthalpy and a high(more negative) makes the enthalpy of solution more negative.

Ionic salts that dissolve exothermically include ***sodium hydroxide, calcium chloride, sodium carbonate***

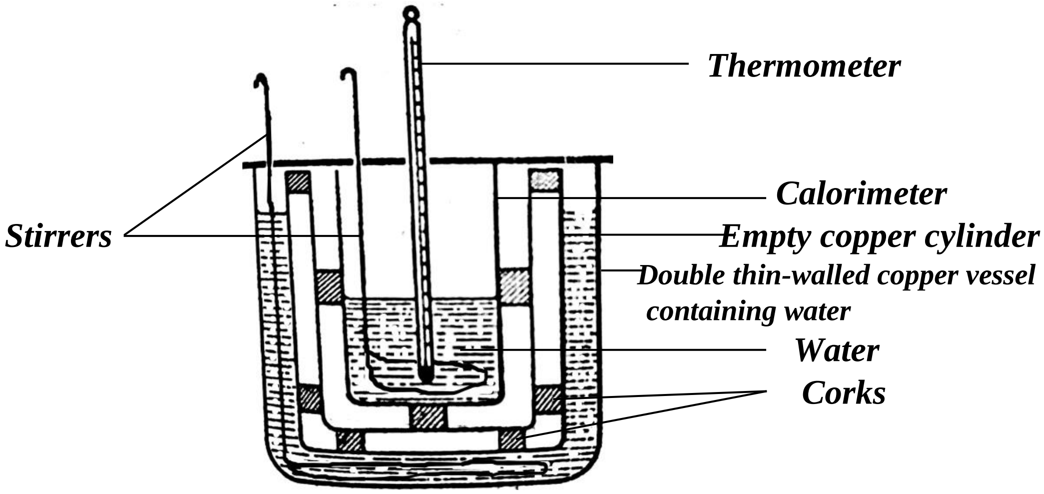
The more negative the enthalpy of solution, the more soluble a compound is. The less negative the enthalpy of solution, the less soluble the compound is.

Experiments to determine enthalpy of solution

Experiment to determine enthalpy of solution for an ionic salt that dissolves exothermically

For example sodium hydroxide

Set up



A ***known volume*** ($\boldsymbol{V\ cm^3}$) of ***water*** is put in a ***calorimeter*** fitted with a ***thermometer*** and ***stirrer.***

The ***initial temperature, T_1°C of the water*** is recorded from the ***thermometer***

A ***known mass***($\boldsymbol{m\ g}$) ***of solid sodium hydroxide*** is added to the water and the solution is ***stirred until there is no further change in temperature.***

The ***final steady temperature T_2°C*** is read and recorded from the thermometer.

Assumptions:

Density of solution is equal to density of water = $\boldsymbol{1.0gcm^{-3}}$

Specific heat capacity of solution is equal to specific heat capacity of water

$$= \boldsymbol{4.2Jg^{-1}K^{-1}}$$

No heat is lost to the surroundings

Heat capacity of the calorimeter is negligible

Treatment of results

$$Temperature\ rise = \Delta T = (\boldsymbol{T_2} - \boldsymbol{T_1})°C$$

$$Mass\ of\ water\ used = (volume\ \times density) = (V \times 1) = V\ g$$

$$Total\ mass\ of\ solution = (m + V)\ g$$

$$Heat\ change = mass\ of\ solution \times specific\ heat\ capacity \times temperature\ rise$$

$$Heat\ change = \big((m + V) \times 4.2 \times \Delta T\big)J$$

$$Molar\ mass\ of\ NaOH = 23 + 16 + 1 = 40g$$

$$m\ g\ \ of\ NaOH\ \ evolve\ \ \big((m + V)\ \times 4.2 \times \Delta T\big)J$$

$$40\ g\ \ of\ NaOH\ \ evolve\ \ \left(\frac{40 \times (m + V) \times 4.2 \times \Delta T}{m}\right)J$$

$$Enthalpy\ of\ solution\ of\ NaOH\ = -\left(\frac{40 \times (m + V) \times 4.2 \times \Delta T}{m}\right)Jmol^{-1}$$

$$\boldsymbol{Enthalpy\ of\ solution\ of\ NaOH\ = -\left(\frac{40 \times (m + V) \times 4.2 \times \Delta T}{m \times 1000}\right)kJmol^{-1}}$$

Experiment to determine enthalpy of solution for an ionic salt that dissolves endothermically

For example ammonium chloride

A ***known volume*** (***$V\ cm^3$***) of ***water*** is put in a ***calorimeter*** fitted with a ***thermometer*** and ***stirrer.***
The ***initial temperature, T_1°C of the water*** is recorded from the ***thermometer***
A ***known mass***(***$m\ g$***) ***of solid ammonium chloride*** is added to the water and the solution is ***stirred until there is no further change in temperature.***
The ***final steady temperature T_2°C*** is read and recorded from the thermometer.

Assumptions:

Density of solution is equal to density of water = $\boldsymbol{1.0gcm^{-3}}$
Specific heat capacity of solution is equal to specific heat capacity of water
$$\boldsymbol{= 4.2Jg^{-1}K^{-1}}$$
No heat is lost to the surroundings
Heat capacity of the calorimeter is negligible

Treatment of results

$$Temperature\ change = \Delta T = (\boldsymbol{T_1 - T_2})°C$$

$$Mass\ of\ water\ used = (volume\ \times density) = (V \times 1) = V\ g$$

$$Total\ mass\ of\ solution = (m + V)\ g$$

$$Heat\ change = mass\ of\ solution \times specific\ heat\ capacity \times temperature\ rise$$

$$Heat\ change = \big((m + V) \times 4.2 \times \Delta T\big)J$$

$$Molar\ mass\ of\ NH_4Cl = 14 + 4 + 35.5 = 53.5g$$

$$m\ g\ \ of\ NH_4Cl\ \ evolve\ \ \big((m + V)\ \times 4.2 \times \Delta T\big)J$$

$$53.5\ g\ \ of\ NH_4Cl\ \ evolve\ \ \left(\frac{53.5 \times (m + V) \times 4.2 \times \Delta T}{m}\right)J$$

$$Enthalpy\ of\ solution\ of\ NH_4Cl\ = +\left(\frac{53.5 \times (m + V) \times 4.2 \times \Delta T}{m}\right)Jmol^{-1}$$

$$\boldsymbol{Enthalpy\ of\ solution\ of\ NH_4Cl} = +\left(\frac{53.5\times(\boldsymbol{m}+\boldsymbol{V})\times\boldsymbol{4.2}\times\Delta \boldsymbol{T}}{\boldsymbol{m}\times\boldsymbol{1000}}\right)\boldsymbol{kJmol^{-1}}$$

Note the difference in the two experiments is the temperature rise and the sign on the enthalpy value.

Calculations involving enthalpy of solution

1. **The table below shows enthalpies of hydration and lattice energies of potassium chloride and lithium chloride.**

Salt	Lattice energy ($kJmol^{-1}$)	Hydration energy ($kJmol^{-1}$)
Potassium chloride	-862	-883
Lithium chloride	-718	-695

   (a) **Calculate the enthalpy of solution of potassium chloride and lithium chloride.**

   (b) **State which of the two salts is more soluble in water at a given temperature and give a reason for your answer.**

(a) ***Note that the given values of lattice energy are negative but for the compounds to dissolve in water, the lattice enthalpy involved is lattice dissociation enthalpy which is endothermic.***

For potassium chloride	*For Lithium chloride*
$\underset{KCl}{\Delta H_{solution}} = \underset{KCl}{\Delta H_{lattice}} + \underset{KCl}{\Delta H_{hydration}}$ $\underset{KCl}{\Delta H_{solution}} = +862 + -883$ $= \boldsymbol{-21\ kJmol^{-1}}$	$\underset{LiCl}{\Delta H_{solution}} = \underset{LiCl}{\Delta H_{lattice}} + \underset{LiCl}{\Delta H_{hydration}}$ $\underset{LiCl}{\Delta H_{solution}} = +718 + -695$ $= \boldsymbol{+23\ kJmol^{-1}}$

(b) ***Potassium chloride is more soluble in water because its enthalpy of solution is exothermic.***

3. **The enthalpies of hydration of sodium ions and hydroxyl ions are $\boldsymbol{424}$ and $\boldsymbol{kJmol^{-1}}$. Calculate the lattice enthalpy of sodium hydroxide if its enthalpy of solution is $\boldsymbol{-44.5\ kJmol^{-1}}$.**

   Note that although the values given for enthalpy of hydration have no negative sign, it should be known that hydration enthalpies are always exothermic.

$$\underset{NaOH}{\Delta H_{solution}} = \underset{NaOH}{\Delta H_{lattice}} + \underset{NaOH}{\Delta H_{hydration}}$$

$$\underset{NaOH}{\Delta H_{solution}} = \underset{NaOH}{\Delta H_{lattice}} + \left(\underset{Na^+}{\Delta H_{hydration}} + \underset{\bar{O}H}{\Delta H_{hydration}}\right)$$

$$-44.5 = \underset{NaOH}{\Delta H_{lattice}} + (-424 + -519)$$

$$-44.5 = \underset{NaOH}{\Delta H_{lattice}} - 943$$

$$\Delta H_{\underset{NaOH}{lattice}} = (-44.5 + 943)kJmol^{-1}$$

$$\boldsymbol{\Delta H_{\underset{NaOH}{lattice}} = +898.5\ kJmol^{-1}}$$

4. **In an experiment, $5.05g$ of potassium nitrate is added to $100\ cm^3$ of water in a polystyrene foam cup at $25.0\ °C$ and the mixture stirred. If the solution achieved a minimum final temperature of $21.7\ °C$. Determine the enthalpy of solution of potassium nitrate**

$$(Density\ of\ the\ solution\ is\ 1.0gcm^{-3}\ and\ the\ specific\ heat\ capacity\ of\ the\ solution\ is\ 4.2J°C^{-1}g^{-1})$$

$$Temperature\ change = \Delta T = (\mathbf{25.0 - 21.7}) = 3.3°C$$

$$Mass\ of\ water\ used = (volume\ \times density) = (100 \times 1) = 100\ g$$

$$Total\ mass\ of\ solution = (100 + 5.05) = 105.05g$$

$$Heat\ change = mass\ of\ solution \times specific\ heat\ capacity \times temperature\ rise$$

$$Heat\ change = (105.05 \times 4.2 \times 3.3) = 1455.993\ J$$

$$Molar\ mass\ of\ KNO_3 = 39.1 + 14 + 48 = 101.1\ g$$

$$5.05\ g\ \ of\ KNO_3\ \ \boldsymbol{absorb}\ \ 1455.993\ Joules$$

$$101.1\ g\ \ of\ KNO_3\ \ \boldsymbol{absorb}\ \ \left(\frac{101.1 \times 1455.993}{5.05}\right)J$$

$$Enthalpy\ of\ solution\ of\ KNO_3\ = +29148.692\ Jmol^{-1}$$

$$\boldsymbol{Enthalpy\ of\ solution\ of\ KNO_3\ = +29.149\ kJmol^{-1}}$$

Questions

1. In an experiment, $4.00g$ of sodium hydroxide was added to $100\ g$ of water in a well-insulated polystyrene foam cup the mixture stirred. The temperature of the solution rose by $10.0\ °C$. Determine the enthalpy of solution of sodium hydroxide.$(The\ specific\ heat\ capacity\ of the\ solution\ is\ 4.2J°C^{-1}g^{-1})$
2. When 3.21g of solid ammonium nitrate dissolves in 50.0g of water at $24.9\ °C$ in a calorimeter, the temperature decreased to $20.3\ °C$. Calculate the enthalpy of solution of ammonium nitrate. State any assumptions made.
3. The table below shows hydration enthalpies of magnesium and chloride ions.

Ion	Enthalpy of hydration ($kJmol^{-1}$)
$\boldsymbol{Mg^{2+}}$	$\mathbf{-1923}$
$\boldsymbol{Cl^-}$	$\mathbf{-338}$

If the lattice dissociation enthalpy of magnesium chloride is $+2526\ kJmol^{-1}$. Calculate the enthalpy of solution of magnesium chloride.

4. The enthalpies of hydration for calcium ion and fluoride ion are -1616 and $-504\ kJmol^{-1}$respectively. If the lattice enthalpy of calcium fluoride is $+2651\ kJmol^{-1}$. Calculate the enthalpy of solution of calcium fluoride.
5. (a) Define the terms;
   (i) enthalpy of hydration
   (ii) enthalpy of solution

   (b) The enthalpies of solution and lattice energies of salts AX and BX are given in the table below.

Salt	**Enthalpy of solution $(kJmol^{-1})$**	**Lattice enthalpy$(kJmol^{-1})$**
AX	$+20$	-880
BX	-10	-790

   (i) Calculate the enthalpy of hydration of each salt
   (ii) State the salt which has a larger value of hydration energy

Application of enthalpy of solution in real life situation

In instant cold and hot packs already explained in the beginning subtopics of the topic**.(Pages 284-285)**

Heat of precipitation

When two aqueous solutions are added together and a **precipitate** is formed, the reaction is called a **precipitation reaction** or **double decomposition reaction**. This reaction is used to prepare insoluble salts for example silver chloride, barium sulphate, lead sulphate and others.

The heat given out or absorbed is called heat of precipitation.

The heat of precipitation is the heat change that occurs when one mole of a precipitate is formed from its ions in aqueous solution.

Heat of precipitation can be **exothermic** or **endothermic**.

Experiment to determine heat of precipitation of silver chloride

A ***known volume, $V\ cm^3$*** of ***silver nitrate*** of ***known concentration, $C\ moldm^{-3}$*** is measured and placed in a ***plastic beaker***.

The ***initial temperature of the silver nitrate solution, T_1°C*** is noted from the ***thermometer***.

An ***equal volume, $V\ cm^3$*** of ***sodium chloride*** solution of the ***same concentration*** is also measured and poured into a separate beaker and its ***initial temperature, T_2°C*** is noted from the ***thermometer***.

The ***two solutions are added together*** quickly and carefully while ***stirring*** and the ***maximum temperature, T_3°C*** attained is noted.

Assumptions

The solution has the same specific heat capacity as water $= 4.2Jg^{-1}{}^\circ C^{-1}$
Heat loss to the surroundings is negligible
Heat capacity of the beaker is negligible
Density of solution is $1gcm^{-3}$

Treatment of results

$$Initial\ temperature\ of\ silver\ nitrate\ solution = T_1{}^\circ C$$

$$Initial\ temperature\ of\ sodium\ chloride\ solution = T_2{}^\circ C$$

$$Average\ initial\ temperature\ of\ solution = \left(\frac{T_1 + T_2}{2}\right){}^\circ C$$

$$Temperature\ rise = \Delta T = \left[T_3 - \left(\frac{T_1 + T_2}{2}\right)\right]{}^\circ C$$

$$Total\ volume\ of\ solution = (V + V) = 2V\ cm^3$$

$$Total\ mass\ of\ solution = (volume\ \times density) = (2V \times 1) = 2V\ g$$

$$Heat\ change = mass\ of\ solution \times specific\ heat\ capacity \times temperature\ rise$$

$$Heat\ change = (2V \times 4.2 \times \Delta T)J$$

$$Moles\ of\ silver\ ions\ that\ reacted = \left(\frac{V \times C}{1000}\right)$$

$$\boldsymbol{Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)}$$

$$mole\ ratio\ \boldsymbol{Ag^+ : AgCl = 1 : 1}$$

$$\left(\frac{V \times C}{1000}\right) moles\ of\ \boldsymbol{Ag^+}\ precipitate\ \left(\frac{V \times C}{1000}\right) moles\ of \boldsymbol{AgCl}$$

$$\left(\frac{V \times C}{1000}\right)\ moles\ of \boldsymbol{AgCl}\ are\ precipitated\ with\ evolution\ of\ (2V \times 4.2 \times \Delta T)\ J$$

$$1\ mole\ of \boldsymbol{AgCl}\ is\ precipitated\ with\ evolution\ of\ \left(\frac{1000 \times 2V \times 4.2 \times \Delta T}{V \times C}\right)J$$

$$Enthalpy\ of\ precipitation\ of\ \boldsymbol{AgCl} = -\left(\frac{1000 \times 2V \times 4.2 \times \Delta T}{V \times C}\right)Jmol^{-1}$$

$$\boldsymbol{Enthalpy\ of\ precipitation\ of\ AgCl = -\left(\frac{2V \times 4.2 \times \Delta T}{V \times C}\right)kJmol^{-1}}$$

Calculations involving heat of precipitation

Example

25.0 cm^3 of 0.5 M silver nitrate solution was added to 25.0 cm^3 of 0.5 M sodium chloride solution in a plastic cup. The temperature of the resulting mixture rose by 3 $°C$. Assuming the container has a negligible heat capacity and the specific heat capacity of the resulting mixture is $4.2Jg^{-1}{}^\circ C^{-1}$. Calculate the heat of precipitation of silver chloride.

$$Temperature\ rise = \Delta T = 3\ °C$$
$$Total\ volume\ of\ solution = (25.0 + 25.0) = 50\ cm^3$$
$$Total\ mass\ of\ solution = (volume\ \times density) = (50 \times 1) = 50\ g$$
$$Heat\ change = mass\ of\ solution \times specific\ heat\ capacity \times temperature\ rise$$
$$Heat\ change = (50 \times 4.2 \times 3) = 630\ Joules$$
$$Moles\ of\ silver\ ions\ \ that\ reacted = \left(\frac{250 \times 0.5}{1000}\right) = 0.125$$
$$\boldsymbol{Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)}$$
$$mole\ ratio\ \boldsymbol{Ag^+ : AgCl = 1 : 1}$$
$$0.125\ moles\ of\ \boldsymbol{Ag^+}\ precipitate\ 0.125\ moles\ of\ \boldsymbol{AgCl}$$
$$0.125\ moles\ of\ \boldsymbol{AgCl}\ are\ precipitated\ with\ evolution\ of\ 630\ \ J$$
$$1\ mole\ of\ \boldsymbol{AgCl}\ is\ precipitated\ with\ evolution\ of\ \left(\frac{1 \times 630}{0.125}\right) J$$
$$Enthalpy\ of\ precipitation\ of\ \boldsymbol{AgCl} = -5040\ Jmol^{-1}$$
$$\boldsymbol{Enthalpy\ of\ precipitation\ of\ AgCl = -5.04\ kJmol^{-1}}$$

Questions

1. In an experiment carried out to determine heat of precipitation of silver chloride, $25.0\ cm^3$ of $1.0\ moldm^{-3}$ of silver nitrate solution is poured in a polystyrene cup and its initial temperature recorded as $29\ °C$. $25.0\ cm^3$ of $1.0\ moldm^{-3}$ of sodium chloride solution was added and the resulting mixture stirred. The highest temperature attained by the solution was $37\ °C$. Calculate the heat of precipitation of silver chloride.
2. When $100\ cm^3$ of $0.200M$ of sodium chloride solution and $100\ cm^3$ of $0.200M$ of silver nitrate solution, both at $21.9\ °C$ were mixed in a coffee cup calorimeter, the temperature increases to $23.5\ °C$. Calculate the heat of precipitation of silver chloride. State any assumptions made.
3. $50\ cm^3$ of $0.5\ moldm^{-3}$ silver nitrate solution at $29.5\ °C$ is added to $50\ cm^3$ of $0.5\ moldm^{-3}$ potassium chloride solution which is at a temperature of $28.5\ °C$. The mixture is stirred and the highest temperature reached is $32.0\ °C$. Calculate the heat of precipitation of silver chloride.

$$(Density\ of\ the\ solution\ is\ 1.0gcm^{-3}\ and\ the\ specific\ heat\ capacity\ of\ the\ solution\ is\ 4.2J°C^{-1}g^{-1})$$

Bond energy

Bond energy is heat given out when one mole of a single covalent bond of a diatomic molecule is formed from free gaseous atoms.

$$H(g) + H(g) \longrightarrow H_2(g) \qquad \Delta H = -436\ kJmol^{-1}$$
$$H(g) + Cl(g) \longrightarrow HCl(g) \qquad \Delta H = -431\ kJmol^{-1}$$
$$Cl(g) + Cl(g) \longrightarrow Cl_2(g) \qquad \Delta H = -242\ kJmol^{-1}$$

This enthalpy change resulting into formation of a covalent bond is ***exothermic***. It is more correctly known as ***bond energy of formation***.

Bond energies are very important because all chemical reactions involve forming and breaking bonds. The strength of a covalent bond is represented by its ***bond dissociation energy***.

Bond dissociation energy

Bond dissociation energy is energy required to break one mole of a single covalent bond of a diatomic molecule to form free gaseous atoms.

Bond dissociation enthalpy is **endothermic** because energy must be absorbed to break a covalent bond.

$$H_2(g) \longrightarrow 2H(g) \qquad \Delta H = +436\ kJmol^{-1}$$
$$HCl(g) \longrightarrow H(g) + Cl(g) \qquad \Delta H = +431\ kJmol^{-1}$$
$$Cl_2(g) \longrightarrow 2Cl(g) \qquad \Delta H = +242\ kJmol^{-1}$$

Bond dissociation energy is related to atomization energy.

$$\boldsymbol{Bond\ dissociation\ energy = 2 \times Atomisation\ energy}$$
$$\boldsymbol{Atomisation\ energy = \frac{1}{2} \times Bond\ dissociation\ energy}$$

Consider the reaction;

$$O_2(g) \longrightarrow 2O(g)$$
$$\Delta H_{BDE} = +498\ kJmol^{-1}$$
$$\Delta H_a = (\frac{1}{2} \times 498) kJmol^{-1}$$

$$\tfrac{3}{2} O_2(g) \longrightarrow \tfrac{3}{2}(2O)(g)$$
$$\tfrac{3}{2} O_2(g) \longrightarrow 3O(g)$$
$$\frac{3}{2}\Delta H_{BDE} = \frac{3}{2}(+498)\ kJmol^{-1}$$

Since $\Delta H_{BDE} = 2\Delta H_a$

$$\frac{3}{2}\Delta H_{BDE} = 3\Delta H_a$$
$$\Delta H_a = (2 \times 498) kJmol^{-1}$$

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Average bond energies (enthalpies)

For a polyatomic molecule such as AX_3, the average bond enthalpy is $\frac{1}{3}$ of the enthalpy change of the process;

$$AX_3(g) \longrightarrow A(g) + 3X(g)$$

In methane, for example, the average bond enthalpy is given as

$$\boldsymbol{Average\ bond\ enthalpy\ of\ C-H\ bond = \frac{Bond\ enthalpy\ of\ CH_4}{4}}$$

Since $\quad \boldsymbol{CH_4(g) \longrightarrow C(g) + 4H(g) \qquad \Delta H = 1661.8\ kJmol^{-1}}$

$$\boldsymbol{Average\ bond\ enthalpy\ of\ C-H\ bond = \frac{1661.8}{4} = 415.45\ kJmol^{-1}}$$

This is because methane has four $C-H$ bonds

Average bond enthalpies are obtained from standard molar enthalpies of formation and molar enthalpies of atomization

If the average bond enthalpy of one covalent bond in a molecule is known, then the average bond enthalpy if the other bond can be determined.

Using bond energies to calculate enthalpy of a reaction

Enthalpy of any given reaction can be obtained if the average bond enthalpies of the bonds involved are known. The relationship used is;

$$\boldsymbol{\Delta H_{reaction} = \begin{pmatrix} sum\ of\ bond\ enthalpies\ of\ bonds - sum\ of\ bond\ enthalpies\ of\ bonds \\ broken \qquad\qquad\qquad\qquad\qquad formed \end{pmatrix}}$$

$$\boldsymbol{\Delta H_{reaction} = \sum \begin{matrix} bond\ enthalpies\ of\ bonds \\ broken \end{matrix} - \sum \begin{matrix} bond\ enthalpies\ of\ bonds \\ formed \end{matrix}}$$

Calculations involving bond energies

Examples

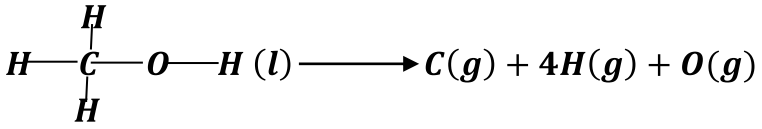
1. **(a) Define the term "*standard enthalpy of atomization*"**

   (b) Bond energies for some bonds are given below.

   Calculate the standard enthalpy of atomization of methanol

Bond	Bond energy($kJmol^{-1}$)
$C—O$	**358**
$C—H$	**413**
$O—H$	**464**

(b) Equation; $CH_3OH(l) \longrightarrow C(g) + 4H(g) + O(g)$



$$\mathbf{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}O{-}H\ (l) \longrightarrow C(g) + 4H(g) + O(g)}$$

$$\Delta H_a = \sum \begin{matrix} bond\ enthalpies\ of\ bonds \\ broken \end{matrix} - \sum \begin{matrix} bond\ enthalpies\ of\ bonds \\ formed \end{matrix}$$

$$\Delta H_a = [3(C-H) + (C-O) + (O-H)] - 0$$

$$= 3(413) + 358 + 464$$

$$\boldsymbol{\Delta H_a = +2061\ kJmol^{-1}}$$

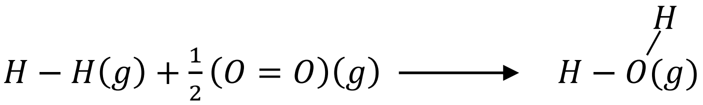
2. **(a) Write equation for formation of steam.**

   (b) The enthalpy of formation of steam is $\boldsymbol{-241.8\ kJmol^{-1}}$. The bond energies of some bonds are also given below.

Bond	Bond energy($kJmol^{-1}$)
$H-H$	436
$O-H$	463

   Calculate the oxygen-oxygen bond energy in $\boldsymbol{O_2}$.

(a) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$



$$H-H(g) + \tfrac{1}{2}(O=O)(g) \longrightarrow H-\overset{\displaystyle H}{O}(g)$$

$$\Delta H_{f,H_2O} = \sum \begin{matrix} bond\ enthalpies\ of\ bonds \\ broken \end{matrix} - \sum \begin{matrix} bond\ enthalpies\ of\ bonds \\ formed \end{matrix}$$

$$\Delta H_{f,H_2O} = \left[(H-H) + \frac{1}{2}(O=O)\right] - [2(O-H)]$$

$$-241.8 = \left[436 + \frac{1}{2}(O=O)\right] - 2(463)$$

$$\frac{1}{2}(O=O) = -241.8 - 436 + 2(463)$$

$$(O=O)\ bond\ energy = (248.2 \times 2)$$

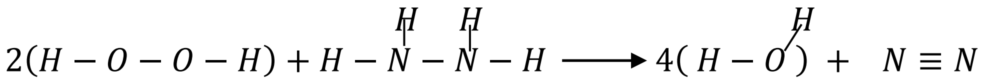
$$\boldsymbol{(O=O)\ bond\ energy = 496.4\ kJmol^{-1}}$$

3. **Hydrazine reacts exothermically with hydrogen peroxide when used as a rocket fuel. The table below shows some bond energies.**

Bond	$O-H$	$N-H$	$N-N$	$O-O$	$N\equiv N$
Bond energy($kJmol^{-1}$)	**463**	**388**	**163**	**146**	**944**

Calculate the enthalpy change for the reaction;

$$\boldsymbol{2H_2O_2 + N_2H_4 \longrightarrow 4H_2O + N_2}$$



$$2(H-O-O-H)+H-\overset{H}{\underset{|}{N}}-\overset{H}{\underset{|}{N}}-H \longrightarrow 4(H-\overset{H}{O})+\ N\equiv N$$

$$\Delta H_{reaction}=\sum \begin{matrix}bond\ enthalpies\ of\ bonds\\ broken\end{matrix}-\sum \begin{matrix}bond\ enthalpies\ of\ bonds\\ formed\end{matrix}$$

$$\Delta H_{reaction}=\ [4(O-H)+2(O-O)+4(N-H)+(N-N)]-[8(O-H)+N\equiv N]$$

$$\Delta H_{reaction}=[4(436)+2(146)+4(388)+163]-[8(463)+944]$$

$$=3751-4648$$

$$\boldsymbol{\Delta H_{reaction}=-897\ kJmol^{-1}}$$

Questions

1. Bond energies for some bonds are given below.
   Calculate the standard enthalpy of atomization of CH_2Cl_2

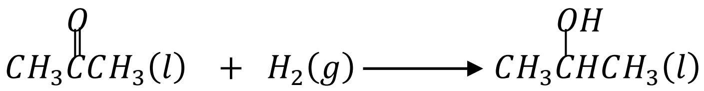
Bond	**Bond energy**$(\boldsymbol{kJmol^{-1}})$
$\boldsymbol{C-H}$	415
$\boldsymbol{C-Cl}$	326

2. Bond energies for some bonds are given below.

Bond	**Bond energy**$(\boldsymbol{kJmol^{-1}})$
$\boldsymbol{C\equiv C}$	+813
$\boldsymbol{C-C}$	+346
$\boldsymbol{C-H}$	+413
$\boldsymbol{H-H}$	+436

   (a) Calculate enthalpy of hydrogenation of ethyne
   (b) State whether hydrogenation of ethyne is feasible or not. Give a reason for your answer.

3. Propan-2-ol can be prepared from propanone by the reaction;



$$CH_3\overset{O}{\overset{\|}{C}}CH_3(l)\ +\ H_2(g)\longrightarrow CH_3\overset{OH}{\overset{|}{C}}HCH_3(l)$$

   Given the data below;

Bond	Bond energy$(kJmol^{-1})$
$C{=}O$	715
$C-C$	345
$C-H$	414
$C-O$	351
$O-H$	464
$H-H$	436

Calculate the enthalpy change for the reaction above.

4. The table below shows some bond energies.

Bond	$H-H$	$C-Br$	$C-C$	$C{=}C$	$Br-Br$
Bond energy$(kJmol^{-1})$	**435**	**415**	**284**	**256**	**193**

(a) What is meant by the term bond energy?

(b) Calculate the enthalpy of formation of;

  (i) 1,2-dibromopropane

  (ii) Propane

(c) Calculate the enthalpy change for the reaction;

$$CH_3CH = CH_2 + Br_2 \longrightarrow CH_3CHBrCH_2Br$$

Note; Factors that affect strength of a covalent bond also affect bond energy. Refer to one of the previous topics (STRUCTURE AND BONDING) and also for trends in bond energy.

Hess's law of constant heat summation

Hess's law states that the enthalpy change in a chemical reaction at constant temperature and pressure is the same whether the reaction is brought about in one stage or through intermediate stages but depends on the initial and final states of the reactants and products.

Demonstration of Hess's law using an experiment

The validity of Hess's law can be demonstrated experimentally by measuring enthalpy changes when a reaction is brought about in two or more different ways.

For example ammonium chloride solution can be made using 17g of ammonia , 36.5g of hydrogen chloride and water in two ways;

(i) Reacting ammonia gas and hydrogen chloride gas to form ammonium chloride which is then dissolved in water

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s) \qquad \Delta H_1$$

$$NH_4Cl(s) + aq \longrightarrow NH_4Cl(aq) \qquad \Delta H_2$$

$$\boldsymbol{\Delta H_{total\,1} = \Delta H_1 + \Delta H_2}$$

(ii) ***Dissolving ammonia gas and hydrogen chloride gas separately in water and the solutions added to each other***

$$NH_3(g) + aq \longrightarrow NH_3(aq) \qquad \Delta H_3$$
$$HCl(g) + aq \longrightarrow HCl(aq) \qquad \Delta H_4$$
$$NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq) \qquad \Delta H_5$$
$$\boldsymbol{\Delta H_{total\,2} = \Delta H_3 + \Delta H_4 + \Delta H_5}$$

According to Hess' law, the heat change in both cases is the same and then;

$$\boldsymbol{\Delta H_{total\,1} = \Delta H_{total\,2}}$$
$$\boldsymbol{\Delta H_1 + \Delta H_2 = \Delta H_3 + \Delta H_4 + \Delta H_5}$$

The Hess's law is very important in determining heats of reaction if direct determination is not possible. It has already been applied in calculations involving heats of combustion.

Application of Hess's law in some more calculations

Examples

1. (a**) Calculate the enthalpy of formation of sodium chloride using the following data**

	$\Delta H^{\theta}(kJmol^{-1})$
$\boldsymbol{Na(s) \longrightarrow Na(g)}$	$\boldsymbol{+109}$
$\boldsymbol{Cl_2(g) \longrightarrow 2Cl(g)}$	$\boldsymbol{+242}$
$\boldsymbol{Na(g) \longrightarrow Na^+(g) + e}$	$\boldsymbol{+494}$
$\boldsymbol{Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)}$	$\boldsymbol{-771}$
$\boldsymbol{Cl(g) + e \longrightarrow Cl^-(g)}$	$\boldsymbol{-364}$

(b) Comment on the stability of sodium chloride. Give a reason for your answer.

(a) *Equation for the reaction required;*

$$\boldsymbol{Na(s) + \tfrac{1}{2}Cl_2(g) \longrightarrow NaCl(s)} \qquad \boldsymbol{\Delta H^{\theta}_{f,NaCl(s)}} = ?$$

Equations for reactions given;

$$\boldsymbol{Na(s)} \longrightarrow \cancel{Na(g)} \qquad \Delta H_1 = +109$$
$$\boldsymbol{\tfrac{1}{2}Cl_2(g)} \longrightarrow \cancel{Cl(g)} \qquad \frac{1}{2}\Delta H_2 = \frac{1}{2}(+242)$$
$$\cancel{Na(g)} \longrightarrow \cancel{Na^+(g)} + \cancel{e} \qquad \Delta H_3 = +494$$
$$\cancel{Na^+(g)} + \cancel{Cl^-(g)} \longrightarrow \boldsymbol{NaCl(s)} \qquad \Delta H_4 = -771$$
$$\cancel{Cl(g)} + \cancel{e} \longrightarrow \cancel{Cl^-(g)} \qquad \Delta H_5 = -364$$

$$\boldsymbol{\Delta H^{\theta}_{f,NaCl(s)} = \Delta H_1 + \frac{1}{2}\Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5}$$
$$= +109 + \frac{1}{2}(+242) + 494 + (-771) + (-364)$$
$$\boldsymbol{\Delta H^{\theta}_{f,NaCl(s)} = -411\ kJmol^{-1}}$$

2. (a) **Define the term** ***standard heat of reaction***

   (b) **Given the following data:**

Enthalpy of formation of magnesium chloride = $\boldsymbol{-641.62\ kJmol^{-1}}$
Lattice energy of Magnesium chloride = $\boldsymbol{+2495.6\ kJmol^{-1}}$
Hydration energy of chloride ions = $\boldsymbol{-378.0\ kJmol^{-1}}$
Enthalpy of solution of hydrogen chloride gas = $\boldsymbol{-74.8\ kJmol^{-1}}$
Heat of formation of hydrogen chloride gas = $\boldsymbol{-92.32\ kJmol^{-1}}$
Hydration energy of magnesium ions = $\boldsymbol{-1926\ kJmol^{-1}}$

Calculate the enthalpy of the reaction;

$$\boldsymbol{Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)}$$

N.B The lattice energy given is positive(endothermic). This means its lattice dissociation energy.

(b) Equations given;

$$Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s) \qquad \Delta H^{\theta}_{f,MgCl_2(s)} = -641.62\ kJmol^{-1}$$

$$MgCl_2(s) \longrightarrow Mg^{2+}(g) + 2Cl^-(g) \qquad \Delta H^{\theta}_{lattice} = +2495.6\ kJmol^{-1}$$

$$Cl^-(g) \longrightarrow Cl^-(aq) \qquad \Delta H^{\theta}_{\underset{Cl^-}{hydration}} = -378.0\ kJmol^{-1}$$

$$HCl(g) \longrightarrow HCl(aq) \qquad \Delta H^{\theta}_{\underset{HCl}{solution}} = -74.8\ kJmol^{-1}$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g) \qquad \Delta H^{\theta}_{f,HCl(g)} = -92.32\ kJmol^{-1}$$

$$Mg^{2+}(g) \longrightarrow Mg^{2+}(aq) \qquad \Delta H^{\theta}_{\underset{Mg^{2+}}{hydration}} = -1962\ kJmol^{-1}$$

Rearrangement

$$\boldsymbol{Mg(s)} + \cancel{Cl_2(g)} \longrightarrow \cancel{MgCl_2(s)} \qquad \Delta H^{\theta}_{f,MgCl_2(s)} = -641.62$$

$$\cancel{MgCl_2(s)} \longrightarrow \cancel{Mg^{2+}(g)} + \cancel{2Cl^-(g)} \qquad \Delta H^{\theta}_{lattice} = +2495.6$$

$$\cancel{2Cl^-(g)} \longrightarrow \boldsymbol{2Cl^-(aq)} \qquad \boldsymbol{2\Delta H^{\theta}_{\underset{Cl^-}{hydration}} = 2(-378.0)}$$

$$\boldsymbol{2HCl(aq)} \longrightarrow \cancel{2HCl(g)} \qquad \boldsymbol{-2\Delta H^{\theta}_{\underset{HCl}{solution}} = -2(-74.8)}$$

$$2\cancel{HCl(g)} \longrightarrow \boldsymbol{H_2(g)} + \cancel{Cl_2(g)} \qquad \boldsymbol{-2\Delta H^{\theta}_{f,HCl(g)} = -2(-92.32)}$$

$$\cancel{Mg^{2+}(g)} \longrightarrow \boldsymbol{Mg^{2+}(aq)} \qquad \Delta H^{\theta}_{\underset{Mg^{2+}}{hydration}} = -1962$$

$$\boldsymbol{Mg(s) + 2HCl(aq) \longrightarrow Mg^{2+}(aq) + 2Cl^-(aq) + H_2(g) \qquad \Delta H^{\theta}_{reaction}} = ?$$

The equation generated above and the equation given in the question are the same.

$$\boldsymbol{\Delta H^{\theta}_{reaction} = \Delta H^{\theta}_{f,MgCl_2(s)} + \Delta H^{\theta}_{lattice} + 2\Delta H^{\theta}_{\underset{Cl^-}{hydration}} - 2\Delta H^{\theta}_{\underset{HCl}{solution}} - 2\Delta H^{\theta}_{f,HCl(g)} + \Delta H^{\theta}_{\underset{Mg^{2+}}{hydration}}}$$

$$= -641.62 + 2495.6 + 2(-378.0) - 2(-74.8) - 2(-92.32) - 1962$$

$$\boldsymbol{\Delta H^{\theta}_{reaction} = -529.78\ kJmol^{-1}}$$

Questions

1. The enthalpies of some reactions are given below.

	$\Delta H^{\theta}(kJmol^{-1})$
$H_2(g) \longrightarrow 2H(g)$	$+432$
$H(g) + e \longrightarrow H^-(g)$	-72
$Na(s) \longrightarrow Na(g)$	$+107$
$Na(g) \longrightarrow Na^+(g) + e$	$+494$
$Na(s) + \frac{1}{2}H_2(g) \longrightarrow NaH(s)$	-57

(a) Calculate the lattice energy of sodium hydride

(b)(i) From your answer in (a); state whether sodium hydride is a stable compound or not.

(ii)Give a reason for you answer in b(i)

2. (a) State what is meant by the term enthalpy of atomization

(b) Given the thermochemical data below

Lattice energy of rubidium chloride = $665\ kJmol^{-1}$
Enthalpy of bond dissociation of chlorine = $226\ kJmol^{-1}$
Enthalpy of atomisation of rubidium = $84\ kJmol^{-1}$
Ionisation energy of rubidium atom = $397\ kJmol^{-1}$
Standard enthalpy of formation of solid rubidium chloride = $-439\ kJmol^{-1}$

Calculate the electron affinity of chlorine

(c) Sodium chloride and potassium chloride have lattice enthalpies $-788\ kJmol^{-1}$ and $-718\ kJmol^{-1}$respectively. Explain the difference.

3. The thermochemical data for some processes are given below

	$\Delta H^{\theta}(kJmol^{-1})$
$Rb(s) \longrightarrow Rb(g)$	$+78$
$Rb(g) \longrightarrow Rb^+(g) + e$	$+402$
$F_2(g) \longrightarrow 2F(g)$	$+160$
$Rb^+(g) + F^-(g) \longrightarrow RbF(s)$	-762
$F_2(g) + Rb(s) \longrightarrow 2RbF(s)$	-1104

Calculate the electron affinity of the fluorine atom.

ENTHALPY CYCLES (BORN HABER CYCLES)

A Born-Haber cycle is a technique for applying Hess's law to the standard enthalpy changes. Born Haber cycles are used to calculate enthalpy changes which are difficult, or impossible to evaluate directly. These include theoretical values for **lattice energies**, **electron affinities** and **enthalpies of formation**. The only energy term in the cycle that cannot be measured experimentally is the lattice enthalpy and the cycle enables its value to be determined.

The cycle can be an energy level diagram or enthalpy cycle.

Terms used in Born-Haber cycle

The common energy terms below which have been previously defined the subtopics above, are used in the Born Haber cycle;

- ***Standard enthalpy of sublimation***
- ***Standard enthalpy of ionisation***
- ***Standard bond dissociation enthalpy***
  The standard bond dissociation energy is twice atomization energy
- ***Electron affinity***
- ***Standard lattice enthalpy***
- ***Standard enthalpy of formation***

Point to note when drawing Born Haber cycles

- ***The cycles should have well balanced equations***
- ***Ions should have correct charges***
- ***The chemical symbols of the elements must be correct***
- ***State symbols must be shown and should be correct***
- ***The enthalpy values should be shown along with the reactions they represent in the cycle.***
- ***For the energy level diagram it's important to consider the ranges between any two energy terms***

(a) Enthalpy diagram or energy level diagram

An energy level diagram shows the energy changes in the order they happen. Endothermic (positive) enthalpy changes are shown upwards and the exothermic (negative) enthalpy changes are shown down wards. The diagram also must have well balanced equations for the reactions that take place, with state symbols inclusive and the energy changes must be labelled.

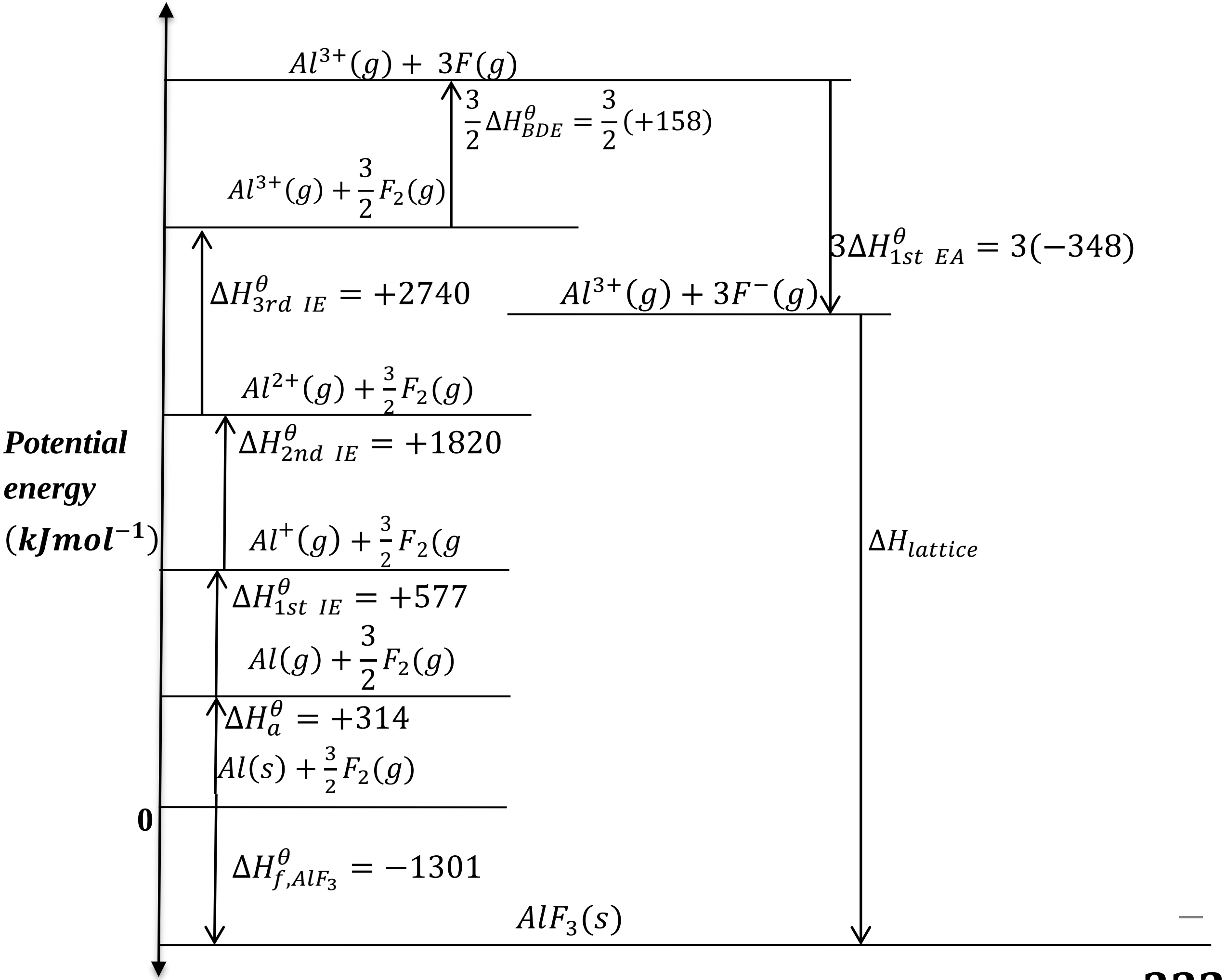
Examples

1. **Given the following data;**

Standard enthalpy of formation of aluminium fluoride= $-1301\ kJmol^{-1}$
Enthalpy of atomization of aluminium = $+314\ kJmol^{-1}$
Bond dissociation energy of fluorine = $+158\ kJmol^{-1}$
First ionisation energy of aluminium = $+577\ kJmol^{-1}$
Second ionisation energy of aluminium = $+1820\ kJmol^{-1}$
Third ionisation energy of aluminium = $+2740\ kJmol^{-1}$
First electron affinity of fluorine= $-348\ kJmol^{-1}$

- **(i)** **Draw an energy level diagram for the formation of aluminium fluoride**
- **(ii)** **Calculate the lattice energy of aluminium fluoride**
- **(iii)** **If the hydration energies of aluminium ions and fluoride ions are 4690 and 364 $kJmol^{-1}$ respectively, calculate the enthalpy of solution of aluminium fluoride.**

(i) ***Energy level diagram for formation of aluminium fluoride;***



(ii) **By Hess' law;**

$$\Delta H^{\theta}_{f,AlF_3} = \Delta H^{\theta}_{a} + \Delta H^{\theta}_{1st\ IE} + \Delta H^{\theta}_{2nd\ IE} + \Delta H^{\theta}_{3rd\ IE} + \frac{3}{2}\Delta H^{\theta}_{BDE} + 3\Delta H^{\theta}_{1st\ EA} + \Delta H_{lattice}$$

$$-1301 = 314 + 577 + 1820 + 2740 + \frac{3}{2}(+158) + 3(-348) + \Delta H_{lattice}$$

$$\Delta H_{lattice} = -1301 - 314 - 577 - 1820 - 2740 - 237 + 1044$$

$$\boldsymbol{\Delta H_{lattice} = -5945\ kJmol^{-1}}$$

(iii) $AlF_3(aq) \longrightarrow Al^{3+}(aq) + 3F^{-}(aq)$

$$\Delta H_{\substack{hydration\\ AlF_3}} = \Delta H_{\substack{hydration\\ Al^{3+}}} + 3\Delta H_{\substack{hydration\\ F^{-}}}$$

$$= -4690 + 3(-364) = \boldsymbol{-5782\ kJmol^{-1}}$$

$$\Delta H_{\substack{solution\\ AlF_3}} = \Delta H_{\substack{lattice\\ AlF_3}} + \Delta H_{\substack{hydration\\ AlF_3}}$$

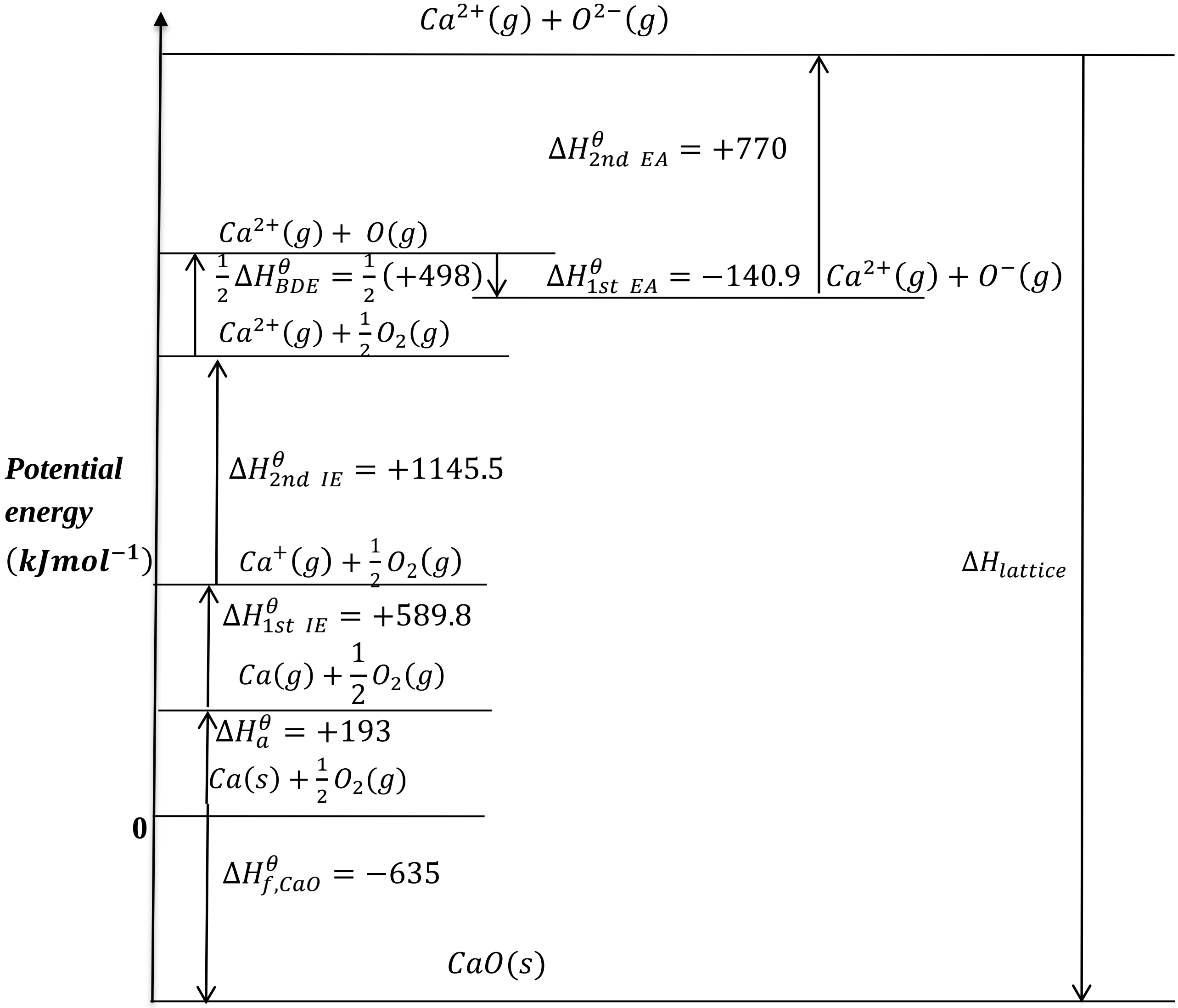
$$\boldsymbol{\Delta H_{\substack{solution\\ AlF_3}} = +5945 + (-5782) = +163 kJmol^{-1}}$$

Note that lattice energy substituted in the equation for $\Delta H_{\substack{solution\\ AlF_3}}$ ***above is the lattice dissociation enthalpy hence it must be positive. Hydration enthalpies are also known to be negative although given as positive values in the question.***

2. **(a) Use the data below to calculate the lattice enthalpy of calcium oxide**

Enthalpy of formation of calcium oxide= $\boldsymbol{-635\ kJmol^{-1}}$
Bond dissociation energy of oxygen $\boldsymbol{= +498\ kJmol^{-1}}$
First electron affinity of oxygen = $\boldsymbol{-140.9\ kJmol^{-1}}$
Second electron affinity of oxygen = $\boldsymbol{+770\ kJmol^{-1}}$
Atomization energy of calcium = $\boldsymbol{+193\ kJmol^{-1}}$
First ionisation energy of calcium $\boldsymbol{= +589.8\ kJmol^{-1}}$
Second ionisation energy of calcium $\boldsymbol{= +1145.5\ kJmol^{-1}}$

Using an energy level diagram;



Similarly, since oxygen shows both positive and negative values of first and second electron affinities, they can be summed up. The value got is positive and the sum got is represented by one arrow facing upwards. The arrow can then be labelled as $(\Delta \boldsymbol{H}^{\boldsymbol{\theta}}_{\boldsymbol{1st\ EA}} + \Delta \boldsymbol{H}^{\boldsymbol{\theta}}_{\boldsymbol{2nd\ EA}})$

By Hess' law;

$$\Delta H^{\theta}_{f,CaO} = \Delta H^{\theta}_{a} + \Delta H^{\theta}_{1st\ IE} + \Delta H^{\theta}_{2nd\ IE} + \frac{1}{2}\Delta H^{\theta}_{BDE} + \Delta H^{\theta}_{1st\ EA} + \Delta H^{\theta}_{2nd\ EA} + \Delta H_{lattice}$$

$$-635 = 193 + 589.8 + 1145.5 + \frac{1}{2}(+498) - 140.9 + 770 + \Delta H_{lattice}$$

$$\Delta H_{lattice} = -635 - 193 - 589.8 - 1145.5 - 249 + 140.9 - 770$$

$$\Delta H_{lattice} = -3441.7\ kJmol^{-1}$$

(b) Born-Haber cycle in form of a usual enthalpy cycle

Examples

1. **Below is thermochemical data about sodium chloride.**

	$\Delta H^{\theta}(kJmol^{-1})$
Enthalpy of sublimation of sodium	$+109$
Bond dissociation energy of chlorine	$+242$
First ionisation energy of sodium	$+494$
Lattice energy of sodium chloride	-771
Enthalpy of formation of sodium chloride	-411

(a) **Draw a Born Haber cycle of sodium chloride and use it to calculate the electron affinity of chlorine using the following data above**

(b) **If the hydration enthalpies of sodium and chloride ions are $406\ kJmol^{-1}$ and $363\ kJmol^{-1}$ respectively, calculate the enthalpy of solution of sodium chloride.**

(c) **Comment on your answer in (b) above and give a reason for your answer.**

(a)

$$\begin{tikzcd}
Na^{+}(g) & + & Cl^{-}(g) \arrow[ddrr, "-771kJmol^{-1}"] & & \\
Na(g) \arrow[u, "+494kJmol^{-1}"'] & & Cl(g) \arrow[u, "\Delta H_{EA}"'] & & \\
Na(s) \arrow[u, "+109kJmol^{-1}"'] & + & \frac{1}{2}Cl_2(g) \arrow[u, "\frac{+242}{2}kJmol^{-1}"'] \arrow[rr, "\Delta H^{\theta}_{f,NaCl}=-411kJmol^{-1}"] & & NaCl(s)
\end{tikzcd}$$

By Hess' law;

$$\Delta H^{\theta}_{f,NaCl} = \Delta H^{\theta}_{Sublimation} + \Delta H^{\theta}_{1st\ IE} + \frac{1}{2}\Delta H^{\theta}_{BDE} + \boldsymbol{\Delta H^{\theta}_{EA}} + \Delta H_{lattice}$$

$$-411 = 109 + 494 + \frac{1}{2}(242) + \boldsymbol{\Delta H^{\theta}_{EA}} - 771$$

$$\boldsymbol{\Delta H^{\theta}_{EA}} = -411 - 109 - 494 - 121 + 771$$

$$\boldsymbol{\Delta H^{\theta}_{EA} = -364\ kJmol^{-1}}$$

(b)

$$\underset{NaCl}{\Delta H_{solution}} = \underset{NaCl}{\Delta H_{lattice}} + \underset{NaCl}{\Delta H_{hydration}}$$

$$\underset{NaCl}{\Delta H_{solution}} = +771 + \left(\underset{Na^{+}}{\Delta H_{hydration}} + \underset{Cl^{-}}{\Delta H_{hydration}}\right)$$

$$\underset{NaCl}{\Delta H_{solution}} = +771 + (-406 + -363)$$

$$\underset{\boldsymbol{NaCl}}{\boldsymbol{\Delta H_{solution}}} = \boldsymbol{+2\ kJmol^{-1}}$$

Note that lattice energy substituted in the equation in (b) above is the lattice dissociation enthalpy hence it must be positive. Hydration enthalpies are also known to be negative although given as positive values in the question.

(c) *The enthalpy of solution of sodium chloride is* **endothermic** *because the* ***magnitude of its lattice energy is higher than the magnitude of its hydration energy.***

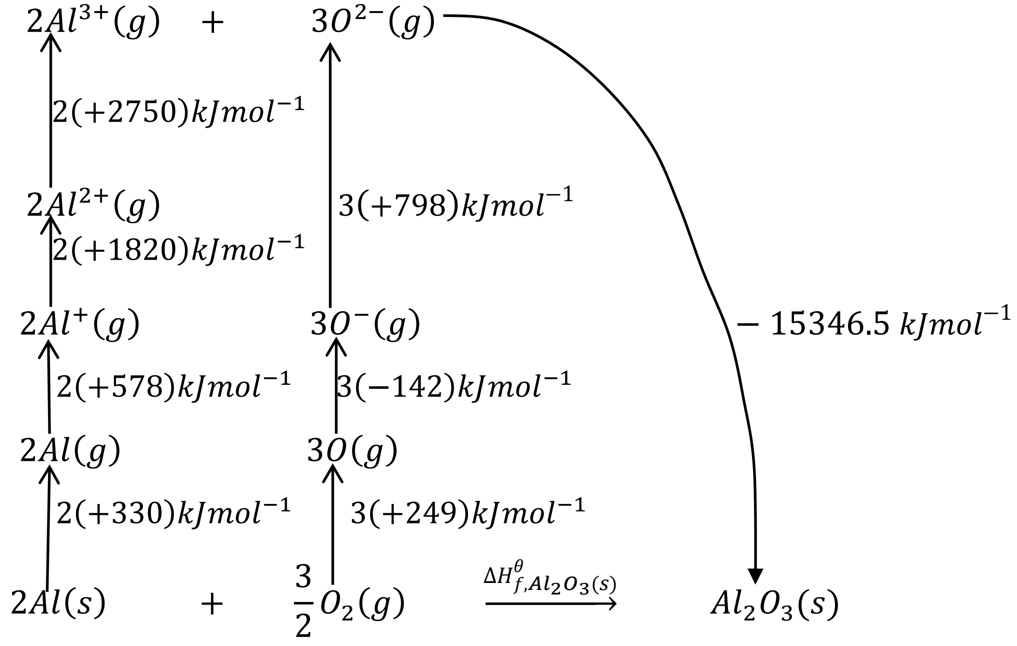
1. **The information below shows thermochemical data of aluminium oxide.**

	$\boldsymbol{\Delta H^{\theta}(kJmol^{-1})}$
Enthalpy change of atomisation of Aluminium	**330**
First ionisation energy of Aluminium	**578**
Second ionisation energy of Aluminium	**1820**
Third ionisation energy of Aluminium	**2750**
Lattice energy of aluminium oxide	**−15346.5**
Atomisation energy of oxygen	**249**
First electron affinity of oxygen	**−142**
Second electron affinity of oxygen	**798**

(a) **Construct a Born Haber cycle relating the enthalpy changes and use it to calculate the enthalpy of formation of aluminium oxide**

(b) **Comment on the stability of aluminium oxide. Give a reason for your answer.**

(a)



By Hess' law;

$$\Delta H^{\theta}_{f,Al_2O_3(s)} = 2\Delta H^{\theta}_{a,Al} + 2\Delta H^{\theta}_{1st\ IE} + 2\Delta H^{\theta}_{2nd\ IE} + 2\Delta H^{\theta}_{3rd\ IE} + 3\Delta H^{\theta}_{a,O_2} + 3\Delta H^{\theta}{}_{1\ st\ EA} + 3\Delta H^{\theta}{}_{2\ nd\ EA} + \Delta H_{lattice}$$

$$\Delta H^{\theta}_{f,Al_2O_3(s)} = 2(+330) + 2(+578) + 2(+1820) + 2(+2750) + 3(+249) + 3(-142) + 3(+798) - 15346.5$$

$$\boldsymbol{\Delta H^{\theta}_{f,Al_2O_3(s)} = -1675.5\ kJmol^{-1}}$$

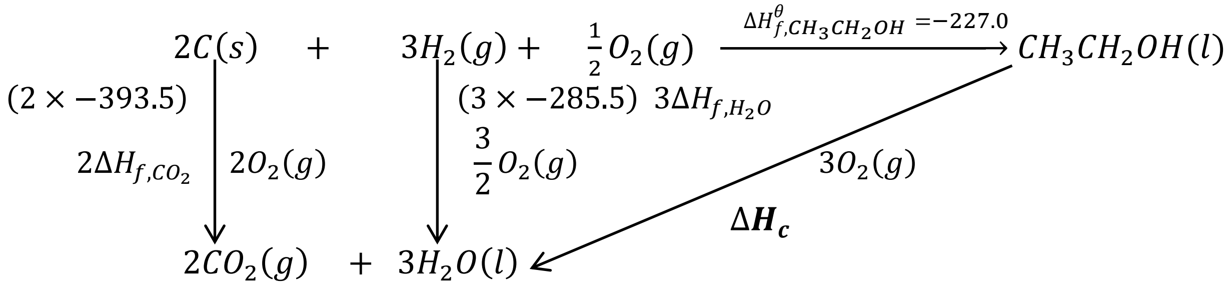
(b) ***Aluminium oxide is stable because its enthalpy of formation is exothermic.***

Born-Haber cycle involving enthalpies of combustion and formation

The standard heats of formation of ethanol, carbon dioxide and water -227.0, -393.5 and $-285.5\ kJmol^{-1}$ respectively.

- **(a) Draw a Born-Haber cycle to relate the energy changes stated above**
- **(b) Calculate the standard heat of combustion of ethanol using the drawn cycle.**
- **(c) From your answer in (b) above and the energy changes in (a) , state one ideal use of ethanol in chemistry. Give a reason for your answer.**

(a)



(b) **By Hess' law**

$$2\Delta H_{f,CO_2} + 3\Delta H_{f,H_2O} = \Delta H^{\theta}_{f,CH_3CH_2OH} + \Delta \boldsymbol{H_c}$$

$$\Delta \boldsymbol{H_c} = 2\Delta H_{f,CO_2} + 3\Delta H_{f,H_2O} - \Delta H^{\theta}_{f,CH_3CH_2OH}$$

$$= (2 \times -393.5) + (3 \times -285.5) - (-227.0)$$

$$\Delta \boldsymbol{H_c} = \boldsymbol{-1416.5\ kJmol^{-1}}$$

(c) ***Ethanol is used as a fuel because its enthalpy of combustion is highly exothermic.***

Determination of heat of hydration of hydrated and anhydrous compounds by use of the Born Haber cycle and applying Hess' law

Example

In an experiment to determine hydration energy of anhydrous copper(II) sulphate $\boldsymbol{4.0g}$ of the anhydrous salt was added to $\boldsymbol{50g}$ of water and the temperature rose by $\boldsymbol{8.0\ °C}$. When $\boldsymbol{4.0g}$ of the hydrated copper(II) sulphate was added to $\boldsymbol{50g}$ of water and the temperature dropped from $\boldsymbol{25.0\ °C}$ to $\boldsymbol{23.7\ °C}$.

($\boldsymbol{Specific\ heat\ capacity\ of\ solution\ is\ 4.2Jg^{-1}°C^{-1}}$)

(a) Calculate the enthalpy of solution of;

(i) anhydrous copper(II) sulphate

(ii) hydrated copper(II) sulphate

(b) State which of the two salts is more soluble in water and explain your answer.

(c) Construct a Born Haber cycle and use it to determine the heat of hydration of anhydrous copper(II) sulphate.

Solution

(a) (i) $$Temperature\ rise = \Delta T = 8.0°C$$

$$Mass\ of\ water\ used = 50\ g$$

$$Total\ mass\ of\ solution = (50 + 4.0) = 54.0g$$

$$Heat\ evolved = mass\ of\ solution \times specific\ heat\ capacity \times temperature\ rise$$

$$Heat\ evolved = (54.0 \times 4.2 \times 8.0) = 1814.4\ J$$

$$Molar\ mass\ of\ anhydrous\ CuSO_4 = 63.5 + 32.1 + (16 \times 4) = 159.6\ g$$

$$4.0\ g\ \ of\ anhydrous\ CuSO_4\ \ \boldsymbol{evolve}\ \ 1814.4\ Joules$$

$$159.6\ g\ \ of\ CuSO_4\ \ \boldsymbol{evolve}\ \ \left(\frac{159.6 \times 1814.4}{4.0}\right)J$$

$$Enthalpy\ of\ solution\ of\ anhydrous\ CuSO_4\ = -72{,}394.56\ Jmol^{-1}$$

$$\boldsymbol{Enthalpy\ of\ solution\ of\ anhydrous\ CuSO_4\ = -72.39456\ kJmol^{-1}}$$

N.B The enthalpy of solution for this reaction is negative (exothermic) because there is an increase in temperature.

(ii)
$$Temperature\ change = \Delta T = (25.0 - 23.7) = 1.3°C$$
$$Mass\ of\ water\ used = 50\ g$$
$$Total\ mass\ of\ solution = (50 + 4.0) = 54.0g$$
$$Heat\ absorbed = mass\ of\ solution \times specific\ heat\ capacity \times temperature\ rise$$
$$Heat\ absorbed = (54.0 \times 4.2 \times 1.3) = 294.84\ J$$
$$Molar\ mass\ of\ \ CuSO_4.5H_2O = 63.5 + 32.1 + (16 \times 4) + (5 \times 18) = 249.6\ g$$
$$4.0\ g\ \ of\ CuSO_4.5H_2O\ \ \boldsymbol{absorb}\ \ 294.84\ Joules$$
$$249.6\ g\ \ of\ CuSO_4.5H_2O\ \boldsymbol{absorb}\ \ \left(\frac{249.6 \times 294.84}{4.0}\right)J$$
$$Enthalpy\ of\ solution\ of\ CuSO_4.5H_2O\ \ = +18398.016\ Jmol^{-1}$$
$$\boldsymbol{Enthalpy\ of\ solution\ of\ CuSO_4.5H_2O\ \ = +18.398016\ kJmol^{-1}}$$

N.B The enthalpy of solution for this reaction is positive (endothermic) because there is a decrease in temperature.

(b) Anhydrous copper(II) sulphate **is more soluble** than hydrated copper(II) sulphate since its enthalpy of solution is **exothermic** whereas that of the hydrated salt is **endothermic**.

This is because the copper(II) ion and sulphate ion in hydrated copper(II) sulphate are already **partly hydrated**. When the hydrated salt is dissolved in water, its **lattice energy outweighs the enthalpy of hydration** associated **with any further hydration**. This makes the **enthalpy of solution positive**. For the anhydrous salt, the **hydration energy outweighs the lattice energy** making the **enthalpy of solution negative**.

(c)
$$\begin{tikzcd}
CuSO_4(s) \arrow[rr, "\Delta H_1 = \mathbf{-72.39456\ kJmol^{-1}}", "(aq)"'] \arrow[dr, "5H_2O"', "\Delta H^{\theta}_{hydration}"] & & Cu^{2+}(aq) + SO_4^{2-}(aq) \\
& CuSO_4.5H_2O(s) \arrow[ur, "(aq)", "\Delta H_2 = \mathbf{+18.398016\ kJmol^{-1}}"'] &
\end{tikzcd}$$

By Hess' law

$$\Delta H_1 = \Delta H^{\theta}_{hydration} + \Delta H_2$$
$$-72.39456 = \Delta H^{\theta}_{hydration} + +18.398016$$
$$\Delta H^{\theta}_{hydration} = -72.39456 - (+18.398016)$$
$$\boldsymbol{\Delta H^{\theta}_{hydration} = -90.7926\ kJmol^{-1}}$$

Born-Haber cycle involving bond energies

1. **(a) Distinguish between atomization energy and bond energy**

   (b) Draw a labelled Born Haber cycle and identify the energy changes involved at each step when carbon reacts with hydrogen to form methane

   (c) Given the enthalpy of formation of methane and atomisation energy of carbon and hydrogen are $\boldsymbol{-75\ kJmol^{-1}}$, $\boldsymbol{218\ kJmol^{-1}}$ and $\boldsymbol{436\ kJmol^{-1}}$respectively, calculate the average bond energy for $\boldsymbol{C - H}$ bond.

(b)

$$\begin{tikzcd}
C(s) \arrow[d, "715kJmol^{-1}\ \Delta H_{a,C}"] & + & 2H_2(g) \arrow[d, "(4\times 218)\ 4\Delta H_{a,H_2}"] \arrow[rr, "\Delta H_f^{\theta}\quad =-75kJmol^{-1}"] & & CH_4(g) \\
C(g) & + & 4H(g) \arrow[urr, "4\ \Delta H_{BE}(C-H)"'] & &
\end{tikzcd}$$

By Hess' law

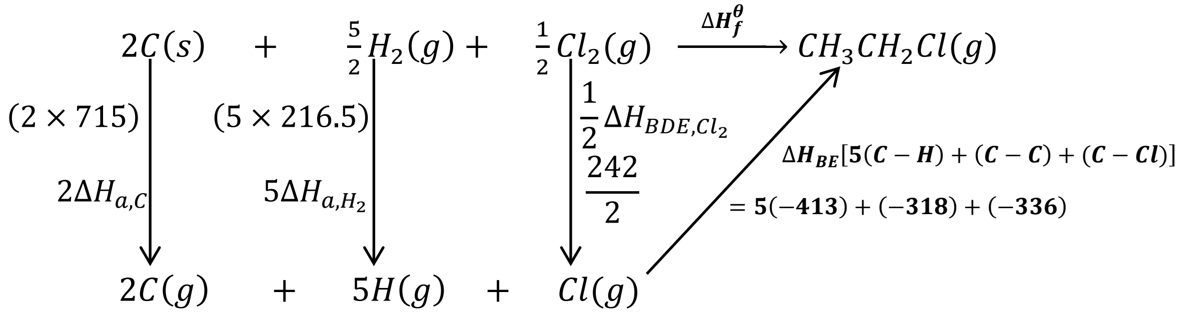
$$\Delta H_f^{\theta} = \Delta H_{a,C} + 4\Delta H_{a,H_2} + 4\Delta H_{BE}(C-H)$$
$$-75 = 715 + (4\times 218) + 4\Delta H_{BE}(C-H)$$
$$4\Delta H_{BE}(C-H) = -75 - 715 - (4\times 218)$$
$$4\Delta H_{BE}(C-H) = -1662$$
$$\Delta H_{BE}(C-H) = \frac{-1662}{4}$$
$$\boldsymbol{\Delta H_{BE}(C-H) = -415.5\ kJmol^{-1}}$$

2. **(a) Draw a Born Haber cycle for formation of chloroethane**

   (b) Calculate the enthalpy of formation of chloroethane using following thermochemical data.

Bond energy of $\boldsymbol{C - C}$ bond = $\boldsymbol{318\ kJmol^{-1}}$
Bond energy of $\boldsymbol{C - Cl}$ bond = $\boldsymbol{336\ kJmol^{-1}}$
Bond energy of $\boldsymbol{C - H}$ bond = $\boldsymbol{413\ kJmol^{-1}}$
Atomization energy of hydrogen = $\boldsymbol{216.5\ kJmol^{-1}}$
Bond dissociation energy of chlorine = $\boldsymbol{242\ kJmol^{-1}}$
Enthalpy of atomization of graphite = $\boldsymbol{715\ kJmol^{-1}}$

Solution



In this calculation you should clearly note that bond energy of formation is exothermic (negative)

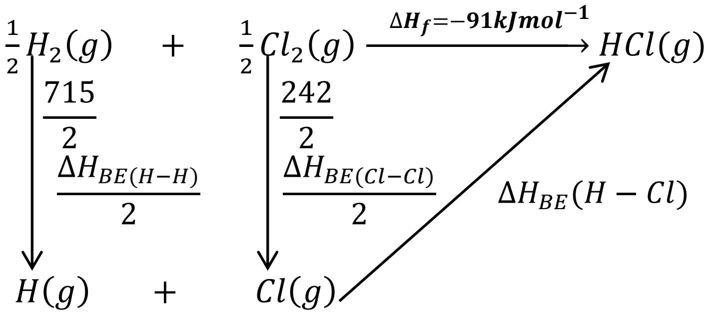
By Hess' law

$$\Delta H_f^\theta = 2\Delta H_{a,C} + 5\Delta H_{a,H_2} + \frac{1}{2}\Delta H_{BDE,Cl_2} + \Delta H_{BE}[5(C-H) + (C-C) + (C-Cl)]$$

$$\Delta H_f^\theta = (2 \times 715) + (5 \times 216.5) + \frac{242}{2} - 5(413) - 318 - 336$$

$$\boldsymbol{\Delta H_f^\theta = -85.5\ kJmol^{-1}}$$

3. **Calculate the bond energy of HCl given that the $H-H$ bond energy is $433\ kJmol^{-1}$, $Cl-Cl$ bond energy is $242\ kJmol^{-1}$ and the enthalpy of formation of hydrogen chloride is $-91\ kJmol^{-1}$**



By Hess' law

$$\Delta H_f = \frac{\Delta H_{BE(H-H)}}{2} + \frac{\Delta H_{BE(Cl-Cl)}}{2} + \Delta H_{BE}(H-Cl)$$

$$-91 = \frac{715}{2} + \frac{242}{2} + \Delta H_{BE}(H-Cl)$$

$$\Delta H_{BE}(H-Cl) = -91 - \frac{715}{2} - \frac{242}{2}$$

$$\boldsymbol{\Delta H_{BE}(H-Cl) = -569.5\ kJmol^{-1}}$$

4. **The standard heat of formation of phosphorus trichloride is $-306\ kJmol^{-1}$. The bond dissociation energy and enthalpy of atomisation of chlorine and phosphorus are 242 and 314 $kJmol^{-1}$ respectively.**
   (i) Draw a Born-Haber cycle for the formation of phosphorus trichloride.
   (ii) Use the Born-Haber cycle to calculate the $P-Cl$ bond energy.

$$\begin{tikzcd}
\frac{1}{4}P_4(s) \arrow[d, "\begin{matrix}314\\ \Delta H_{a,P}\end{matrix}"] & + & \frac{3}{2}Cl_2(g) \arrow[d, "\begin{matrix}\frac{3}{2}\times 242\\ \frac{3}{2}\Delta H_{BDE,Cl_2}\end{matrix}"] \arrow[r, "\Delta H_f=-306\ kJmol^{-1}"] & PCl_3(g) \\
P(g) & + & 3Cl(g) \arrow[ur, "3\Delta H_{BE}(P-Cl)"'] &
\end{tikzcd}$$

$$\Delta H_f = \Delta H_{a,P} + \frac{3}{2}\Delta H_{BDE,Cl_2} + 3\Delta H_{BE}(P-Cl)$$

$$-306 = 314 + \left(\frac{3}{2}\times 242\right) + 3\Delta H_{BE}(P-Cl)$$

$$3\Delta H_{BE}(P-Cl) = -306 - 314 - \frac{726}{2}$$

$$\Delta H_{BE}(P-Cl) = -\frac{983}{3}$$

$$\boldsymbol{\Delta H_{BE}(P-Cl) = -327.667\ kJmol^{-1}}$$

Questions

Questions involving enthalpy cycles

1. The thermochemical data of lithium and oxygen are given below.

$$2Li(s) + \tfrac{1}{2}O_2(g) \longrightarrow Li_2O(s) \quad \Delta H = -596\ kJmol^{-1}$$
$$Li_2O(s) \longrightarrow 2Li^+(g) + O^{2-}(g) \quad \Delta H = +2852.8\ kJmol^{-1}$$
$$Li(s) \longrightarrow Li(g) \quad \Delta H = +161 kJmol^{-1}$$
$$Li(g) \longrightarrow Li^+(g) + e \quad \Delta H = +519 kJmol^{-1}$$
$$O_2(g) \longrightarrow 2O(g) \quad \Delta H = +496\ kJmol^{-1}$$
$$O(g) + e \longrightarrow O^-(g) \quad \Delta H = -141.4\ kJmol^{-1}$$

(a) (i) Draw an energy level diagram for the formation of lithium oxide
    (ii) Use your diagram to find the second electron affinity of oxygen
(b) Comment on the electron affinities of oxygen

2. (a)Draw an energy level diagram for formation of lithium fluoride.

   (b) Using the diagram in (a) above and the data below calculate the standard enthalpy of formation of lithium fluoride

   Atomization energy of fluorine = 150 kJmol^{-1}
   Electron affinity of fluorine = -351 kJmol^{-1}
   Atomization energy of lithium = 155 kJmol^{-1}
   Ionisation energy of lithium = 518 kJmol^{-1}
   Lattice energy of lithium fluoride = -1030 kJmol^{-1}

3. Carefully study the information given below. Enthalpy changes are given in kJmol^{-1} .

   First ionisation energy of calcium = 59
   Atomization energy of calcium = 117
   Second ionisation energy of calcium = 1100
   Heat of atomization of oxygen = 249
   First electron affinity of oxygen = -141
   Second electron affinity of oxygen = 790
   Heat of formation of calcium oxide = -636

From the information above, draw a labelled Born Haber cycle for calcium oxide. Calculate the lattice energy for calcium oxide.

4. Using the information below, draw a Born-Haber cycle and use it to calculate the lattice energy of potassium bromide.

   Enthalpy of formation of potassium bromide = -395.9kJmol^{-1}
   Atomization energy of potassium = 90 kJmol^{-1}
   Dissociation energy of bromine = 113.1 kJmol^{-1}
   Electron affinity of bromine = -342.4 kJmol^{-1}
   Ionisation energy of potassium = 434.2 kJmol^{-1}

5. Construct a Born-Haber cycle for the formation of solid potassium chloride from its elements in their standard states. Use the data below to calculate the standard enthalpy of formation of potassium chloride.

$$K^+(g) + Cl^-(g) \longrightarrow KCl(s) \quad \Delta H = -718\ kJmol^{-1}$$
$$K(s) \longrightarrow K(g) \quad \Delta H = 90\ kJmol^{-1}$$
$$K(g) \longrightarrow K^+(g) + e \quad \Delta H = 418\ kJmol^{-1}$$
$$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g) \quad \Delta H = 122\ kJmol^{-1}$$
$$Cl(g) + e \longrightarrow Cl^-(g) \quad \Delta H = -348\ kJmol^{-1}$$

6. (a) State Hess' law of heat summation.

   (b) Some thermochemical data for silver, fluorine and silver fluoride are given below;

   $F_2(g) \longrightarrow 2F(g)$ $\Delta H_1^\theta = +158\ kJmol^{-1}$

   $Ag^+(g) + F^-(g) \longrightarrow AgF(s)$ $\Delta H_2^\theta = -969\ kJmol^{-1}$

   $Ag(s) \longrightarrow Ag(g)$ $\Delta H_3^\theta = +278\ kJmol^{-1}$

   $Ag(g) + \frac{1}{2}F_2(g) \longrightarrow AgF(s)$ $\Delta H_4^\theta = -203\ kJmol^{-1}$

   $Ag(g) \longrightarrow Ag^+(g) + e$ $\Delta H_5^\theta = +731\ kJmol^{-1}$

   $Ag^+(g) + F^-(g) \longrightarrow Ag^+(aq) + F^-(aq)$ $\Delta H_6^\theta = -991\ kJmol^{-1}$

   (i) Draw an energy level for the formation of solid silver fluoride.

   (ii) Use the energy level diagram above to calculate the first electron affinity of fluorine.

   (c) (i) Define the term enthalpy of solution.

   (ii) Describe an experiment to determine enthalpy of solution of silver fluoride.

   (iii) Explain the energy terms that determine the magnitude of the enthalpy of solution of any ionic salt.

   (iv) Sketch a labelled energy diagram for the dissolution of silver fluoride.

7. (a) Draw a Born Haber for the formation of solid Rubidium chloride

   (b) Calculate the electron affinity of chlorine atom using the following data;

   Enthalpy of formation of rubidium chloride = -439 kJmol^{-1}

   Lattice enthalpy of rubidium chloride = -665 kJmol^{-1}

   Enthalpy of sublimation of rubidium = 84 kJmol^{-1}

   Ionisation energy of rubidium = 397 kJmol^{-1}

   Bond dissociation energy of chlorine = 242 kJmol^{-1}

8. The enthalpies of formation of water and carbon dioxide are -286 and $-393\ kJmol^{-1}$ respectively. The enthalpy of combustion of methane is $-891\ kJmol^{-1}$. Construct a Born-Haber cycle and use it to calculate the enthalpy of formation of methane.

9. The heat of formation of carbon dioxide is $-393kJmol^{-1}$, heat of formation of water is $-286kJmol^{-1}$ and heat of combustion of butane is $-2877kJmol^{-1}$

   (a) Draw a Born Haber cycle to relate the energy changes above.

   (b) Calculate the standard heat of formation of butane using the Born Haber cycle in(a) above.

10. Draw a Born-Haber cycle that can be used to calculate the heat of oxidation of ethanol to ethanal if the enthalpies of combustion of ethanol and ethanal are -1367 kJmol^{-1} and -1167kJmol^{-1} respectively.

    Use your cycle to calculate the enthalpy change for oxidation of ethanol to ethanal.

11. The bond dissociation energies of hydrogen, chlorine and hydrogen chloride are 435, 242 and 431 $kJmol^{-1}$ respectively. Using a Born-Haber cycle, calculate the enthalpy of formation of hydrogen chloride.
12. Calculate the standard enthalpy of formation of ethene from the following data using a Born-Haber cycle.

Bond energy of $C - H$ bond $= 413\ kJmol^{-1}$
Bond energy of $C = C$ bond $= 606\ kJmol^{-1}$
Bond energy of $H - H$ bond $= 435\ kJmol^{-1}$
Bond dissociation energy of hydrogen $= 433\ kJmol^{-1}$
Bond dissociation energy of chlorine $= 242\ kJmol^{-1}$
Enthalpy of sublimation of carbon $= 715\ kJmol^{-1}$

13. The average bond enthalpy and some atomization enthalpies are given below.

Bond	**Bond energy**$(\boldsymbol{kJmol^{-1}})$	**Atomization energy**$(\boldsymbol{kJmol^{-1}})$	
$\boldsymbol{C}$——$\boldsymbol{C}$	318	$C(s) \longrightarrow C(g)$	718
$\boldsymbol{C}$——$\boldsymbol{H}$	416	$\frac{1}{2}H_2(g) \longrightarrow H(g)$	218

(a) Draw a Born Haber cycle for formation of ethane
(b) Use the information above and your cycle to calculate the enthalpy of formation of ethane.

14. (a) Define the term bond energy.
(b) Draw the structure and name the shape of phosphorus trichloride molecule
(c) The heats of atomization of phosphorus and chlorine are given below

	$\Delta \boldsymbol{H_a^{\theta}}(\boldsymbol{kJmol^{-1}})$
$P(s) \longrightarrow P(g)$	$+314$
$Cl_2(g) \longrightarrow 2Cl$	$+242$

Calculate the average bond energy for $P - Cl$ bond.
$(The\ heat\ of\ formation\ of\ PCl_3\ is\ -360\ kJmol^{-1})$

15. The standard enthalpy change of formation of silicon(IV) chloride is $-610\ kJmol^{-1}$. The standard enthalpy change of atomization of silicon and chlorine are $+338\ kJmol^{-1}$ and $+122\ kJmol^{-1}$respectively.
(a) Use these values to construct a Born-Haber cycle for formation of silicon(IV) chloride from its elements and indicate the energy changes involved.
(b) Calculate the average bond energy of the $Si - Cl$ bond.
16. The standard enthalpy change of formation of tin(IV) chloride is $-508\ kJmol^{-1}$. The standard enthalpy change of atomization of tin and chlorine are $+301\ kJmol^{-1}$ and $+121\ kJmol^{-1}$respectively.

(a) Use the above to construct a Born-Haber cycle for formation of tin(IV) chloride.

(b) Calculate the average bond energy of the $Sn - Cl$ bond.

17. The molar enthalpy of solution of anhydrous copper(II) sulphate and copper(II) sulphate pentahydrate are $-66.5\ kJmol^{-1}$ and $+11.70\ kJmol^{-1}$ respectively.

(a)Explain the difference in the values above.

(b) Calculate the enthalpy of hydration of anhydrous copper(II) sulphate.

18. Chemical reactions are accompanied by enthalpy changes.

(a) Explain what is meant by the term standard enthalpy change of a reaction

(b) The enthalpy change for hydration of anhydrous magnesium sulphate can be calculated by carrying out two separate experiments.

(i) In the first experiment, $45.0g$ of water was put in a polystyrene cup and $3.01g$ of anhydrous magnesium sulphate was added and stirred until it completely dissolved. The temperature of the water rose from $23.5\ °C$ to $34.7\ °C$. Calculate the enthalpy of solution of magnesium sulphate.

(ii) In the second experiment, $45.0g$ of water was put in a polystyrene cup and $3.01g$ of hydrated magnesium sulphate($MgSO_4.7H_2O$) was added and stirred until it completely dissolved. The temperature of the water decreased from $23.5\ °C$ to $22.9\ °C$. Calculate the enthalpy of solution of hydrated magnesium sulphate.

(iii) Draw a well labelled Born-Haber cycle and use it to calculate the enthalpy change for the reaction;

$$MgSO_4(s) + 7H_2O(l) \longrightarrow MgSO_4.7H_2O(s)$$

Miscellaneous questions

1. (a) State Hess' law

(b) State four factors that affect the enthalpy change of any system.

(c) The enthalpy of combustion of ethene is $-1411\ kJmol^{-1}$ while that of ethyne is $-1299.5\ kJmol^{-1}$ and that of hydrogen is $-285.8\ kJmol^{-1}$ .Calculate the enthalpy change of hydrogenation of ethyne to ethene.

2. (a) What is meant by the term bond energy?

(b) The bond energies of $C = O,\ C - H, C - O, C - C, C \equiv N$ and $O - H$ bonds respectively are $743, 412, 360, 348, 887$ and $463kJmol^{-1}$. Calculate the enthalpy change for the reaction below.

$$(\boldsymbol{CH_3})_2\boldsymbol{C} = \boldsymbol{O} \quad + \quad \boldsymbol{HCN} \longrightarrow (\boldsymbol{CH_3})_2\underset{\boldsymbol{OH}}{\underset{|}{\boldsymbol{C}}}\boldsymbol{CN}$$

(c) For each of the following compounds state the type of bonding and structure adopted.

Compound	Bonding type	Structure
Iodine		
Calcium fluoride		
Silicon(IV) oxide		

3. (a) Copper like other transition elements forms compounds in oxidation states $+1$ and $+2$. Write the electronic configuration of:
   (i) copper(I) ions
   (ii) copper(II) ions

   (b) The enthalpies of reduction of copper(I) and copper(II) ions are given below:

$$Cu^{+}(aq) + e \longrightarrow Cu(s) \qquad \Delta H_1 = -602 kJmol^{-1}$$
$$Cu^{2+}(aq) + 2e \longrightarrow Cu(s) \qquad \Delta H_2 = -795\ kJmol^{-1}$$

   (i) Calculate the enthalpy of disproportionation of copper(I) ions to copper(II) ions and copper
   (ii) Using your answer in b(i), comment on the stability of copper(I) ions with respect to copper(II) ions. Give a reason for your answer.

   (c) State any two other properties that make copper a typical transition metal.

4. (a) Describe an experiment to determine enthalpy of combustion of butanol

   (b) The standard enthalpies of combustion of the first five straight chain alkanes and alcohols are shown in the table below

Number of carbon atoms	0	1	2	3	4	5
Enthalpy of combustion of alkanes($kJmol^{-1}$)	-286	-890	-1560	-2220	-2877	-3509
Enthalpy of combustion of alcohols($kJmol^{-1}$)	0	-715	-1371	-2010	-2673	-3305

   (i) On the same axes, plot a graph of enthalpies of combustion of both alkanes and alcohols against number of carbon atoms
   (ii) Use the graph to determine the enthalpy of combustion of hexane.
   (iii) Explain the shape of the graph

   (c) The standard enthalpies of combustion of carbon and hydrogen are $-393\ kJmol^{-1}$ and $-286\ kJmol^{-1}$ respectively. The standard enthalpies of atomization of carbon and hydrogen are $+715\ kJmol^{-1}$ and $+218\ kJmol^{-1}$ respectively. Calculate;
   (i) Standard enthalpy of formation of hexane
   (ii) Standard enthalpy of atomization of hexane

CHAPTER FIVE

PHYSICAL EQUILIBRIA

Equilibrium represents the state of a process in which the properties like temperature, pressure, concentration of the system do not show any change with passage of time.

A physical equilibrium is an equilibrium that exists between different phases or physical properties. It represents the existence of the same substance in different physical states. This equilibrium does not involve any chemical change. It involves only physical changes like phase changes or solubility.

SYSTEMS, PHASES, COMPONENTS AND PHASE DIAGRAMS

System

A system is that part of the universe, the set of substances and energy associated with them, that is being studied.

For example if reactions are occurring in a conical flask, everything inside the flask is a system.

Phase

A phase is a homogeneous part of a system which is physically distinct from other parts of the system by a definite boundary.

Each of the three homogeneous states (***solid, liquid and gas***) in which a substance can exist is called a **phase**.

- For example a mixture of gases is one phase
- A solution is one phase
- A saturated solution in the presence of an excess of the solute is a two-phase system

Except under special conditions, only two phases can exist in equilibrium.

Component

A pure substance in a system that defines part of the composition of that system

A mixture of water and ethanol has two components but one phase

A mixture of ice and water has two phases but one component

Phase diagram

When a substance can exist in different phases, for example water which can exist as a liquid, gas (water vapour) or solid (ice), the conditions under which each phase exists, and the various equilibria that can exist between the three phases can be represented by a phase diagram.

***A phase diagram is a graph on which pressure is plotted against temperature showing equilibria between different phases of a substance and the temperatures and pressures at which each phase exists*.**

- An **area/ region** of a phase diagram represents one phase
- A **line or curve** represents the temperatures and pressures under which two phases can exist in equilibrium
- A **triple point** represents the temperature and pressure under which three phases can coexist in equilibrium.

COMPONENT SYSTEMS

There are two types of components systems namely;

(i) ***One-component system***

Only one pure chemical substance is involved in the equilibrium

(ii) ***Two-component system***

Two chemically independent components are involved in the equilibrium

One component systems

Examples of one component systems include;

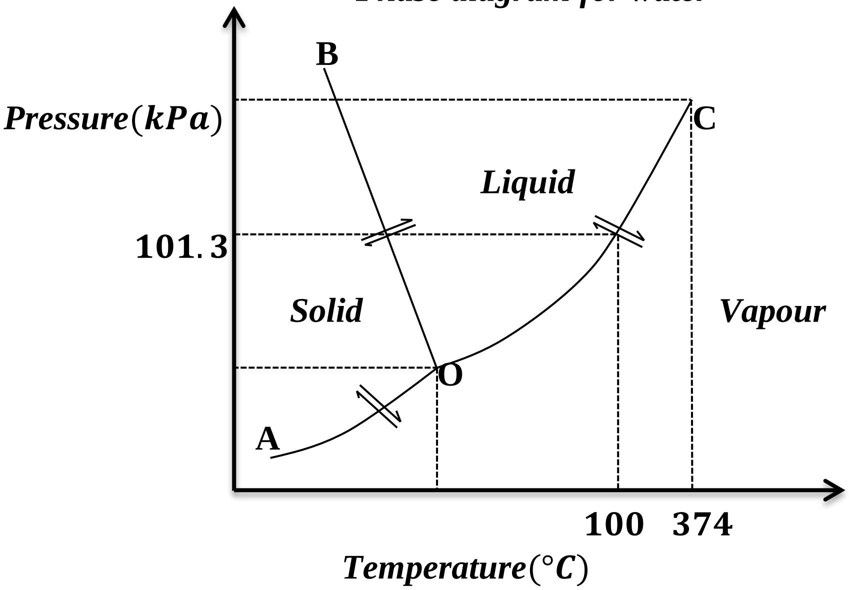
- ***The water system***
- ***The sulphur system***
- ***The carbon dioxide system***

The water system

Water can exist as liquid, as a solid(ice) or as a vapour. It is called steam when its temperature is above $100°C$.

Below is a phase diagram for the water system.

Phase diagram for water



At low temperature and low pressure, water exists as **ice**. At low temperature and high pressure, it exists as **vapour**. At high temperatures and high pressures, it exists as a **liquid**.

Curves/lines	
OA	shows the **variation of vapour pressure of ice with temperature** The line summarises the conditions under which solid ice and water vapour can be in equilibrium. This curve is called the **sublimation curve of ice**.
OC	shows the **variation of vapour pressure of liquid water with temperature** The line summarises the conditions of temperature and pressure under which liquid water and water vapour are in equilibrium. This curve is called the **vapourisation curve of liquid water**.
OB	shows the **effect of pressure on the melting point of ice or freezing point of water.** The line shows equilibrium between ice and liquid water. It is called the **freezing curve/ fusion curve**.

Note: ***Line OB slopes upwards to the left because the melting point of ice decreases as the pressure increases***.

This decrease in melting point with increase in pressure is related to Le Chatelier's principle. (**Check next Chapter**)

Points	
O	***Triple point of water***
C	***Critical point of water***

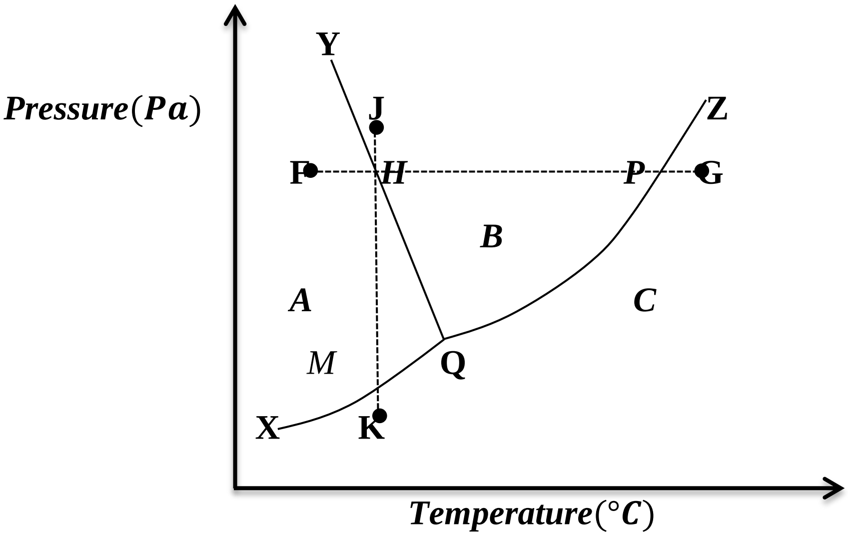
***The triple point refers to the particular temperature and the particular pressure at which ice, water vapour and liquid water co-exist at equilibrium*.**

***The critical point represents the particular temperature and particular pressure above which water vapour cannot condense to liquid water no matter how much pressure is applied*.**

***The critical temperature($374°C$) is the temperature above which vapour cannot be converted into liquid water no matter how much pressure is exerted*.**

Beyond the critical temperature, liquid water and water vapour are undistinguishable

Effect of temperature and pressure on the phases



1. The diagram above is a phase diagram for the water system
   (a) Name the ;
      (i) regions **A, B** and **C**
      (ii) points **Q** and **Z**

(iii) curves **QY, QX** and **QW**

   (b) State why line QY slants to the left

2. **Explain the changes that take place when ;**
   (i) temperature of the system is increased from F to G at a constant pressure
   (ii) pressure of the system is reduced from J to K at constant temperature.

(i) At **F**, water exists in the solid phase (ice).
Increase in the temperature of ice moves the system from **F to H** without change in phase.
At **H**, ice begins to melt and the temperature remains constant until all the ice has melted.

After all the ice has melted, further increase in temperature will move the system from **H to P** in the liquid phase.

At point **P**, liquid water begins to vapourise and the temperature remains constant until all the water has vapourised.

Further increase in temperature moves the system from **P to G** in the vapour phase.

(ii) At **J**, water exists in the liquid phase.

Reducing the pressure of liquid water moves the system from **J to H** without change in phase.

At **H**, liquid water begins to freeze and the pressure remains constant until all the water has frozen.

After all the liquid water has frozen, a further decrease in pressure will move the system from **H to M** in the solid phase.

At point **M**, ice begins to sublime and the pressure remains constant until all the ice has sublimed.

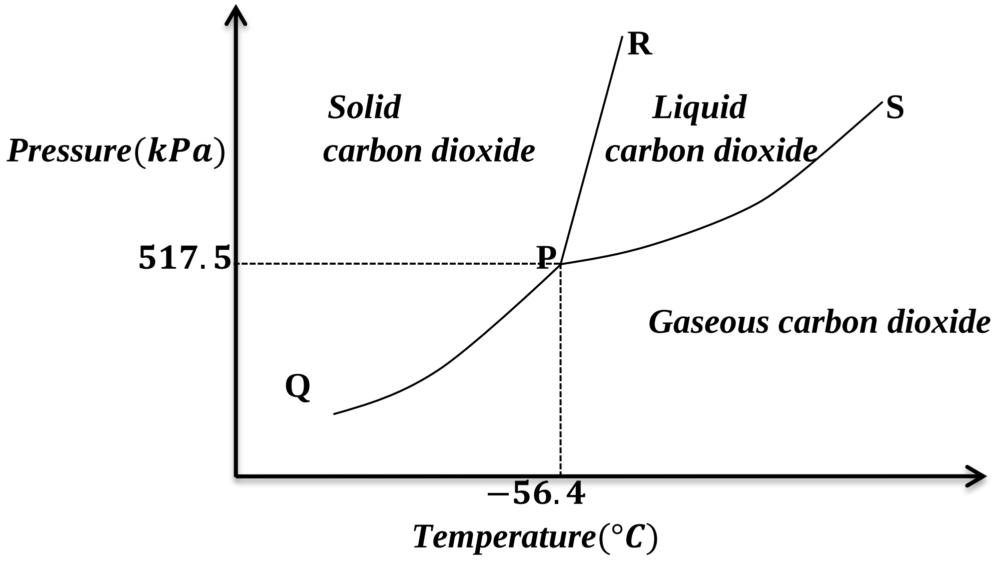
Further decrease in pressure moves the system from **M to K** in the vapour phase.

The carbon dioxide system

Like water, carbon dioxide can also exist as liquid, as solid or as a gas.

Below is a phase diagram for the carbon dioxide system.

Phase diagram for carbon dioxide



Curves/lines	
PQ	This curve is called the **sublimation curve of solid carbon dioxide**. It shows the **variation of vapour pressure of solid carbon dioxide with temperature** The line summarises the conditions under which solid carbon dioxide and carbon dioxide gas can be in equilibrium.
PS	This curve is called the **vapourisation curve of liquid carbon dioxide**. It shows the **variation of vapour pressure of liquid carbon dioxide with temperature** The line summarises the conditions of temperature and pressure under which liquid carbon dioxide and gaseous carbon dioxide are in equilibrium.
PR	It is called the **freezing curve/ fusion curve**. It shows the **effect of pressure on the melting point solid carbon dioxide or freezing point of liquid carbon dioxide.** The line shows equilibrium between solid carbon dioxide and liquid carbon dioxide.

Note: ***Line PR slopes to the right because the melting point of solid carbon dioxide increases as the pressure increases***.

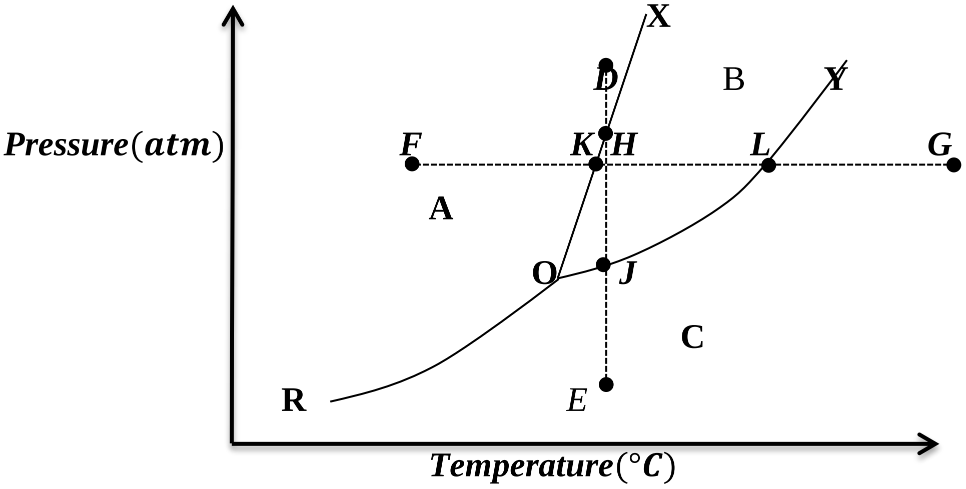
Points

P	***Triple point of carbon dioxide***
S	***Critical point of carbon dioxide***

The triple point of carbon dioxide is $-56.4\,^{\circ}C$ and $517500\,Pa$. This means that liquid carbon dioxide cannot exist at ordinary atmospheric pressure and solid carbon dioxide sublimes when exposed to a warm temperature.

Effect of temperature and pressure on the phases

The figure below shows the phase diagram for carbon dioxide.



(a) State what the following represent.
- **(i)** Regions; **A, B** and **C**
- (ii) Points; **O** and **Y**
- (iii) Curves **OX**, **OR** and **OY**

(b) State why line OX slopes to the right**.**

(c) **Explain the changes that take place when ;**
- **(i)** **pressure of the system is decreased from D to E at a constant temperature**
- **(ii)** **temperature of the system is increased from F to G at constant pressure.**

(i) At **D**, carbon dioxide is a solid.

Decrease in the pressure of solid carbon dioxide moves the system from **D to H** without change in phase.

At **H**, solid carbon dioxide begins to melt and the pressure remains constant until all the solid carbon dioxide has melted.

After all the solid carbon dioxide has melted, further decrease in pressure will move the system from **H to J** in the liquid phase.

At point **J**, liquid carbon dioxide begins to vapourise and the pressure remains constant until all the liquid carbon dioxide has vapourised.

Further decrease in pressure moves the system from **J to E** in the vapour phase.

(ii) At **F**, carbon dioxide is a solid.

Increasing the temperature of solid carbon dioxide moves the system from **F to K** without change in phase.

At **K**, solid carbon dioxide begins to melt and the temperature remains constant until all the solid carbon dioxide has melted.

After all the solid carbon dioxide has melted, a further increase in temperature will move the system from **K to L** in the liquid phase.

At point **L**, liquid carbon dioxide begins to vapourise and the temperature remains constant until all the liquid carbon dioxide has vapourised.

Further increase in temperature moves the system from **L to G** in the gaseous phase.

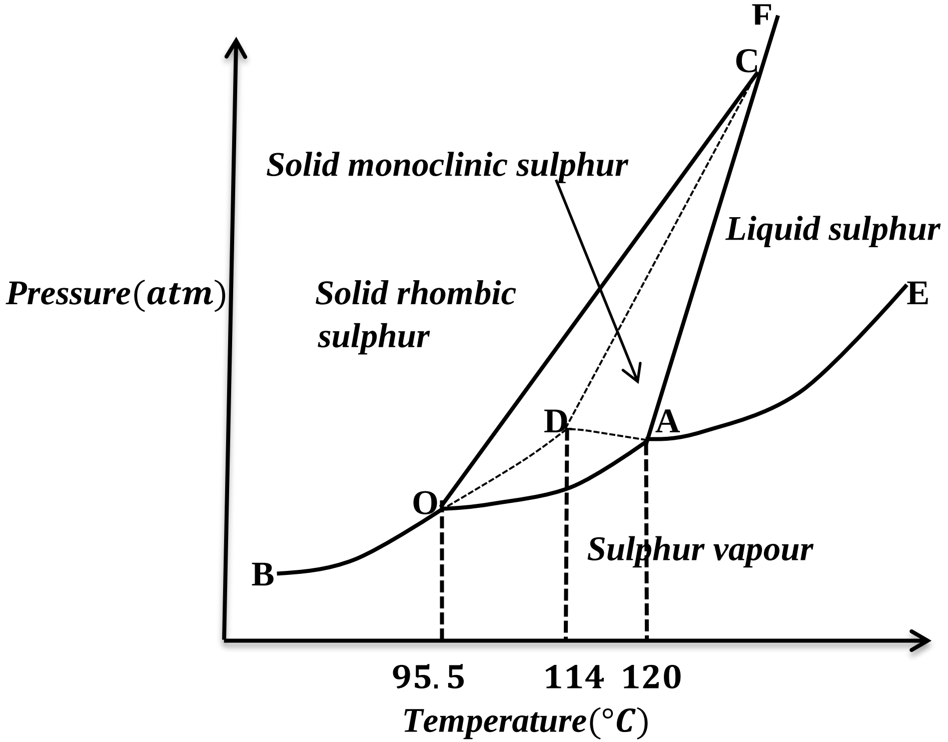
The sulphur system

Sulphur exhibits **enantiotropic allotropy**.

Enantiotropic allotropy occurs when one form of an element after being heated is converted into another form at a definite transition temperature.

Sulphur exists in two crystalline forms; **rhombic sulphur** (or $\alpha-$sulphur) and **monoclinic sulphur**($\beta -$ sulphur)

These changes can be represented in the **phase diagram for sulphur** below.



Curves	
OB	This is the **sublimation curve of solid rhombic sulphur**. It shows the **variation of vapour pressure of solid rhombic sulphur with temperature** Along this curve, solid rhombic sulphur is in equilibrium with sulphur vapour.
OA	This is the **sublimation curve of solid monoclinic sulphur**. It shows the **variation of vapour pressure of solid monoclinic sulphur with temperature** Along this curve, solid monoclinic sulphur is in equilibrium with sulphur vapour.
AE	This is the **vapourisation curve of liquid sulphur**. It shows the **variation of vapour pressure of liquid sulphur with temperature** Along this curve, liquid sulphur is in equilibrium with its vapour.
OC	It is called the **transition curve**. shows the **effect of pressure on the transition point between rhombic and monoclinic sulphur.** The line shows equilibrium between ice and liquid water.
AC	This is the **fusion curve of monoclinic sulphur**. It shows the **effect of pressure on the melting point of monoclinic sulphur.**
CF	This is the **fusion curve of rhombic sulphur**. It shows the **effect of pressure on the melting point of rhombic sulphur.**

Points

O	***Triple point for rhombic sulphur, monoclinic sulphur and sulphur vapour***
C	***Triple point for rhombic sulphur, monoclinic sulphur and liquid sulphur***
A	***Triple point for monoclinic sulphur, liquid sulphur and sulphur vapour***
D	***Melting point of rhombic sulphur***

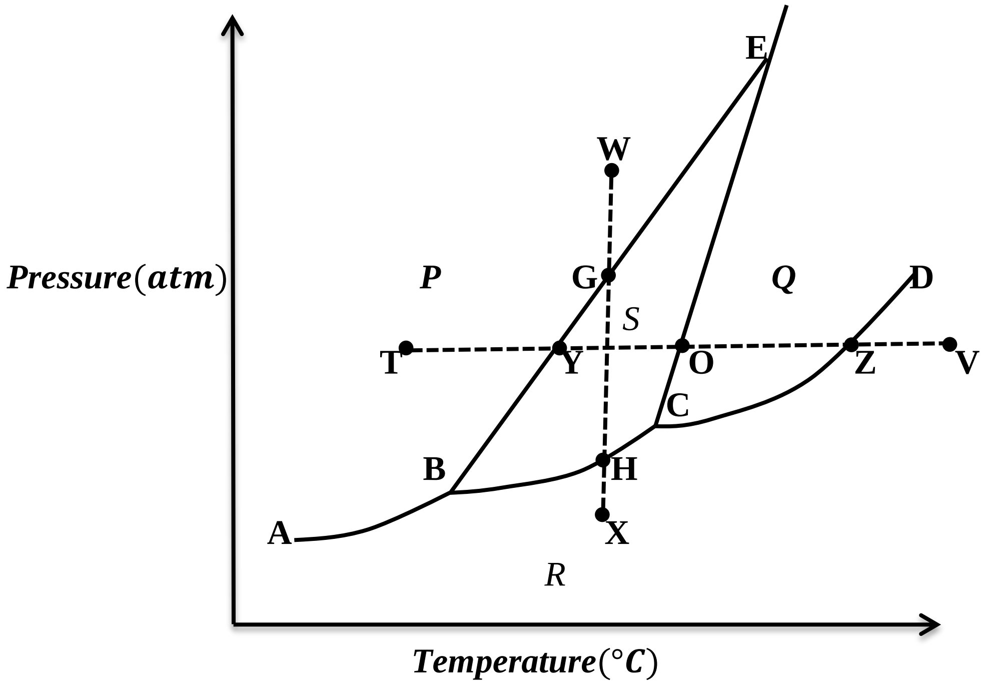
At **ordinary temperatures** and **under one atmosphere**, sulphur exists as in the stable allotropic form of **rhombic sulphur**.
If its heated slowly to a ***temperature just above*** $\boldsymbol{95.5\,°C}$ ***(the transition temperature)*** , it changes completely into **monoclinic sulphur** which is stable until a temperature of $120°C$ is reached, which is the melting point of monoclinic sulphur.
This transition is marked by a change in direction of the vapour pressure-temperature curve at **O** in the phase diagram.
On cooling monoclinic sulphur up to $95.5°C$, it changes to rhombic sulphur**.**

$$\boldsymbol{rhombic\ (\alpha)S \overset{95.5°C}{\rightleftharpoons} monoclinic(\beta)S \overset{120°C}{\rightleftharpoons} liquid\ S}$$

- When rhombic sulphur is heated rapidly, its temperature is raised rapidly to point **D** without conversion into monoclinic sulphur. Melting occurs at $114°C$, above the transition temperature.
- Rhombic sulphur is only stable below the transition temperature but unstable the transition temperature.
- Liquid sulphur when cooled forms needle shaped crystals of monoclinic sulphur. These can exist below the transition temperature but change in a few hours to rhombic sulphur.
- The more stable rhombic sulphur has a lower vapour pressure that the unstable monoclinic sulphur at the same temperature.

Curves OC, AC and CF all slope upwards to the right because the transition temperature, melting point of monoclinic sulphur and melting point of rhombic sulphur all increase with increase in pressure respectively.

Effect of temperature and pressure on the phases



(a) State what the following represent.

- **(i)** phases; **P, Q, R** and **S**
- (ii) Points; **B, C** and **E**
- (iii) Curves **AB**, **BC, CD, BE** and **CE**

(b) State why curves **BE** and **CE** slope to the right**.**

(c) Explain the changes that take place when ;

- **(i) P is heated T to V at constant pressure.**
- **(ii) pressure of the system is decreased from W to X at a constant temperature**

(i) At **T**, sulphur is in the solid rhombic form.

Heating increases the temperature of solid rhombic sulphur from **T to Y** without change in phase.

At **Y**, solid rhombic sulphur begins to change to solid monoclinic sulphur and the temperature remains constant until all the solid rhombic sulphur has changed to monoclinic sulphur.

Further heating increases the temperature of solid monoclinic sulphur, moving the system from **Y to O**.

At point **O**, monoclinic sulphur begins to melt into liquid sulphur and the temperature remains constant until all the monoclinic sulphur has melted.

Further heating increases the temperature of liquid sulphur, moving the system from **O to Z** in the liquid phase.

At **Z**, liquid sulphur begins to turn into sulphur vapour and the temperature remains constant until all the liquid sulphur has vapourised.

Further heating moves the system from **Z** to **V** in the vapour phase.

(ii) At **W**, sulphur is in the solid rhombic form.

Decrease in the pressure of solid rhombic sulphur moves the system from **W to G** without change in phase.

At **G**, solid rhombic sulphur begins to change to solid monoclinic sulphur and the pressure remains constant until all the solid rhombic sulphur has changed to monoclinic sulphur.

Further decreases in vapour pressure of monoclinic sulphur moves the system from **G to H**.

At point **H**, solid monoclinic sulphur begins to sublime and the pressure remains constant until all the solid monoclinic sulphur has sublimed.

Further decrease in pressure moves the system from **H to X** in the vapour phase.

Two component systems

Types of two component systems

There are three types of two component systems (liquid mixtures) which include;

- ***Completely miscible liquid mixtures***
- ***partially miscible liquid mixtures***
- ***immiscible liquid mixtures***

Completely miscible liquid mixtures

These are liquids which when shaken mix completely, in any proportions to form a solution at a given temperature.

Depending on the forces of attraction between the molecules in the solution there are two types of miscible solutions which are;

(i) Ideal solution
(ii) Non-ideal solutions

These will be explained later

Examples of miscible liquid mixture include;

- Ethanol and water
- Methanol and water
- Ethoxyethane and benzene

- Benzene and methylbenzene
- Propan-1-ol and propan-2-ol

For completely miscible liquids, the vapour pressure of the mixture is not constant at a given temperature but varies with the proportions of the two liquids and also depends on the nature of the two liquids

Completely miscible liquid mixtures can be separated by **fractional distillation.**

Partially miscible liquid mixtures

Partially miscible liquids are liquids which in given proportions dissolve in each other to some extent to form conjugate solutions.

Examples of partly miscible liquid mixtures include;

- Ethoxyethane and water
- Triethylamine and water
- Phenol and water(partially miscible below $66°C$)

When a few drops of ethoxyethane are shaken with a lot of water, a solution of ethoxyethane in water is formed. If a few drops of water are shaken with a lot of ethoxyethane, a solution of water in ethoxyethane is formed. If about equal volumes of the two liquids are shaken, two layers are formed. The upper layer consists of a saturated ***solution of water in ethoxyethane*** and the lower layer consists of a ***saturated solution of ethoxyethane in water***.

Phenol and water are only completely miscible, forming one solution above $66°C$, but two immiscible solutions are formed below the same temperature depending on the composition of the mixture. One of the solutions is a ***solution of phenol in water*** and the other is a ***solution of water in phenol***.
The two solutions are called **conjugate solutions**.

The complete miscibility of phenol and water with increasing temperature is because their mutual solubilities increase with increase in temperature.
Steam distillation method may be used to separate partially miscible liquid mixtures**.**

Immiscible liquid mixtures

Immiscible liquids are liquids which when shaken and allowed to settle, they do not mix but form separate layers.
In most cases, immiscible liquids involve organic substances and water.
Examples of immiscible liquid mixtures include;

- Oil and water
- Chloroform(trichloromethane) and water

- Tetrachloromethane and water
- Paraffin and water
- Benzene and water
- Carbon disulphide and water
- Mercury and water

Immiscible liquids can be separated by using **steam distillation method.**

IDEAL SOLUTIONS AND NON-IDEAL SOLUTIONS

Ideal solutions

Ideal solutions can also be called perfect solutions.

An ideal solution is a solution in which the cohesive forces are equal to adhesive forces, made with no heat or volume change and obeys Raoult's law over all concentration ranges at a given temperature.

If a solution is made from two components **A** and **B**, the solution is ideal if forces between **A** and **B** are equal to the forces between **A** and **A** and those between **B** and **B**.

$$\boldsymbol{A}\text{——}\boldsymbol{A} \quad \boldsymbol{B}\text{——}\boldsymbol{B} \quad \boldsymbol{A}\text{——}\boldsymbol{B}$$

$$\boldsymbol{intramolecular\ forces}(\boldsymbol{cohesive\ forces}) = \boldsymbol{intermolecular\ forces}(\boldsymbol{adhesive\ forces})$$

Raoult's law

Raoult's law states that the partial vapour pressure of a pure component in a solution at a given temperature is equal to the vapour pressure of the pure component at the same temperature, multiplied by its mole fraction in the solution.

$$\boldsymbol{P_i = x_i P_i^0} \text{ where}$$

$$\boldsymbol{P_i} = Partial\ vapour\ pressure\ of\ i$$

$$\boldsymbol{x_i} = mole\ fraction\ of\ i$$

$$\boldsymbol{P_i^0} = vapour\ pressure\ of\ pure\ i$$

Vapour pressure of a pure substance is the pressure exerted the vapour over the surface at a given temperature.

Substances with lower vapour pressure have strong intermolecular forces, while those with higher vapour pressure have weak intermolecular forces. The higher the vapour pressure, the faster the evaporation rate.

Mole fraction <u>of a component</u> (x)in a solution is the ratio of the number of moles of that component present to the total number of moles of all the components in the mixture.

$$x = \frac{n_i}{n_{total}}$$

Therefore for a mixture of two liquids A and . The mole fractions of liquids A and B are given respectively as

$$x_A = \frac{n_A}{n_A + n_B} \quad and\ x_B = \frac{n_B}{n_A + n_B}$$

$$x_A = \frac{n_A}{n_{total}} \quad and\ x_B = \frac{n_B}{n_{total}}$$

Where n_A is number of moles of A and n_B is number of moles of B

$$we\ should\ also\ note\ that\ the\ total\ mole\ fraction\ should\ always\ be\ one$$

$$x_A + x_B = 1$$

$$Therefore\ \ x_A = 1 - x_B$$

According to Raoult's law; $P_A = x_A P_A^0$

Similarly ; $P_B = x_B P_B^0$

$$P_{total} = P_A + P_B$$

$$\boldsymbol{P_{total} = x_A P_A^0 + x_B P_B^0}$$

The vapour composition of each component can be obtained from the expressions;

$$\boldsymbol{vapour\ composition\ of\ A = \frac{P_A}{P_{total}}}$$

$$\boldsymbol{vapour\ composition\ of\ B = \frac{P_B}{P_{total}}}$$

The percentage vapour composition of each component can be obtained from the expressions;

$$\boldsymbol{percentage\ vapour\ composition\ of\ A = \frac{P_A}{P_{total}} \times 100}$$

$$\boldsymbol{percentage\ vapour\ composition\ of\ B = \frac{P_B}{P_{total}} \times 100}$$

Characteristics of ideal solutions

Two substances when mixed form an ideal solution only when;

(i) they obey Raoult's law.

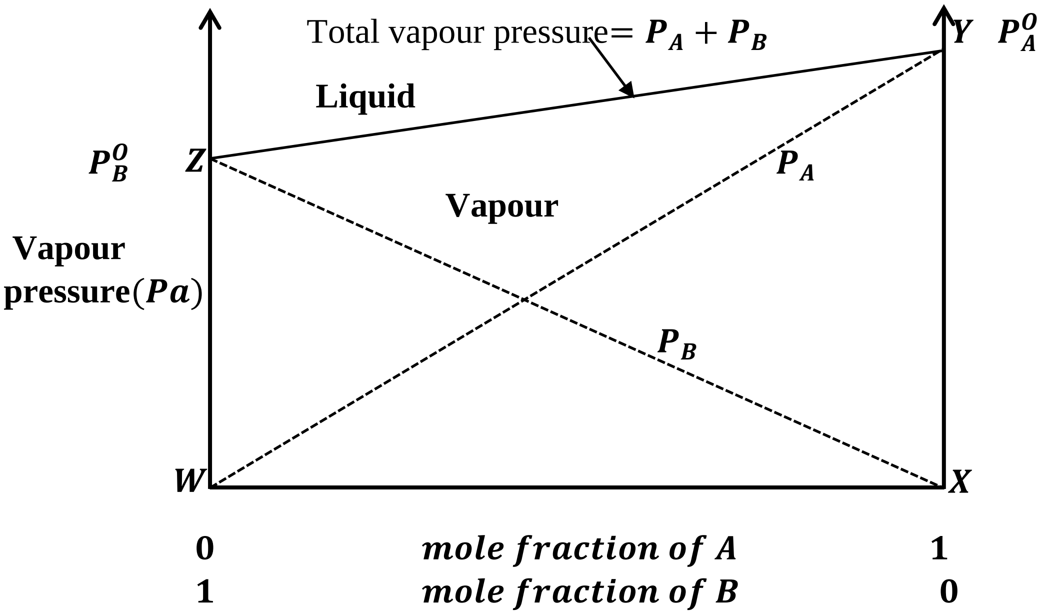
(ii) no heat change occurs on mixing

(iii) the total volume of the solution is equal to the sum of the volumes of the pure components mixed to make the solution.

Examples of ideal solutions

- Benzene and methylbenzene
- Hexane and heptane
- Chlorobenzene and bromobenzene
- Bromoethane and iodoethane
- Propan-2-ol and propan-1-ol

Vapour pressure-composition diagram for an ideal solution



Instead of mole fraction, percentage composition by mass may be used

P_A^O is the vapour pressure of pure A

P_B^O is the vapour pressure of pure B

Line WY shows variation in partial vapour pressure of A with its composition/ mole fraction

Line XZ shows variation in partial vapour pressure of B with its composition/ mole fraction

Line ZY shows variation in total vapour pressure of the mixture with composition/ mole fraction

- The more volatile component has a higher saturated vapour pressure at a given temperature if the composition is the same.
- From the above diagram, A is more volatile than B
- The steeper the line ZY, the higher the difference in the vapour formation tendency of the two components. In the case the two components have equal vapour formation tendencies; the line would have been horizontal.
- Ideal solutions do not form an azeotropic mixture

Boiling point-composition diagram for an ideal solution

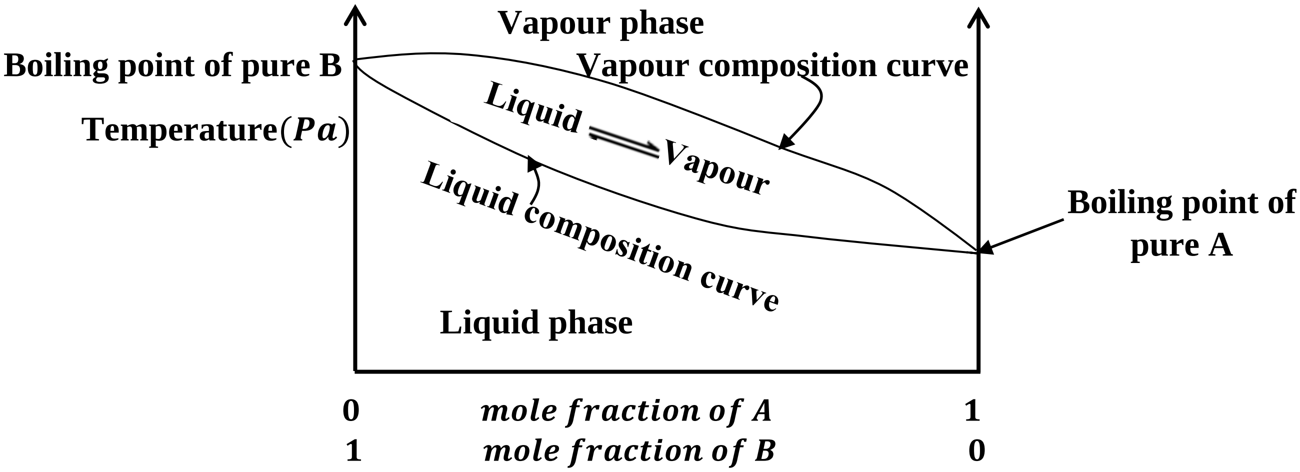
Boiling point composition diagram is a plot of boiling point of the mixture against composition.

Using the saturated vapour pressures, a boiling point of a substance can be predicted.

The component with a ***higher saturated vapour pressure*** has a ***lower boiling point*** and the component with a ***lower saturated vapour pressure*** has a ***higher boiling point***.

From the vapour pressure-composition diagram above; $P_A^O > P_B^O$. Therefore liquid A is more volatile (has a lower boiling point) than liquid B

Increasing temperature increases the vapour pressure of both liquids in the mixture but the vapour pressure of a more volatile component increases more rapidly, such that the vapour above the liquid mixture boiling is richer in the more volatile component.



Instead of mole fraction, percentage composition by mass may be used

Questions

1. A mixture of benzene and methylbenzene at 330K is an ideal solution. The partial vapour pressure of benzene above the solution varies according to Raoult's law as shown in the table below.

Partial vapour pressure of benzene in solution (kPa)	10.0	15.0	25.0	30.0	40.0
Mole fraction of benzene in solution	0.20	0.30	0.50	0.60	0.80

State the effect of adding methyl benzene to the temperature and volume of a fixed mass of benzene.

(a) On the same axes, plot a graph of ;
  (i) Vapour pressure of benzene.
  (ii) Total vapour pressure above the solution against mole fraction of benzene.

(the composition of benzene in the vapour is 50% when its mole fraction in solution is 0.27).

(b) Sketch a well labeled boiling point-composition diagram for the above mixture.

2. A mixture of methanol and water at $50°C$ is an ideal solution. The partial vapour pressure of methanol in the vapour above the solution varies according to Raoult's law as shown in the table below.

Partial vapour pressure of methanol (mmHg)	40.0	100.0	200.0	260.0	320.0
Mole fraction of methanol in solution	0.10	0.25	0.50	0.65	0.80

(a) (i) Define the term ideal solution.
  (ii) State Raoult's law
(b) On the same axes, plot a graph of;
  (i) Vapour pressure of methanol
  (ii) Total vapour pressure above the solution against mole fraction of methanol.
  (the composition of methanol in the vapour is 50% when its mole fraction in solution is 0.19)
(c) Use your graphs in (b) above to determine the;
  (i) Saturated vapour pressure of methanol at $50°C$.
  (ii) Saturated vapour pressure of water at $50°C$
(d) Compare the volatility of methanol and water at $50°C$. Give a reason for your answer.
(e) Draw a well labeled boiling point composition diagram for methanol-water mixture.

3. (a) The table below shows the composition of ***X*** in the vapour and the liquid mixture of ***X*** and ***Y*** at different temperatures.

Temperature($°C$)	110	107	100	95	90	85	80
Mole fraction of *X* in the liquid	0	0.06	0.19	0.32	0.5	0.73	1.0
Mole fraction of *X* in the vapour	0	0.19	0.48	0.65	0.79	0.91	1.0

  (i) Plot a boiling point-composition diagram for the system
  (ii) Explain how this mixture deviates from Raoult's law
(b) Sketch a well labeled vapour-pressure composition diagram for the system.

Calculations involving Raoult's law

Examples

1. **The vapour pressure of a pure liquid A is $5332.9\ Pa$ at $310\ K$. The vapour pressure of this liquid in a solution with liquid B is $4266.3\ Pa$. Calculate the mole fraction of A in the solution if it obeys Raoult's law.**

$$P_A^0 = 5332.9\ Pa$$
$$P_A = 4266.3\ Pa$$
$$x_A = ?$$

According to Raoult's law

$$P_A = x_A P_A^0$$
$$4266.3 = x_A \times 5332.9$$
$$x_A = \frac{4266.3}{5332.9}$$
$$\boldsymbol{x_A = 0.8}$$

---

2. **Benzene and methylbenzene are two hydrocarbons that form an ideal solution. At 313K, the vapour pressures of the pure benzene and methylbenzene are 160 mmHg and 60 mmHg respectively. Calculate the total pressure over the following solutions;**
   - **(i)** **One made by combining 4 moles of methylbenzene and 1mole of benzene.**
   - **(ii)** **One made by combining an equal number of moles of benzene and methylbenzene**.
   - **(iii)** **One made by combining equal masses of methylbenzene and benzene.**

(i) One made by combining 4 moles of methylbenzene and 1mole of benzene

$$P_{C_6H_6}^0 = 160\ mmHg$$
$$P_{C_7H_8}^0 = 60\ mmHg$$
$$n_{C_6H_6} = 1\ mole \qquad n_{C_7H_8} = 4\ moles$$
$$n_{total} = 1 + 4 = 5\ moles$$
$$x_{C_6H_6} = \frac{1}{5} = \mathbf{0.2}$$
$$x_{C_7H_8} = \frac{4}{5} = \mathbf{0.8}$$

According to Raoult's law

$$P_{C_6H_6} = x_{C_6H_6} P_{C_6H_6}^0$$
$$= 0.2 \times 160 = \mathbf{32\ mmHg}$$
$$P_{C_7H_8} = x_{C_7H_8} P_{C_7H_8}^0$$
$$= 0.8 \times 60 = \mathbf{48\ mmHg}$$
$$P_{total} = P_{C_6H_6} + P_{C_7H_8}$$
$$\boldsymbol{P_{total} = 32 + 48 = 80mmHg}$$

(ii)

$$P_{C_6H_6}^0 = 160\ mmHg$$
$$P_{C_7H_8}^0 = 60\ mmHg$$
$$let\ the\ number\ of\ \mathbf{moles}\ of\ C_6H_6 = \boldsymbol{N}$$
$$number\ of\ \mathbf{moles}\ of\ C_7H_8 = \boldsymbol{N}$$
$$n_{C_6H_6} = N \qquad n_{C_7H_8} = N$$
$$n_{total} = N + N = \boldsymbol{2N}$$
$$x_{C_6H_6} = \frac{N}{2N} = \mathbf{0.5} \qquad x_{C_7H_8} = \frac{N}{2N} = \mathbf{0.5}$$

According to Raoult's law

$$P_{C_6H_6} = x_{C_6H_6} P_{C_6H_6}^0$$
$$= 0.5 \times 160 = \mathbf{80mmHg}$$
$$P_{C_7H_8} = x_{C_7H_8} P_{C_7H_8}^0$$
$$= 0.5 \times 60 = \mathbf{30mmHg}$$
$$P_{total} = P_{C_6H_6} + P_{C_7H_8}$$
$$\boldsymbol{P_{total} = 80 + 30 = 110mmHg}$$

(iii)

$$P^0_{C_6H_6} = 160\ mmHg$$

$$P^0_{C_7H_8} = 60\ mmHg$$

$$let\ the\ \boldsymbol{mass}\ of\ C_6H_6 = \boldsymbol{m}$$

$$\boldsymbol{mass}\ of\ C_7H_8 = \boldsymbol{m}$$

Molar mass of $C_6H_6 = (6 \times 12) + (6 \times 1) = \boldsymbol{78g}$

Molar mass of $C_7H_8 = (7 \times 12) + (8 \times 1) = \boldsymbol{92g}$

mass of $C_6H_6\ in\ solution = (y \times 78)g$

mass of $C_7H_8\ in\ solution = (y \times 92)g$

$$n_{C_6H_6} = \frac{\boldsymbol{m}}{\boldsymbol{78}} \qquad n_{C_7H_8} = \frac{\boldsymbol{m}}{\boldsymbol{92}}$$

$$n_{total} = \frac{m}{78} + \frac{m}{92} = \boldsymbol{0.02369m}$$

$$x_{C_6H_6} = \left(\frac{m}{78} \div 0.02369m\right)$$

$$x_{C_6H_6} = \left(\frac{m}{78} \times \frac{1}{0.02369m}\right) = \boldsymbol{0.541178}$$

$$x_{C_7H_8} = \left(\frac{m}{92} \div 0.02369m\right)$$

$$x_{C_7H_8} = 1 - x_{C_6H_6}$$

$$x_{C_7H_8} = (1 - 0.541178) = \boldsymbol{0.458822}$$

$$P_{C_6H_6} = x_{C_6H_6}P^0_{C_6H_6}$$

$$= 0.541178 \times 160 = \boldsymbol{86.58848mmHg}$$

$$P_{C_7H_8} = x_{C_7H_8}P^0_{C_7H_8}$$

$$= 0.458822 \times 60 = \boldsymbol{27.52932\ mmHg}$$

$$P_{total} = P_{C_6H_6} + P_{C_7H_8}$$

$$\boldsymbol{P_{total} = 86.58848 + 27.52932}$$

$$= \boldsymbol{114.1178\ mmHg}$$

---

3. **A solution contains 20% heptane in pure methylbenzene. The vapour pressures of pure heptane and pure methylbenzene 92.1 mmHg and 59.1 mmHg respectively. Calculate the total pressure of the solution.**

20% heptane means the solution has $\boldsymbol{20g}$ of heptane and $(\boldsymbol{100 - 20})\boldsymbol{g}$ of methylbenzene

$$mass\ of\ C_7H_{16} = \boldsymbol{20g}$$

$$mass\ of\ C_7H_8 = \boldsymbol{80g}$$

$$P^0_{C_7H_{16}} = 92.1\ mmHg \qquad P^0_{C_7H_8} = 59.1\ mmHg$$

Molar mass of $C_7H_{16} = (7 \times 12) + (16 \times 1)$

$= \boldsymbol{100g}$

Molar mass of $C_7H_8 = (7 \times 12) + (8 \times 1) = \boldsymbol{92g}$

$$n_{C_7H_{16}} = \frac{20}{100} = \boldsymbol{0.2\ moles}$$

$$n_{C_7H_8} = \frac{80}{92} = \boldsymbol{0.869565\ moles}$$

$$n_{total} = 0.2 + 0.869565 = \boldsymbol{1.069565\ moles}$$

$$x_{C_7H_{16}} = \left(\frac{0.2}{1.069565}\right) = \boldsymbol{0.186992}$$

$$x_{C_7H_8} = 1 - x_{C_7H_{16}}$$

$$x_{C_7H_8} = (1 - 0.186992\ ) = \boldsymbol{0.813008}$$

$$P_{C_7H_{16}} = x_{C_7H_{16}}P^0_{C_7H_{16}}$$

$$= 0.186992\ \times 92.1 = \boldsymbol{17.22196\ mmHg}$$

$$P_{C_7H_8} = x_{C_7H_8}P^0_{C_7H_8}$$

$$= 0.813008 \times 59.1 = \boldsymbol{48.04877\ mmHg}$$

$$P_{total} = P_{C_7H_{16}} + P_{C_7H_8}$$

$$P_{total} = 17.22196 + 48.04877$$

$$= \boldsymbol{65.27073\ mmHg}$$

---

4. **The vapour pressures of methanol and ethanol at $20°C$ are 94mmHg and 44mmHg. If 20g of methanol and 100g of ethanol gave ideal solution after being mixed together, calculate ;**
   - **(i) Partial pressure exerted by each component in a mixture**
   - **(ii) Total vapour above the mixture**
   - **(iii) Composition of vapour above the liquid mixture.**

(i)

$$P^0_{CH_3OH} = 94\ mmHg \qquad P^0_{CH_3CH_2OH} = 44\ mmHg$$

$$mass\ of CH_3OH = \mathbf{20g}$$

$$mass\ of CH_3CH_2OH = \mathbf{100g}$$

Molar mass of $CH_3OH = 12 + 4 + 16 = \mathbf{32g}$

Molar mass of $CH_3CH_2OH = 24 + 6 + 16 = \mathbf{46g}$

$$n_{CH_3OH} = \frac{20}{32} = \mathbf{0.625\ moles}$$

$$n_{CH_3CH_2OH} = \frac{100}{46} = \mathbf{2.173913\ moles}$$

$$n_{total} = 0.625 + 2.173913 = \mathbf{2.798913\ moles}$$

$$x_{CH_3OH} = \left(\frac{0.625}{2.798913}\right) = \mathbf{0.223301}$$

$$x_{CH_3CH_2OH} = 1 - x_{CH_3OH}$$

$$x_{CH_3CH_2OH} = (1 - 0.223301\ ) = \mathbf{0.776699}$$

$$P_{CH_3OH} = x_{CH_3OH}P^0_{CH_3OH}$$

$$= 0.223301\ \ \times 94$$

$$\boldsymbol{P_{CH_3OH} = 20.9903\ mmHg}$$

$$P_{CH_3CH_2OH} = x_{CH_3CH_2OH}P^0_{CH_3CH_2OH}$$

$$= 0.776699 \times 44$$

$$\boldsymbol{P_{CH_3CH_2OH} = 34.1748\ mmHg}$$

(ii)

$$P_{total} = P_{CH_3OH} + P_{CH_3CH_2OH}$$

$$P_{total} = 20.9903 + 34.1748$$

$$\boldsymbol{P_{total} = 55.1651\ mmHg}$$

(iii) Vapour composition of $CH_3OH = \frac{\boldsymbol{P_{CH_3OH}}}{\boldsymbol{P_{total}}}$

$$= \frac{20.9903}{55.1651} = \mathbf{0.3805}$$

Vapour composition of $CH_3CH_2OH = \frac{\boldsymbol{P_{CH_3CH_2OH}}}{\boldsymbol{P_{total}}} = \frac{34.1748}{55.1651} = \mathbf{0.6195}$

---

5. **Two liquids Y and Z on mixing form an ideal solution. At 30°C, the vapour pressure of the solution containing 3 moles of Y and 1 mole of Z is 550 mmHg. When 4 moles of Y and 1 mole of Z are mixed, the vapour pressure of the solution formed is 560mmHg. Calculate the vapour pressure of pure Y and pure Z.**

For case one;

$$n_Y = 3, \qquad n_Z = 1$$

$$P_{total} = 550\ \ mmHg$$

$$P^0_Y = ? \qquad P^0_Z = ?$$

$$n_{total} = 3 + 1 = \mathbf{4}$$

$$x_Y = \frac{3}{4} = \mathbf{0.75} \qquad x_Z = \frac{1}{4} = \mathbf{0.25}$$

$$P_Y = x_YP^0_Y = \boldsymbol{0.75P^0_Y}$$

$$P_Z = x_ZP^0_Z = \boldsymbol{0.25P^0_Z}$$

$$P_{total} = P_Y + P_Z$$

$$P_{total} = 0.75P^0_Y + 0.25P^0_Z$$

$$\boldsymbol{0.75P^0_Y + 0.25P^0_Z = 550} \ldots\ldots\ldots\ldots..(\boldsymbol{i})$$

For case two;

$n_Y = 4, \qquad n_Z = 1$

$P_{total} = 560\ mmHg$

$P_Y^0 = ? \qquad P_Z^0 = ?$

$n_{total} = 4 + 1 = \mathbf{5}$

$x_Y = \frac{4}{5} = \mathbf{0.8} \qquad x_Z = \frac{1}{5} = \mathbf{0.2}$

$P_Y = x_Y P_Y^0 = \mathbf{0.8P_Y^0}$

$P_Z = x_Z P_Z^0 = \mathbf{0.2P_Z^0}$

$P_{total} = P_Y + P_Z$

$P_{total} = 0.8P_Y^0 + 0.2P_Z^0$

$\mathbf{0.8P_Y^0 + 0.2P_Z^0 = 560} \ldots\ldots\ldots\ldots..(\boldsymbol{ii})$

Solving equations $(\boldsymbol{i})$ and $(\boldsymbol{ii})$ simultaneously yields;

$\boldsymbol{P_Y^0 = 600\ mmHg \quad and\ P_Z^0 = 400\ mmHg}$

6. **The saturated vapour pressures of liquids A and B form an ideal solution at $20°C$ are $15\ KNm^{-2}$ and $35\ KNm^{-2}$ respectively. If the total vapour pressure above the solution is KNm^{-2} , calculate the;**
   (i) mole fraction of A in the liquid mixture.
   (ii) composition of the vapour above the liquid mixture of A and B.

(i)

$P_A^0 = 15\ KNm^{-2} \qquad P_B^0 = 35\ KNm^{-2}$

$P_{total} = 29\ KNm^{-2}$

$x_A = ? \qquad x_B = ?$

$Since\ x_A + x_B = 1$

$x_B = 1 - x_A$

$P_A = x_A P_A^0 = x_A \times 15$

$P_B = x_B P_B^0 = x_B \times 35 = 35(1 - x_A)$

$P_{total} = P_A + P_B$

$29 = 15x_A + 35(1 - x_A)$

$29 = 15x_A + 35 - 35x_A$

$20x_A = 6$

$\boldsymbol{x_A = 0.3}$

(ii)

$P_A = x_A P_A^0 = 0.3 \times 15 = 4.5KNm^{-2}$

$P_B = x_B P_B^0 = x_B \times 35 = 35(1 - 0.3)$

$= 24.5KNm^{-2}$

Vapour composition of A = $\frac{P_A}{P_{total}} = \frac{4.5}{29} = \mathbf{0.155}$

Vapour composition of B = $\frac{P_B}{P_{total}} = \frac{24.5}{29} = \mathbf{0.845}$

Questions

1. Calculate the partial vapour pressure of 1,1-dibromoethane at $85°C$ for an ideal solution with a mole fraction of 0.25. The vapour pressure of pure 1,1-dibromoethane is 170mmHg at $85°C$.

2. (a) Explain what is meant by the term **ideal solution**.
   (b) The vapour pressures of liquids $\boldsymbol{X}$ and $\boldsymbol{Y}$ are $473.5\ Nm^{-2}$ and $139.8\ Nm^{-2}$ respectively at $20°C$. Calculate the composition of the vapour above an ideal solution containing 3 moles of $\boldsymbol{X}$ and 4 moles of $\boldsymbol{Y}$ at $20°C$.
3. Benzene when mixed with toluene form an essentially ideal solution. 24g of Benzene were mixed with 61.3 g of toluene. At 80°C. At this temperature, vapour pressure of pure benzene and toluene are 740 mmHg and 290 mmHg respectively. Calculate the;
   (i) partial pressure of each component above the solution
   (ii) total vapour pressure and vapour composition.
4. The vapour pressures of benzene and methyl benzene at $298K$ are 43.98 and $36.54\ mmHg$ respectively.
   (i) Calculate the vapour pressure of a solution containing 5.6 g of benzene and 6.3 g of methylbenzene assuming the mixture is ideal.
   (ii) Calculate the composition of the vapour above the liquid mixture.
5. An ideal solution contains an equal number of moles of benzene and methylbenzene at 60°C. At this temperature vapour pressure of pure benzene and pure methylbenzene are 94 mmHg and 28.4 mmHg respectively. Calculate partial vapour pressure, total vapour pressure and vapour composition above the liquid mixture.
6. An ideal solution containing 3 moles of benzene and 2 moles of methylbenzene has a total vapour pressure of 280 mmHg at 60°C. When one mole of methylbenzene was added at the same temperature, the new total pressure was found to be 300 mmHg. Calculate the vapour pressure of pure benzene and pure toluene at 60°C.
7. (a) State **Raoult's** law
   (b) A liquid mixture of ***A*** and ***B*** obeys Raoult's law. The vapour pressures of ***A*** and ***B*** are $9.978kNm^{-2}$ and $2.875kNm^{-2}$ respectively at 20ºC.
   (i) Calculate the composition of the vapour of a mixture containing 0.7 mole fraction of liquid ***A*** at 20ºC
   (ii) Which of the liquids is more volatile? Give a reason for your answer.
8. The vapour pressures of pure propyl alcohol and pure isopropyl alcohol are 20.9mmHg and 45.2mmHg at 25ºC. If the two form an ideal solution, and the mole fraction of propyl alcohol in the solution is 0.25. Calculate;
   (i) the partial pressure of each component in equilibrium with the solution
   (ii) the total pressure over the solution
9. An ideal solution containing benzene and methylbenzene has composition of 0.62 benzene in the vapour. Calculate mole fraction of benzene and toluene in the liquid given that, vapour pressure of pure benzene and toluene are 94 mmHg and 28.4 mmHg respectively.

10. Assuming that urea, $CO(NH_2)_2$,forms an ideal solution in water. Calculate the vapour pressure of an aqueous solution containing 10% by mass of urea at 40. (Vapour pressure of water at 40°C is 55.3mmHg)
11. (a) State what is meant by the term ideal solution.
    (b) The vapour pressure of water and methanol are 3.173kPa and 16.785kPa respectively at 293K. Assuming that the mixture of the two liquids behaves as an ideal solution and that it contains 0.88 mole fraction of water. Calculate the:
        (i) vapour pressure of the mixture
        (ii) percentage of methanol in the vapour.
12. (a) Heptane and octane form an ideal solution.
        (i) Explain what is meant by the term **'ideal solution'**
        (ii) State **Raoult's** law
        (iii) Calculate the vapour pressure of a solution containing 49.8g of heptane and 33.2g of octane. The vapour pressures of heptane and octane are $473.2Pa$ and $139.8Pa$ respectively
    (b) Compound ***X*** (**boiling point 370ºC**) and compound ***Y*** (**boiling point 400ºC**) form an ideal solution.
        (i) Sketch a labelled boiling point-composition diagram for the mixture
        (ii) Using the diagram, describe and explain how pure ***Y*** can be obtained from a mixture containing 50% compound ***Y.***

Non-ideal (real) solutions

An ideal solution is a solution which the cohesive forces are either stronger or weaker than adhesive forces, made with change in volume or heat does not obey Raoult's law over all concentration ranges at a given temperature.

Characteristics of real solutions

(i) The components do not obey Raoult's law.
(ii) Heat is either absorbed or given off when they are formed
(iii) The solutions are formed with a change in volume.

Deviation from Raoult's law

For non-ideal solutions, the intramolecular forces of attraction are not equal to the intermolecular forces of attraction hence such solutions deviate from both Raoult's law.
There are two deviations from Raoult's law that can occur for non- ideal solutions.

Negative deviation from Raoult's law

For a solution that deviates negatively from Raoult's law, ***the total vapour pressure above the liquids is less than what it would be if the liquids were ideal(lower than what is predicted by Raoult's law or calculated value)*** as a result of a ***lower tendency for the molecules to escape from the solution*** than from the pure liquids. This is due to ***stronger forces of attraction between the molecules in solution than between those in pure liquids***.

The stronger forces between the components of the solution are commonly due to association through intermolecular hydrogen bonding.

Solutions that deviate negatively from Raoult's law are commonly made with a ***contraction in volume*** and ***an evolution of heat***.

Examples of solutions that deviate negatively from Raoult's law

They include;

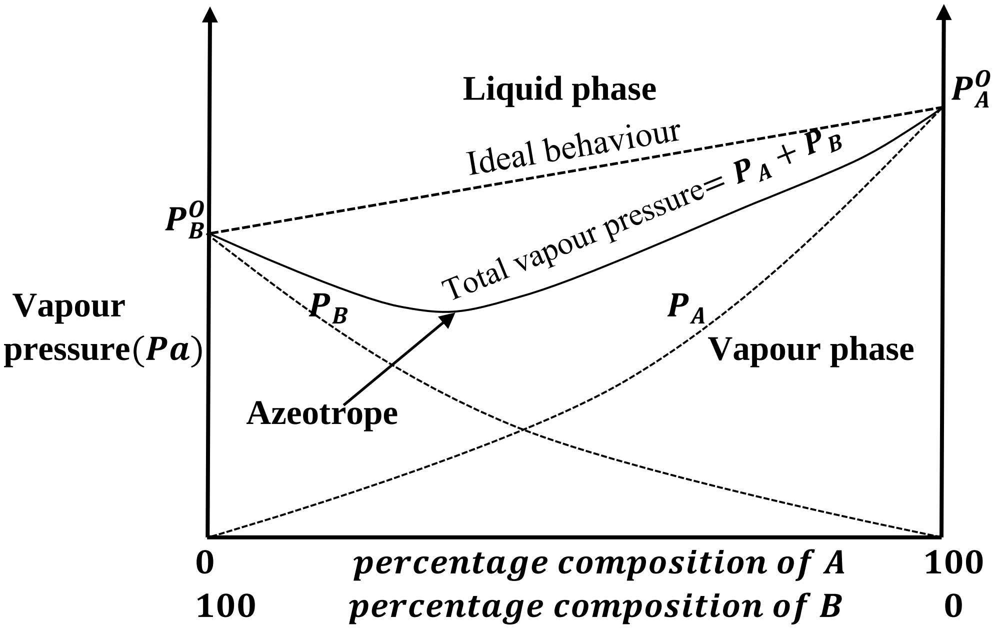
- Water and nitric acid
- Water and hydrofluoric acid
- Water and hydrochloric acid
- Water and hydrobromic acid
- Water and hydroiodic acid
- Water and chloric(VI) acid
- Water and sulphuric acid
- Methanol and ethanoic acid
- Water and methanoic acid
- Trichloromethane(chloroform) and ethoxyethane
- Trichloromethane and benzene
- Trichloromethane and propanone
- Propanone(acetone)and aminobenzene(aniline or phenylamine)
- Propanone and ethanol
- Phenol and phenylamine

N.B. Please refer to bonding and structure to identify forces of attraction between the individual molecules and when each of the two liquids above are mixed.

In general, for solutions that deviate negatively from Raoult's law;

- ***Forces of attraction between different molecules(A and B) are stronger than forces of attraction between similar molecules (A and A) or (B and B)***
- ***Heat is evolved on mixing the components of the solution***
- ***Volume of the solution is less than the sum of the volumes of the two liquids mixed***
- ***The solution has a lower vapour formation tendency compared to the ideal solution.***
- ***The solution can't be separated to its pure components by fractional distillation because at a certain point during distillation the solution form an azeotropic mixture whose liquid and vapour composition are at equilibrium and boils at constant temperature.***

Characteristic vapour pressure-composition diagram for negative deviation from Raoult's law



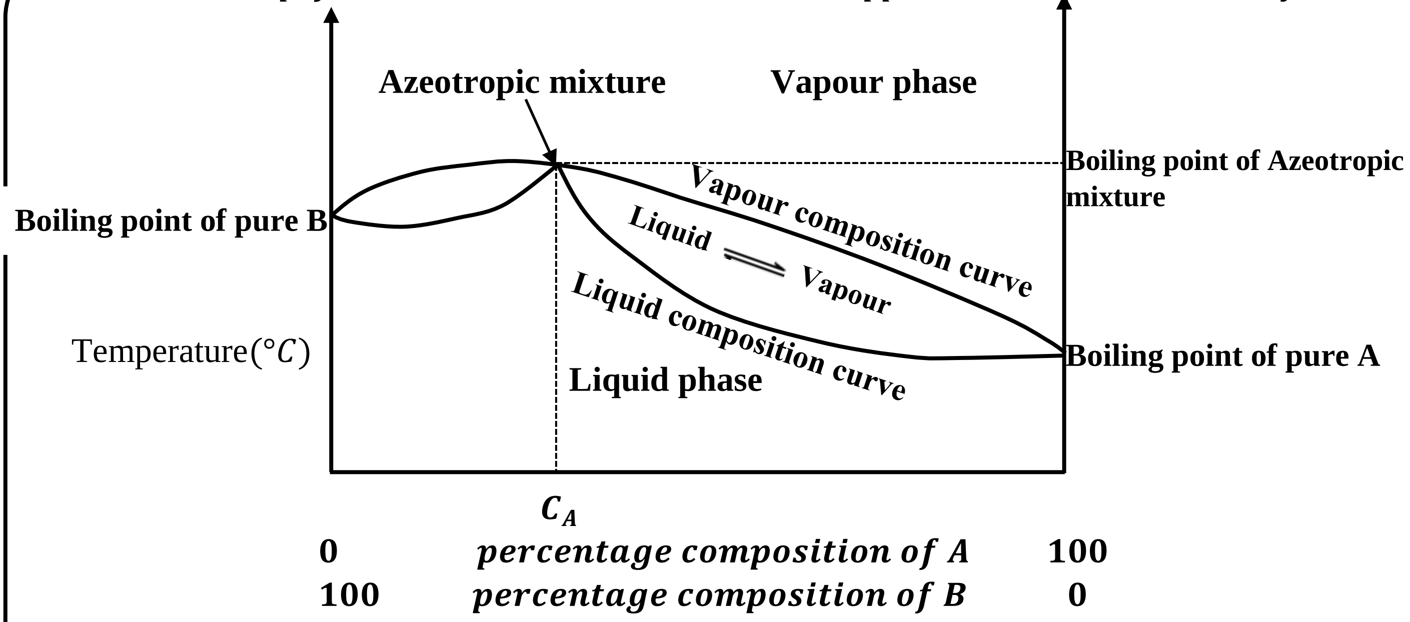
Instead of percentage composition, mole fraction may be used

Component A is more volatile than B (A has a higher saturated vapour than B)

Maximum boiling point-composition diagram (Negative deviation from Raoult's law)

When two liquids in solution associate through intermolecular bonding, their escaping tendencies into vapour reduce, hence a reduction in vapour pressure than what is expected basing on Raoult's law. For such solutions, a minimum is seen in the vapour pressure-composition diagram. The minimum vapour pressure implies that the boiling point at that composition will be maximum.

Considering the mixture of A and B above, the boiling-point composition diagram can be drawn a shown below.



C_A is the composition of the Azeotropic mixture

Positive deviation from Raoult's law

For a solution that deviates positively from Raoult's law, ***the total vapour pressure above the liquids is greater than what it would be if the liquids were ideal(higher than what is predicted by Raoult's law or calculated value)*** as a result of a ***greater tendency for the molecules to escape from the solution*** than from the pure liquids. This is due to ***weaker forces of attraction between the molecules in solution than between those in pure liquids***. Stronger forces between the molecules of the independent pure liquids that must be broken to form such a solution are commonly hydrogen bonds.

Solutions that deviate negatively from Raoult's law are commonly made with ***an increase in volume*** and ***an absorption of heat***.

Examples of solutions that deviate positively from Raoult's law

They include;

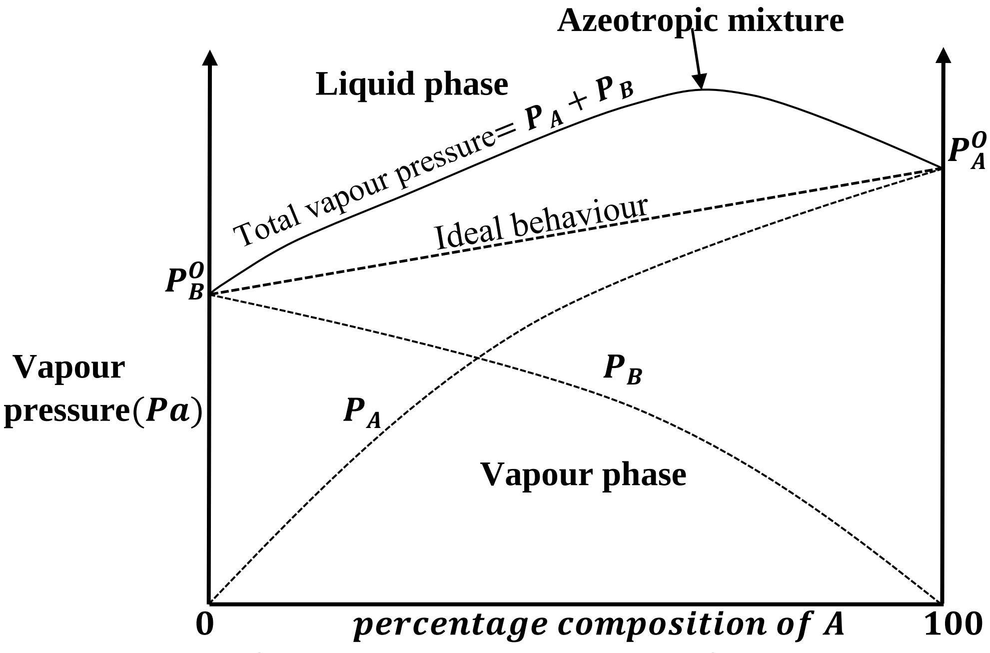
- Water and ethanol
- Water and propan-1-ol
- Water and butanol
- Water and pyridine
- Hexane and ethanol
- Propanone(Acetone) and ethanol
- Propanone and carbon disulphide
- Propanone and benzene
- Ethanol and trichloromethane
- Ethanol and methylbenzene
- Carbon tetrachloride(tetrachloromethane) and benzene
- Tetrachloromethane and chloroform
- Tetrachloromethane and methylbenzene

N.B. Please refer to bonding and structure to identify forces of attraction between the individual molecules and when each of the two liquids above are mixed.

In general, for solutions that deviate positively from Raoult's law;

- ***Forces of attraction between different molecules(A and B) are weaker than forces of attraction between similar molecules (A and A) or (B and B)***
- ***Heat is absorbed on mixing the components of the solution***
- ***Volume of the solution is bigger than the sum of the volumes of the two liquids mixed***
- ***The solution has a higher vapour formation tendency compared to the ideal solution.***
- ***The solution can't be separated to its pure components by fractional distillation because at a certain point during distillation the solution form an azeotropic mixture whose liquid and vapour composition are similar at equilibrium and boils at constant temperature.***
- ***The azeotropic mixture formed in this case has a maximum vapour pressure and a minimum boiling point.***

Characteristic vapour pressure-composition diagram for positive deviation from Raoult's law



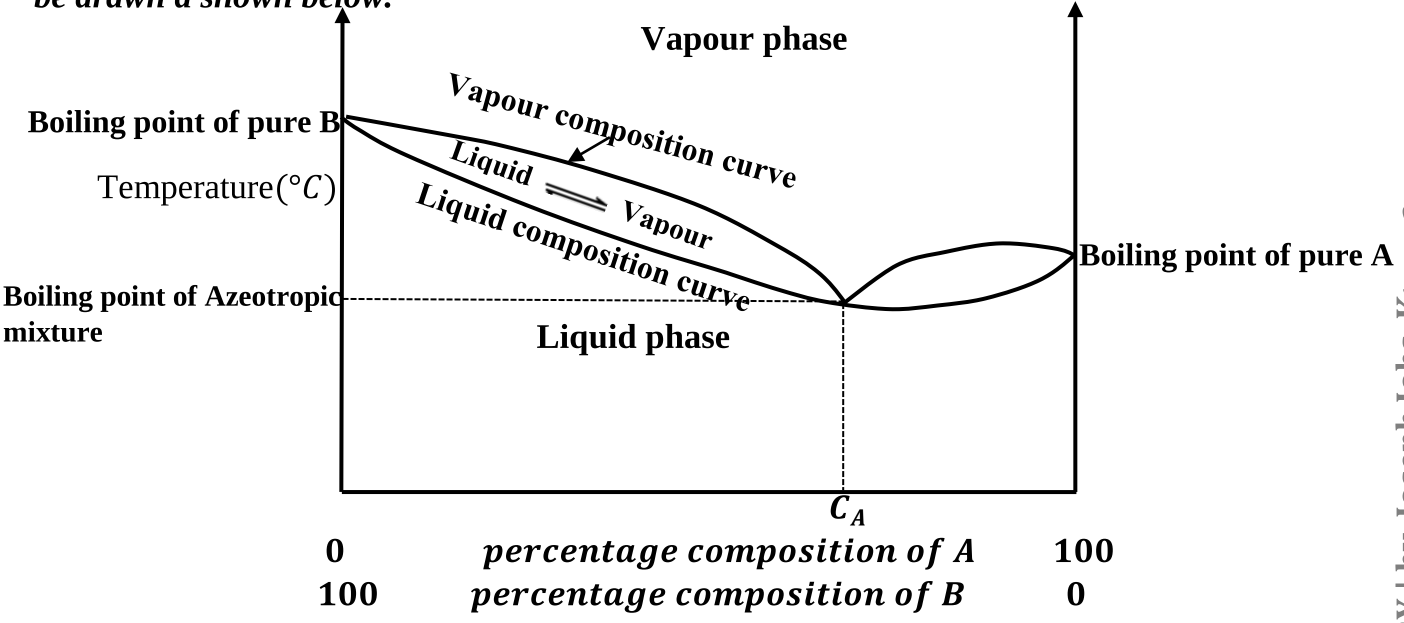
Instead of percentage composition, mole fraction may be used

Component A is more volatile than B (A has a higher saturated vapour than B)

Minimum boiling point-composition diagram
(Positive deviation from Raoult's law)

When two liquids in solution have weaker adhesive forces than cohesive forces, their escaping tendencies into vapour increase, hence an increase in vapour pressure than what is expected basing on Raoult's law. For such solutions, a maximum is seen in the vapour pressure-composition diagram. The maximum vapour pressure implies that the boiling point at that composition will be minimum.

Considering the mixture of A and B above, the boiling-point composition diagram can be drawn a shown below.



C_A *is the composition of the Azeotropic mixture*

Azeotropic mixtures and azeotropes

An **azeotrope** is also called a **constant-boiling mixture**.

An azeotropic is the mixture of two or more compounds that boils at a constant temperature to form a vapour of the same composition as that of mixture at a constant pressure.

An azeotropic mixture may have either a maximum or a minimum boiling point depending on the type of variation from Raoult's law, but any one pressure, its composition is fixed.

Each non-ideal solution has its own azeotropic point as well as azeotropic composition

Azeotropes are not classified as compounds because;

- ***their compositions vary with pressure.***
- ***the azeotropic mixture can also be separated into its components fairly easily by physical means***
- ***azeotropes cannot be represented by simple chemical formulae***

An azeotropic mixture cannot be separation by fractional distillation because the mixture boils at a ***fixed constant temperature*** with ***no change in composition***.

Methods of separation of components of azeotropes

(i) ***Addition of quick lime to remove the water*** for example to separate an azeotropic mixture of water and ethanol.

When the mixture is shaken with calcium oxide, the calcium oxide reacts with water to form non-volatile insoluble calcium hydroxide which is then filtered off leaving behind ethanol.

$$CaO(s) + H_2O(l) \longrightarrow Ca\,(OH)_2\,(s)$$

(ii) ***Addition of concentrated sulphuric acid*** to remove aromatic or unsaturated hydrocarbons from their azeotropic mixture with saturated hydrocarbons.

(iii) ***Distillation with a third component.***

The azeotropic mixture of ethanol and water can be separated by adding benzene and then distilled. At first an azeotropic mixture containing three components; water, ethanol and benzene is obtained. Then a binary azeotropic mixture of ethanol and benzene is formed and finally absolute ethanol on further distillation.

(iv) ***Adsorption***

Addition of charcoal or silica gel can **adsorb** one of the components.

(v) ***Solvent extraction***

Organic compounds are more soluble in organic solvents like ether or benzene than in water. The organic solvents (benzene or ether) are immiscible with water. Azeotropic mixtures containing water and some organic compounds can be separated by adding small volumes of ether or benzene and shaking. The organic compounds dissolve in the organic solvents. The benzene or ether can then be distilled off from the mixture with the organic compound.

Distillation of a binary liquid mixture

When a liquid is heated, its saturated vapour pressure increases until it becomes equal to the atmospheric pressure, normally 1 atm. At this point, boiling of the liquid takes place and the temperature remains constant. Further heating causes the liquid to vapourise. The vapourisation of a liquid and condensation of the resulting vapour is called distillation. Distillation under reduced pressure is used is used in purification of substances that decompose at their boiling points.

The process of fractional distillation

Fractional distillation is used to separate the components of a mixture of liquids, depending on the **difference in their boiling points** and also on the fact that **the vapour above the liquids is richer in the more volatile component** (component with a lower boiling point).

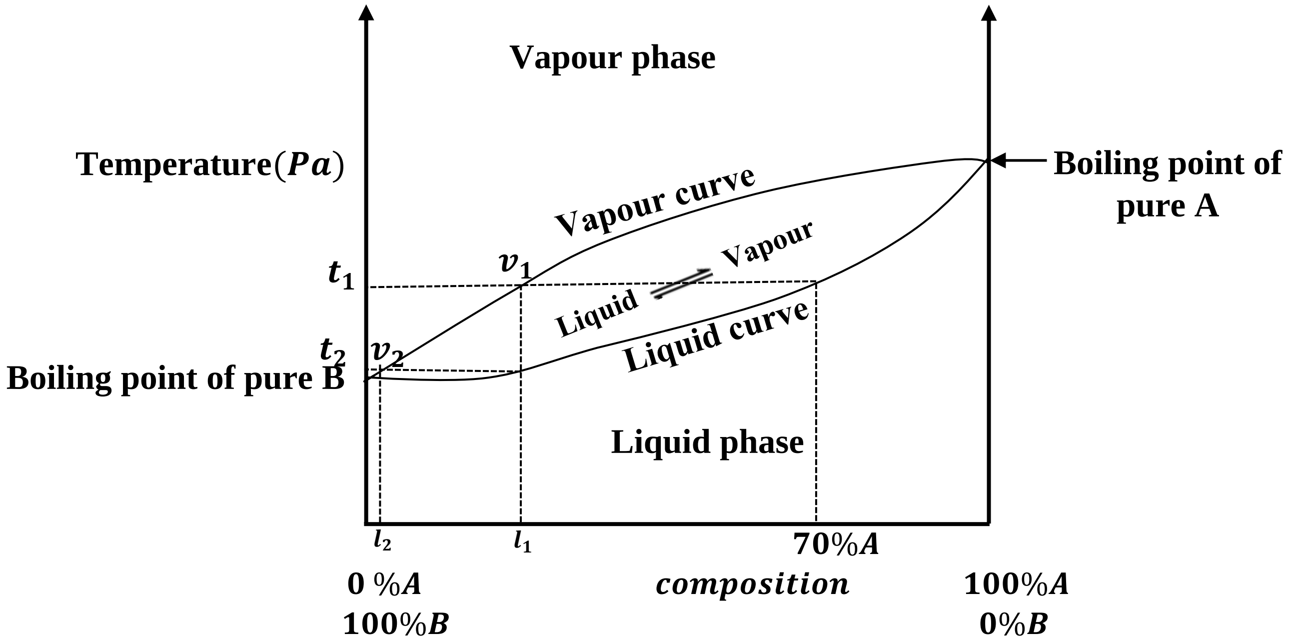
The apparatus used for fractional distillation has **a fractionating column** with a **large surface area** on which the **ascending vapour and the descending liquid come into contact**. A mixture **richer in the more volatile component** distills over at the top of the column and the **thermometer** registers its **boiling temperature**.

As distillation continues, the temperature rises and towards the boiling temperature of the **next most volatile component**.

The receiver is changed to collect the second component.

In the process, the components are distilled over at their boiling temperatures.

Distillation of an ideal solution



When a liquid of containing $70\%A$ *or* $30\%B$ *is heated, it boils at a temperature* $t_1{}^\circ C$ *to form a vapour of composition ,*v_1*, containing a higher proportion of the more volatile component,* B *.*

When the vapour is condensed, it forms a liquid, l_1 *of the same composition as the vapour*

When this liquid is heated, it boils at a temperature $t_2{}^\circ C$ *to form a vapour of composition ,*v_2 *still containing a higher proportion of the more volatile component , B.*

When the vapour is condensed, it forms a liquid **,l_2** *of the same composition as the vapour. Repeated vapourisation and condensation, will yield* ***pure B as distillate*** *and* ***pure A as residue***.

Trial question

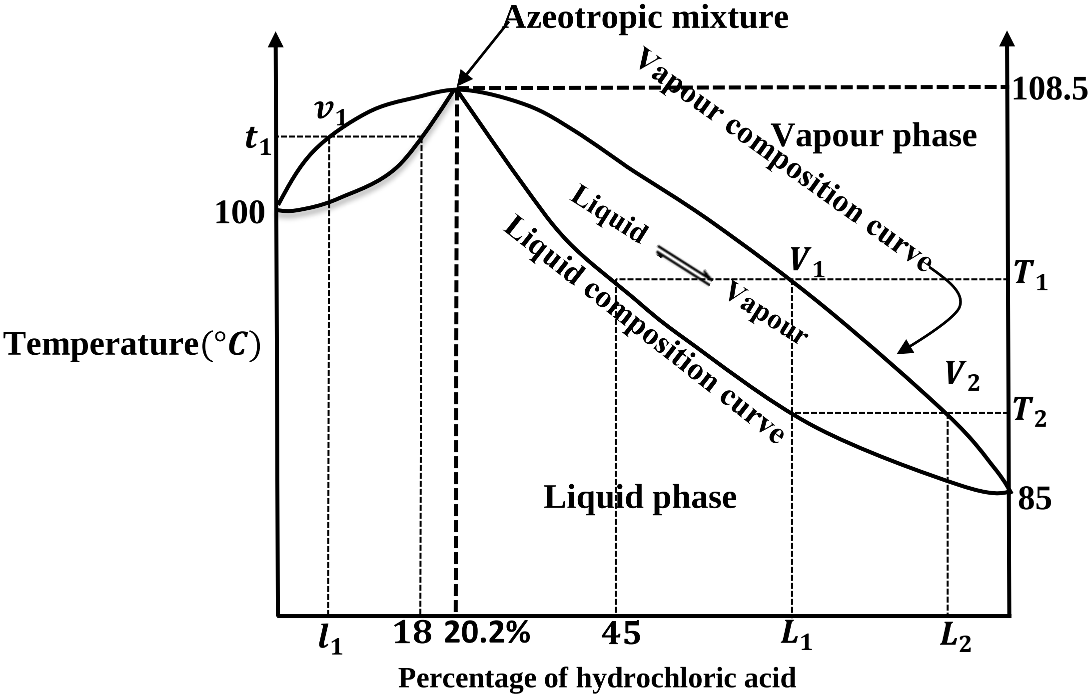
Methanol and water form an ideal solution. If the boiling point of pure methanol is $66°C$ and that of pure water is $100°C$.

- **(a) Explain why the two liquids form an ideal solution**
- **(b) Sketch a well labeled vapour pressure-composition diagram for the solution**
- **(c) Draw a well labeled boiling point-composition diagram for the solution**
- **(d) Using your diagram in (c) above, explain the changes that take place when;**
  - **(i) a solution containing 50% methanol is distilled.**
  - **(ii) a solution containing 85% water is distilled.**

Distillation of non-ideal solutions

1. **A non-ideal solution that deviates negatively from Raoult's law e.g. hydrochloric acid- water solution.**

   A mixture of water and hydrochloric acid forms a constant boiling mixture containing 20.2% hydrochloric acid with a boiling point of 108.5°C. The boiling points of pure water and hydrochloric acid are 100°C and 85°C respectively.



(a) Explain why the solution shows such a deviation from Raoult's law

The acid ***ionises in water*** to form hydrogen ions and chloride ions. When the ions are hydrated, there exist ***ion-dipole attractions (forces of attraction between hydrochloric acid molecules and water molecules).*** The ion-dipole attractions are ***on average stronger*** than the ***hydrogen bonds (forces of attraction) between individual water molecules*** and the ***van der Waal's forces (forces of attraction) between individual hydrochloric acid molecules.*** This ***reduces the tendency for the molecules to escape from the solution*** than from the pure liquids. Therefore the ***total vapour pressure above the liquids is less than what is predicted by Raoult's law.*** The solution therefore has ***a maximum boiling point*** and ***a minimum vapour pressure at 20.2% hydrochloric acid***, ***deviating negatively*** from Raoult's law.

(b) Using your diagram in (c) above, explain the changes that take place when;

(i) a solution containing 82% water is distilled.

When a solution containing 82% ***water*** *(or* 18% *hydrochloric acid)* ***is heated****, it* ***boils at a temperature*** $t_1°C$ *to form a* ***vapour of composition*** *,*v_1*, containing* ***a higher percentage of water than the solution*** *.*
When the ***vapour is condensed****, it* ***forms a liquid,*** l_1 *of the* ***same composition as the vapour*** *, still* ***richer in water****.*
Repeated ***vapourisation and condensation****, will yield* ***pure water as distillate*** *and* ***the azeotropic mixture as residue****.*

(ii) a solution containing 45% hydrochloric acid is distilled.

When a solution containing 45% ***hydrochloric acid*** *(or* 55% *water)* ***is heated****, it* ***boils at a temperature*** $T_1°C$ *to form a* ***vapour of composition*** *,*V_1*, containing* ***a higher percentage of hydrochloric acid than the solution*** *.*
When the ***vapour is condensed****, it* ***forms a liquid,*** L_1 *of the* ***same composition as the vapour*** *, still* ***richer in hydrochloric acid****.*
When the liquid ***is heated again****, it* ***boils at a temperature*** $T_2°C$ *to form a* ***vapour of composition*** *,*V_2***, still*** *containing* ***a higher percentage of hydrochloric.***
When the ***vapour is condensed****, it* ***forms a liquid,*** L_2 *of the* ***same composition as the vapour*** *, still* ***richer in hydrochloric acid****.*
Repeated ***vapourisation and condensation****, will yield* ***pure hydrochloric acid as distillate*** *and* ***the azeotropic mixture as residue****.*

Trial question

The boiling point of pure methanoic acid is 101°C. Methanoic acid and water are miscible in all proportions and form a maximum boiling azeotrope containing 77.5% methanoic acid with a boiling point of 108°C.

(i) **Sketch a labeled diagram of the mixture of methanoic acid and water showing the variation of the boiling points with composition**

(ii) **Explain the shape of the diagram above.**

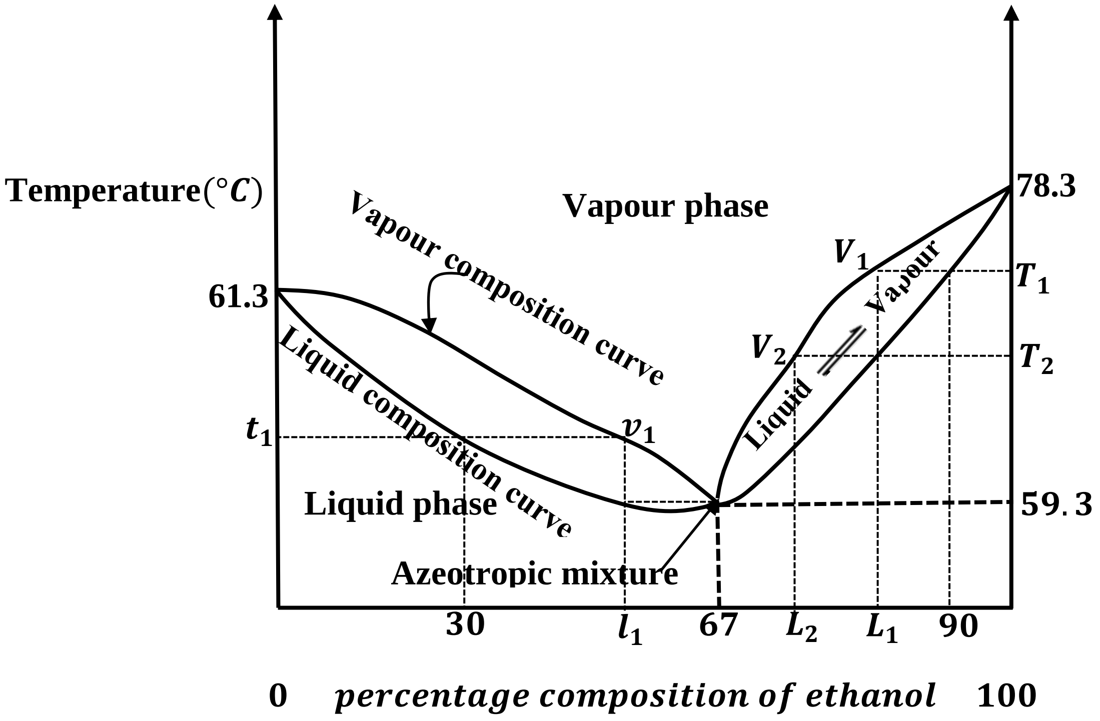
(iii) **Describe briefly what happens when a mixture containing 40% methanoic acid is distilled**

(iv) **Explain what will happen when a mixture containing 22.5% water is heated.**

(v) **Suggest one method by which methanoic acid may be obtained from the mixture.**

2. A non-ideal solution that deviates positively from Raoult's law e.g. trichloromethane-ethanol solution.

A mixture of chloroform and ethanol forms a constant boiling mixture containing 67% ethanol with a boiling point of 59.3 °C. The boiling points of pure chloroform and pure ethanol are 61.3°C and 78.3°C respectively.



(a) Explain the shape of the graph

The solution has a ***minimum boiling point at 67% of ethanol which implies it deviates positively from Raoult's law.*** This is because ***forces of attraction between ethanol molecules and trichloromethane molecules*** are ***on average weaker*** than the ***forces of attraction between individual ethanol molecules*** and the ***forces of attraction between individual trichloromethane molecules.*** This ***increases the tendency for the molecules to escape from the solution*** than from the pure liquids. Therefore the ***total vapour pressure above the liquids greater than what is predicted by Raoult's law.***

(b) Using your diagram in (c) above, explain the changes that take place when;

(i) a solution containing 90% ethanol is distilled.

When a solution containing 90% ***ethanol is heated****, it* ***boils at a temperature*** $T_1°C$ *to form a* ***vapour of composition,*** V_1, *containing* ***a lower percentage of ethanol than the original solution*** *.*
When the ***vapour is condensed****, it* ***forms a liquid,*** L_1 *of the* ***same composition as the vapour****, still containing* ***a lower percentage of ethanol****.*
When the liquid ***is heated again****, it* ***boils at a temperature*** $T_2°C$ *to form a* ***vapour of composition,*** V_2, ***still*** *containing* ***a lower percentage of ethanol.***
When the ***vapour is condensed****, it* ***forms a liquid,*** L_2 *of the* ***same composition as the vapour****, still* ***a lower percentage of ethanol.***
Repeated ***vapourisation and condensation*** *will yield* ***the azeotropic mixture as distillate*** *and* ***pure ethanol as residue****.*

(ii) a solution containing 30% ethanol is distilled.

When a solution containing 30% ***ethanol is heated****, it* ***boils at a temperature*** $t_1°C$ *to form a* ***vapour of composition,*** v_1, *containing* ***a higher percentage of ethanol than the solution*** *.*
When the ***vapour is condensed****, it* ***forms a liquid,*** l_1 *of the* ***same composition as the vapour****, still* ***richer in ethanol****.*
Repeated ***vapourisation and condensation*** *will yield* ***the azeotropic mixture as distillate*** *and* ***pure ethanol as residue****.*

Trial question

The boiling point of pure propan-1-ol is 97°C. Propan-1-ol and water are miscible in all proportions and form a constant boiling mixture containing 72% propan-1-ol with a boiling point of 88°C.

(i) Sketch a labeled diagram of the mixture of propan-1-ol and water showing the variation of the boiling points with composition
(ii) Explain why the mixture has such a deviation from Raoult's law.
(iii) Describe briefly what happens when a mixture containing 50% propan-1-ol is distilled.

NOTE;

(a) **Fractional distillation of a liquid mixture that deviates negatively from Raoult's law must yield a pure component as distillate the azeotropic mixture as residue**

(b) **Fractional distillation of a liquid mixture that deviates positively from Raoult's law must yield the azeotropic mixture as distillate a pure component as residue**

(c) **Further distillation of the azeotropic mixture cannot separate its components any further but methods of separation of azeotropes discussed before can be used depending on which azeotrope to separate.**

Miscellaneous questions

Some of the questions require you to plot graphs which you can use to identify the type of deviation that is shown and use the graphs to answer questions. By attempting them, you will improve your graph plotting skills.

1. (a)(i) What is a constant boiling mixture?

   (ii) Explain how it is known that a constant boiling mixture is a mixture but not a compound

   (iii) Give two types of constant boiling mixtures

   (b) A mixture of equal parts by weight of ethanol and water is fractionally distilled.

   (i) What will be the composition of the distillate first collected?

   (ii) How will the distillate change during the distillation?

   (c) State one advantage of using a fractionating column as a better method of separating liquid mixtures than its absence.
2. (a) State Raoult's law.

   (b) A solution containing 1 mole of trichloromethane and 4 moles of propanone has a vapour pressure of 0.4 atmospheres at $25°C$. At this temperature, the vapour pressure of pure trichloromethane and propanone are 0.359 and 0.453 atmospheres respectively.

   (i) Calculate the vapour pressure of the solution. State your assumption(s)

   (ii) State whether trichloromethane and propanone form a minimum or maximum boiling azeotrope. Give a reason.
3. Ethanol and acetone are completely miscible in all proportions. A solution was prepared by mixing $10g$ of ethanol and $18g$ of acetone at $90\ °C$. At this temperature total vapour pressure above the liquid surface was measured to be $553\ mmHg$. If the saturated vapour pressure of a pure ethanol and pure acetone of $90\ °C$ was found to be $200\ mmHg$ and $300\ mmHg$ respectively.

(a) (i) State the deviation from Raoult's law shown by the solution.
(All your working must be shown)
(ii) Explain your answer in (a)(i) above.
(b) Sketch the vapour pressure- composition diagram for this solution.
(c) Explain why ethanol and acetone cannot completely be separated by fractional distillation.

4. (a) Define a '**constant boiling point mixture**'
(b) At atmospheric pressure, hydrochloric acid and water forms a constant boiling point mixture (Azeotropic mixture) with a boiling point of $110°C$ and composition of 20% by mass hydrochloric acid.
   (i) State the type of deviation of the mixture from Raoult's law.
   (ii) Explain why the mixture shows this type of deviation.
(c) Sketch a labeled
   (i) Vapour pressure -composition diagram,
   (ii) Boiling point-composition diagram of the mixture.
   (iii) Give two reasons why the boiling point mixture is a mixture and not a compound.
   (iv) Using the diagram describe what will happen if a mixture containing 10% of hydrochloric acid is fractionally distilled.
(d) A constant boiling point mixture in (b) above has a density of $1.18gcm^{-3}$.
   (i) Calculate the molarity of the solution.
   (ii) Calculate the volume of the solution required to prepare $250\ cm^3$ of a $2M$ hydrochloric acid solution.

5. (a) What is meant by the term "**azeotropic mixture**" ?
(b) Nitric acid solution forms an azeotropic mixture containing 32% water at $121℃$. Its density is $1.42gcm^{-3}$ .The boiling points of water and nitric acid are $100℃$ and $86℃$ respectively.
(i) Draw boiling point-composition diagram for an aqueous solution of nitric acid.
(ii) State the type of deviation from Raoult's law shown by the mixture and explain your answer.
(c) Explain what will happen when a nitric acid solution containing;
   (i) less than 68% of the acid is distilled.
   (ii) more than 68% of the acid is distilled.
(d) Calculate the:
   (i) molar concentration of nitric acid in the solution in(b) above
   (ii) calculate the volume of the acid required to prepare $250cm^3$ of a 0.05M solution the acid.

(e) Describe any three methods of separating components of an azeotropic mixture.

6. An aqueous solution of ethanol forms an azeotropic mixture which boils at $73°C$ and contains 90% ethanol. Pure ethanol and pure water boil at $78°C$ and $100°C$ respectively.
   (a) (i) Draw the temperature-mole fraction phase diagram for an aqueous solution of ethanol.
   (ii) Explain what will happen if dilute solution containing less than 40% ethanol and concentrated solution containing more than 96% ethanol are separately boiled in a beaker.
   (b) (i) Give a reason(s) why it is not possible to obtain pure ethanol from its aqueous solution by fractional distillation method.
   (ii) After obtaining a 90% ethanol aqueous solution, state how a higher percentage of ethanol be obtained.
7. The table below shows the variation in the vapour pressure of the mixture of $\boldsymbol{X}$ and $\boldsymbol{Y}$ at 298K with composition of $\boldsymbol{Y}$.

Mole fraction of $\boldsymbol{Y}$	0.8	0.6	0.4	0.2	0
Vapour pressure of mixture (Pa)	362.5	355	372.5	395	427

   The vapour pressure of pure $\boldsymbol{Y}$ at 298K is $4 \times 10^{-1} kPa$
   (a) (i) Plot a vapour pressure – composition diagram for the above system
   (ii) Name the type of deviation from Raoult's law and give a reason for your answer.
   (iii) Explain the shape of the curve in relation to Raoult's law.
   (b) (i) Draw a well labelled boiling point -composition diagram for the system
   (ii) Describe the changes that occur when a mixture of 25% of $\boldsymbol{Y}$ is fractionally distilled.
8. (a) Explain what is meant by the term azeotropic mixture.
   (b) The boiling points and percentage composition by mass of methanol in the liquid mixture and in the vapour above the mixture of methanol and cyclohexane are given in the table below.

Boiling point of mixture($°C$)	70	60	55	57	61
Percentage composition of CH_3OH in the liquid mixture	12	13	50	82	94
Percentage composition of CH_3OH in the vapour above the mixture	27	47	56	69	83

(i) Use the data to plot a boiling-point composition diagram for solutions of cyclohexane in methanol. *(Boiling points of pure cyclohexane and pure methanol are 81°C and 65°C respectively)*

(ii) Use your graph to determine the composition of the azeotropic mixture and azeotropic temperature.

(c) (i) State the type of deviation from Raoult's law shown by the mixture of methanol and cyclohexane.

(iii) Explain your answer in (i)

9. The table below shows the partial vapour pressures for a two component mixture of propanone and trichloromethane at 35ºC for a range of mole fractions of trichloromethane.

Mole fraction of trichloromethane	0.0	0.2	0.4	0.6	0.8	1.0
Partial pressure of trichloromethane$(mmHg)$	0	35	82	142	219	293
Partial pressure of propanone$(mmHg)$	347	270	185	102	37	0

(i) Plot a graph to show how this system deviates from Raoult's law
(ii) Name the type of deviation shown by the system
(iii) State the cause of such a deviation and the characteristics of such a system showing this deviation.

10. Explain the following observations;
    (a) When propanone is mixed with tetrachloromethane, a warm miscible mixture was formed whose volume was lower than the sum of the volumes of the individual components.
    (b) Methanol and ethanol form an ideal mixture while a mixture of cyclohexane and ethanol shows a positive deviation.

Immiscible liquid mixtures

Immiscible liquids are liquids which when shaken and allowed to settle, they do not mix but form separate layers.

Examples of immiscible liquid mixtures include;

- Oil and water
- Chloroform(trichloromethane) and water
- Tetrachloromethane and water
- Paraffin and water
- Benzene and water
- Carbon disulphide and water
- Mercury and water
- Phenylamine and water

Vapour pressure of a system of two immiscible liquid

Each liquid behaves independently of the other and the vapour above an agitated/ heated mixture of two immiscible liquids at any temperature is the sum of the vapour pressures of the individual liquids at the same temperature.

$$P_{total} = P_A + P_B$$

$$P_A = Vapour\ pressure\ of\ liquid\ A$$

$$P_B = Vapour\ pressure\ of\ liquid\ B$$

Agitation of the mixture is necessary to enable each liquid to establish its own vapour phase.

Immiscible liquids have the following characteristics;

- The total vapour pressure above the immiscible liquid is equal to the sum of vapour pressure exerted by each liquid in pure state.
- Total vapour pressure above the immiscible liquid is greater than that of any of the individual components.
- Both the vapour pressure of each liquid and the total vapour pressure increase with increase in temperature. When the total vapour pressure above the mixture is equal to atmospheric pressure, the mixture will boil and the boiling point will be lower than the boiling point of either of the two liquids.
- The immiscible liquid mixture always boil at lower temperature than boiling point pure components
- Each component in the immiscible liquid retains its vapour formation tendency
- The forces of attraction between the components in the immiscible liquid mixture are negligibly small because there is no interaction of the components.

Question one : Phenylamine and water have boiling points of $184°C$ and $100°C$ respectively but a mixture of phenylamine and water boils at $98°C$

*Phenylamine and water are **immiscible**. When a mixture of the two liquids is heated, each **component exerts its own vapour pressure independently**. The **vapour pressure of the above mixture is the sum of the vapour pressure of phenylamine and the vapour pressure of water**. When **heating continues**, both the **vapour pressure of the independent components and the total vapour pressure above the mixture increases**. The mixture will **boil** when the **total vapour pressure is equal to the atmospheric pressure** at a **temperature lower than the boiling point of either phenylamine or water** in the mixture.*

Question two: Benzene (boiling point $°C$) and water (boiling point $100°C$) form a mixture that boils at $70°C$ at a pressure of one atmosphere.

The principle explained above is applied in separation of components of an immiscible liquid mixture by **steam distillation**.

STEAM DISTILLATION

Steam distillation is the technique of separating a volatile substance, immiscible with water, at a temperature below its boiling point from another substance by bubbling steam through the hot mixture.

The volatile substance to be separated vapourises off with steam leaving behind the non-volatile substance.

Steam distillation depends on properties of immiscible liquids.

The process in commonly used to extract organic substances with high boiling points, decompose on heating and cannot be distilled at atmospheric pressure.

The principle on which steam distillation is based

- When a mixture of two immiscible liquids is agitated (heated), each of the liquids exerts its own vapour pressure independently.
- The vapour pressure above the liquid mixture is the sum of the vapour pressures of the two components
- When heating continues, both the vapour pressure of each liquid and the total vapour pressure above the mixture increases.
- The mixture boils when the total vapour pressure is equal to the atmospheric pressure at a temperature below the boiling points of the two components in the mixture.

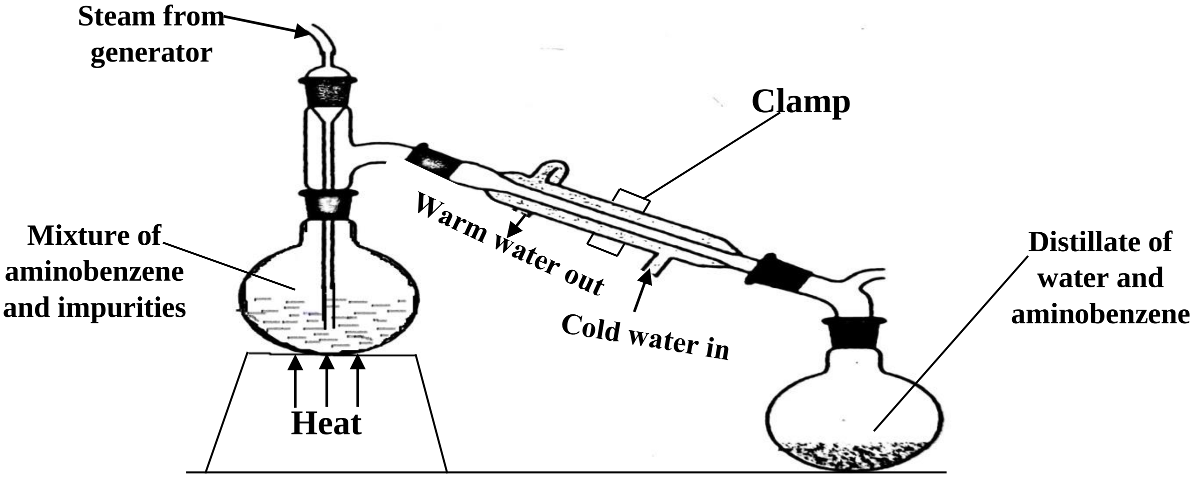
The process of purification of a liquid mixture by steam distillation

Example; The boiling point of phenylamine is $184°C$ and a mixture of phenylamine and water boils at $98°C$. Describe how an impure mixture of phenylamine can be purified by steam distillation

- The impure mixture containing phenylamine is heated
- Steam is passed into the heated mixture
- At a temperature $98°C$ and one atmosphere, a mixture of water and phenylamine distills off
- The distillate, which is two separate layers containing phenylamine and water is collected in the receiver.
- Phenylamine is then separated from the water in the distillate by using a separating funnel and then dried using a drying agent.

  Similarly, the distillate containing phenylamine and water can be shaken with ether (ethoxyethane) in a separating funnel and the two layers are separated
  The extract is the purified by distillation to remove ether.

Set up of apparatus



A mixture of **2-nitrophenol** and **4-nitrophenol** can also be separated by steam distillation as described for aniline above. 2-nitrophenol boils at $214°C$ and 4-nitrophenol boils $279°C$ respectively. In this case, the distillate contains 2-nitrophenol ***(which has a lower boiling point that the meta-substituted isomer, for reasons explained in bonding and structure)*** and water.

The distillate is then shaken with ether which dissolves the 2-nitrophenol. The 2-nitrophenol is then separated from ether by distillation.

Conditions necessary for steam distillation

The substance to be separated/purified by steam distillation;

(i) must be immiscible or insoluble in water
(ii) must have a high relative molecular mass
(iii) must exert a high vapour pressure at about $100°C$
(iv) Any impurities present must be non-volatile under the conditions used.

Advantages of steam distillation

(i) It purifies substances that decompose at temperatures near their boiling points
(ii) Distillation takes place at a lower temperature than during fractional distillation

The composition of the distillate

Assume that the vapour collected above the mixture, behave ideal, and so obeys ideal gas equation.

$$pV = nRT$$

Considering the vapour to contain water vapour and the immiscible liquid, L,

$$For\ water\ vapour;\ p_wV = n_wRT \ldots\ldots\ldots\ldots\ldots..(i)$$

$$For\ the\ liquid, L;\ p_LV = n_LRT \ldots\ldots\ldots\ldots\ldots(ii)$$

Dividing equation (i) by equation(ii) yields;

$$\frac{p_wV}{p_LV} = \frac{n_wRT}{n_LRT}$$

$$\boldsymbol{\frac{p_w}{p_L} = \frac{n_w}{n_L}}$$

The above equation gives the relative amounts of water and the liquid in the distillate where;

$\boldsymbol{p_w}$ *is the vapour pressure of water at the distillation temperature*
$\boldsymbol{p_L}$ *is the vapour pressure of the liquid at the distillation temperature*
$\boldsymbol{n_w}$ *is the number of moles of water*
$\boldsymbol{n_L}$ *is the number of moles of the liquid*

If instead of number of moles, it is the masses of water and the liquid given respectively; then the expression becomes;

$$\boldsymbol{\frac{p_w}{p_L} = \frac{n_w}{M_{r_w}} \Big/ \frac{n_L}{M_{r_L}}}$$

Where; $\boldsymbol{M_{r_w}}$ *and* $\boldsymbol{M_{r_L}}$ *are the molar masses of water and the liquid respectively.*

The vapour pressure of liquid is normally got from the expression for the total vapour pressure

$$\boldsymbol{p_{Total} = p_w + p_L}$$
$$\boldsymbol{p_L = p_{Total} - p_w}$$

Application of Dalton's law of partial pressure in distillation

In 1801, Dalton came up with Dalton's law of partial pressure which states that; in ***a mixture of gases which do not react chemically, the total pressure is the sum of the partial pressures of the components***.

Considering the vapour mixture of the two components; water and liquid, L each having partial vapour pressures p_w and p_L respectively

According to Dalton's law of partial pressures; the total vapour pressure exerted is;

$$p_{total} = p_w + p_L$$

and if the number of moles of water and liquid, L are n_w and n_L respectively,

Then the mole fractions of water and liquid, L are given by;

$$x_w = \frac{n_w}{n_w + n_L} \text{ and } x_L = \frac{n_L}{n_w + n_L}$$
$$x_w = \frac{n_w}{n_{total}} \text{ and } x_L = \frac{n_L}{n_{total}}$$

The partial pressures of water and the liquid respectively are given as a product of their respective mole fractions and the total pressure, p_{total}.

$$p_w = x_w p_{total}$$
$$p_w = \left(\frac{n_w}{n_{total}}\right) p_{total} \ldots\ldots\ldots\ldots\ldots\ldots (i)$$
$$p_L = x_L p_{total}$$
$$p_L = \left(\frac{n_L}{n_{total}}\right) p_{total} \ldots\ldots\ldots\ldots\ldots\ldots (ii)$$

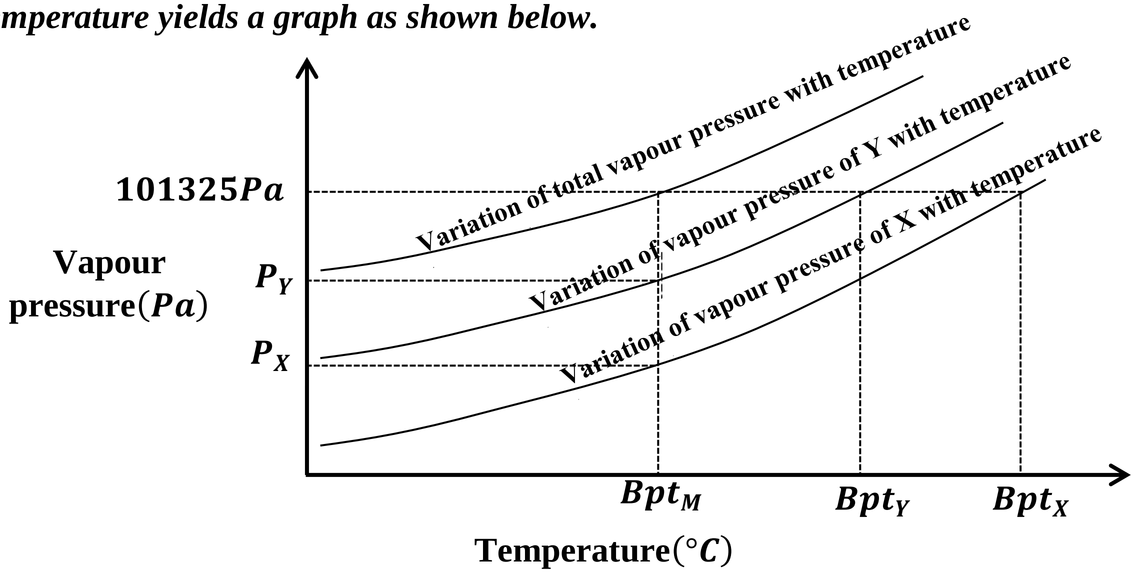
Dividing equation (i) and equation (ii) yields;

$$\frac{p_w}{p_L} = \left(\frac{n_w}{n_{total}}\right) p_{total} \Big/ \left(\frac{n_L}{n_{total}}\right) p_{total}$$
$$\boldsymbol{\frac{p_w}{p_L} = \frac{n_w}{n_L}}$$

Using graphical approach to determine composition of distillate

It is known that during steam distillation, the vapour pressure above the liquid mixture is the sum of the vapour pressures of the two components and that both the vapour pressure of each liquid and the total vapour pressure above the mixture increase with increase in temperature.

A plot of vapour pressure of each of the components and the total vapour pressure against temperature yields a graph as shown below.



- The boiling points of the mixture, component **X** and component **Y** are the temperatures that correspond to the standard atmospheric pressure ($101325\ Pa\ or\ 101.325kPa\ or\ 760mmHg$)
- The vapour pressures of the components $\boldsymbol{P_X}$ and $\boldsymbol{P_Y}$ can be obtained from the graph at the boiling point of the mixture and used to find the composition of the distillate using the expression below and substituting otherwise;

$$\frac{p_X}{p_Y} = \frac{n_X}{n_Y}$$

Use the information to try out questions 9-11 in the exercise on steam distillation.

Calculations involving steam distillation

Examples

1. **An organic compound X is steam distilled at normal atmospheric pressure and the distillate was found to contain 75% by composition of X at a given temperature. If at the same temperature, the vapour pressure of water is 640mmHg. Calculate the relative molecular mass of X.**

$$p_{H_2O} = 640\ mmHg$$

$$p_X = 760 - 640 = 120\ mmHg$$

Percentage composition of water in the distillate $= 75$

Percentage composition of X in the distillate $= (100 - 75) = 25$

Molar mass of $H_2O = 2 + 16 = 18g$

$$\frac{p_{H_2O}}{p_X} = \frac{n_{H_2O}}{n_X}$$

$$\frac{640}{120} = \frac{75}{18}\Big/\frac{25}{M_{rX}}$$

$$\frac{640}{120} = \frac{75 \times M_{rX}}{18 \times 25}$$

$$M_{rX} = \frac{640 \times 18 \times 25}{120 \times 75}$$

$$= 32g$$

The relative molecular mass of X is 32.

2. **A mixture of nitrobenzene and distilled water boiled at $99°C$ at one atmosphere. Calculate the percentage composition of the distillate. The saturated vapor pressure of water at $99°C$ is $723mmHg$.**

$$p_{H_2O} = 723\ mmHg$$

$$p_{nitrobenzene} = 760 - 723 = 37mmHg$$

Molar mass of $C_6H_5NO_2$

$$= (6 \times 12) + (5 \times 1) + (14 \times 1) + (2 \times 16)$$

$$= 123g$$

Molar mass of $H_2O = 2 + 16 = 18g$

Let the percentage composition of water in the distillate be y

The percentage composition of nitrobenzene in the distillate

$$= (100 - y)$$

$$\frac{p_{H_2O}}{p_{C_6H_5NO_2}} = \frac{n_{H_2O}}{n_{C_6H_5NO_2}}$$

$$\frac{723}{37} = \frac{y}{18}\Big/\frac{(100 - y)}{123}$$

$$\frac{723}{37} = \frac{123y}{18(100 - y)}$$

$$y = \frac{723 \times 18 \times 100}{17565}$$

$$y = 74.09$$

The distillate contains 74.09% water and 29.91% nitrobenzene.

3. **The vapour pressure of water at $95°C$ is $84.7kPa$. A liquid Y is insoluble in water and has a relative molecular mass of 160. A mixture of Y and water steam distills at $95°C$ under standard atmospheric pressure. Calculate the mass of water collected in the distillate if the mass of Y in the distillate is 40g.**

$$p_{H_2O} = 84700\ Pa$$

$$p_Y = 101325 - 84700 = 16625Pa$$

Molar mass of $Y = 160g$

Molar mass of $H_2O = 2 + 16 = 18g$

Mass of y in distillate $= 40g$

Let the mass of H_2O in the distillate $= m$

$$\frac{p_{H_2O}}{p_Y} = \frac{n_{H_2O}}{n_Y}$$

$$\frac{84700}{16625} = \frac{m}{18}\Big/\frac{40}{160}$$

$$\frac{84700}{16625} = \frac{m \times 160}{18 \times 40}$$

$$m = \frac{84700 \times 18 \times 40}{16625 \times 160}$$

$$m = 22.92$$

The mass of water in the distillate is 22.92g.

4. **Chlorobenzene forms an immiscible mixture with water. It's mixture with steam distills at $91°C$ an atmospheric pressure of $100300\ Pa$. A sample of distillate contains $23.7g$ chlorobenzene for every $10g$ of water. Calculate the vapour pressure of water and chlorobenzene at $91°C$.**

$$p_{H_2O} = ?$$

$$p_{C_6H_5Cl} = ?$$

But $\boldsymbol{p_{C_6H_5Cl} = 100300 - p_{H_2O}}$

$$Molar\ mass\ of\ C_6H_5Cl$$

$$= (6 \times 12) + (5 \times 1) + (35.5 \times 1) = 112.5g$$

$$Molar\ mass\ of\ H_2O = 2 + 16 = 18g$$

$$Mass\ of\ C_6H_5Cl\ in\ distillate = 23.7g$$

$$Mass\ of\ H_2O\ in\ the\ distillate = 10g$$

$$\frac{p_{H_2O}}{p_{C_6H_5Cl}} = \frac{n_{H_2O}}{n_{C_6H_5Cl}}$$

$$\frac{p_{H_2O}}{100300 - p_{H_2O}} = \frac{10}{18} \Big/ \frac{23.7}{112.5}$$

$$\frac{p_{H_2O}}{100300 - p_{H_2O}} = \frac{10 \times 112.5}{18 \times 23.7}$$

$$p_{H_2O} = \frac{1125 \times 100300}{1551.6}$$

$$\boldsymbol{p_{H_2O} = 72723.318Pa}$$

$$\boldsymbol{p_{C_6H_5Cl} = 100300 - p_{H_2O}}$$

$$\boldsymbol{p_{C_6H_5Cl} = 100300 - 72723.318}$$

$$\boldsymbol{= 27576.682Pa}$$

Questions on steam distillation

1. (a) Explain what is meant by the term **steam distillation**.

   (b) Naphthalene ($C_{10}H_8$) distils in steam at $98.30°C$ under a pressure of $753mmHg$. The vapor pressure of water at this temperature is $715mmHg$. Calculate the percentage by mass of Naphthalene in the distillate.
2. When an organic compound was distilled in steam at $101325\ Pa$ at a temperature of $99°C$. The vapour pressure of water at $99°C$ was $97700Pa$. If the distillate was found to contain 80% by mass of water. Calculate the relative molecular mass of organic compound.
3. An organic liquid distills in steam with partial vapour pressure $5.3\ kPa$ and $96kPa$ water. The distillate contains the liquid in the ration of $0.48g$ organic liquid and $1g$ of water. Calculate the relative molecular mass of organic compound.
4. (a) Bromobenzene can be separated from it impurities by steam distillation. State the conditions that enable purification of bromobenzene by steam distillation.

   (b) $20.0g$ of impure bromobenzene were steam distilled at $95°C$ and $760\ mmHg$ to form a distillate containing $15.345g$ of water. The saturated vapour pressure of water at $95°C$ is $680\ mmHg$. Calculate the percentage purity of bromobenzene.
5. (a) Explain what is meant by the term steam distillation

   (b) (i) Draw a diagram of the set-up of apparatus that can be used to purify aminobenzene by steam distillation

(ii) Name one other substance apart from aminobenzene that can be isolated by steam distillation.

(c) (i) State the requirements of a substance to be isolated by steam distillation

(ii) Explain how the properties you have named in c(i) enable the substance to be purified by steam distillation.

6. (a) The melting point of 4-nitrophenol is much higher than that of 2-nitrophenol. The two compounds can be separated by steam distillation.
   - (i) Explain why the melting point of 4-nitrophenol is higher than that of 2nitrophenol
   - (ii) Explain the principles of steam distillation
   - (iii) Describe how a mixture of 2-nitrophenol and 4-nitrolphenol can be separated by steam distillation

   (b) When substance ***W*** was steam distilled at 93ºC and 750mmHg, the distillate contained 55% by mass of ***W***. calculate the relative molecular mass of ***Y***. (The vapour pressure of water at 93ºC is 654mmHg)

7. Compound ***Q*** contains 62.1% carbon, 10.3% hydrogen, the rest being oxygen.

   (a) Calculate the empirical formula of ***Q***.

   (b) ***Q*** distills in steam at $98°C$ and $1.01 \times 10^5 Nm^{-2}$. If the vapour pressure of water at $98°C$ is $9.5 \times 10^4 Nm^{-2}$.
   - (i) Calculate the molecular mass of ***Q*** if the distillate contained 16.67% by mass of ***Q***
   - (ii) ***Q*** formed a grey precipitate when treated with ammoniacal silver nitrate. Write an equation and outline a mechanism for the reaction between ***Q*** and sodium hydrogensulphite solution.

8. A gaseous hydrocarbon ***Q*** after complete combustion produced 2.025g of water and 6.72 dm^3 of carbon dioxide at standard temperature and pressure.

   (a) Determine the empirical formula of ***Q***.

   (b) ***Q*** steam distills at a given temperature under a pressure of 750mmHg.The vapour pressure of water at the same temperature is 726mmHg and the percentage of water in the distillate was found to be 84.22%. Determine the molecular formula of ***Q***.

   (c) ***Q*** burns with a sooty flame and reacts with 2 moles of hydrogen gas in presence poisoned palladium catalyst supported on barium sulphate to form phenylethene. Write the structural formula of ***Q***.

   (d) Write an equation to shown how ***Q*** can be converted to phenylethanone.

   (e) Write equation(s) and indicate conditions and mechanism(s) for the reaction between;

(i) **Q** and excess dry hydrogen bromide
(ii) Phenylethanone and semicarbazide

9. 4.7g of compound **Z** contains carbon, hydrogen and oxygen only. **Z** on combustion gave 13.2g of carbon dioxide and 2.7g of water.
   (a) Calculate the empirical formula of **Z**.
   (b) When a mixture containing compound **Z** was steam distilled at 760mmHg and 98℃, the distillate contained 12.75g of water and 3.7g of **Z**. If the vapour pressure of water is 720mmHg at 98℃, determine the molecular formula of **Z**.
   (c) **Z** burns with a sooty flame and the pH of its aqueous solution is less than 7. Write the molecular structure of **Z**.
   (d) **Z** was reacted with benzene diazonium chloride in presence of sodium hydroxide.
      (i) State what was observed.
      (ii) Write equation for the reaction that took place.

10. (a) Define the terms;
      (i) Saturated vapour pressure
      (ii) Partial pressure
   (b) Explain the principle of steam distillation, using a suitable example.
   (c) The saturated vapour pressures of phenylamine and water at various temperatures are shown in the table below.

Temperature ($^{\circ}C$)	70	80	90	100	110
Vapour pressure of phenylamine(Pa)	1,400	2,400	3,900	6,100	9,200
Vapour pressure of water(Pa)	31,200	47,300	70,100	101,300	143,300

      (i) On the same axes plot a graph of vapour pressures of each of the components and the total vapour pressure.
      (ii) Calculate the proportion of phenylamine and water in the distillate under standard atmospheric pressure.

11. The vapour pressure of water and that of an immiscible liquid **X** at different temperatures are given in the table below.

Temperature ($^{\circ}C$)	92	94	96	98	100
Vapour pressure of X (Nm^{-2})	6000	8000	1200	15000	17000
Vapour pressure of water(Nm^{-2})	74000	80000	88000	94000	101000

   (a) On the same axes, plot graphs of vapour pressure against temperature
   (b) (i) Determine the vapour pressure of the mixture of **X** and water at the temperatures given in the table above.

(ii) On the same axes in (a), plot a graph of the vapour pressure of the mixture versus the temperature.

(c) The distillate obtained from the mixture at 101kPa contained 1.6g of water and 1.1g of $\boldsymbol{X}$. Calculate the relative molecular mass of $\boldsymbol{X}$ using the graphs you have drawn.

(d) State:

(i) properties a substance to be separated from its mixture by steam distillation should have

(ii) advantages of steam distillation

12. (a) State what is meant by the term steam distillation

(b) Aminobenzene and water are immiscible liquids. The saturated vapour pressures of pure water and pure aminobenzene at various temperatures are given in the table below.

Temperature $(°C)$	85	90	95	100	105
Vapour pressure of aminobenzene(kPa)	3.0	4.0	5.0	6.0	7.0
Vapour pressure of pure water(kPa)	58	70	84.6	101.3	120.7

(i) Plot on the same axes, graphs of vapour pressure of aminobenzene, water and the mixture against temperature.

(ii) Using the graphs, determine the boiling point of the mixture of aminobenzene and water at atmospheric pressure.

(iii) Calculate the percentage by mass of aminobenzene in the distillate if the mixture was steam distilled.

Industrial application of steam distillation

Extraction of natural products from plant materials such as essential oils used in fragrances, perfumes and personal hygiene products

THE DISTRIBUTION LAW (PARTITION LAW)

When a **non-volatile solute** is shaken with **two immiscible solvents in contact**, both in which it is **soluble**, it distributes itself such that the **ratio of concentration of the solute in one solvent to the other** is **a constant**, at a **given temperature when equilibrium is established** and when the **solute remains in the same molecular state**.

This is called the ***distribution law*** or ***partition law***. The constant is called the ***distribution coefficient*** or ***partition coefficient***.

The **distribution coefficient** or **partition coefficient** is therefore defined as;

This is the constant ratio of the molar concentrations of a non-volatile solute in a mixture of two immiscible solvents in contact when equilibrium is established at a given temperature provided the solute remains in the same molecular state.

Consider a solute, X, in a mixture of two immiscible solvents, A and B;

The partition coefficient, K_D is given by;

$$K_D = {[X]_A}/{[X]_B}$$

Limitations of the partition law/ conditions under which partition law is valid

(i) Solvents should be immiscible
(ii) Solution should be dilute
(iii) Temperature must be constant
(iv) No association or dissociation of solute occurs in the solvents

Experimental determination of K_D

(a) To determine partition coefficient of iodine between water and trichloromethane

A ***known mass of iodine*** is added to a ***known volume of trichloromethane*** in a ***separating funnel***.

A ***known volume of water*** is added to the separating funnel

The ***mixture is shaken for some time*** and ***left to stand*** for equilibrium to be established at ***a given temperature.***

After settling, a ***known volume of the aqueous layer is pipetted*** and titrated against a ***standard solution of sodium thiosulphate*** using ***starch indicator***.

The ***concentration of iodine in the aqueous layer*** is calculated using the equation;

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

A ***known volume of the organic layer is also pipetted*** and titrated against a ***standard solution of sodium thiosulphate*** using ***starch indicator***.

The ***concentration of iodine in the organic layer*** is also calculated.

The partition coefficient is then calculated using the expression;

$$K_D = \frac{[I_2]_{H_2O}}{[I_2]_{CHCl_3}}$$

(b) To determine partition coefficient of butane-1,4-dioic acid (succinic acid) between ethoxyethane(ether) and water.

A ***known mass of butane-1,4-dioic acid*** is added to a ***known volume of ether*** in a ***separating funnel***.

A ***known volume of water*** is added to the separating funnel

The ***mixture is shaken for some time*** and ***left to stand*** for equilibrium to be established at ***a fixed temperature.***

After settling, a ***known volume of the ether layer is pipetted*** and titrated against a ***standard solution of sodium hydroxide*** using ***methyl orange indicator***.

The ***concentration of butane-1,4-dioic acid in the ether layer*** is calculated using the equation;

$$HOOCCH_2CH_2COOH(aq) + 2NaOH(aq) \longrightarrow NaOOCCH_2CH_2COONa(aq)(aq) + H_2O(aq)$$

A ***known volume of the aqueous layer is also pipetted*** and titrated against a ***standard solution of sodium hydroxide*** using ***methyl orange indicator***.

The ***concentration of butane-1,4-dioic acid in the aqueous layer*** is also calculated.

The partition coefficient is then calculated using the expression;

$$K_D = \frac{[HOOCCH_2CH_2COOH]_{ether}}{[HOOCCH_2CH_2COOH]_{water}}$$

(c) To determine partition coefficient of ammonia between water and trichloromethane.

A ***known mass of volume of ammonia*** is added to a ***known volume of trichloromethane*** in a ***separating funnel***.

A ***known volume of water*** is added to the separating funnel

The ***mixture is shaken for some time*** and ***left to stand*** for equilibrium to be established at ***a fixed temperature.***

After settling, a ***known volume of the aqueous layer is pipetted*** and titrated against a ***standard solution of hydrochloric acid*** using ***methyl orange indicator***.

The ***concentration of ammonia in the aqueous layer*** is calculated using the equation;

$$NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$$

A ***known volume of the trichloromethane layer is also pipetted*** and titrated against a ***standard solution of hydrochloric acid*** using ***methyl orange indicator***.

The ***concentration of ammonia in the trichloromethane layer*** is also calculated.

The partition coefficient is then calculated using the expression;

$$K_D = \frac{[NH_3]_{water}}{[NH_3]_{trichloromethame}}$$

Question; Describe how partition coefficient of ethanoic acid between water and butan-1-ol can be determined.

Calculations involving K_D

Examples

1. **To determine the partition coefficient of ammonia between water and trichloromethane, 10 cm^3 of aqueous layer required 13.2 cm^3 of 0.25M hydrochloric for complete neutralization. 25 cm^3 of organic layer required**

6.6 cm^3 of 0.05M hydrochloric for complete neutralization. Calculate the partition coefficient.

$$\boldsymbol{moles\ of\ HCl\ that\ reacted\ with\ aqueous\ layer} = \left(\frac{13.2 \times 0.25}{1000}\right) = 0.0033$$

$$\boldsymbol{NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)}$$

$$mole\ ratio\ of\ NH_3{:}\,HCl = 1{:}\,1$$

$$moles\ of\ ammonia\ in\ aqueous\ layer\ that\ reacted\ with\ HCl = 0.0033$$

$$10\ cm^3 of\ \ trichloromethane\ layer\ \ contain\ 0.0033\ moles\ of\ NH_3$$

$$1000\ cm^3 of\ \ trichloromethane\ layer\ \ contain\ \left(\frac{1000 \times 0.0033}{10}\right) moles\ of\ NH_3$$

$$\boldsymbol{[NH_3]_{H_2O} = 0.33\ M}$$

$$\boldsymbol{moles\ of\ HCl\ that\ reacted\ with\ trichloromethane\ layer} = \left(\frac{6.6 \times 0.05}{1000}\right)$$

$$= 0.00033M$$

$$mole\ ratio\ of\ NH_3{:}\,HCl = 1{:}\,1$$

$$moles\ of\ ammonia\ in\ aqueous\ layer\ that\ reacted\ with\ HCl = 0.00033$$

$$25\ cm^3 of\ \ trichloromethane\ layer\ \ contain\ 0.00033\ moles\ of\ NH_3$$

$$1000\ cm^3 of\ \ trichloromethane\ layer\ \ contain\ \left(\frac{1000 \times 0.00033}{25}\right) moles\ of\ NH_3$$

$$\boldsymbol{[NH_3]_{CHCl_3} = 0.0132\ M}$$

$$\mathbf{K_D} = \frac{\boldsymbol{[NH_3]_{H_2O}}}{\boldsymbol{[NH_3]_{CCl_4}}} = \frac{\mathbf{0.33}}{\mathbf{0.0132}} = \mathbf{25}$$

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2. 50 cm^3 of 1.5M ammonia solution was shaken with 50 cm^3 of trichloromethane in a separating funnel. After the layers had settled, 20 cm^3 of trichloromethane layer was pipetted and titrated with 0.05M hydrochloric acid. 22.9 cm^3 of the acid were required for complete neutralization.

(a) Write the expression for the partition coefficient for ammonia between water and trichloromethane.

(b) Calculate the partition coefficient (State any assumptions made)

(a) $\mathbf{K_D} = \frac{\boldsymbol{[NH_3]_{H_2O}}}{\boldsymbol{[NH_3]_{CCl_4}}}$

(b)

$$1000\ cm^3\ of\ solution\ contain\ 0.05\ moles\ of\ HCl$$

$$22.9\ cm^3\ of\ solution\ contain\ \left(\frac{22.9 \times 0.05}{1000}\right)\ moles\ of\ HCl$$

$$\boldsymbol{= 1.145 \times 10^{-3} moles}$$

$$\boldsymbol{NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)}$$

$$mole\ ratio\ of\ NH_3{:}\,HCl = 1{:}\,1$$

$$moles\ of\ ammonia\ that\ reacted = 1.145 \times 10^{-3} moles$$

$$20\ cm^3 of\ \ trichloromethane\ layer\ \ contain\ 1.145 \times 10^{-3} moles\ of\ NH_3$$

$$1000\ cm^3 of\ \ trichloromethane\ layer\ \ contain\ \left(\frac{1000 \times 1.145 \times 10^{-3}}{20}\right) moles\ of\ NH_3$$

$$= \mathbf{0.05725\ M}$$

$$[NH_3]_{CCl_4} = 0.05725M$$

$$[NH_3]_{H_2O} = (1.5 - 0.05725) = 1.44275M$$

$$\mathrm{K_D} = \frac{[NH_3]_{H_2O}}{[NH_3]_{CCl_4}} = \frac{1.44275}{0.05725} = \mathbf{25.2}$$

Assumptions made

- *Water and tetrachloromethane are immiscible*
- *Temperature is constant*
- *Ammonia neither associates nor dissociates in water or trichloromethane*

3. **25 cm^3 portion of a 0.2M solution of iodine in carbontetrachloride was shaken with 50 cm^3 of water at $25°C$. After equilibrium had been attained 25 cm^3 of the aqueous layer required 2.74 cm^3 of 0.2M sodium thiosulphate solution to react completely with iodine. Calculate the partition coefficient of iodine between carbontetrachloride and water.**

$$Moles\ \ of\ sodium\ thiosulphate\ solution\ that\ reacted\ with\ iodine$$

$$= \left(\frac{2.74 \times 0.2}{1000}\right) = \mathbf{0.000548\ moles}$$

$$\boldsymbol{I_2(aq) + \ 2S_2O_3^{2-}(aq) \longrightarrow S_4O_6^{2-}(aq)\ \ +\ 2I^-(aq)}$$

$$mole\ ratio\ of\ S_2O_3^{2-} : I_2 = 2:1$$

$$moles\ of\ I_2\ that\ reacted = \frac{0.000548}{2} = 0.000274\ moles$$

$$25\ cm^3 of\ \ aqueous\ layer\ \ contain\ 0.000274\ moles\ of\ I_2$$

$$1000\ cm^3 of\ \ aqueous\ layer\ \ \ layer\ \ contain\ \left(\frac{1000 \times 0.000274}{25}\right) moles\ of\ I_2$$

$$= \mathbf{0.01096\ M}$$

$$[I_2]_{H_2O} = 0.01096M$$

$$[I_2]_{CCl_4} = (0.2 - 0.01096) = 0.18904\ M$$

$$\mathrm{K_D} = \frac{[I_2]_{CCl_4}}{[I_2]_{H_2O}} = \frac{0.18904}{0.01096} = \mathbf{17.2}$$

4. **(a) When 100 cm^3 of an aqueous solution containing 30g of ethanoic acid were shaken with 50 cm^3 of butan-1-ol, 12g of ethanoic acid remained in the aqueous layer. Calculate the distribution coefficient of ethanoic acid between water and butan-1-ol at $25°C$.**

   (b) If 100 cm^3 of butan-1-ol were used instead, what would be the distribution coefficient at $°C$?

(a)

$Mass\ of\ ethanoic\ acid\ in\ aqueous\ layer = 12g$

$Mass\ of\ ethanoic\ acid\ in\ butan-1-ol\ \ layer = (30-12) = 18g$

$$\mathrm{K_D} = \frac{[CH_3COOH]_{H_2O}}{[CH_3COOH]_{CH_3CH_2CH_2CH_2OH}}$$

$$\mathrm{K_D} = \frac{{}^{12}/_{100}}{{}^{18}/_{50}}$$

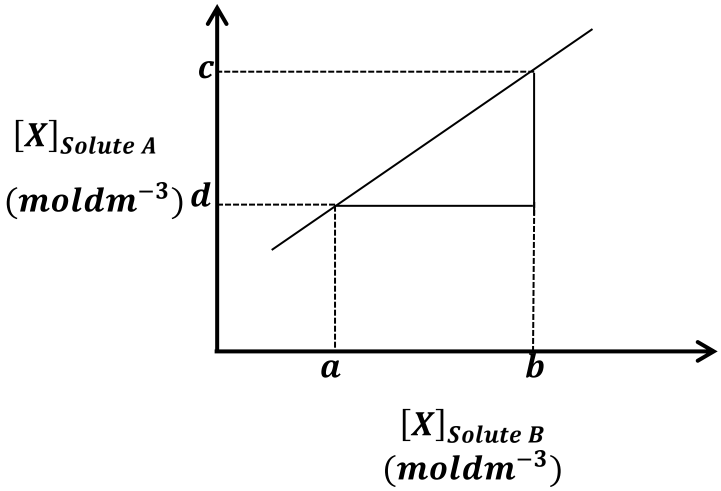
$$\mathrm{K_D} = \frac{12 \times 50}{100 \times 18} = \mathbf{0.333}$$

(b) The distribution coefficient would be the same because the ethanoic acid redistributes itself in the two solvents to maintain the same value of distribution coefficient.

Obtaining values of partition coefficients using graphical approach

Consider a solute $\boldsymbol{X}$, soluble in two immiscible solvents $\boldsymbol{A}$ and $\boldsymbol{B}$.

A graph of concentration of the solute in one solvent against the concentration of the solute in another solvent can be plotted.



A graph of $[\boldsymbol{X}]_{\boldsymbol{Solute\ A}}$ against $[\boldsymbol{X}]_{\boldsymbol{Solute\ B}}$ is usually a straight line.

The slope of the graph gives the partition coefficient of X between solute A and solute B

$$K_D = \frac{\Delta[\boldsymbol{X}]_{\boldsymbol{Solute\ A}}}{\Delta[\boldsymbol{X}]_{\boldsymbol{Solute\ B}}} = \frac{\boldsymbol{c-d}}{\boldsymbol{b-a}}$$

Questions

1. 50 cm^3 of $0.1M$ ammonia solution was shaken to equilibrium with 50 cm^3 of trichloromethane in a stoppered bottle at $25°C$. 25.0 cm^3 of the aqueous layer reacted completely with 24 cm^3 of 0.1M hydrochloric acid. Calculate the partition coefficient of ammonia between water and trichloromethane.
2. A weak tribasic acid, $\boldsymbol{X}$ is soluble in benzene and water. 2.800g of the acid was shaken with 100 cm^3 of benzene and 50 cm^3 of water. 25 cm^3 of the aqueous layer required 14.50 cm^3 of 1M sodium hydroxide solution for neutralisation. Calculate the distribution coefficient of $\boldsymbol{X}$ in water and benzene. $(Molar\ mass\ of\ X = 210g)$
3. (a) Explain is meant by partition coefficient.

   (b) The table below shows the concentrations of iodine in the two layers shaken with a mixture of carbon tetrachloride and water at $25°C$.

Concentration of I_2 in $CCl_4 (moldm^{-3})$	6.12	12.24	15.20	22.38
Concentration of I_2 in $water\ (moldm^{-3})$	0.072	0.143	0.178	0.260

Plot a graph of concentration of iodine in carbon tetrachloride against concentration of iodine in water.

(c) From the graph determine the partition coefficient for iodine distributed between carbon tetrachloride and water.

(d) State two applications of partition coefficient.

The applications of partition coefficients

Partition coefficients are applied in the following processes;

- ***Solvent extraction***
- ***Determining formulae of complex ions***
- ***Paper chromatography and column chromatography***
- ***Ion exchange***
- ***Determining equilibrium constants***

(a) Solvent extraction

During preparation of organic compounds, the product is obtained as an aqueous solution and the organic compound must be separated from the water. This is done by solvent extraction.

Organic compounds are more soluble in organic solvents like ether or benzene than in water and the organic solvents (ether or benzene) are immiscible with water.
An organic compound like phenylamine is more soluble in ethoxyethane (ether) than in water. When a mixture of phenylamine and water with ether is shaken, in a separating funnel, most of the phenylamine dissolves in dissolves in ether. Two separate layers are formed and they can be separated by opening the tap on the separating funnel.
The phenylamine can then be removed from the ether layer by distillation.

Solvent extraction can therefore be defined as the removal of a solute from one solvent in which it is less soluble by shaking the solution with another solvent in which it is more soluble and both solvents being immiscible with each other, the solute remaining in the same molecular state in both solvents.

Conditions for isolation of a solute by solvent extraction

- Solvents must be immiscible with each other
- The two solvents should not react with each other
- The solute should not associate or dissociate in any of the solvents
- Solute must be more soluble in the extracting organic solvent

Ethoxyethane is most commonly used in solvent extraction of organic compounds from their aqueous solution because;

- It is a good solvent for many organic compounds
- Ether is immiscible with water
- It does not react with most organic compounds
- It has a very volatile hence can be distilled off or removed after use

Solvent extraction is always more effective when the extracting liquid is divided into several portions and each portion used separately rather than using the whole of the liquid in one extraction. ***This is because smaller portions used successively extract more of the solute than one big portion used once.***

Applications of solvent extraction

- Separation of azeotropic mixtures
- Extraction of oil from simsim
- Purification of zinc ores
- Separation of inorganic solids for example iron(III) chloride from manganese(II) chloride

Calculations involving solvent extraction

Examples

1. **(a) Explain the principle of solvent extraction.**

   (b) $1.00\ dm^3$ of aqueous solution contains 5.00g of butanoic acid. Calculate the mass of butanoic acid extracted when the solution was shaken:

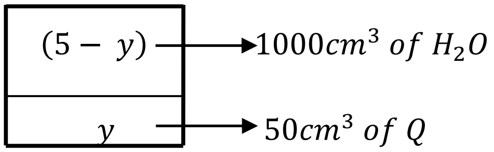
   (The distribution coefficient, K_D of butanoic acid between Q and water is 40)

(i) with 50 cm^3 of a solvent Q.

(ii) twice with 25 cm^3 of solvent Q

(b) (i) $Let\ the\ mass\ of\ CH_3CH_2CH_2COOH\ extracted\ by\ 50\ cm^3 of\ Q\ be\ y\ g$

$mass\ of\ CH_3CH_2CH_2COOH\ that\ remain\ in\ aquoeus\ layer = (5 - y)g$



$$K_D = \frac{[CH_3CH_2CH_2COOH\ ]_Q}{[CH_3CH_2CH_2COOH\ ]_{H_2O}}$$

$$40 = \frac{y/_{50}}{(5-y)/_{1000}}$$

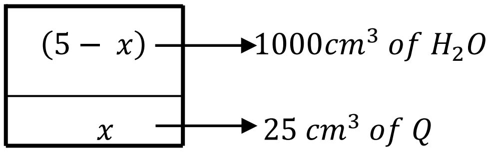
$$40 = \frac{1000y}{50(5-y)}$$

$$y = 3.3333$$

The mass of butanoic acid extracted by $50cm^3$ of Q is 3.3333g

(ii) *Let the mass of* $CH_3CH_2CH_2COOH$ *extracted by* $\boldsymbol{first\ 25\ cm^3\ portion}$ *of Q be x g*

mass of $CH_3CH_2CH_2COOH$ *that remain in aquoeus layer* $= (5 - x)g$



$K_D = 40$

$$40 = \frac{x/25}{(5-x)/1000}$$

$$40 = \frac{1000x}{25(5-x)}$$

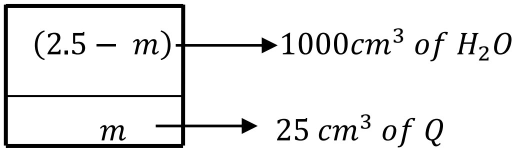
$$x = 2.5$$

The mass of butanoic acid extracted by first $25cm^3$ portion of Q is 2.5 g

Mass of $CH_3CH_2CH_2COOH$ *that remains in water* $= (5 - 2.5) = 2.5g$

Let the mass of $CH_3CH_2CH_2COOH$ $\boldsymbol{second\ 25\ cm^3\ portion}$ *of Q be m g*

mass of $CH_3CH_2CH_2COOH$ *that remain in aqueous layer* $= (2.5 - m)g$



$$40 = \frac{m/25}{(2.5-m)/1000}$$

$$40 = \frac{1000m}{25(2.5-m)}$$

$$m = 1.25$$

The mass of butanoic acid extracted by second $25cm^3$ portion of Q is 1.25 g

The total mass extracted by two successive $25\ cm^3$ portions of Q is $(2.5 + 1.25) = 3.75g$

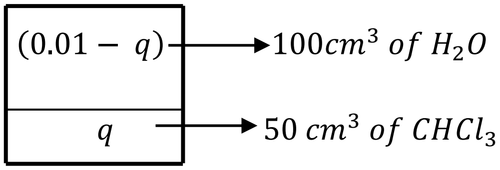
2. **100 $cm^3$of 0.1M ammonia solution was shaken with 50 cm^3 of chloroform. The partition coefficient of ammonia between chloroform and aqueous solution is 25.2. Calculate percentage of ammonia extracted.**

Moles of ammonia in $100cm^3$ *solution*

$$= \left(\frac{100 \times 0.1}{1000}\right) = 0.01$$

Let the moles of NH_3 *extracted by* $50cm^3$*of* $= q$

moles that remain in water $= (0.01 - q)$



$$K_D = \frac{[NH_3\ ]_{CHCl_3}}{[NH_3\ ]_{H_2O}}$$

$$25.2 = \frac{q/50}{(0.01-q)/100}$$

$$25.2 = \frac{100q}{50(0.01-q)}$$

$$q = 0.009265$$

Percentage of ammonia extracted

$$= \frac{0.009265}{0.01} \times 100 = 92.65\%$$

3. (a) 0.9656g of iodine was shaken with a mixture of 50 cm^3 of trichloromethane and 50 cm^3 of water in separating funnel for some time until equilibrium was attained at 25°C. After the layers had settled, 25 cm^3 of the aqueous layer required 4.4 cm^3 of $0.01M$ sodium thiosulphate solution using starch indicator.

- **(i) Determine the distribution coefficient of iodine between trichloromethane and water at 25°C.**
- **(ii) If 50 cm^3 of trichloromethane layer in (a) above was again shaken with 100 cm^3 of water at 25°C , determine the mass of iodine that remained in the trichloromethane layer.**

(b) Explain why trichloromethane is a better solvent in the extraction of iodine than water.

(a) (i) $Moles\ \ of\ sodium\ thiosulphate\ solution\ that\ reacted\ with\ iodine$

$$= \left(\frac{4.4 \times 0.01}{1000}\right) = \mathbf{4.4 \times 10^{-5}\ moles}$$

$$\boldsymbol{I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)}$$

$$mole\ ratio\ of\ S_2O_3^{2-}: I_2 = 2:1$$

$$moles\ of\ I_2\ that\ reacted = \frac{4.4 \times 10^{-5}}{2} = 2.2 \times 10^{-5}\ moles$$

$$25\ cm^3 of\ \ aqueous\ layer\ \ contain\ 2.2 \times 10^{-5}\ moles\ of\ I_2$$

$$50\ cm^3 of\ \ aqueous\ layer\ \ \ layer\ \ contain\ \left(\frac{50 \times 2.2 \times 10^{-5}}{25}\right) moles\ of\ I_2$$

$$= \mathbf{4.4 \times 10^{-5}\ moles}$$

$$Molar\ mass\ of\ I_2 = (2 \times 127) = 254g$$

$$Mass\ of\ I_2 that\ remain\ in\ aqueous\ layer$$

$$= (254 \times 4.4 \times 10^{-5}) = 0.011176g$$

$$Mass\ of\ I_2\ extracted\ by\ \ CHCl_3$$

$$= (0.9656 - 0.011176) = 0.954424g$$

$0.011176g \longrightarrow 50cm^3\ of\ H_2O$

$0.954424g \longrightarrow 50cm^3\ of\ CHCl_3$

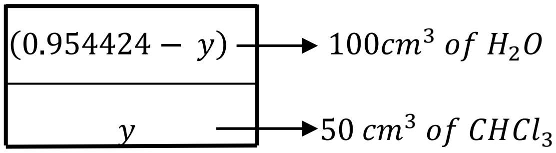
$$\mathrm{K_D} = \frac{[I_2]_{CHCl_3}}{[I_2\ ]_{H_2O}}$$

$$\mathrm{K_D} = \frac{0.954424/50}{0.011176/50}$$

$$\mathrm{K_D} = \frac{0.954424 \times 50}{0.011176 \times 50} = \mathbf{84.4}$$

(ii) $Let\ the\ mass\ of\ I_2\ extracted\ by\ CHCl_3\ be\ y\ g$

$Mass\ of\ I_2\ that\ remain\ in\ aqueous\ layer$
$= (0.954424 - y)g$



$K_D = 84.4$

$$84.4 = \frac{y/50}{(0.954424 - y)/100}$$

$$84.4 = \frac{100y}{50(0.954424 - y)}$$

$$y = 0.932331$$

The mass of Iodine extracted by trichloromethane is 0.932331 g

(b) Both iodine and trichloromethane are non-polar hence iodine is very soluble in non-polar trichloromethane but insoluble in water which is a polar solvent.

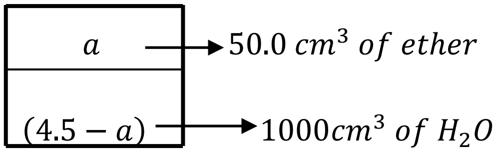
4. A solute Q is three times as soluble in ethoxyethane as in water. An aqueous solution containing 4.5g of Q per litre of solution was shaken by ethoxyethane in a separating funnel. Calculate the mass of Q that is extracted by two successive 50.0 cm^3 portions of ethoxyethane.

$Let\ [Q\ ]_{H_2O} = x$

$Then\ \ [Q\ ]_{ether} = 3x$

$$K_D = \frac{[Q\ ]_{ether}}{[Q\ ]_{H_2O}} = \frac{3x}{x} = 3$$

$Let\ the\ mass\ of\ Q\ extracted\ by\ first\ 50.0cm^3\ portion\ of\ ethoxyethane\ be\ a\ g$



$K_D = 3$

$$3 = \frac{a/50.0}{(4.5 - a)/1000}$$

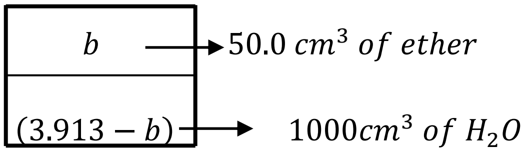
$$3 = \frac{1000a}{50(4.5 - a)}$$

$$m = 0.587$$

The mass of Q extracted by first $\mathbf{50.0cm^3}$ portion of ether is 0.587g

$Mass\ of\ Q\ remaining\ \ in\ water = (4.5 - 0.587)$
$= 3.913g$

$Let\ the\ mass\ of\ Q\ extracted\ by\ second\ 50.0cm^3\ portion\ of\ ethoxyethane\ be\ b\ g$



$$3 = \frac{b/50.0}{(3.913 - b)/1000}$$

$$3 = \frac{1000b}{50(3.913 - b)}$$

$$m = 0.510$$

The mass of Q extracted by second $\mathbf{50.0cm^3}$ portion of ether is 0.510g

The total mass extracted by two successive $\mathbf{50.0\ cm^3}$ portions of ether is
$\mathbf{(0.587 + 0.510) = 1.097g}$

5. (a) An aqueous solution contains 10g of Y in a litre of solution.100 cm^3 of this solution was shaken with 20 cm^3 of ether and the ether extracted 0.8g of Y . Calculate the volume of ether that is required to extract 80% of Y from 500 cm^3 of the aqueous solution.

(b) Give a reason why using small aliquots improves the yield.

(a) $1000cm^3\ solution\ contain\ 10g$

$$100cm^3\ of\ solution\ \left(\frac{100\times 10}{1000}\right)=1g$$

$$0.8g \longrightarrow 20cm^3\ of ether$$

$$0.2g \longrightarrow 100\ cm^3\ of\ H_2O$$

$$\mathrm{K_D}=\frac{[Y\,]_{ether}}{[Y\,]_{H_2O}}$$

$$\mathrm{K_D}=\frac{0.8/20}{0.2/100}$$

$$\mathrm{K_D}=\frac{0.8\times 100}{20\times 0.2}=20$$

$$1000cm^3\ solution\ contain\ 10g$$

$$500cm^3\ of\ solution\ \left(\frac{500\times 10}{1000}\right)=5g$$

$Let\ the\ volume\ of\ ether\ required\ be\ Vcm^3$

$Mass\ of\ Y\ extracted\ Vcm^3 of\ ether$

$$=\left(\frac{80}{100}\times 5\right)=4g$$

$$4.0g \longrightarrow V\ cm^3\ of ether$$

$$1.0g \longrightarrow 500\ cm^3\ of\ H_2O$$

$$\mathrm{K_D}=\frac{4.0/\boldsymbol{V}}{1.0/500}=20$$

$$\frac{4.0\times 500}{\boldsymbol{V}\times 1.0}=20$$

$$\boldsymbol{V=100\ cm^3}$$

(b) This is because after every extraction, the solute redistributes itself uniformly in the two solvents making it available for subsequent extractions

6. A crude sample of lead contained 2% of silver by mass. Calculate the percentage of silver left in 150 kg of lead if it was thoroughly agitated with 10kg of zinc at 800°C. The solubility of silver in a given mass of zinc is 300 times its solubility in an equal mass of lead at 800°C.

$$Mass\ of\ Ag\ in\ 150kg\ of\ Pb=\left(\frac{2}{100}\times 150\right)=3\ kg$$

$Let\ mass\ of\ Ag\ that\ remains\ in\ Pb\ be\ x\ kg$

$$(3-x) \longrightarrow 10\ kg\ of\ Zn$$

$$x \longrightarrow 150\ kg\ of\ Pb$$

$$\mathrm{K_D}=\frac{[Ag\,]_{Zn}}{[Ag\,]_{Pb}}=\frac{300[Ag\,]_{Pb}}{[Ag\,]_{Pb}}=300$$

$$300=\frac{(3-x)/10}{x/150}$$

$$300=\frac{150(3-x)}{10x}$$

$$\boldsymbol{x=0.1429}$$

Percentage of Ag left in 150kg of Pb= $\frac{\mathbf{0.1429}}{\mathbf{3}}\times\mathbf{100=4.76\%}$

Questions

1. The partition coefficient of ***J*** between ethoxyethane and water is 5.0. A solution containing 10.0g of ***J*** in 5000 cm^3 of water is extracted with 100cm^3 of ethoxyethane. Calculate the mass of ***J*** extracted from the water.
2. (a) (i) What is meant by the term **solvent extraction**
   - (ii) State three limitations of solvent extraction
   - (iii) Explain why small portions of solvent are preferred to large portions in solvent extraction of solute.

   (b) An aqueous solution contains 5.0g of ***X*** in 100 cm^3 of solution. The partition coefficient of ***X*** between water and an organic solvent is 0.200. Calculate the mass of ***X*** extracted by shaking 100 cm^3 of the aqueous solution with;

   (i) 50 cm^3 of the solvent

   (ii) Two successive 25 cm^3 portions of the solvent.
3. (a) Define the term partition coefficient.

   (b) A compound ***Z*** has a partition coefficient of 4.00 between ether and water. Calculate the mass of ***Z*** extracted from 100 cm^3 of an aqueous solution of 4.00g of ***Z*** by two successive extractions with 50 cm^3 of ether.
4. (a) Explain the partition law

   (b) 18g of a compound ***X*** distributes itself between an immiscible solvent ***Y*** and an equal volume of water such that 2g of ***X*** are left in water. Calculate the percentage of ***X*** left in water if 1000 cm^3 of water containing 1g of ***X*** are extracted by:
   - (i) One litre of ***Y***
   - (ii) Half a litre of ***Y*** two times successively.
5. An aqueous solution contains 10g of butane-1,4-dioic acid per litre. When 100 cm^3 of this solution was shaken with 20 cm^3 of ethoxyethane, the ethoxyethane layer extracted 0.8g of butane-1,4-dioic acid .Calculate the mass of butane-1,4-dioic acid extracted when 500 cm^3 the aqueous layer was shaken with:

   (a) with 50 cm^3 of ethoxyethane.

   (b) two successive 25 cm^3 portions of ethoxyethane.

   (c) Comment on your results in (a) and (b) above.
6. 100 cm^3 of a solution containing 0.171g of ammonia in trichloromethane was shaken with 100 cm^3 of water until equilibrium was attained at room temperature. Calculate the number of moles of ammonia in the trichloromethane layer. (The distribution coefficient of ammonia between water and trichloromethane is 27.5)
7. 100 cm^3 of an aqueous solution containing 10g of compound ***Q*** was shaken with 100 cm^3 of benzene. ***Q*** is more soluble in benzene than and the partition coefficient of ***Q*** is 12.2. Calculate the mass of ***Q*** left in the aqueous layer.

8. Industrially, silver is extracted from molten lead using molten zinc which is insoluble in lead. The solubility of silver is 300 times greater in zinc than it is in an equal volume of lead. Calculate the mass of silver extracted using $0.01dm^3$ of molten zinc and $0.2dm^3$ of molten lead containing 5g of silver.
9. (a) (i) State the distribution law.
   (ii) Under what conditions is the law you have stated in (i) valid?
   (b) The table below shows the concentrations of succinic acid in ether and water at equilibrium in $moldm^{-3}$.

Experiment number	1	2	3	4	5	6
$[\boldsymbol{Succinic\ acid}]_{\boldsymbol{water}}$	0.023	0.028	0.036	0.044	0.052	0.055
$[\boldsymbol{Succinic\ acid}]_{\boldsymbol{ether}}$	0.15	0.18	0.24	0.3	0.36	0.38

   (i) Plot a graph of concentration of succinic acid in water against concentration of succinic acid in water.
   (ii) From the graph determine the distribution constant for succinic acid between ether and water.
   (c) 100 cm^3 of ether was shaken with an aqueous solution containing 18g of succinic acid per dm^3 of solution. Calculate the mass of succinic acid that remained in the aqueous layer.
   (d) State one application of the distribution constant

(b) Determining formulae of complex ions

The partition coefficient of solute between water and another solvent is used to investigate the composition of a complex ion in aqueous solution.

This is normally applied to cations that are soluble in excess ammonia, excess aminoethane or any other excess ammine solution i.e. copper(II) ions, zinc ions, chromium(III) ions, nickel(II) ions, silver ions and cobalt(II) ions

Theory:

When excess aqueous ammonia is added to a solution of each of the above ions, complex ions are formed.

$$Cu^{2+}(aq) + 4NH_3(aq) \longrightarrow [Cu(NH_3)_4]^{2+}\ (aq)$$
$$Zn^{2+}(aq) + 4NH_3(aq) \longrightarrow [Zn(NH_3)_4]^{2+}\ (aq)$$
$$Cr^{3+}(aq) + 6NH_3(aq) \longrightarrow [Cr(NH_3)_6]^{3+}\ (aq)$$
$$Ni^{2+}(aq) + 6NH_3(aq) \longrightarrow [Ni(NH_3)_6]^{2+}\ (aq)$$
$$Ag^{+}(aq) + 2NH_3(aq) \longrightarrow [Ag(NH_3)_2]^{+}\ (aq)$$
$$Co^{2+}(aq) + 6NH_3(aq) \longrightarrow [Co(NH_3)_6]^{2+}\ (aq)$$

Each of the above complex ions has a characteristic colour in solution from which we can tell that it is formed. For example $[Cu(NH_3)_4]^{2+}$is a deep blue solution and $[Zn(NH_3)_4]^{2+}$is a colourless solution.

The general equation for all the above reactions is;

$$\boldsymbol{M^{x+}(aq) + nNH_3(aq) \longrightarrow [M(NH_3)_n]^{x+}\ (aq)}$$

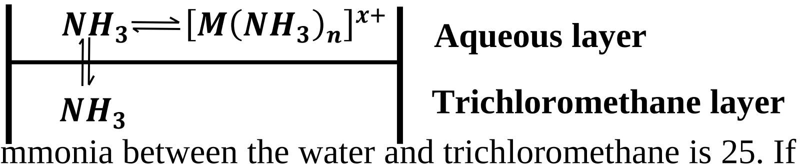
If aminoethane is used then;

$$\boldsymbol{M^{x+}(aq) + nCH_3NH_2(aq) \longrightarrow [M(CH_3NH_2)_n]^{x+}\ (aq)}$$

On addition of excess aqueous ammonia to any of the ions forms a solution containing both free and fixed (complexed) ammonia.

This solution when shaken with chloroform (trichloromethane) and left to settle, two layers are formed.

The upper aqueous layer contains the complex ion and free ammonia in equilibrium with free ammonia in the lower trichloromethane layer.



The partition coefficient of ammonia between the water and trichloromethane is 25. If the concentration of ammonia in the trichloromethane layer is obtained by titrating a portion of it with standard hydrochloric acid, then concentration of free ammonia in the aqueous layer can be calculated from;

$$\mathrm{K_D} = \frac{[NH_3]_{free\ in\ water}}{[NH_3]_{CHCl_3}}$$

$$[NH_3]_{free\ in\ water} = 25 \times [NH_3]_{CHCl_3}$$

The total concentration of ammonia (free and complexed) in the aqueous layer is also obtained by titrating a portion of it with standard hydrochloric acid. During this titration, the equilibrium is displaced to the left. The concentration of complexed ammonia is then got by subtraction as shown below.

$$[NH_3]_{total} = [NH_3]_{free\ in\ water} + [NH_3]_{complexed}$$

$$[NH_3]_{complexed} = [NH_3]_{total} - [NH_3]_{free\ in\ water}$$

Assuming that all the cation is complexed and that the concentration of the solution of the complexed cation, $[\ M^{x+}]$ is known, then the value of n in the complex, $[M(NH_3)_n]^{x+}$ can be obtained by;

$$n = \frac{[NH_3]_{complexed}}{[M^{x+}]}$$

Experimental determination of formula of a complex ion

Experiment to determine formula of complex formed between excess ammonia and zinc ions.

A ***known volume of excess ammonia*** solution is shaken with ***an equal volume*** of a ***standard solution of zinc ions.***

The resultant solution formed, that contains the complex, $[Zn(NH_3)_n]^{2+}$ and excess ammonia is shaken with a ***known volume of trichloromethane*** for about 15 minutes.

The mixture is ***left to stand*** for equilibrium to be established ***at a constant temperature***.

A ***known volume of the trichloromethane layer*** is ***pipetted and titrated*** against a ***standard solution of hydrochloric acid*** using ***methyl orange indicator***.

The ***concentration of ammonia in the trichloromethane layer*** is calculated using the equation;

$$\boldsymbol{NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)}$$

A ***known volume of the aqueous layer*** is also ***pipetted and titrated*** against ***a standard solution of hydrochloric acid*** using ***methyl orange indicator***.

The ***total concentration of ammonia in the aqueous layer*** determined

<u>Treatment of results</u>

$$Concentration\ of\ zinc\ ions\ used\ = [\boldsymbol{Zn^{2+}}]$$

$$Concentration\ of\ ammonia\ in\ the\ trichloromethane\ layer = [\boldsymbol{NH_3}]_{\boldsymbol{CHCl_3}}$$

$$Total\ concentration\ of\ ammonia\ in\ the\ aqueous\ layer = [\boldsymbol{NH_3}]_{\boldsymbol{total}}$$

For a known value of partition coefficient, $\mathbf{K_D}$ of ammonia between water and trichloromethane, the ***concentration of free ammonia*** in the aqueous layer is calculated;

$$\mathbf{K_D} = \frac{[\boldsymbol{NH_3}]_{\boldsymbol{free\ in\ water}}}{[\boldsymbol{NH_3}]_{\boldsymbol{CHCl_3}}}$$

$$[\boldsymbol{NH_3}]_{\boldsymbol{free\ in\ water}} = \mathbf{K_D} \times [\boldsymbol{NH_3}]_{\boldsymbol{CHCl_3}}$$

$$But\ [\boldsymbol{NH_3}]_{\boldsymbol{total}} = [\boldsymbol{NH_3}]_{\boldsymbol{free\ in\ water}} + [\boldsymbol{NH_3}]_{\boldsymbol{complexed}}$$

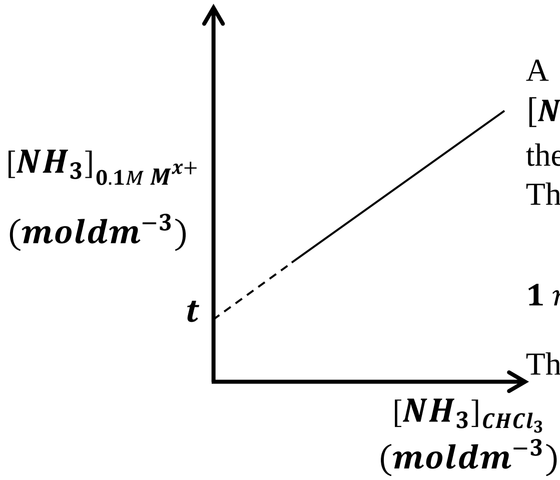
$$[\boldsymbol{NH_3}]_{\boldsymbol{complexed}} = [\boldsymbol{NH_3}]_{\boldsymbol{total}} - [\boldsymbol{NH_3}]_{\boldsymbol{free\ in\ water}}$$

$$Then\quad \boldsymbol{n} = \frac{[\boldsymbol{NH_3}]_{\boldsymbol{complexed}}}{[\boldsymbol{Zn^{2+}}]}$$

The same procedure can be used for an experiment to determine the formulae of ; $[Cu(NH_3)_n]^{2+}$, $[Cr(NH_3)_n]^{3+}$, $[Ni(NH_3)_n]^{2+}$, $[Ag(NH_3)_n]^{+}$ and $[Co(NH_3)_n]^{2+}$

Determining formula of a complex, $[M(NH_3)_n]^{x+}$ using graphical approach

A graph of concentration of ammonia in a standard solution of complexed cation i.e. $[NH_3]_{0.1M\ M^{x+}}$ ***against the concentration of ammonia in trichloromethane,*** $[NH_3]_{CHCl_3}$ ***is plotted***.



A graph of $[NH_3]_{0.1M\ M^{x+}}$ against $[NH_3]_{CHCl_3}$ is usually a straight line with an intercept (t) on the $[NH_3]_{0.1M\ M^{x+}}$ axis (obtained by extrapolation).
Then;

$$\mathbf{0.1}\ moles\ of\ \boldsymbol{M^{x+}} complex\ with\ \boldsymbol{t}\ moles\ of\ NH_3$$

$$\mathbf{1}\ moles\ of\ \boldsymbol{M^{x+}} will\ complex\ with\ \left(\frac{1 \times t}{0.1}\right)\ moles\ of\ NH_3$$

The value of $\boldsymbol{n}$ in $[\boldsymbol{M(NH_3)_n}]^{x+}$ **is therefore** $\left(\frac{\boldsymbol{t}}{\mathbf{0.1}}\right)$

Examples

1. **(a) Define the term partition coefficient**

   (b) 50 cm^3 of a $0.8M$ ammonia solution was added to 50 cm^3 of trichloromethane in a flask. To the resultant mixture was added $0.1M$ cobalt(II) chloride solution. The mixture was shaken and allowed to stand at constant temperature. When the layers had separated, 25 cm^3 of the trichloromethane layer required 20 cm^3 of $0.01M$ hydrochloric acid for complete reaction. (K_D of ammonia between water and trichloromethane is 25.0).

   Calculate the molar concentration of ;

   (i) ammonia in the trichloromethane layer.

   (ii) free ammonia in the aqueous layer

   (iii) ammonia fixed in the complex $[Co(NH_3)_n]^{2+}$

   (c) Determine the value of n in the complex in b(ii)

(b) (i) $Moles\ of\ HCl\ that\ reacted\ with\ NH_3\ in\ trichloromethane\ layer\ \left(\frac{20\times0.01}{1000}\right)\ moles.$

$$= \mathbf{0.0002\ moles}$$

$$\boldsymbol{NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)}$$

$$mole\ ratio\ of\ NH_3 : HCl = 1:1$$

$$moles\ of\ ammonia\ NH_3\ in\ trichloromethane\ layer\ that\ reacted\ with\ HCl = \mathbf{0.0002\ moles}$$

$$25\ cm^3 of\ \ trichloromethane\ layer\ \ contain\ 0.0002\ moles\ of\ NH_3$$

$$1000\ cm^3 of\ \ trichloromethane\ layer\ \ contain\ \left(\frac{1000\times0.0002}{25}\right) moles\ of\ NH_3$$

$$\boldsymbol{[NH_3]_{CHCl_3} = 0.008\ M}$$

(ii) $$K_D = \frac{[NH_3]_{free\ in\ water}}{[NH_3]_{CHCl_3}}$$

$$25 = \frac{[NH_3]_{free\ in\ water}}{0.008}$$

$$[NH_3]_{free\ in\ water} = 25 \times 0.008$$

$$\boldsymbol{[NH_3]_{free\ in\ water} = 0.2\text{M}}$$

(iii) $$[NH_3]_{total} = [NH_3]_{free\ in\ water} + [NH_3]_{complexed}$$

$$[NH_3]_{complexed} = [NH_3]_{total} - [NH_3]_{free\ in\ water}$$

$$[NH_3]_{complexed} = 0.8 - 0.2$$

$$= \mathbf{0.6}$$

(c) $$\boldsymbol{n = \frac{[NH_3]_{complexed}}{[Co^{2+}]} = \frac{0.6}{0.1} = 6}$$

---

2. **To a solution of 25 cm^3 of a $0.1M$ copper(II) ions was added 25 $cm^3$of ammonia solution at and the resulting solution was shaken with trichloromethane and allowed to stand to form two layers. 20 cm^3 of the organic layer required 10.2 cm^3 of $0.05M$ hydrochloric acid for complete neutralization. 10 cm^3 of the aqueous layer was titrated with 16.5 cm^3 of $0.5M$ hydrochloric acid. The partition coefficient of ammonia between water and trichloromethane is 25.0. Calculate the value of n in the complex below.**

$$\boldsymbol{Cu^{2+}(aq) + nNH_3(aq) \longrightarrow [Cu(NH_3)_n]^{2+}\ (aq)}$$

$Moles\ of\ HCl\ that\ reacted\ with\ NH_3\ in\ trichloromethane\ layer\ \left(\frac{10.2\times0.05}{1000}\right)\ moles.$

$$= \mathbf{0.00051\ moles}$$

$$\boldsymbol{NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)}$$

$$mole\ ratio\ of\ NH_3 : HCl = 1:1$$

$$moles\ of\ ammonia\ NH_3\ in\ trichloromethane\ layer\ that\ reacted\ withHCl = \mathbf{0.00051\ moles}$$

$$20\ cm^3 of\ \ trichloromethane\ layer\ \ contain\ 0.00051\ moles\ of\ NH_3$$

$$1000\ cm^3 of\ \ trichloromethane\ layer\ \ contain\ \left(\frac{1000\times0.00051}{20}\right) moles\ of\ NH_3$$

$$\boldsymbol{[NH_3]_{CHCl_3} = 0.0255\ M}$$

$$\mathrm{K_D} = \frac{[NH_3]_{free\ in\ water}}{[NH_3]_{CHCl_3}}$$

$$25.0 = \frac{[NH_3]_{free\ in\ water}}{0.0255}$$

$$[NH_3]_{free\ in\ water} = 25.0 \times 0.0255$$

$$\boldsymbol{[NH_3]_{free\ in\ water} = 0.6375\mathrm{M}}$$

$$Moles\ of\ HCl\ that\ reacted\ with\ NH_3\ in\ aqueous\ layer\ \left(\frac{16.5 \times 0.5}{1000}\right)\ moles.$$

$$= \boldsymbol{0.00825\ moles}$$

$$\boldsymbol{NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)}$$

$$mole\ ratio\ of\ NH_3 : HCl = 1:1$$

$$moles\ of\ ammonia\ NH_3\ in\ aqueous\ layer\ that\ reacted\ with\ HCl = \boldsymbol{0.00825\ moles}$$

$$10\ cm^3 of\ \ aqueous\ layer\ \ contain\ 0.00825\ moles\ of\ NH_3$$

$$1000\ cm^3 of\ aqueous\ layer\ \ contain\ \left(\frac{1000 \times 0.00825}{10}\right) moles\ of\ NH_3$$

$$= \boldsymbol{0.825\ M}$$

$$Therefore\ total\ concentration\ of\ NH_3\ in\ aqueous\ layer, [NH_3]_{total} = 0.825M$$

$$But \qquad [NH_3]_{total} = [NH_3]_{free\ in\ water} + [NH_3]_{complexed}$$

$$[NH_3]_{complexed} = [NH_3]_{total} - [NH_3]_{free\ in\ water}$$

$$[NH_3]_{complexed} = 0.825 - 0.6375$$

$$= \boldsymbol{0.1875M}$$

Note that when an equal volume of ammonia solution is added to a solution of copper(II) ions, the concentration of copper(II) ions is halved. This is shown by the calculation below;

$$Moles\ of\ \mathbf{Cu^{2+}}\ in\ 25\ cm^3 of\ solution = \left(\frac{25 \times 0.1}{1000}\right) = 0.0025\ moles.$$

$$\text{Total volume of solution} = (25 + 25) = 50\ cm^3$$

$$50\ cm^3 of\ solution\ contain\ 0.0025\ moles$$

$$1000\ cm^3 of\ solution\ contain\ \left(\frac{1000 \times 0.0025}{50}\right) = \boldsymbol{0.05M}$$

$$\boldsymbol{n = \frac{[NH_3]_{complexed}}{[Cu^{2+}]} = \frac{0.1875}{0.05} = 3.75 \approx 4}$$

---

3. **$3.0g$ of a zinc ore was dissolved in excess concentrated ammonia and the solution made up to $500\ cm^3$ with water. The resultant solution was shaken with chloroform and left to stand. 25 cm^3 of the organic layer required 12.50 cm^3 of 0.025M hydrochloric acid for complete neutralisation. 12.50 cm^3 of the aqueous layer was neutralised by 20.0 cm^3 of 0.25M hydrochloric acid. Calculate the percentage of zinc in the ore. ($Zn = 65.7$ and the partition coefficient of ammonia between chloroform and water is 0.04.)**

$$Moles\ of\ HCl\ that\ reacted\ with\ NH_3\ in\ trichloromethane\ layer\ \left(\frac{12.5 \times 0.025}{1000}\right)\ moles.$$

$$= \mathbf{0.000312\ moles}$$

$$\mathbf{NH_3(aq) + HCl(aq) \xrightarrow{\quad} NH_4Cl(aq)}$$

$$mole\ ratio\ of\ NH_3 : HCl = 1:1$$

$$moles\ of\ ammonia\ NH_3\ in\ trichloromethane\ layer\ that\ reacted\ with\ HCl$$

$$= \mathbf{0.000312\ moles}$$

$$25\ cm^3 of\ \ trichloromethane\ layer\ \ contain\ 0.000312\ moles\ of\ NH_3$$

$$1000\ cm^3 of\ \ trichloromethane\ layer\ \ contain\ \left(\frac{1000 \times 0.000312}{25}\right) moles\ of\ NH_3$$

$$\mathbf{[NH_3]_{CHCl_3} = 0.0125\ M}$$

$$\mathrm{K_D} = \frac{[NH_3]_{CHCl_3}}{[NH_3]_{free\ in\ water}}$$

$$0.04 = \frac{0.0125}{[NH_3]_{free\ in\ water}}$$

$$[NH_3]_{free\ in\ water} = \frac{0.0125}{0.04}$$

$$\mathbf{[NH_3]_{free\ in\ water} = 0.3125\ M}$$

$$Moles\ of\ HCl\ that\ reacted\ with\ NH_3\ in\ aqueous\ layer\ \left(\frac{20 \times 0.25}{1000}\right)\ moles.$$

$$= \mathbf{0.005\ moles}$$

$$\mathbf{NH_3(aq) + HCl(aq) \xrightarrow{\quad} NH_4Cl(aq)}$$

$$mole\ ratio\ of\ NH_3 : HCl = 1:1$$

$$moles\ of\ ammonia\ NH_3\ in\ aqueous\ layer\ that\ reacted\ with\ HCl = \mathbf{0.005\ moles}$$

$$12.5\ cm^3 of\ \ aqueous\ layer\ \ contain\ 0.005\ moles\ of\ NH_3$$

$$1000\ cm^3 of\ \ trichloromethane\ layer\ \ contain\ \left(\frac{1000 \times 0.005}{12.5}\right) moles\ of\ NH_3$$

$$= \mathbf{0.4\ M}$$

$$Therefore\ total\ concentration\ of\ NH_3\ in\ aqueous\ layer, [NH_3]_{total} = 0.4M$$

$$But \qquad [NH_3]_{total} = [NH_3]_{free\ in\ water} + [NH_3]_{complexed}$$

$$[NH_3]_{complexed} = [NH_3]_{total} - [NH_3]_{free\ in\ water}$$

$$[NH_3]_{complexed} = 0.4 - 0.3125$$

$$= \mathbf{0.0875M}$$

$$1000\ cm^3 contain\ 0.0875\ moles\ of\ NH_3\ that\ complex\ with\ Zn^{2+}$$

$$500\ cm^3 contain\ \left(\frac{500 \times 0.0875}{1000}\right)\ moles\ that\ complex\ with\ Zn^{2+}$$

$$= 0.04375\ moles\ of\ NH_3$$

$$\mathbf{Equation\ ;\ Zn^{2+}(aq) + 4NH_3(aq) \xrightarrow{\quad\quad} [Zn(NH_3)_4]^{2+}\ (aq)}$$

$$4\ moles\ of\ NH_3\ complex\ with\ 1\ mole\ of Zn^{2+}$$

$$0.04375\ moles\ of\ NH_3\ complex\ with\ \left(\frac{1 \times 0.04375}{4}\right)\ moles\ of Zn^{2+}$$

$$= 0.0109\ moles\ of Zn^{2+}$$

$$Mass\ of\ pure\ Zn\ in\ 500\ cm^3\ of\ solution = (0.0109 \times 65.7) = 0.71613g$$

$$\boldsymbol{Percentage\ of\ zinc\ in\ the\ ore = \frac{0.71613}{3.0} \times 100 = 23.87\%}$$

This calculation is done on an assumption that all the zinc in the ore was complexed.

Questions

1. (a) Explain the term **partition coefficient**.

   (b) State two conditions under which partition coefficient is valid.

   (c) Excess ammonia was shaken with equal volume of trichloromethane and a 0.05M aqueous solution of zinc sulphate and allowed to stand. Some ammonia reacted with zinc to form a complex, $[Zn(NH_3)_n]^{2+}$. At equilibrium, the concentrations of ammonia in the trichloromethane layer and the aqueous layer were 0.0254 mol l^{-1} and 0.835 mol l^{-1} respectively. (The partition coefficient of ammonia between water and trichloromethane is 25). Calculate;

   (i) the concentration of free ammonia in the aqueous layer

   (ii) the concentration of ammonia that formed the complex with zinc ions

   (iii) the formula of the complex ion.
2. $25\,cm^3$ of a $0.1M$ zinc ions was mixed with $25\,cm^3$ of ammonia solution and the resulting solution was shaken with trichloromethane and allowed to stand to form two layers. 20 cm^3 of the organic layer required 10.2 cm^3 of $0.05M$ hydrochloric acid for complete neutralisation. 10 cm^3 of the aqueous layer was titrated with 16.5 cm^3 of $0.5M$ hydrochloric acid. If the partition coefficient of ammonia between water and trichloromethane is 25. Calculate the value of n in the zinc complex, $[Zn(NH_3)_n]^{2+}$**.**
3. $50\,cm^3$ of a $0.1M$ solution of chromium(III) ions was mixed with $50\,cm^3$of ammonia solution at and the resulting solution was shaken with $50\,cm^3$ trichloromethane and the mixture left to settle. At equilibrium, the aqueous layer required 70 cm^3 of $1M$ hydrochloric acid for complete reaction while the organic layer required $20\,cm^3$ of $0.04M$ hydrochloric acid for complete reaction. The partition coefficient of ammonia between water and chloroform is 25.0 and chromium forms a complex, $[Cr(NH_3)_n]^{2+}$ with ammonia. Find the value of n in the complex.
4. (a) The partition coefficient of ammonia between water and trichloromethane at $25°C$ is 25.0.

   (i) Define the term partition coefficient.

   (ii) State two conditions under which the partition coefficient ($K_D = 25.0$) is valid other than constant temperature.

(b) 25 cm^3 of $0.0056M$ nickel(II) sulphate solution were added to an equal volume of ammonia solution at $25°C$. The mixture was shaken with 50 cm^3 of trichloromethane and allowed to stand until equilibrium was established. The trichloromethane layer required 32 cm^3 of $0.0025M$ hydrochloric acid for complete neutralization. 7.06 cm^3 of the aqueous layer required 20 cm^3 of $0.02M$ hydrochloric acid.

Nickel (II) ions react with ammonia according to the equation;

$$\boldsymbol{Ni^{2+}(aq) + nNH_3(aq) \longrightarrow [Ni(NH_3)_n]^{2+}\ (aq)}$$

Calculate;

(i) Molar concentration of the free ammonia in the aqueous layer.

(ii) Molar concentration of ammonia that reacted with nickel (II) ions

(iii) Use your answer b(ii) above to determine the value of n in $[Ni(NH_3)_n]^{2+}$

5. (a) In an experiment to determine the partition coefficient of ammonia between water and trichloromethane, equal volumes of 0.1M copper(II) sulphate solution and 2M ammonia were mixed and the mixture shaken with trichloromethane in a closed vessel. At equilibrium, the concentration of ammonia in trichloromethane was 0.0308M.

   (i) Calculate the concentration of ammonia that reacted with copper(II) ions.

$$\boldsymbol{Cu^{2+}(aq) + 4NH_3(aq) \longrightarrow [Cu(NH_3)_4]^{2+}\ (aq)}$$

   (ii) Determine the partition coefficient K_D of ammonia between water and trichloromethane.

   (b) State any two:

   (i) assumptions made in (a)(ii) above

   (ii) practical application of the partition law other than determining the formulae of complexes.

6. Excess ammonia and trichloromethane was shaken with $0.025moldm^{-3}$ of an aqueous solution of copper(II) sulphate and allowed to reach an equilibrium. At equilibrium, the concentrations of ammonia in the aqueous layer and the trichloromethane layer were found to be 0.400 moldm^{-3} and 0.012 mol dm^{-3} respectively. If the partition coefficient of ammonia between water and trichloromethane is 25.

   (a) Calculate the concentration of complexed ammonia in the aqueous layer

   (b) Hence determine the value of n in the formula of the complex ion, $[Cu(NH_3)_n]^{2+}$.

7. (a) Describe briefly how the formula of the silver complex, $[Ag(NH_3)_n]^+$ can be determined in the laboratory.

   (b) 25.0 cm^3 of excess ammonia was mixed with 25.0 cm^3 of $0.1M$ silver nitrate solution. The resultant mixture containing the complex, $[Ag(NH_3)_n]^+$ was shaken with 50 cm^3 of trichloromethane and allowed to stand until equilibrium was established at room temperature. The aqueous layer required 27.5 cm^3 of 1.0M hydrochloric acid while the organic layer required 18.0 cm^3 of 0.05M hydrochloric acid for complete neutralization. Determine the value of n. (K_D of ammonia between water and trichloromethane is 25.0 at 25°C)

8. 25 cm^3 of 1.7M amminomethane were added to 25 cm^3 of a 0.1M zinc sulphate solution. The resultant solution was shaken with trichloromethane and left to settle. 10 cm^3 of the aqueous layer required 16.5 cm^3 of 0.5M nitric acid. If the partition coefficient of aminomethane between water and trichloromethane is 25 at 25°C.

   (a)Calculate;

   (i) the concentration of aminomethane in the organic layer

   (ii) the concentration of aminomethane that formed a complex with zinc ions

   (iii) the formula of the complex ion.

   (b) Use your answer in (a)(ii) to write an equation for the reaction between aminomethane and zinc ions

9. The table below shows the results for partition of aminoethane between trichloromethane and 0.1M copper(II) sulphate solution

$[\boldsymbol{CH_3NH_2}]_{\boldsymbol{0.1MCuSO_4}}$	0.88	1.10	1.34	1.58	1.80
$[\boldsymbol{CH_3NH_2}]_{\boldsymbol{CHCl_3}}$	0.02	0.03	0.04	0.05	0.06

   (a) Plot a graph of $[CH_3NH_2]_{0.1MCuSO_4}$ against $[CH_3NH_2]_{CHCl_3}$.

   (b) Determine the number of moles of aminomethane that form a complex with copper(II) ion.

   (c) Write equation for the reaction between copper(II) ions and aminomethane .

10. Copper(II) ions form a complex, $[Cu(NH_3)_n]^{2+}$ with ammonia. The table below shows the results for partition of ammonia between 0.1M copper(II) ions solution and trichloromethane.

$[\boldsymbol{NH_3}]_{\boldsymbol{0.1MCu^{2+}}}$	0.88	1.08	1.34	1.56	1.80
$[\boldsymbol{NH_3}]_{\boldsymbol{CHCl_3}}$	0.02	0.03	0.04	0.05	0.06

   (a) Plot a graph of $[NH_3]_{0.1MCu^{2+}}$ against $[NH_3]_{CHCl_3}$.

   (b) Determine the value of n in the complex.

   (c) Determine the partition coefficient of ammonia between aqueous copper(II) ions and trichloromethane

   (d) State what the value of partition coefficient obtained in (c) above indicates about the distribution of ammonia.

11. Cobalt(II) ions form a complex, $[Co(NH_3)_n]^{2+}$ with ammonia. The table below shows the results for partition of ammonia between 0.1M cobalt(II) sulphate solution and trichloromethane.

$[NH_3]_{0.1M\ CoSO_4}$	0.72	0.94	1.19	1.43	1.70	1.92
$[NH_3]_{CHCl_3}$	0.01	0.03	0.05	0.07	0.09	0.11

(a) Plot a graph of $[NH_3]_{0.1M\ CoSO_4}$ against $[NH_3]_{CHCl_3}$.

(b) Determine the value of n in $[Co(NH_3)_n]^{2+}$.

12. The table below shows the results for partition of ammonia between 0.1M Nickel(II) sulphate solution and trichloromethane.

$[NH_3]_{0.1M\ NiSO_4}$	0.87	1.10	1.33	1.57	1.80
$[NH_3]_{CHCl_3}$	0.02	0.03	0.04	0.05	0.06

(a) Plot a graph of $[NH_3]_{0.1M\ NiSO_4}$ against $[NH_3]_{CHCl_3}$.

(b) Determine the number of moles of ammonia that formed a complex with nickel(II) ions.

(c) Write equation for the reaction between nickel(II) ions and aminomethane.

Ion exchange

Ion exchange is a type of partition of ionic compounds

An ion exchanger can be a solid which releases one ion and adsorbs another.

When the ions exchanged are cations, the material is known as a ***cation exchanger*** and when anions are exchanged, then it's an ***anion exchanger***.

A cation exchanger is usually a polymer containing an acidic group such as $-SO_3H$, $-COOH$, or $-OH$.

Anion exchangers contain basic groups such as secondary, tertiary or quaternary amine groups.

Ion exchangers are used in softening of water by removing calcium ions and magnesium ions by using an insoluble sodium salt of a cation exchanger

$$2NaR(s) + Ca^{2+}(aq) \rightleftharpoons 2Na^+(aq) + CaR_2(s)$$

$$where\ R\ is\ a\ resin$$

Water can also be purified further so that all dissolved salts are removed(deionisation/demineralisation) by using both a cation and an anion exchanger.

When the water is passed through a cation exchanger, all the cations in it are replaced by hydrogen ions.

$$HR(s) + X^{2+}(aq) \rightleftharpoons H^+(aq) + XR(s)$$

The partially purified water is then passed through an anion exchanger and all the anions are replaced by hydroxyl ions.

$$ROH(s) + Y^{-}(aq) \rightleftharpoons \bar{O}H(aq) + RY(s)$$

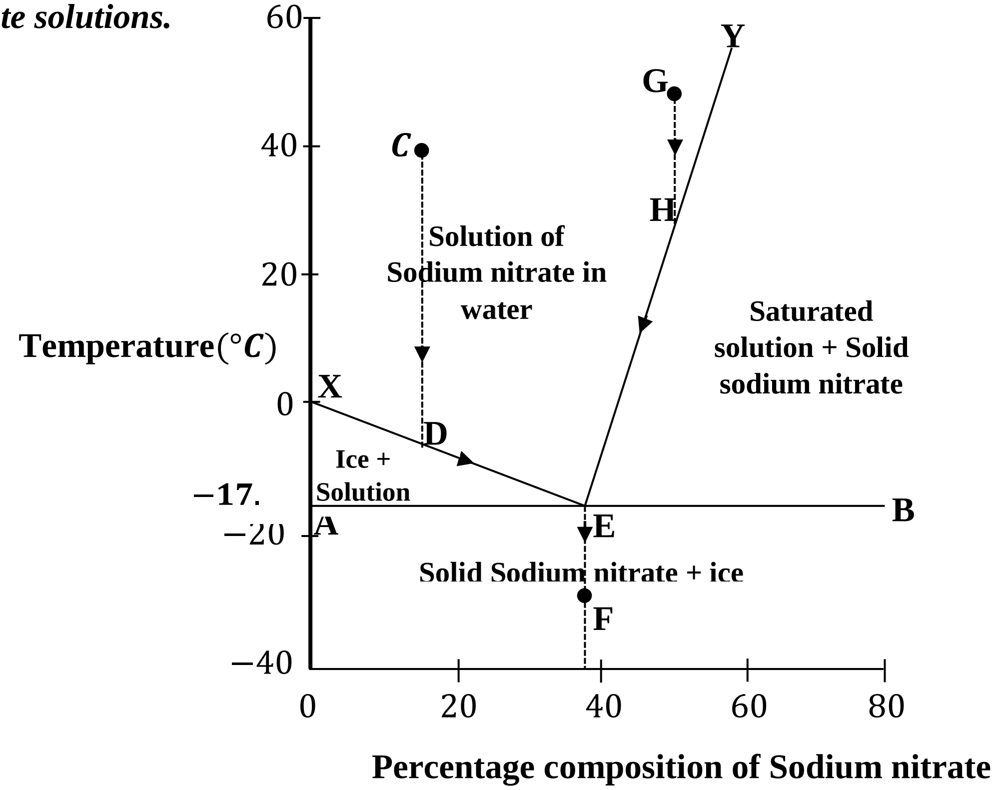
The hydrogen ions and hydroxyl ions then combine to form water.

Determining equilibrium constants using partition coefficients
(refer to next Chapter; Chemical equilibria)

EUTECTICS

1. Solidification of an aqueous solution of solids

The diagram below is a temperature-composition diagram (phase diagram) for sodium nitrate solutions.



When a dilute solution of sodium nitrate in water is cooled from room temperature, there is no phase change but the temperature reduces up to $0°C$.

On cooling the solution below $0°C$, pure ice forms when the freezing point of the solution is reached.

The freezing point of the solution is less than the freezing point of pure water ($0°C$) because the solute added lowers the freezing point of water.

When the solution is cooled further, more ice is formed and the solution becomes richer in sodium nitrate.

At $-17.5°C$, the remaining solution becomes saturated and any further cooling will deposit a mixture of ice and solid sodium nitrate and the temperature remains constant until the whole system solidifies.

Curves/lines	
YE	**The solubility curve of sodium nitrate in water**
XE	**The decrease in freezing point of water as increasing quantities of sodium nitrate are added**
AB	**The solid curve.** Below it **only the solid phase** exists.
XEY	**The liquid curve.** Above it **only liquid phase** exists.

Point E is the Eutectic point

At this only point; **ice**, **solid sodium nitrate** and a **saturated solution of sodium nitrate in water** are in equilibrium.

At the eutectic point, the **solid formed from the solution has the same composition as the solution**.

From the phase diagram above, this composition is 38.62% by mass of sodium nitrate and the point occurs at an **eutectic temperature** of $-17.5°C$.

The mixture formed at this composition and temperature is called an **eutectic mixture**.

Important definitions

A* eutectic mixture *is a liquid mixture which at constant pressure will solidify at constant temperature to form a solid mixture without change in composition.

Or a* eutectic mixture *is a solid mixture which melts at constant temperature to form a liquid mixture without change in composition.

***A* eutectic temperature *is the constant temperature at which a liquid mixture solidifies at a given pressure without change in composition*.**

Effect of change in temperature on the mixture

Question; Using the phase diagram for sodium nitrate- water system above, describe what happens when;

- **(i) a solution containing 15% potassium nitrate is cooled from $40°C$ to $-30°C$.**
- **(ii) a solution containing 50% water is cooled from $50°C$ to $-30°C$.**

(i) ***From $40°C$, at point C, the solution cools to point D without change in phase***

At point D, ***ice begins to solidify*** as the ***composition of sodium nitrate in the solution increases***.

As the solution is ***further cooled***, ***more ice solidifies***, the solution ***becoming richer in sodium nitrate*** and the ***freezing point decreases along DE*** up to the ***eutectic point, $E(-17.5°C)$***.

At the eutectic point, E ($-17.5°C$), sodium nitrate also begins to solidify and the ***temperature and composition remain constant*** until the ***whole system solidifies***. ***The solid mixture then cools with no change in phase up to $-30°C$***.

(ii) ***From $50°C$, at point G, the solution cools to point H without change in phase***

At point H, ***sodium nitrate begins to solidify*** as the ***composition of water in the solution increases***.

As the solution is ***further cooled***, ***more sodium nitrate solidifies***, the solution ***becoming richer in water*** and the ***freezing point decreases along HE*** up to the ***eutectic point, $E(-17.5°C)$***.

At the eutectic point, E ($-17.5°C$), ice also begins to solidify and the ***temperature and composition remain constant*** until the ***whole system solidifies***. ***The solid mixture then cools with no change in phase up to $-30°C$***.

2. Solidification of mixtures of two liquids without compound formation

Eutectic mixtures can also be formed between two metals or two organic solids.

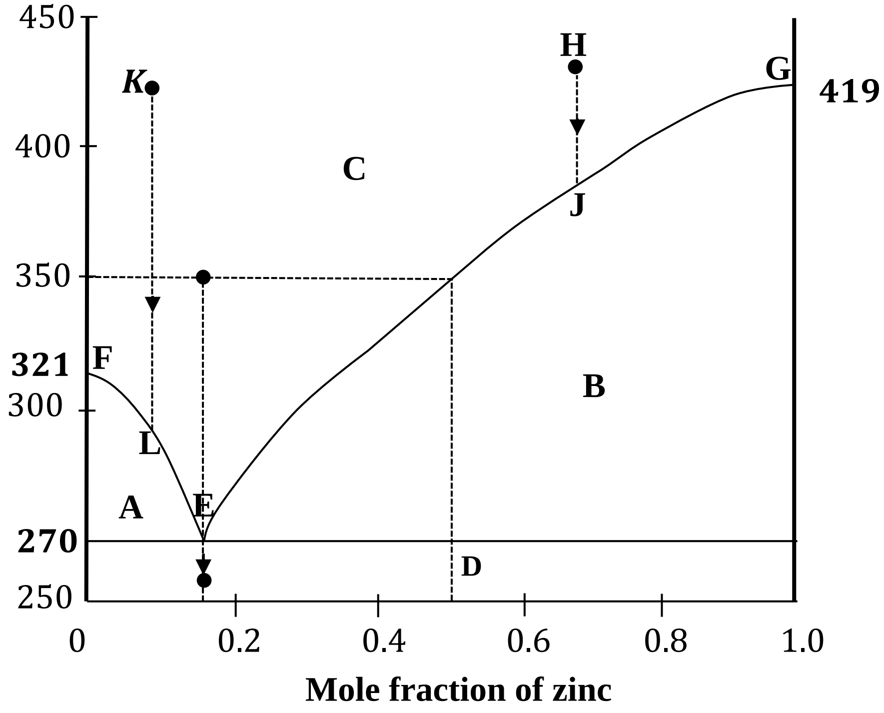
The two must be completely miscible when melted into liquids. A mixture of the two liquids forms a eutectic mixture on freezing in the same way as an aqueous solution of a solid.

Examples of substances that form eutectic mixtures

These include;

- ***Zinc and cadmium***
- ***Tin and lead***
- ***Antimony and lead***
- ***Bismuth and cadmium***
- ***Gold and thallium***
- ***Bromoethane and benzene***
- ***Camphor and naphthalene***
- ***Naphthalene and biphenyl***

The diagram below is a temperature-composition diagram (phase diagram) for a Zinc-cadmium mixture.



Percentage composition may be used instead of mole fraction.

Note that the word solution should not be used for these kinds of mixtures. Only the liquid and solid phases are emphasized.

(a) Describe how the phase diagram of a mixture of zinc and cadmium can be obtained in the laboratory.

Mixtures of various compositions of solid zinc and solid cadmium are prepared

Each mixture is heated separately until it melts

Each mixture is ***allowed to cool*** while ***stirring*** and the ***constant temperature*** at ***which it freezes is recorded***.

The ***melting points of pure zinc and pure cadmium*** are determined in the same way

Then a ***graph of melting points against composition is plotted*** and a ***phase diagram is drawn***.

(b) State what the following represent;

(i) Regions: A, B, C and D

A-***Solid cadmium and liquid***
B-***Solid Zinc and liquid***

C-***Liquid mixture***
D-***Solid cadmium and solid zinc***

(ii) Points E, F and G

E-***Eutectic point***
F-***Melting point of pure cadmium***

G-***Melting point of pure zinc***

Note: *From the phase diagram, the eutectic mixture has a mole fraction of* 0.17 *zinc. This is the same as* 17% *zinc. In terms of cadmium, it is* 0.83 *mole fraction of cadmium (*83% *cadmium). The eutectic temperature is* $270°C$*.*
The melting point of pure cadmium is $321°C$ *and that of pure zinc is* $419°C$*.*

(iii) Curves FE and GE

FE- *Decrease in freezing point of Cadmium as zinc is added*
GE- *Decrease in freezing point of zinc as cadmium is added*

(c) Using the phase diagram for the zinc-cadmium system above, describe what would happen when;

(i) a mixture containing 70% zinc is cooled from $435°C$ to $260°C$.
(ii) a mixture containing 90% cadmium is cooled from $425°C$ to $260°C$.
(iii) a mixture containing 83% cadmium is cooled from $350°C$ to $260°C$
(iv) a mixture containing 17% zinc is heated.

(i) ***From*** $435°C$***, at point H, the liquid mixture cools to point J without change in phase***

At point J, ***zinc begins to solidify*** as the ***composition of cadmium in the liquid mixture increases***.

As the liquid mixture is ***further cooled***, ***more zinc solidifies***, the liquid ***becoming richer in cadmium*** and the ***freezing point decreases along JE*** up to the ***eutectic point, E(*** $270°C$***)***.

At the eutectic point, E ($270°C$***), cadmium also begins to solidify*** and the ***temperature and composition remain constant*** until the ***whole system solidifies***.

The solid mixture then cools with no change in phase up to $260°C$.

(ii) ***From*** $425°C$***, at point K, the liquid mixture cools to point L without change in phase***

At point L, ***cadmium begins to solidify*** as the ***composition of zinc in the liquid mixture increases***.

As the liquid mixture is ***further cooled***, ***more cadmium solidifies***, the liquid ***becoming richer in zinc*** and the ***freezing point decreases along LE*** up to the ***eutectic point, E(*** $270°C$***)***.

At the eutectic point, E ($270°C$***), zinc also begins to solidify*** and the ***temperature and composition remain constant*** until the ***whole system solidifies***.

The solid mixture then cools with no change in phase up to $260°C$.

(iii) ***From $350°C$, the liquid mixture cools to $270°C$ without change in phase***

At the eutectic point, E ($270°C$), both ***zinc and cadmium begin to solidify*** and the ***temperature and composition remain constant*** until the ***whole system solidifies***.

The solid mixture then cools with no change in phase up to $260°C$.

(iv) ***The solid mixture melts at a constant temperature of $270°C$ to form a liquid mixture of the same composition***.

(d) Explain what will happen when;

  (i) increasing quantities of zinc are added to molten cadmium

  (ii) increasing quantities of cadmium are added to molten zinc

(i) ***The freezing point of cadmium decreases, more and more cadmium solidifies up to the eutectic point (at $270°C$ and when the mixture contains 17% zinc). At the eutectic point, the freezing point is constant, zinc also solidifies. Further addition of zinc increases freezing point towards that of pure zinc. More and more zinc solidifies out of the mixture.***

(ii) ***The freezing point of zinc decreases, more and more zinc solidifies up to the eutectic point (at $270°C$ and when the mixture contains 83% cadmium). At the eutectic point, the freezing point is constant, solid cadmium also solidifies. Further addition of cadmium increases freezing point towards that of pure cadmium. More and more cadmium solidifies out of the mixture.***

(e) Calculate the mass of cadmium that remained in the liquid mixture when $150g$ of the liquid mixture containing 16% zinc was cooled from $400°C$ to $350°C$.

$$Mass\ of\ zinc\ in\ the\ liquid\ mixture\ before\ freezing\ = \frac{16}{100} \times 150 = 24g$$

$$From\ the\ graph;\ composition\ of\ the\ liquid\ mixture\ at\ 350°C = 50\%$$

$$At\ 350°C, mass\ of\ zinc = 24g$$

$$Let\ the\ mass\ of\ cadmium\ be\ x\ g$$

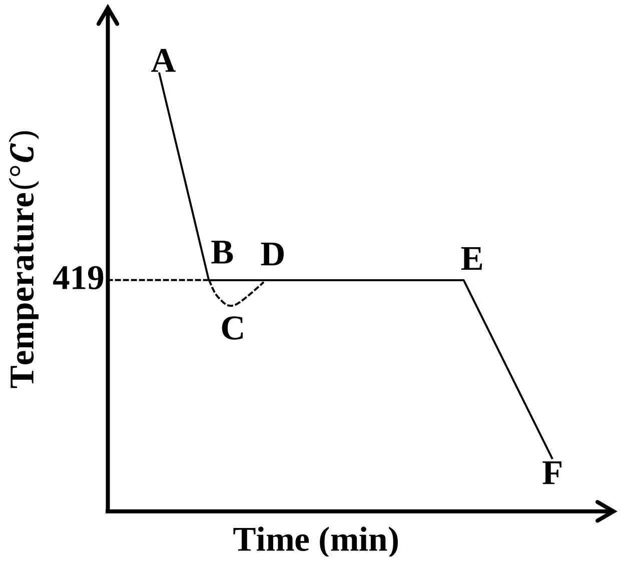
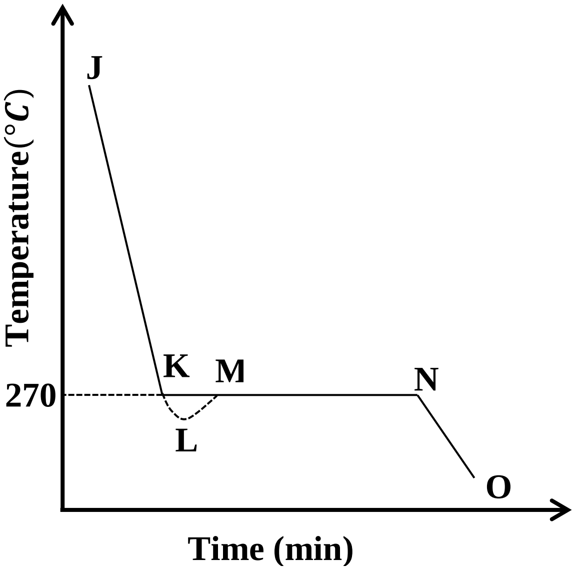
$$Then\ \frac{24}{x + 24} \times 100 = 50$$

$$x = 24\ g$$

Cooling curve for a pure substance or a eutectic mixtures

The cooling curve of a pure substance is similar to that of a eutectic mixture. Both a pure substance and a eutectic mixture have a sharp freezing and melting point.

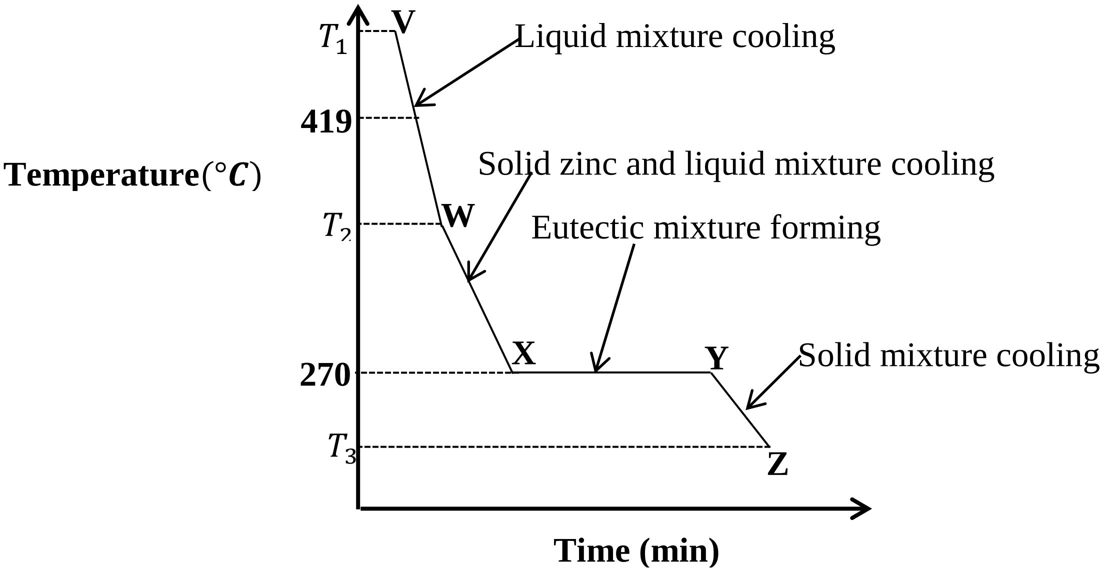
Considering pure hot molten zinc that is allowed to cool until it solidifies and also a eutectic mixture of zinc and cadmium from the information already shown above. The cooling curves for the changes are shown below.

Cooling curve for pure zinc	***Cooling curve for an eutectic mixture of zinc and cadmium***$(17\%\ Zn\ and\ 83\%\ Cd)$
	
AB- ***Decrease in temperature of Liquid zinc*** **BE-*Freezing of Liquid zinc*** **EF-*Decrease in temperature of Solid zinc*** **Curve BCD-** ***Supercooling of liquid zinc*** ***Along AB, the temperature of liquid zinc decreases. At B, liquid zinc begins to freeze and the temperature remains constant until all the zinc freezes along BE. At E, all the zinc has frozen. Along EF, the temperature of solid zinc decreases.***	**JK-** ***Decrease in temperature of Liquid eutectic mixture of zinc and cadmium*** **KN-*Freezing of Liquid zinc and liquid cadmium*** **NO-*Decrease in temperature of Solid eutectic mixture of zinc and cadmium*** **Curve KLM-** ***Supercooling of liquid eutectic mixture of zinc and cadmium*** ***Along JK, the temperature of the liquid eutectic mixture decreases. At K, the liquid euctectic mixture begins to freeze and the eutectic temperature remains constant until all the liquid mixture freezes along KN. At N, all the liquid eutectic mixture has frozen. Along NO, the temperature of solid eutectic mixture of zinc and cadmium decreases.***

The cooling curve of pure zinc is similar to and can be used for any other pure substance and that of the eutectic mixture can be used for any other eutectic mixture

Cooling curve for a mixture

For a mixture other than a eutectic mixture, the cooling curve similar to the one below is obtained. ***The one sketched below is a cooling curve for a liquid mixture of zinc and cadmium.***



The liquid mixture of zinc and cadmium cools from point V(temperature , $T_1°C$) to point W(temperature, $T_2°C$) below the freezing point of pure zinc.

At W, solid zinc begins to freeze and the liquid mixture becomes richer in cadmium.

The zinc begins to freeze at a temperature, $T_2°C$ below the freezing point of pure zinc because adding cadmium to it lowers its freezing point.

The temperature of the solid zinc and liquid mixture then decreases from W to X(at the eutectic temperature, 270°C).

At X, cadmium also begins to freeze and the temperature remains constant until all the mixture freezes along XY. A eutectic mixture is formed.

At Y, the whole mixture has frozen.

Further cooling of the solid mixture decreases the temperature to $T_3°C$

Differences between a eutectic mixture and a compound

Eutectic mixture	Compound
Its composition changes with change in pressure	Its composition is fixed and does not change with pressure
Its melting point changes with pressure	It has a fixed melting point
Can be separated into its components by physical means	Cannot be separated into its components by physical means
Microscopic examination shows that it is a heterogenous in composition	It is homogenous

Tests that can show that a eutectic mixture is not a pure compound

- Microscopic examination shows that it is a heterogeneous mixture of individual crystals of the components that make it up
- X-ray diffraction pattern of an eutectic mixture does not conform to that of a pure compound
- Determining its composition shows that it does not correspond to a chemical formula of any known compound.
- Changing pressure changes the composition of an eutectic mixture

Similarities between a pure substance and a eutectic mixture

- Both have sharp melting points
- Have similar cooling curves

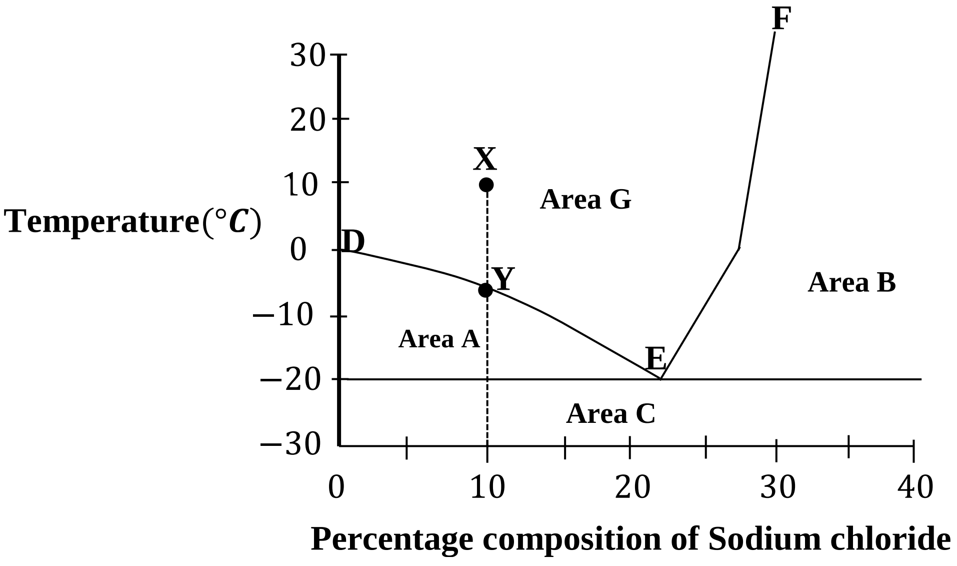
Application of eutectic mixtures

Formation of solder, an alloy of lead and tin which is used for joining other metals at temperatures which are not so high to melt the pure metal

Questions

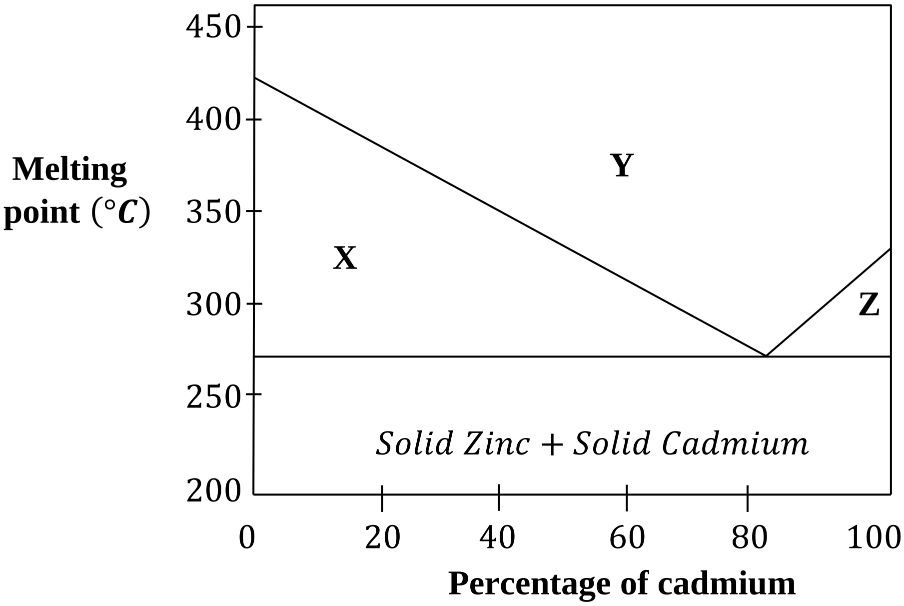
1. Sodium chloride and water form a eutectic mixture which melts at $-22°C$ and contains 23.6% by mass of sodium chloride. Draw a well labelled temperature-composition diagram for sodium chloride-water mixture.
2. (a) Explain what is meant by;
    - (i) Saturated solution
    - (ii) Mole fraction
    - (iii) Eutectic mixture
    - (iv) Azeotropic mixture

   (b) The diagram below shows a temperature-composition diagram for a dilute sodium chloride system



(i) State what lines **DE** and **EF** represent
(ii) Name the substances present at each of the areas **A, B, C** and **G**.
(iii) Describe what happens when a solution at X is cooled slowly to a temperature below the eutectic temperature.
(iv) State two reasons why eutectic mixtures are not compounds

3. (a) The graph below shows the variation in melting point of a mixture of zinc and cadmium with composition.



Use the graph to:
(i) Determine the eutectic point of the system
(ii) Name the phases in the regions X, Y and Z.
(b) Estimate the melting points of zinc and cadmium
(c) Describe the changes that take place when a mixture containing 88% zinc is cooled from 450°C to 280°C.
(d) Calculate the mass of zinc that remained in the liquid when 120g of the liquid mixture containing 12% cadmium was cooled from 450°C to 280°C.
(e) State one difference and one similarity between a eutectic mixture and a pure compound.

4. (a) Define the terms;
(i) Eutectic point
(ii) Eutectic mixture
(b) Two metals A and B form a eutectic mixture with an eutectic point 80°C and 72%B. Draw a well labelled phase diagram for the two metals. (Melting points of A and B are 242°C and 185°C
(c) State two similarities between a eutectic mixture and a metal.

5. (a) Define the term **“Phase”**

(b) The melting points of various composition of Naphthalene-biphenyl system are given below:

Mole fraction of naphthalene	0.800	0.625	0.275	0.125
Melting points$(°C)$	72.6	58.0	56.0	64.5

Naphthalene-biphenyl system forms an eutectic mixture of composition of 0.47 mole fraction of naphthalene at temperature of $41.0°C$

(i) Plot a phase diagram for naphthalene-biphenyl system and label all regions.

$(Melting\ point\ pure\ Naphthalene\ =\ 80°C\ and\ melting\ point\ of\ biphenyl\ =\ 71°C)$

(ii) Describe what happens when a mixture containing 0.70 mole fraction of biphenyl is cooled.

(c) Draw a well labeled cooling curve for a mixture naphthalene and biphenyl and explain the shape of your curve.

(d) State one application of eutectic mixture

6. (a) Define the terms:

(i) Eutectic mixture

(ii) Eutectic point

(b) Briefly describe how a phase diagram of a mixture of cadmium and bismuth can be determined in the laboratory.

(c) The table below shows the melting points of various mixtures of cadmium and bismuth.

Percentage of bismuth	5	20	35	50	65	80	100
Melting point$(°C)$	300	242	184	156	190	226	271

(i) Draw a labeled phase diagram for the bismuth-cadmium system. (The melting point of pure cadmium are is $321°C$ respectively)

(ii) State the composition and melting point of the eutectic mixture.

(iii) Using the diagram, describe what happens when a liquid mixture containing 90% bismuth at $350°C$ is gradually cooled.

(iv) Explain what is observed when increasing quantities cadmium are added to bismuth.

(v) Draw a well labeled cooling curve for the eutectic mixture formed and explain the shape of your curve.

(c) State two similarities and two differences between an eutectic mixture and a compound.

7. (a) The melting points of mixtures of zinc and cadmium of different compositions are shown below.

Percentage of zinc	0	10	17	30	60	100
Melting point(°C)	321	295	270	305	360	491

(i) Draw a fully labelled phase diagram for the zinc-cadmium system.
(ii) Determine the temperature and composition of the eutectic mixture.
(iii) Using the diagram in a(i) , describe the changes that will take place when a liquid mixture containing 5% zinc at 300°C was gradually cooled.

(b) State any three tests that can be carried out on the eutectic mixture to show that it is not a pure compound.

8. (a) Define the following terms:
(i) Eutectic temperature
(ii) Eutectic mixture

(b) The table below shows the melting points and compositions of various mixtures of cadmium and bismuth.

Percentage of cadmium	20	35	50	65	80	95
Melting point(°C)	226	190	156	184	242	300

Draw a labelled phase diagram for the cadmium-bismuth system.
Use your graph to;
(i) determine the melting points of pure cadmium and pure bismuth
(ii) determine the composition and melting point of the eutectic mixture
(iii) describe what happens when a liquid mixture containing 90% bismuth at 350°C is gradually cooled.
(iv) determine the mass of bismuth that crystallized when 200g of the mixture containing 25% cadmium was cooled from 300°C to 168°C.

COLLIGATIVE PROPERTIES

All solutions containing non-volatile solutes have certain properties in common. All these properties vary with the compositions of the solutions in a similar way.
Each of these properties can be measures over a range of concentrations of the solutions and the results obtained depend on the ***total number of solute particles present in a fixed amount of solvent*** and hold for ***dilute solutions***.
The properties are called ***colligative properties***.

Colligative properties are therefore defined as physical properties of a dilute solution which depend on the number of non-volatile dissolved particles in the solution but do not depend on the chemical nature of the solute particles.

$$Colligative\ property\ measured\ \propto number\ of\ particles\ of\ solute\ in\ solution$$

The greater the number of particles in solution, the greater the extent to which the colligative property is affected.

The colligative properties include:

1. ***Lowering of the vapour pressure of a solvent***
2. ***Elevation of boiling point***
3. ***Freezing point depression***
4. ***Osmotic pressure of solution***

Colligative properties are important and useful for the determination of molecular masses for non-volatile solutes

Limitations of colligative properties

A correct value of relative molecular mass obtained by use of any colligative property is only obtained if;

(i) Solute does not associate or dissociate in solution.

When solute particles associate in solution, the number of particles in solution decreases, lowering the colligative property and increasing the relative molecular mass.

Molecular mass obtained by a colligative property for a solute that associates in solution is always twice the actual value

$$2HCOOH \rightleftharpoons (HCOOH)_2$$
$$2CH_3CH_2COOH \rightleftharpoons (CH_3CH_2COOH)_2$$

When solute particles dissociate in solution, the number of particles in solution increases, and the colligative property also increases, reducing the relative molecular mass.

Molecular mass obtained by a colligative property for a solute that dissociates in solution is lower than the actual value.

$$NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq)$$
$$CaCl_2(s) \longrightarrow Ca^{2+}(aq) + 2Cl^-(aq)$$

(ii) The solution is dilute

(iii) There is no chemical reaction between the solute and the solvent.

(iv) The solute is non-volatile

Vapour pressure lowering

Vapour pressure of a liquid is the pressure exerted by the vapour when it is in equilibrium with the liquid at a given temperature.

The vapour pressure of a solvent in solution is less than the vapour pressure of the pure solvent at the same temperature.

This is because the non-volatile solute particles occupy some of the surface of the solution. This reduces the escaping tendency of the solvent particles into the vapour

phase. The solution there has a lower vapour pressure than that that would be exerted by a pure solvent.

Question; Explain why an aqueous solution of glucose has a lower vapour pressure than water at a given temperature

Glucose is ***non-volatile solute .*** When dissolved in water, ***glucose particles occupy some of the surface of the solution.*** This ***reduces the escaping tendency of the solvent particles into the vapour phase. The solution there has a lower vapour pressure than that that would be exerted by a pure water.***

For a solvent in solution, the vapour pressure lowering ($\Delta \boldsymbol{p}$) is given by;

$$\Delta \boldsymbol{p} = \boldsymbol{p^0_{solvent}} - \boldsymbol{p_{solution}},\ where;$$

$$\boldsymbol{p^0_{solvent}}\ \ is\ the\ vapour\ pressure\ of\ pure\ solvent\ and$$

$$\boldsymbol{p_{solution}}\ is\ the\ vapour\ pressure\ of\ the\ solvent\ in\ solution$$

Derivation of expression for relative vapour pressure lowering

For a solution made up of a volatile solvent and a non-volatile solute, the total vapour pressure of the solution is equal to the partial vapour pressure of the solvent ($\boldsymbol{p_{solvent}}$) because the solute does not contribute to the vapour pressure.

$$But\ \ p_{solvent} = p^0_{solvent} \times x_{solvent}$$, where

$$x_{solvent}\ is\ mole\ fraction\ of\ solvent$$

$$p_{solution} = p_{solvent}$$

$$p_{solution} = p^0_{solvent} \times x_{solvent}$$

$$From\ \ \Delta p = p^0_{solvent} - p_{solution}$$

$$\Delta p = p^0_{solvent} - p^0_{solvent} \times x_{solvent}$$

$$\Delta p = p^0_{solvent}(1 - x_{solvent})$$

$$From\ \ x_{solvent} + x_{solute} = 1$$

$$x_{solute} = 1 - x_{solvent}$$

$$Then\ \Delta p = p^0_{solvent} \times x_{solute}$$

$$\frac{\Delta \boldsymbol{P}}{\boldsymbol{p^0_{solvent}}} = \boldsymbol{x_{solute}}$$

$$\frac{\boldsymbol{p^0_{solvent}} - \boldsymbol{p_{solution}}}{\boldsymbol{p^0_{solvent}}} = \frac{\boldsymbol{n_{solute}}}{\boldsymbol{n_{solute}} + \boldsymbol{n_{solvent}}}$$

Where $\boldsymbol{n}$ represents number of moles.

From the above expression, $\frac{\boldsymbol{p^0_{solvent}} - \boldsymbol{p_{solution}}}{\boldsymbol{p^0_{solvent}}}$ is called **relative lowering of vapour pressure** and the whole expression represents the **Raoult's law of vapour pressure lowering.**

Raoult's law of vapour pressure lowering therefore states that the relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution at a given temperature.

For dilute solutions, $\boldsymbol{n_{solute}}$ is small compared to $\boldsymbol{n_{solvent}}$ this implies that;

$$n_{solute} + n_{solvent}\ \approx\ n_{solvent}$$

$$Therefore \quad \frac{p^0_{solvent} - p_{solution}}{p^0_{solvent}} = \frac{n_{solute}}{n_{solvent}}$$

$$\frac{p^0_{solvent} - p_{solution}}{p^0_{solvent}} = \frac{n_{solute}}{n_{solvent}}$$

$$\frac{\boldsymbol{p^0_{solvent} - p_{solution}}}{\boldsymbol{p^0_{solvent}}} = \frac{\boldsymbol{m_{solute}}}{\boldsymbol{M_{r_{solute}}}} \bigg/ \frac{\boldsymbol{m_{solvent}}}{\boldsymbol{M_{r_{solvent}}}}$$

Where; $\boldsymbol{m_{solute}}$ *and* $\boldsymbol{m_{solvent}}$ *are masses of the solute and solvent respectively*
$\boldsymbol{M_{r_{solute}}}$ *and* $\boldsymbol{M_{r_{solvent}}}$ *are the molar masses of water and the liquid respectively.*

Note: The lowering of vapour pressure of a solvent by a non-volatile solute at a given temperature is directly proportional to the concentration of the solute and inversely proportional to the relative molecular mass of the solute.

$$\boldsymbol{\Delta P \propto concentration\ of\ solute}$$

$$\boldsymbol{\Delta P \propto \frac{1}{M_{r_{solute}}}}$$

Assumptions/ limitations of vapour pressure lowering

(i) Solute does not associate or dissociate in solution.
(ii) The solution is dilute
(iii) There is no chemical reaction between the solute and the solvent.
(iv) The solute is non-volatile

Calculations involving lowering of vapour pressure

Examples

1. **The vapour pressure of pure ethoxyethane at a certain temperature is** $\boldsymbol{32.67kPa}$**. Calculate the vapour pressure of a 3% solution of camphor,**$\boldsymbol{C_{10}H_{16}O}$ **in ethoxyethane at the same temperature**.

$\boldsymbol{3\%\ means\ 3g\ of\ solute\ in\ 100g\ of\ solution}$

$$m_{solute} = 3g$$

$$m_{solution} = 100g$$

$$m_{solvent} = (100 - 3) = 97g$$

$$Molar\ mass\ of CH_3CH_2OCH_2CH_3$$

$$= 48 + 10 + 16 = 74g$$

$$Molar\ mass\ of Camphor, C_{10}H_{16}O$$

$$= 120 + 16 + 16 = 152g$$

$$p_{solution} = ? \quad p^0_{solvent} = 32.67kPa$$

$$\frac{p^0_{solvent} - p_{solution}}{p^0_{solvent}} = \frac{n_{solute}}{n_{solvent}}$$

$$\frac{p^0_{solvent} - p_{solution}}{p^0_{solvent}} = \frac{m_{solute}}{M_{r_{solute}}} \bigg/ \frac{m_{solvent}}{M_{r_{solvent}}}$$

$$\frac{32.67 - p_{solution}}{32.67} = \frac{3}{152} \bigg/ \frac{97}{74}$$

$$\frac{32.67 - p_{solution}}{32.67} = \frac{3 \times 74}{152 \times 97}$$

$$p_{solution} = 32.67 - 0.4919$$

$$p_{solution} = \boldsymbol{32.178\ kPa}$$

2. **(a) Define the term relative lowering of vapour pressure of a solvent.**

   (b) (i) At $50°C$, an aqueous solution of carbamide (CH_3CONH_2) of concentration $60.93gdm^{-3}$ has a vapor pressure of $12100Nm^{-2}$. Determine the vapour pressure of water at this temperature.

   (ii) State the assumptions you have made in b(i).

(a) Relative lowering of vapour pressure is the difference of vapour pressure of a pure solvent and the vapour pressure of the solvent above its solution with a non-volatile solvent divided by the vapour pressure of the pure solvent.

(b) (i) $p_{solution} = 12100Nm^{-2}$

$$m_{solution} = 1000g$$

$$m_{solute} = 60.93g$$

$$m_{solvent} = (1000 - 60.93) = 939.07g$$

$$Molar\ mass\ of CH_3CONH_2$$

$$= 24 + 5 + 16 + 14$$

$$= 59g$$

$$Molar\ mass\ of\ H_2O = 2 + 16 = 18g$$

$$p_{water} = ?$$

$$\frac{p^0_{water} - p_{solution}}{p^0_{water}} = \frac{n_{solute}}{n_{solvent}}$$

$$\frac{p^0_{water} - p_{solution}}{p^0_{water}} = \frac{m_{solute}}{M_{r_{solute}}} \Big/ \frac{m_{solvent}}{M_{r_{solvent}}}$$

$$\frac{p^0_{water} - 12100}{p^0_{water}} = \frac{60.93}{59} \Big/ \frac{939.07}{18}$$

$$\frac{p^0_{water} - 12100}{p^0_{water}} = \frac{60.93 \times 18}{59 \times 939.07}$$

$$p^0_{water} = \frac{59 \times 939.07 \times 12100}{54308.39}$$

$$\boldsymbol{p^0_{water} = 12344.356\ Nm^{-2}}$$

(ii) Carbamide does not associate or dissociate in solution.

The solution is dilute

There is no chemical reaction between the carbamide and water.

Carbamide is non-volatile

Density of solution is $1gcm^{-3}$

3. **The vapour pressure of pure benzene at a certain temperature is 640mmHg. A non-volatile, nonelectrolyte solid weighing 2.175g is added to 39g of benzene, the vapor pressure of a solution of the solid in benzene is 600mmHg. Calculate the molar mass of solid substance.**

$$p^0_{solvent} = 640mmHg$$

$$p_{solution} = 600mmHg$$

$$m_{solute} = 2.175g \qquad m_{solvent} = 39g$$

$$Molar\ mass\ of C_6H_6 = (6 \times 12) +$$

$$= 78g$$

$$Molar\ mass\ of\ solute\ = ?$$

$$\frac{p^0_{solvent} - p_{solution}}{p^0_{solvent}} = \frac{n_{solute}}{n_{solvent}}$$

$$\frac{p^0_{solvent} - p_{solution}}{p^0_{solvent}} = \frac{m_{solute}}{M_{r_{solute}}} \Big/ \frac{m_{solvent}}{M_{r_{solvent}}}$$

$$\frac{640 - 600}{640} = \frac{2.175}{M_{r_{solute}}} \Big/ \frac{39}{78}$$

$$\frac{40}{640} = \frac{2.175 \times 78}{M_{r_{solute}} \times 39}$$

$$M_{r_{solute}} = \frac{2.175 \times 78 \times 640}{39 \times 40}$$

$$M_{r_{solute}} = \boldsymbol{69.6g}$$

3. **The vapour pressure of carbon disulphide at a certain temperature is $400\ mmHg$. At the same temperature, a solution of 5g of sulphur in $63\ cm^3$ of carbon disulphide has a vapour pressure of $392.58\ mmHg$. If the density of carbon disulphide at this temperature is $1.27gcm^{-3}$.**
   (a) Calculate the relative molecular mass of sulphur
   (b) Deduce the molecular formula of sulphur in carbon disulphide.
   $(C = 12, S = 32)$

(a) $p^0_{solvent} = 400\ mmHg$

$p_{solution} = 392.58\ mmHg$

$m_{solute} = 5g$

$m_{solvent} = (63 \times 1.27) = 80.01\ g$

$Molar\ mass\ of CS_2 = 12 + 64 = 76g$

$Molar\ mass\ of\ sulphur\ \ =?$

$$\frac{p^0_{solvent} - p_{solution}}{p^0_{solvent}} = \frac{n_{solute}}{n_{solvent}}$$

$$\frac{p^0_{solvent} - p_{solution}}{p^0_{solvent}} = \frac{m_{solute}}{M_{r_{solute}}} \Big/ \frac{m_{solvent}}{M_{r_{solvent}}}$$

$$\frac{400 - 392.58}{400} = \frac{5}{M_{r_{solute}}} \Big/ \frac{80.01}{76}$$

$$\frac{7.42}{400} = \frac{5 \times 44}{M_{r_{solute}} \times 80.01}$$

$$M_{r\,solute} = \frac{400 \times 5 \times 76}{7.42 \times 80.01}$$

$$M_{r_{solute}} = \mathbf{256g}$$

The relative molecular mass of sulphur is 256

(b) $S_n = 256$

$32n = 256 \quad n = 8$

Molecular formula of sulphur in carbon disulphide is S_8

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4. **The vapour pressure of water is $23.7mmHg$ at a certain temperature. Calculate the lowering in vapour pressure that occurs when 12g of urea, NH_2CONH_2 are dissolved in one litre of water at the same temperature.**

$p^0_{solvent} = 23.7\ mmHg$

$\Delta p =??$

$m_{solute} = 12g$

$m_{solvent} = (1000 \times 1) = 1000\ g$

$Molar\ mass\ of NH_2CONH_2$

$= 28 + 12 + 16 + 4$

$= 60g$

$Molar\ mass\ of\ H_2O\ \ = 2 + 16 = 18g$

$$\frac{\Delta p}{p^0_{solvent}} = \frac{n_{solute}}{n_{solvent}}$$

$$\frac{\Delta p}{p^0_{solvent}} = \frac{m_{solute}}{M_{r_{solute}}} \Big/ \frac{m_{solvent}}{M_{r_{solvent}}}$$

$$\frac{\Delta p}{23.7} = \frac{12}{60} \Big/ \frac{1000}{18}$$

$$\frac{\Delta p}{23.7} = \frac{12 \times 18}{60 \times 1000}$$

$$\Delta p = \frac{12 \times 18 \times 23.7}{60 \times 1000}$$

$$\Delta p = \mathbf{0.08532\ mmHg}$$

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5. **A solution contains 4.45g of solute X in 1kg of carbon disulphide. Another solution contains 6.42g of sulphur in the same mass of carbon disulphide. If the two solutions have the same vapour pressure at the same temperature, calculate:**
   (a) the relative lowering of vapour pressure
   (b) Structural formula of the dissolved sulphur
   (Relative molecular mass of X=178)

(a) For a solution of X in CS_2;

$p^0_{solvent} = ??\quad p_{solution} = ??$

$m_{solute} = 4.45g\qquad m_{solvent} = 1000\ g$

$Molar\ mass\ of X = 178g$

$Molar\ mass\ of CS_2 = 12 + 64 = 76g$

$$\frac{p^0_{solvent} - p_{solution}}{p^0_{solvent}} = \frac{n_{solute}}{n_{solvent}}$$

$$\frac{p^0_{solvent} - p_{solution}}{p^0_{solvent}} = \frac{4.45}{178}\Big/\frac{1000}{76}$$

$$\frac{\boldsymbol{p^0_{solvent} - p_{solution}}}{\boldsymbol{p^0_{solvent}}} = \frac{4.45 \times 76}{178 \times 1000} = \mathbf{0.0019}$$

For a solution of Sulphur in CS_2;

$p^0_{solvent} = ??\quad p_{solution} = ??$

$m_{solute} = 6.42g\qquad m_{solvent} = 1000\ g$

$Molar\ mass\ of X = 178g$

$Molar\ mass\ of CS_2 = 12 + 64 = 76g$

$$\frac{p^0_{solvent} - p_{solution}}{p^0_{solvent}} = \frac{n_{solute}}{n_{solvent}}$$

$$\frac{p^0_{solvent} - p_{solution}}{p^0_{solvent}} = \frac{6.42}{M_{r_{solute}}}\Big/\frac{1000}{76}$$

$$\frac{\boldsymbol{p^0_{solvent} - p_{solution}}}{\boldsymbol{p^0_{solvent}}} = \frac{6.42 \times 76}{M_{r_{solute}} \times 1000}$$

(b) Since the two solutions have the same vapour pressure, and the same solvent(same vapour pressure of pure solvent) is used, then both the lowering of vapour pressure and the relative lowering of vapour pressure is the same.

$$\frac{6.42 \times 76}{M_{r_{solute}} \times 1000} = 0.0019$$

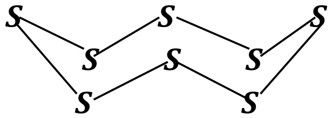
$$M_{r_{solute}} = \frac{6.42 \times 76}{1000 \times 0.0019} = \mathbf{256.8g}$$

$$S_n = 256.8$$

$$32n = 256.8 \quad n = 8$$

Molecular formula is S_8

Structural formula is;



Questions

1. (a) State **Raoult's law of relative lowering of vapour pressure**.
   (b) (i) Calculate the vapour pressure of a solution containing 18g of glucose ($C_6H_{12}O_6$) in 50g of water at $60°C$. (Vapour pressure of water at $60°C$ is 150mmHg.)
   (ii) State any assumptions made in (b)(i).
2. A solvent ***Y*** of molecular mass 62 has a vapor pressure of $1.0\ x\ 10^4 Nm^{-2}$ at $298K$. 23.3g of a non volatile solute of molecular mass 270 was added to 100g of Y at $298K$.
   (i) Calculate the vapor pressure of solution
   (ii) State and explain the effect of increasing the concentration of the solute on the boiling point of ***Y***.
3. The vapor pressure of water at $50°C$ is $12.333kPa$. At this temperature, a solution of $9.14g$ of carbamide in $150.0g$ of water has a vapour pressure of $12106\ Pa$. Find the relative molecular formula of the carbamide.

4. The vapour pressure of a 3% solution of a non-volatile solute ***X*** in ethoxyethane is $3218Nm^{-2}$ at a certain temperature. The vapour pressure of pure ethoxyethane at the same temperature is $32670Nm^{-2}$.
   (i) Calculate the relative molecular mass of ***X***
   (ii) State any other assumptions made in (i) apart from ***X*** being non-volatile
5. $10\ g$ of a certain solute were dissolved in $67g$ in ethoxethane at $60\ ^0C$ and vapour pressure of the solution was measured to be $0.2928\ atm$. At this temperature vapour pressure of ethoxyethane was found to be $0.3618\ atm$. Calculate relative molecular mass of the solute.
6. When $100g$ of sucrose were dissolved in $1kg$ of water at $20\ ^0C$, the vapour pressure decreased by $16.6\ Pa$. Calculate the molar mass of sucrose (Vapour pressure of water at $25\ ^0C$ is $3.17kpa$)
7. The vapour pressure of pure water at $25°C$ is $3167\ Pa$. The vapour pressure of a solution of 4g of a sugar in 100g of water at the same temperature is $3154.5\ Pa$. Calculate the relative molecular mass of the sugar.
8. 19 g of solute ***K***, were dissolved in 90g of water and vapour pressure of the solution was lowered by 42 mmHg. Calculate molar mass of solute ***K*** if vapour pressure of pure water is 92 mmHg.
9. The vapour pressure of a solution containing $108.2g$ of a substance Q in 1000g of water was reduced by $0.186mmHg$ of water at $20°C$ (The vapor pressure of water at $20°C$ is $17.54mmHg$.
   (a) Calculate the relative molecular mass of substance Q.
   (b) State four assumptions made in (a)
   (c) Explain why the vapor pressure of the solution containing a nonvolatile solute is less than the vapor pressure of a pure solvent.

Graphical representation of vapour pressure lowering

From the expression;

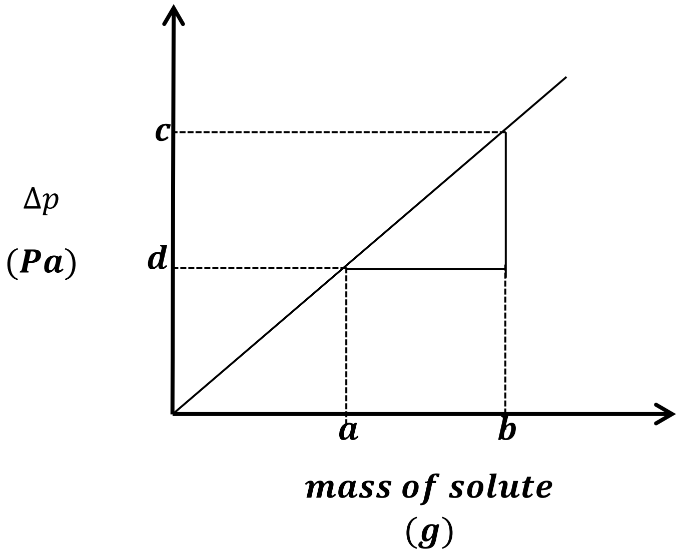
$$\frac{\Delta p}{p^0_{solvent}} = \frac{m_{solute}}{M_{r_{solute}}} \Big/ \frac{m_{solvent}}{M_{r_{solvent}}}$$

$$\frac{\Delta p}{p^0_{solvent}} = \frac{m_{solute} \times M_{r_{solvent}}}{M_{r_{solute}} \times m_{solvent}}$$

$$\Delta p = \frac{m_{solute} \times M_{r_{solvent}} \times p^0_{solvent}}{M_{r_{solute}} \times m_{solvent}}$$

$$\Delta p = \left(\frac{M_{r_{solvent}} \times p^0_{solvent}}{M_{r_{solute}} \times m_{solvent}}\right) m_{solute}$$

Comparing with the equation $y = mx$, a graph of the lowering of vapour pressure(Δp) plotted against mass of solute (m_{solute}) for a given mass of water can be plotted.



A graph of lowering of vapour pressure($\Delta p = p^0_{solvent} - p_{solution}$) against mass of solute is a straight line through the origin.

The slope of the graph gives the value $\left(\frac{M_{r_{solvent}} \times p^0_{solvent}}{M_{r_{solute}} \times m_{solvent}}\right)$

$$Slope = \frac{\boldsymbol{c - d}}{\boldsymbol{b - a}} = \left(\frac{M_{r_{solvent}} \times p^0_{solvent}}{M_{r_{solute}} \times m_{solvent}}\right)$$

The data you are usually given requires you to calculate Δp first before graph plotting. $p^0_{solvent}$ is the vapour pressure at $m_{solute} = 0$. Each $p_{solution}$ value is subtracted from the $p^0_{solvent}$ value to get Δp values at the different m_{solute} values.

Also from the expression;

$$\frac{\Delta p}{p^0_{solvent}} = \frac{n_{solute}}{n_{solvent}}$$

$$\frac{\Delta p}{p^0_{solvent}} = n_{solute} / \frac{m_{solvent}}{M_{r_{solvent}}}$$

$$\frac{\Delta p}{p^0_{solvent}} = \frac{n_{solute} \times M_{r_{solvent}}}{m_{solvent}}$$

Since $m_{solvent} = density \times volume$;

$$\frac{\Delta p}{p^0_{solvent}} = \frac{n_{solute} \times M_{r_{solvent}}}{density\ of\ solvent \times Volume\ of\ solvent}$$

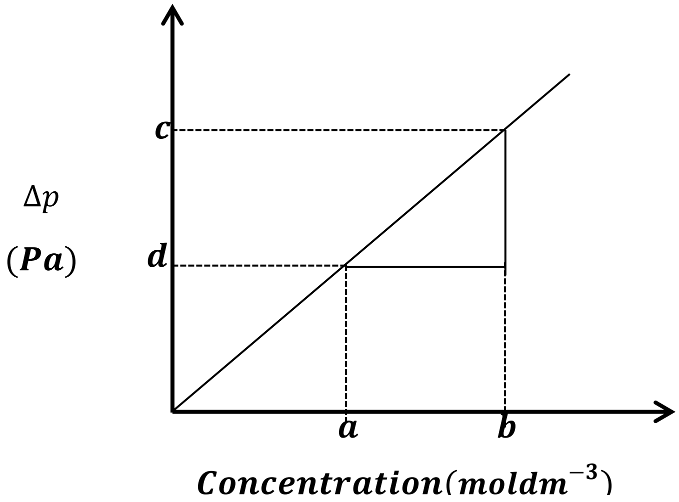
$$\Delta p = \frac{M_{r_{solvent}} \times p^0_{solvent}}{density\ of\ solvent}\left(\frac{n_{solute}}{Volume\ of\ solvent}\right)$$

$$But\ \left(\frac{n_{solute}}{Volume\ of\ solvent}\right) = Concentration\ in\ moldm^{-3}$$

$$\Delta p = \frac{M_{r_{solvent}} \times p^0_{solvent}}{density\ of\ solvent}(concentration)$$

Comparing with the equation $y = mx$, a graph of the lowering of vapour pressure(Δp) plotted against mass of solute $concentration$($moldm^{-3}$) of a solute in a given solvent can be plotted.

The density if given in gcm^{-3} must be multiplied by 1000 to convert it to gdm^{-3} since units of concentration are usually expressed per litre



A graph of lowering of vapour pressure($\Delta p = p^0_{solvent} - p_{solution}$) against $concentration(moldm^{-3})$ of solute in a solvent is a straight line through the origin.

The slope of the graph gives the value $\frac{M_{r_{solvent}} \times p^0_{solvent}}{density\ of\ solvent \times 1000}$

$$Slope = \frac{\boldsymbol{c-d}}{\boldsymbol{b-a}} = \left(\frac{M_{r_{solvent}} \times p^0_{solvent}}{density\ of\ solvent \times 1000}\right)$$

The data you are usually given may require you to calculate Δp first before graph plotting. $p^0_{solvent}$ is the vapour pressure at $concentration = 0$. Each $p_{solution}$ value is subtracted from the $p^0_{solvent}$ value to get Δp values at the different $concentration$ values.

Questions

1. (a) (i) Define the term vapour pressure
   (ii) State Raoult's law of vapour pressure lowering
   (b) The vapour pressure of aqueous solutions of glucose containing 9.0g of water at $27°C$ varies with the mass of glucose dissolved as shown in the table below.

Mass of glucose in 9.0g of water	0.00	0.45	0.90	1.80	3.60	4.50	7.20
Vapour pressure of solution(mmHg)	31.82	31.66	31.50	31.32	30.55	30.23	29.27

   (i) Plot a graph of lowering in vapour pressure(ΔP) against mass of glucose dissolved in 9.0g of water.
   (ii) Use your graph in b(i) above to determine the molar mass of glucose.
   (c) State the effect of water on the molecular state of glucose. Give a reason for your answer using the molar mass calculated in b(i) above.
2. The lowering in vapour pressure of a volatile solvent is a colligative property.
   (a) (i) Define the term colligative property
   (ii) State two other examples of colligative properties
   (b) The vapour pressure of different solutions of solute $\boldsymbol{Y}$ dissolved in solvent $\boldsymbol{X}$ at $40°C$ are shown in the table below.

Concentration of Y$(moldm^{-3})$	0.00	0.10	0.20	0.30	0.40	0.50
Vapour pressure of solution(kNm^{-2})	16.000	15.971	15.942	15.914	15.880	15.860

(i) Plot a graph of lowering in vapour pressure(ΔP) against concentration of Y.

(ii) Use your graph in b(i) above to determine the relative molecular mass of solvent X if its density is $1.0gcm^{-3}$.

(iii) State two assumptions made in b(ii) above.

Elevation of boiling point (Ebullioscopy)

Boiling point of a liquid is the constant temperature at which its saturated vapour pressure becomes equal to the external pressure on the liquid.

A pure liquid will only boil when its saturated vapour pressure is equal to the external pressure. The external pressure is usually the atmospheric pressure$(1\ atm\ or\ 760mmHg\ or\ 101325Pa)$

The vapour pressure of a liquid decreases when a non-volatile solute is dissolved in it The decreased vapour pressure implies that the solution will have to be heated to a higher temperature than the boiling point of the pure liquid so that its equilibrium vapour pressure becomes equal to the atmospheric pressure for boiling to take place.

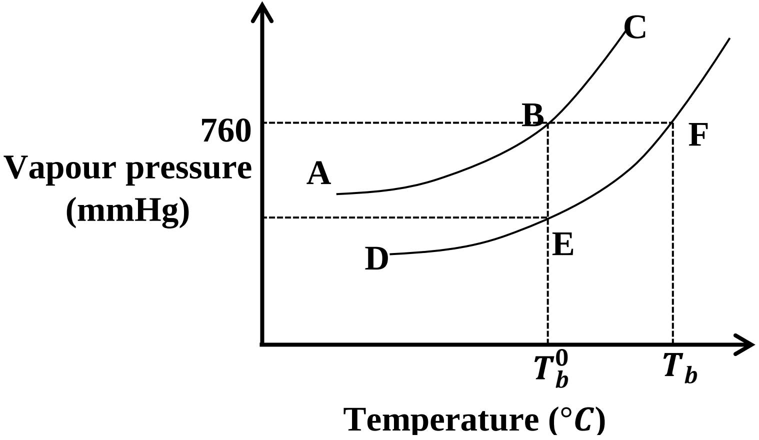
Pure water boils at $100°C$ an aqueous solution of sodium chloride boils at $106°C$ at $760\ mmHg$. Explain

Sodium chloride is ***non-volatile solute.*** When dissolved in water, ***sodium chloride particles occupy some of the surface of the solution.*** This ***reduces the escaping tendency of the solvent particles into the vapour phase. The solution there has a lower vapour pressure than that that would be exerted by pure water. The solution should therefore be heated at a higher temperature*** than the boiling point of pure water so that its equilibrium ***vapour pressure becomes equal to the atmospheric pressure for boiling to take place.***

In simple terms, the boiling point of a solution containing a non-volatile solute $(T_{b(solution)})$ is always higher than the boiling point of pure solvent$\left(T^0_{b(solvent)}\right)$. This increase in boiling point is called the **elevation in boiling point**(ΔT_b).

$$\Delta T_b = T_{b(solution)} - T^0_{b(solvent)}$$

Vapour pressure-temperature diagrams and boiling points



Curve ABC represents the ***variation of vapour pressure of pure solvent with temperature***

Curve DEF represents the ***variation of vapour pressure of solution with temperature***

Curve DEF is below curve ABC at all temperatures because the vapour pressure of the solution is always lower than that of pure solvent

T_b^0 is the boiling point of pure solvent

T_b is the boiling point of the solution.

The elevation in boiling point, $\Delta T_b = T_b - T_b^0$. The greater the concentration of the solute particles in solution, the greater the boiling point elevation.

Therefore a curve of a more concentrated solution will still be below curve DEF at all temperatures.

The boiling point constant of the solvent or molal boiling point constant (Ebullioscopic constant,k_b)

This is the elevation in boiling point caused when one mole of a non-ionizing and non-volatile solute is dissolved in 1000g of a solvent.

The units of the ebullioscopic constant are $°Cmol^{-1}kg^{-1}$ or $°Cmol^{-1}\ per\ 1000g$

Boiling point elevation is directly proportional to magnitude of vapour pressure lowering

$$\Delta T_b \propto \Delta p$$

The vapour pressure lowering is proportional to the **molality, m** (not molarity) of the solute particles.

$$\Delta p \propto m$$

Therefore boiling point elevation is directly proportional to molality of the solute.

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m$$

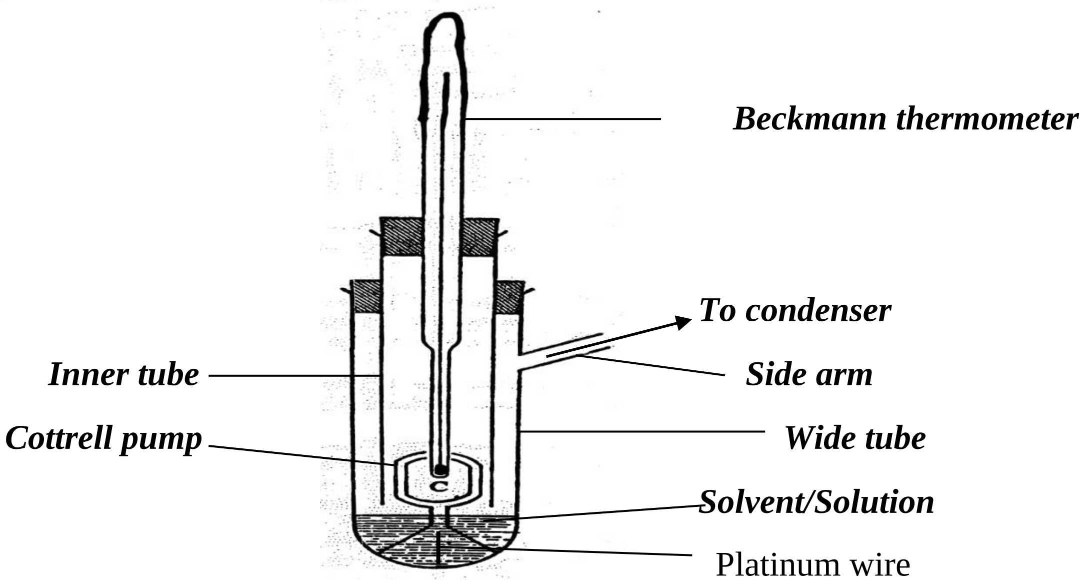
where m is **molality** of the solute in solution and K_b is **the boiling point constant of the solvent or molal boiling point constant or ebullioscopic constant.**

The molal concentration (or molality; symbol m) is the amount of substance per unit mass of solvent, commonly given in units of $mol\ kg^{-1}\ or\ mol\ g^{-1}$.

$$molality = \left(\frac{number\ of\ moles\ of\ solute}{mass\ of\ solvent}\right) mol\ kg^{-1}$$

Experimental determination of molecular mass using boiling point elevation method

Using Cottrell's apparatus to find relative molecular mass of benzoic acid in propanone



A known mass of pure propanone, $x\ g$ is placed in a wide tube fitted with a side arm leading to a reflux condenser.

The boiling tube is closed by a stopper through which is passed a second inner tube, open at the lower end and fitted with a Beckmann thermometer.

In the liquid is immersed a Cottrell pump, C to prevent super heating

The propanone is then heated until the Beckmann thermometer shows a constant temperature and the boiling point, $T_b^0\ °C$ is measured.

A known mass of benzoic acid, $y\ g$ in pellet form is then added through the side arm to the solvent

The resulting solution is also heated until the Beckmann thermometer shows a constant temperature and the boiling point of the solution $T_b\ °C$ is also measured.

<u>Treatment of results</u>

$$Mass\ of\ solvent = x\ g$$

$$Mass\ of\ solute = y\ g$$

Let the boiling point elevation constant of propanone be $K_b °C mol^{-1} kg^{-1}$

$$Elevation\ of\ boiling\ point, \Delta T = (T_b - T_b^0)°C$$

$$x\ g\ of\ propanone\ dissolve\ y\ g\ of\ benzoic\ acid$$

$$1000\ g\ of\ propanone\ will\ dissolve\ \left(\frac{1000 \times y}{x}\right)\ g\ of\ benzoic\ acid$$

$$\Delta T \text{ is elevation of boiling point caused } \left(\frac{1000 \times y}{x}\right) g \text{ of benzoic acid}$$

$$K_b \text{ will be elevation in boiling point caused by } \left(\frac{1000 \times y \times K_b}{x \times \Delta T}\right) g$$

The relative molecular mass of the benzoic acid is $\left(\frac{\mathbf{1000 \times y \times K_b}}{\mathbf{x \times \Delta T}}\right)$

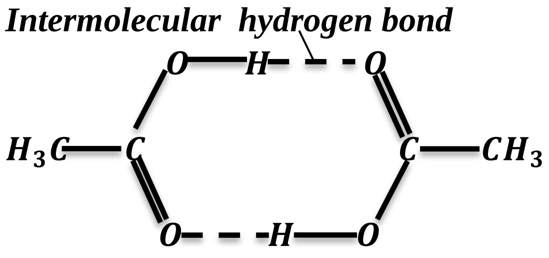
Assumptions/ limitations of the boiling point elevation method for determining relative molecular mass

(i) Solute does not associate or dissociate in solution.
(ii) The solution is dilute
(iii) There is no chemical reaction between the solute and the solvent.
(iv) The solute is non-volatile

Explain why the molecular mass of ethanoic acid obtained by ebullioscopic method is 120g using benzene as a solvent.

Molecular mass of $CH_3COOH = 24 + 32 + 4 = 60g$

The molecular mass of ethanoic acid obtained by boiling point elevation method is ***twice the actual value****. This is because ethanoic acid* ***associates through intermolecular hydrogen bonds*** *to form* ***dimers in benzene.*** *The number of ethanoic acid molecules in benzene solution is* ***half the original number in the pure solute****. This* ***lowers the boiling point elevation*** *but* ***increasing the relative molecular mass to twice the actual value****.*



The relative molecular mass of sodium chloride obtained by boiling point elevation method is 29.25. Explain. $(\boldsymbol{Na = 23, Cl = 35.5})$

Actual relative molecular mass of sodium chloride $= \mathbf{23 + 35.5 = 58.8}$

The obtained relative molecular mass is ***half the actual value****.*

Sodium chloride being a ***strong electrolyte****,* ***completely ionises*** *in water to form* ***sodium ions and chloride ions***

$$\boldsymbol{NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq)}$$

Therefore ***1 mole of sodium chloride will form a total of 2 moles of ions in solution****. Since* ***boiling point elevation is a colligative property****,* ***directly proportional to the number of solute particles in solution****, the ionisation of sodium chloride* ***increases the boiling point elevation*** *but* ***reduces the relative molecular mass*** *to half the actual value.*

Calculations involving boiling point elevation

Examples

1. **(a) A solution containing 60g of $RCOOH$ and 50g of water was boiled. Calculate the boiling point of the solution. ($R = 43, H = 1, C = 12, O = 16, k_b$ *for water is* $0.54°C mol^{-1} kg^{-1}$)**
   (b) State any assumption(s) you have made in your calculation.

(a) $50g\ of H_2O\ dissolve\ 60g\ of\ RCOOH$

$$1000g\ of H_2O\ dissolve \left(\frac{1000 \times 60}{50}\right) g\ of\ RCOOH$$

$$= 1200g\ of\ RCOOH$$

$$Molar\ mass\ of RCOOH = 43 + 12 + 32 + 1 = 88g$$

$$88g\ of\ RCOOH\ elevate\ boiling\ point\ by\ 0.54°C$$

$$1200g\ of RCOOH\ elevate\ boiling\ point\ by\ \left(\frac{1200 \times 0.54}{88}\right) °C$$

$$\Delta T = 7.3636°C$$

$$Elevation\ of\ boiling\ point;$$

$$\Delta T = T_{b(solution)} - T^0_{b(solvent)}$$

$$T_{b(solution)} = \Delta T + T^0_{b(solvent)}$$

$$T_{b(solution)} = 7.3636 + 100$$

$$\boldsymbol{T_{b(solution)} = 107.36°C}$$

(b) ***$RCOOH$ does not associate or dissociate in solution.***
The solution is dilute
There is no chemical reaction between $RCOOH$ and water.
$RCOOH$ is non-volatile

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2. **A 2% aqueous solution of urea (CON_2H_4) has a boiling point of $100.08°C$. Calculate the boiling point of pure water. (k_b *for water is* $0.52°C$ *per mole per* $1000g$)**

$$\boldsymbol{2\%\ means\ 2g\ of\ urea\ in\ 100g\ of\ solution}$$

$$Mass\ of\ water = (100 - 2)g = 98g$$

$$98g\ of H_2O\ dissolve\ 2g\ of\ CON_2H_4$$

$$1000g\ of H_2O\ dissolve \left(\frac{1000 \times 2}{98}\right) g\ of\ CON_2H_4$$

$$= 20.4082g\ of CON_2H_4$$

$$Molar\ mass\ of CON_2H_4 = 12 + 16 + 28 + 4 = 60g$$

$$60g\ of\ CON_2H_4\ elevate\ boiling\ point\ by\ 0.52°C$$

$$20.4082g\ of CON_2H_4\ elevate\ boiling\ point\ by\ \left(\frac{20.4082 \times 0.52}{60}\right) °C$$

$$\Delta T = 0.1769°C$$

$$Elevation\ of\ boiling\ point;$$

$$\Delta T = T_{b(solution)} - T^0_{b(solvent)}$$

$$T^0_{b(solvent)} = T_{b(solution)} - \Delta T$$

$$T^0_{b(solvent)} = 100.08 - 0.1769$$

$$= \boldsymbol{99.9°C}$$

3. **2.00g of phosphorus raise the boiling point of 37.4g carbon disulphide by $\boldsymbol{1.003°C}$**

   (a) Calculate the molar mass of phosphorus in carbon disulphide $(\boldsymbol{k_b\ for\ carbon\ disulphide\ is\ 2.35°C\ mol^{-1}\ (1000g)^{-1}})$

   (b) (i) Hence determine the molecular formula of phosphorus in carbon disulphide.$(\boldsymbol{P = 31})$

   (ii) State any two assumptions made in the calculation in (a) above

   (iii) Comment on the result in b(i) above.

(a)

$$37.4g\ of\ CS_2\ dissolve\ 2.00g\ of\ Phosphorus$$

$$1000g\ of\ CS_2\ dissolve\left(\frac{1000 \times 2}{37.4}\right)g\ of\ Phosphorus$$

$$= 53.4759g\ of\ Phosphorus$$

$$1.003°C\ is\ elevation\ in\ boiling\ point\ caused\ by\ 53.4759g$$

$$2.35°C\ is\ elevation\ in\ boiling\ point\ caused\ by\ \left(\frac{2.35 \times 53.4759}{1.003}\right) = 125.29g$$

$$\boldsymbol{Molar\ mass\ of\ Phosphorus\ in\ Carbon\ disulphide\ is\ 125.29g}$$

(b) (i) $P_n = 125.29$ $\quad n = 4$ $31n = 125.29$	**Molecular formula of Phosphorus in carbon disulphide is $\boldsymbol{P_4}$**

(ii) The solution is dilute

There is no chemical reaction between phosphorus and carbon disulphide.

Phosphorus is non-volatile

(iii) Phosphorus exists as a tetratomic molecules in carbon disulphide

4. **0.900g of a solute was dissolved in $\boldsymbol{100cm^3}$ of benzene at 25°$\boldsymbol{C}$. The solution formed boiled at 0.25°$\boldsymbol{C}$ higher than the boiling point of benzene. Calculate relative molecular mass of the solute.**

$$\boldsymbol{(Molal\ elevation\ constant\ of\ benzene\ is\ 2.52°Cmol^{-1}kg^{-1}}$$
$$\boldsymbol{and\ the\ density\ of\ benzene\ is\ 0.879gcm^{-3})}$$

$$Mass\ of\ benzene = density\ \times volume = (0.879 \times 100) = 87.9g$$

$$87.9g\ of\ benzene\ dissolve\ 0.9g\ of\ solute$$

$$1000g\ of\ benzene\ dissolve\left(\frac{1000 \times 0.9}{87.9}\right)g\ of\ solute$$

$$= 10.2389g\ of\ solute$$

$$0.25°C\ is\ elevation\ in\ boiling\ point\ caused\ by\ 10.2389g\ of\ solute$$

$$2.52°C\ is\ elevation\ in\ boiling\ point\ caused\ by\ \left(\frac{2.52 \times 10.2389}{0.25}\right) = 103.21g$$

$$\boldsymbol{Relative\ molecular\ mass\ of\ solute\ is\ 103.21}$$

3. **(a) The boiling point of pure water is 100°C but when 1.97g of potassium chloride is dissolved in 125g of water, the solution boiled at 100.11°C at a pressure of 760mmHg. Explain this observation.**

   (b) From the information given in (a) above, calculate the boiling point constant of water.($K = 39.1, Cl = 35.4$)

(a) Potassium chloride is ***non-volatile solute.*** When dissolved in water, ***potassium chloride particles occupy part of the surface of the solution.*** This ***reduces the escaping tendency of the water molecules into the vapour phase. The solution there has a lower vapour pressure than that that would be exerted by pure water. The solution should therefore be heated at a higher temperature*** than the boiling point of pure water so that its equilibrium ***vapour pressure becomes equal to the atmospheric pressure for boiling to take place.***

(b)

$$125g\ of\ water\ \ dissolve\ 1.97g\ of\ potassium\ chloride$$

$$1000g\ of\ water\ dissolve \left(\frac{1000 \times 1.97}{125}\right) g\ of\ potassium\ chloride$$

$$= 15.76g\ of\ potassium\ chloride$$

$$Elevation\ in\ boiling\ point, \Delta T = T_{b(solution)} - T^0_{b(solvent)}$$

$$\Delta T = (100.11 - 100) = 0.11°C$$

$$Molar\ mass\ of\ KCl = 39.1 + 35.4 = 74.5g$$

$$15.76g\ of\ KCl\ elevate\ boiling\ point\ by\ 0.11°C$$

$$74.5g\ of\ KCl\ elevate\ boiling\ point\ \ by\ \left(\frac{74.5 \times 0.11}{15.76}\right) = 0.52\ °Cmol^{-1}kg^{-1}$$

$$\boldsymbol{The\ boiling\ point\ constant\ of\ water\ is\ \ 0.52\ °Cmol^{-1}kg^{-1}}$$

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4. **(a) Define the term boiling point elevation constant of a substance.**

   (b) The boiling point of benzene under certain pressure condition is $80.0°C$. Calculate the boiling point elevation constant of benzene, if a solution containing 5g of 2,4,6-trinitrophenol, ($HOC_6H_2(NO_2)_3$ in 100g of benzene, boils at $80.568°C$.

(b)

$$100g\ of\ benzene\ \ dissolve\ 5g\ of\ (HOC_6H_2(NO_2)_3$$

$$1000g\ of\ benzene\ dissolve \left(\frac{1000 \times 5}{100}\right) g\ of\ (HOC_6H_2(NO_2)_3$$

$$= 50g\ of\ (HOC_6H_2(NO_2)_3$$

$$Elevation\ in\ boiling\ point, \Delta T = T_{b(solution)} - T^0_{b(solvent)}$$

$$\Delta T = (80.568 - 80.0) = 0.568°C$$

$$Molar\ mass\ of\ (HOC_6H_2(NO_2)_3 = (3 \times 1) + (7 \times 16) + (6 \times 12) + (3 \times 14) = 229g$$

$$50g\ of\ (HOC_6H_2(NO_2)_3\ elevate\ boiling\ point\ by\ 0.568°C$$

$$229g\ of\ (HOC_6H_2(NO_2)_3\ elevate\ boiling\ point\ \ by\ \left(\frac{229 \times 0.568}{50}\right) = 2.6\ °Cmol^{-1}kg^{-1}$$

$$\boldsymbol{The\ boiling\ point\ constant\ of\ benzene\ is\ \ 2.6\ °Cmol^{-1}kg^{-1}}$$

5. **Calculate the mass of sucrose, $C_{12}H_{22}O_{11}$, that would have to be dissolved in 1000g of water to raise its boiling point to 101.7°C. (k_b for water is $0.52°Cmol^{-1}kg^{-1}$)**

$$Elevation\ in\ boiling\ point, \Delta T = T_{b(solution)} - T^0_{b(solvent)}$$

$$\Delta T = (101.7 - 100) = 1.7°C$$

$$Molar\ mass\ of\ C_{12}H_{22}O_{11} = (12 \times 12) + (22 \times 1) + (11 \times 16) = 342g$$

$$0.52°C\ is\ elevation\ in\ boiling\ point\ caused\ by\ 342g\ of\ C_{12}H_{22}O_{11}$$

$$1.7°C\ is\ elevation\ in\ boiling\ point\ that\ will\ be\ caused\ by\ \left(\frac{1.7 \times 342}{0.52}\right) = 1118.08g$$

$$\boldsymbol{The\ mass\ of\ sucrose\ required\ is\ 1118.08g}$$

Questions

1. Calculate the boiling point of a solution formed by mixing 8g of glucose, $C_6H_{12}O_6$, and 120g of water. (k_b for water is $0.52°Cmol^{-1}kg^{-1}$)
2. Calculate the boiling point of a solution containing 0.360g of glucose dissolved in 100g of water. The boiling point of pure water is 100°C. (k_b for water is $0.52°Cmol^{-1}kg^{-1}$)
3. The boiling point of ethanol is 78°C. Calculate the boiling point of a solution containing 2.7g of ethanamide (CH_3CONH_2) in 75g of ethanol (Boiling point elevation for 1000g of ethanol is $1.15°C\ mol^{-1}$)
4. The boiling point of ethanol is 78°C and its molal boiling point constant is $1.15°Cmol^{-1}kg^{-1}$. A solution containing 0.56g of camphor in 16g of ethanol has a boiling point of 78.278°C. Calculate the relative molecular mass of camphor.
5. 0.900g of a solute was dissolved in $100cm^3$ of benzene at 25°C. The solution formed boiled at 0.25°C higher than the boiling point of benzene. Calculate relative molecular mass of the solute.

   $$(Molal\ elevation\ constant\ of\ benzene\ is\ 2.52°Cmol^{-1}kg^{-1}$$
   $$and\ the\ density\ of\ benzene\ is\ 0.879gcm^{-3})$$
6. The boiling point of an aqueous solution containing 3g of a non-volatile solute in 200g of water is 100.45°C. Calculate the molar mass of the solute. (k_b for water is $0.54°Cmol^{-1}kg^{-1}$)
7. A solution containing 1.00g of a non-volatile solute in 10.0g of benzene boils at 1.22°C higher than pure benzene. Calculate the molecular mass of the solute. (k_b for benzene is $2.53°Cmol^{-1}kg^{-1}$)

8. (a) State what is meant by the term ebullioscopic constant.

   (b) 0.40g of camphor when dissolved in 33.5g of trichloromethane produces a solution boiling at $0.30°C$ above the boiling point of pure solvent. Calculate the ebullioscopic constant of trichloromethane. ($Molar\ mass\ of\ camphor\ =\ 155$).

9. (a) Define the term **boiling point elevation constant of a substance**.

   (b) An aqueous solution of glucose containing 12g of the solute dissolved in 100g of water was found to boil at $100.34°C$ while pure water boils at $100°C$. Calculate the boiling point elevation constant of water.

10. Calculate the mass of sucrose, $C_{12}H_{22}O_{11}$, that would have to be dissolved in 1000g of water to raise the boiling point by $1.0°C$. ($k_b\ for\ water\ is\ 0.54°Cmol^{-1}kg^{-1}$)

11. (a)Explain the terms;
    - (i) Boiling point of a liquid
    - (ii) Boiling point elevation constant of a liquid
    - (iii) Relative molecular mass
    - (iv) Colligative property

    (b) Describe an experiment to determine the relative molecular mass of naphthalene in chloroform by the elevation of boiling point method.

    (c) State, with reasons why the method in (b)(i) above is not suitable for determining relative molecular mass of;
    - (i) polyvinylchloride
    - (ii) ethanoic acid

    (d) (i) A solution of 2.8g of cadmium(II) iodide in 20g of water boiled at $100.2°C$ at standard pressure. Calculate the relative molecular mass of the solute and comment on your answer. ($k_b\ for\ water\ is\ 0.52°Cmol^{-1}per\ 1000g$)

    (ii) A solution contains 1 mole of sugar per kg of water. Another solution contains 1 mole of urea per kg of water. State and explain which of the two solutions will have a higher elevation in boiling point.

Graphical representation of Boiling point elevation

The elevation in boiling point is proportional to the lowering in vapour pressure

$$\Delta T \propto \Delta p$$

Since the lowering in vapour pressure is directly proportional to the concentration of solute and inversely proportional to relative molecular mass of the solute;

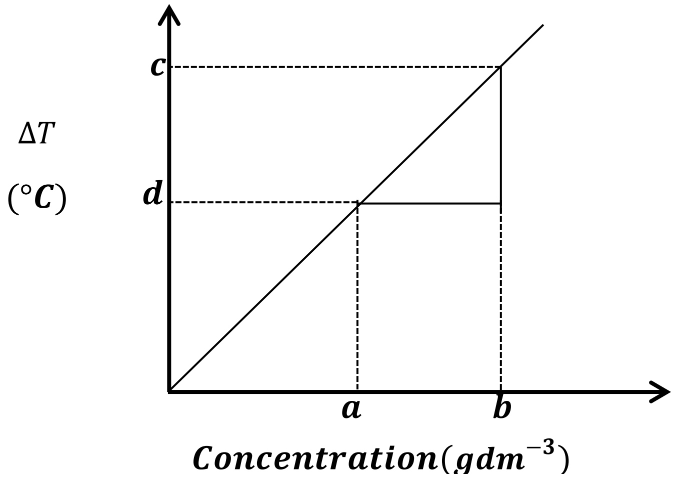
$\Delta p \propto \frac{C}{M_r}$, where C is concentration in grams of solute per litre of solvent

This implies that $\Delta T \propto \frac{C}{M_r}$

$$\Delta T = K_b \frac{C}{M_r}$$

$\Delta T = \frac{K_b}{M_r}C$ where the constant K_b is the boiling point constant

A graph of boiling point elevation , ΔT against concentration can be plotted



A graph of elevation of boiling point (ΔT) against $concentration(gdm^{-3})$ of solute in a solvent is a straight line through the origin.

The slope of the graph gives the value $\frac{K_b}{M_r}$

$$Slope = \frac{c-d}{b-a} = \frac{K_b}{M_r}$$

If K_b of the solvent is known, the relative molecular mass of the solute can be calculated. The data you are usually given may require you to calculate ΔT first before graph plotting.

Freezing point depression (Cryoscopy)

Freezing point of a liquid is the constant temperature at which the liquid coexists with its solid form at the same saturated vapour pressure.

The vapour pressure of a solvent decreases when a solute is dissolved in it and therefore the solid-liquid equilibrium will only exist at a temperature lower than that of the pure solvent.

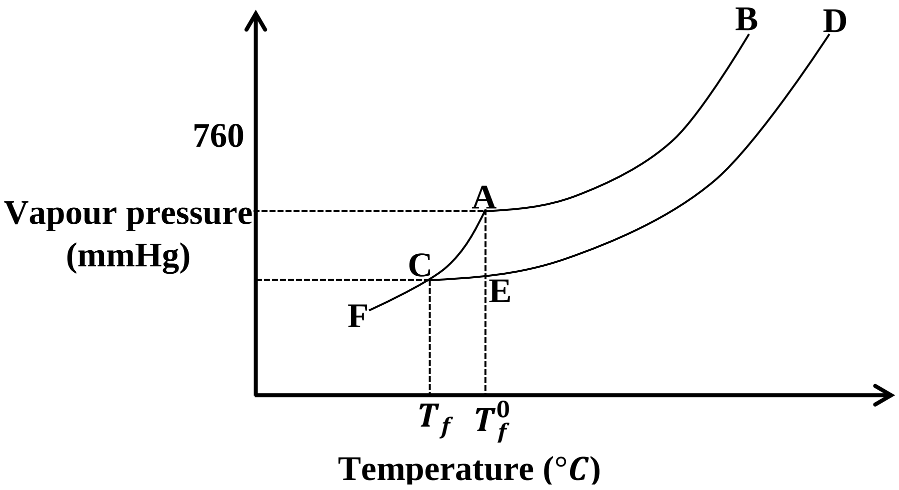
Explain why freezing point of a solution containing a non-volatile solute is always lower than freezing point of the pure solvent

When a non-volatile solute is dissolved in a solvent, ***the solute particles occupy part of the surface of the solution.*** This ***reduces the escaping tendency of the solvent molecules into the vapour phase. The solution there has a lower vapour pressure than that that would be exerted by pure solvent. Therefore the temperature*** at ***which the solution is at equilibrium with the solid solvent is lower than that for the pure solvent.***

In simple terms, the freezing point of a solution($T_{f(solution)}$) containing a non-volatile solute is always lower than the freezing point of pure solvent$\left(T^0_{f(solvent)}\right)$. This decrease in boiling point is called the **freezing point depression**$\left(\Delta T_f\right)$.

$$\Delta T_f = T^0_{f(solvent)} - T_{f(solution)}$$

Vapour pressure-temperature diagrams and freezing point



Curve AB represents the ***variation of vapour pressure of pure solvent with temperature***

Curve CD represents the ***variation of vapour pressure of solution with temperature***

Curve FCA represents the ***variation of vapour pressure of pure solid solvent with temperature.*** It is called the ***sublimation curve of the solid solvent.***

The **point A**, at which curves FCA and AB meet is the ***freezing point of pure solvent***.

Point C is the ***freezing point of the solution***.

Curve CD is below curve AB at all temperatures because the vapour pressure of the solution is always lower than that of pure solvent

T_f^0 is the freezing point of pure solvent

T_f is the free point of the solution.

The depression in freezing point, $\Delta T_f = T_f^0 - T_f$ **.** The greater the concentration of the solute particles in solution, the greater the depression in freezing point

Therefore a curve of a more concentrated solution will still be below curve CD at all temperatures.

The freezing point constant of the solvent or molal freezing point depression constant (Cryoscopic constant, k_f)

This is the amount by which the freezing point of 1000g of a solvent is lowered when one mole of a non-ionizing and non-volatile solute is dissolved in it.

The units of the cryoscopic constant are $°C mol^{-1} kg^{-1}$ or $°C mol^{-1}\ per\ 1000g$

Freezing point depression is directly proportional to magnitude of vapour pressure lowering

$$\Delta T_f \propto \Delta p$$

The vapour pressure lowering is proportional to the **molality, m** (not molarity) of the solute particles.

$$\Delta p \propto m$$

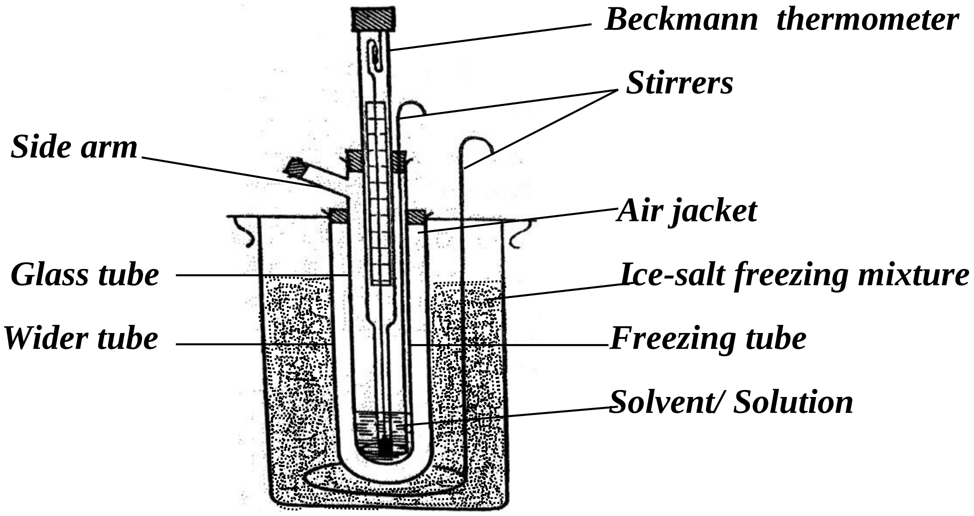
Therefore freezing point depression is directly proportional to molality of the solute.

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m$$

where m is **molality** of the solute in solution and K_f is **the freezing point constant of the solvent or molal freezing point constant or cryoscopic constant.**

Experimental determination of molecular mass using freezing point depression method using Beckmann's freezing point apparatus



A known mass of pure solvent, x g is placed into a glass tube that is fitted with a Beckmann thermometer, stirrer and has a side arm.

The freezing tube is placed in a wider tube that acts as an air jacket to ensure uniform cooling.

The whole apparatus is put in a vessel containing an ice-salt freezing mixture that is kept stirred

The solvent is allowed to cool while stirring until a constant temperature, $T_f^0\ °C$ is obtained when it begins to freeze and recorded from the Beckmann thermometer.

The solvent is warmed until it melts.

A known mass of solute, y g, in pellet form is added to the solvent through a side arm.

The solution is cooled while stirring and the steady temperature, $T_f °C$ at which it freezes, is recorded.

<u>Treatment of results</u>

$$Mass\ of\ solvent = x\ g$$

$$Mass\ of\ solute = y\ g$$

Let the freezing point depression constant of the solvent be $K_f °C mol^{-1} kg^{-1}$

$$Elevation\ of\ boiling\ point, \Delta T = \left(T_f^0 - T_f\right) °C$$

$$x\ g\ of\ solvent\ dissolve\ y\ g\ of\ solute$$

$$1000\ g\ of\ solvent\ will\ dissolve\ \left(\frac{1000 \times y}{x}\right)\ g\ of\ solute$$

$$\Delta T\ is\ elevation\ of\ boiling\ point\ caused\ \left(\frac{1000 \times y}{x}\right)\ g\ of\ solute$$

$$K_f\ will\ be\ elevation\ in\ boiling\ point\ caused\ by\ \left(\frac{1000 \times y \times K_f}{x \times \Delta T}\right) g$$

The relative molecular mass of the solute is $\left(\frac{\mathbf{1000 \times y \times K_f}}{\mathbf{x \times \Delta T}}\right)$

Assumptions/ limitations of the freezing point depression method for determining relative molecular mass

(i) Solute does not associate or dissociate in solution.
(ii) The solution is dilute
(iii) There is no chemical reaction between the solute and the solvent.
(iv) The solute is non-volatile

Explain why 0.1 mole of sodium chloride depresses the freezing point of 1 dm^3 of water twice as much as 0.1 mole of glucose does.

Sodium chloride ***completely ionises*** *in water to form* ***sodium ions and chloride ions***

$$\boldsymbol{NaCl(s)} \longrightarrow \boldsymbol{Na^+(aq)} + \boldsymbol{Cl^-(aq)}$$
$$0.1\ mole \qquad 0.1\ mole \qquad 0.1\ mole$$

Glucose is ***non-ionising solute***

Therefore ***0.1 moles of sodium chloride will form a total of 0.2 moles of ions in solution****. Glucose* ***remains in its molecular state in solution*** *and will still exist as 0.1 moles in solution. Since* ***freezing point depression is a colligative property****,* ***directly proportional to the number of solute particles in solution****, the amount by which freezing point of water is depressed by sodium chloride doubles that of glucose.*

Calculations involving freezing point depression

Examples

1. **Liquid camphor freezes at 175°C. A solution of 1.54g of naphthalene, $C_{10}H_8$, in 18g of camphor freezes at 148.3°C. Calculate the freezing point constant of camphor.**

$$18g\ of\ camphor\ dissolve\ 1.54g\ of\ C_{10}H_8$$

$$1000g\ of\ camphor\ dissolve\left(\frac{1000 \times 1.54}{18}\right) g\ of\ C_{10}H_8$$

$$= 85.556g\ of\ C_{10}H_8$$

$$Freezing\ point\ depression, \Delta T = T^0_{f(solvent)} - T_{f(solution)}$$

$$\Delta T = (175 - 148.3) = 26.7°C$$

$$Molar\ mass\ of\ C_{10}H_8 = (10 \times 12) + (8 \times 1) = 128\ g$$

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$$85.556g\ of\ C_{10}H_8\ lower\ freezing\ point\ by\ 26.7°C$$

$$128g\ of\ C_{10}H_8\ lower\ freezing\ point\ \ by\ \left(\frac{128 \times 26.7}{85.556}\right) = 39.95\ °Cmol^{-1}kg^{-1}$$

$$\boldsymbol{The\ freezing\ point\ constant\ of\ Camphor\ is\ \ 39.95°Cmol^{-1}kg^{-1}}$$

---

2. (a) Explain what is meant by the term cryoscopic constant

(b) Calculate the melting point of a solution made by dissolving 0.36g of naphthalene, $C_{10}H_8$, in 6.0g of camphor. The melting point of camphor is 177°C and k_f for camphor is 40°C for 1 mole in 1000g.

(b) $6.0g\ of\ camphor\ dissolve\ 0.36g\ of\ C_{10}H_8$

$$1000g\ of camphor\ will\ dissolve\left(\frac{1000 \times 0.36}{6.0}\right)g\ of\ C_{10}H_8$$

$$= 60g\ of\ C_{10}H_8$$

$$Molar\ mass\ of C_{10}H_8 = 120 + 8 = 128g$$

$$128g\ of\ C_{10}H_8\ lower\ freezing\ point\ by\ 40°C$$

$$60g\ of C_{10}H_8\ lower\ freezing\ point\ by\ \left(\frac{60 \times 40}{128}\right)°C$$

$$\Delta T_f\ = 18.75\ °C$$

$$Depression\ of\ freezing\ point;$$

$$\Delta T_f\ = T^0_{f(solvent)} - T_{f(solution)}$$

$$T_{f(solution)} = 177 - 18.75$$

$$\boldsymbol{T_{f(solution)} = 158.25°C}$$

---

3. Calculate the mass of water in which 10g of glucose, $C_6H_{12}O_6$ should be dissolved to obtain a solution that freezes at $-0.35\ °C$. ($\boldsymbol{k_f for\ water\ is\ 1.86°Cmol^{-1}kg^{-1}}$)

$$Freezing\ point\ depression, \Delta T = T^0_{f(solvent)} - T_{f(solution)}$$

$$\Delta T = (0 - -0.35) = 0.35°C$$

$$Molar\ mass\ of\ C_6H_{12}O_6 = (6 \times 12) + (12 \times 1) + (6 \times 16) = 180\ g$$

$$1.86°C\ is\ depression\ caused\ by\ 180g\ of\ C_6H_{12}O_6$$

$$0.35°C\ is\ depression\ caused\ by\left(\frac{180 \times 0.35}{1.86}\right)g\ of\ C_6H_{12}O_6$$

$$= 33.87g\ of\ C_6H_{12}O_6$$

$$33.87g\ of\ C_6H_{12}O_6\ are\ dissolved\ in\ 1000g\ of\ water$$

$$10g\ of\ C_6H_{12}O_6\ are\ dissolved\ in\ \ \left(\frac{10 \times 1000}{33.87}\right) = 295.25g$$

$$\boldsymbol{The\ mass\ of\ water\ required\ is\ \ 295.25g}$$

---

4. A solution containing 1.2g of ethanoic acid in 80g of water freezes at $-0.46°C$. Calculate the relative molecular mass of ethanoic acid.

($\boldsymbol{k_f\ for\ water = 1.86°Cmol^{-1}kg^{-1}}$)

$$80g\ of\ water\ dissolve\ 1.2g\ of\ ethanoic\ acid$$

$$1000g\ of\ water\ will\ dissolve\left(\frac{1000 \times 1.2}{80}\right)g\ of\ ethanoic\ acid$$

$$= 15g\ of\ ethanoic\ acid$$

$$\Delta T_f = T^0_{f(solvent)} - T_{f(solution)} = (0 - -0.46) = 0.46°C$$

$$0.46°C\ is\ depression\ in\ freezing\ point\ caused\ by\ 15g\ of\ ethanoic\ acid$$

$$1.86°C\ is\ depression\ in\ freezing\ point\ caused\ by\ \left(\frac{1.86 \times 15}{0.46}\right) = 60.65g$$

$$\boldsymbol{Relative\ molecular\ mass\ of\ ethanoic\ acid\ is\ 60.65}$$

---

5. (a) Explain what is meant by the term colligative property.

(b) 0.72g of a compound X was dissolved in 80g of water and the resultant solution had a freezing point of $-0.14°C$. When 2.9g of the same compound was dissolved in 111g of benzene the freezing point was depressed by $0.6°C$.

($\boldsymbol{k_f\ for\ water\ is\ 1.86°Cmol^{-1}kg^{-1} and\ k_f for\ benzene\ is\ 5.5°Cmol^{-1}kg^{-1}}$)

Calculate the apparent molecular mass of X in ;

(i) water

(ii) benzene

(c) Explain why the molecular mass of X differs in the solvents.

(b)(i)

$$80g\ of\ water\ dissolve\ 0.72g\ of\ X$$

$$1000g\ of\ water\ will\ dissolve\left(\frac{1000 \times 0.72}{80}\right)g\ of\ X$$

$$= 9g\ of\ X$$

$$\Delta T_f = T^0_{f(solvent)} - T_{f(solution)} = (0 - -0.14) = 0.14°C$$

$$0.14°C\ is\ depression\ in\ freezing\ point\ caused\ by\ 9\ g\ of\ X$$

$$1.86°C\ is\ depression\ in\ freezing\ point\ caused\ by\ \left(\frac{1.86 \times 9}{0.14}\right) = 119.57g$$

$$\boldsymbol{Relative\ molecular\ mass\ of\ X\ in\ water\ is\ 119.57}$$

(ii)

$$111g\ of\ benzene\ dissolve\ 2.9g\ of\ X$$

$$1000g\ of\ benzene\ will\ dissolve\left(\frac{1000 \times 2.9}{111}\right)g\ of\ X$$

$$= 26.126g\ of\ X$$

$$\Delta T_f = 0.6°C$$

$$0.6°C\ is\ depression\ in\ freezing\ point\ caused\ by\ 26.126g\ of\ X$$

$$5.5°C\ is\ depression\ in\ freezing\ point\ caused\ by\ \left(\frac{5.5 \times 26.126}{0.6}\right) = 239.49g$$

$$\boldsymbol{Relative\ molecular\ mass\ of\ X\ in\ benzene\ is\ 239.49}$$

(c) The apparent molecular mass is X in benzene is twice that of benzene in water because two molecules of X associate in benzene to give a dimer.

6. (a) An aqueous solution containing 7.2g of a non-cyclic substance Z in 250g of water freezes at $-0.744\ °C$. Calculate the molecular mass of Z.

$$(\textit{the freezing point constant}, k_f, \textit{for water is } 1.86°C mol^{-1} kg^{-1}).$$

(b) If Z contains carbon, 66.7%, hydrogen, 11.1% and the rest being oxygen

- **(i) Calculate the simplest formula of Z**
- **(ii) Determine the molecular formula of Z**
- **(iii) Write the structures of all possible isomers of Z**

(c) Z forms a yellow precipitate with phenyl hydrazine and iodine solution in presence of sodium hydroxide. Name Z.

(a)

$$250g \text{ of water dissolve } 7.2g \text{ of } Z$$

$$1000g \text{ of water will dissolve } \left(\frac{1000 \times 7.2}{250}\right) g \text{ of } Z$$

$$= 28.8g \text{ of } Z$$

$$\boldsymbol{\Delta T_f = T^0_{f(water)} - T_{f(solution)} = (0 - -0.744) = 0.744°C}$$

$$0.744°C \text{ is depression in freezing point caused by } 28.8g \text{ of} Z$$

$$1.86°C \text{ is depression in freezing point caused by } \left(\frac{1.86 \times 28.8}{0.744}\right) = 72g$$

$$\boldsymbol{\text{Molecular mass of } Z \text{ is } 72g}$$

(b) (i) $\text{percentage mass of } O = 100 - 66.7 - 11.1 = 22.2$

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

$$\boldsymbol{\text{Simplest formula is } C_4H_8O}$$

(iii)

$$(C_4H_8O)_n = 72$$

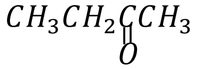
$$(48 + 8 + 16)n = 72$$

$$72n = 72$$

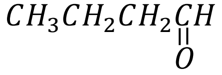
$$n = 1$$

$$\boldsymbol{\text{Molecular formula is } C_4H_8O}$$

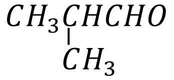
(iv)



$CH_3CH_2\underset{\underset{O}{\|}}{C}CH_3$



$CH_3CH_2CH_2\underset{\underset{O}{\|}}{C}H$



$CH_3\underset{\underset{CH_3}{|}}{C}HCHO$

(c) **Z is Butanone**

Questions

1. A solution containing 0.368g of methanoic acid in 50g of benzene freezes at 5.093°C.
   (a) Calculate the relative molecular mass of methanoic acid.
   $(k_f\ for\ water = 1.86°Cmol^{-1}kg^{-1})$
   (b) Comment on the value in (a)
2. The melting point of camphor is 177.5°C while that of a solution containing 1g of naphthalene in 10g of camphor is 147°C. Calculate the cryoscopic constant of camphor. (Molar mass of naphthalene is 128)
3. The freezing point of a solution of 22.0g of carbon tetrachloride dissolved in 800g of benzene is 4.59 °C. If the freezing point of benzene is 5.50 °C Calculate the molal freezing point depression constant of benzene.
4. Calculate the freezing point of a solution containing 3.33g of ethane-1,2-diol in 14g of water. $(k_f for\ water\ is\ 1.86°Cmol^{-1}kg^{-1})$
5. Calculate the freezing point of a solution containing 60g of glucose, $C_6H_{12}O_6$in 200g of water. $(k_f for\ water\ is\ 1.86°Cmol^{-1}kg^{-1})$
6. A solution containing 25.6g of sulphur dissolved in 1000g of naphthalene gave a freezing point lowering of 0.680°C. Determine the molecular formula of sulphur in naphthalene.
   $(The\ freezing\ point\ and\ k_f for\ sulphur\ are\ 80.1°C\ \ and\ 6.8°Cmol^{-1}kg^{-1})$
7. An organic compound W contains 22.8% nitrogen, 28% oxygen , 8.5% hydrogen and the rest being carbon.
   (a) Calculate the empirical formula of ***W***
   (b) 0.5g of W dissolved in 80g of water forming a solution that freezes at -0.197 °C. Calculate the molecular formula of ***W***.
   $(Cryoscopic\ constant\ for\ water\ is\ 1.86°Cmol^{-1}per\ 1000g\ of\ water)$.
   (c) When ***W*** was refluxed with potassium hydroxide, ethanoic acid and ammonia was produced.
      (i) Identify ***W***
      (ii) Write equations to show how ***W*** is obtained from a carbonyl compound.
8. (a) A compound ***Y*** contains 80% carbon, 6.7% hydrogen, and the rest being oxygen.
   Calculate the empirical formula of ***Y***.
   (b) 0.48g of ***Y*** was dissolved in 50.0g of benzene and caused a freezing point depression of 0.44°C. Determine the molecular formula of ***Y***.
   $(k_f for\ benzene\ is\ 5.5°Cmol^{-1}kg^{-1})$

(c) Compound ***Y*** forms a yellow precipitate with 2,4-dinitrophenylhydrazine and reacts with a mixture of iodine and sodium hydroxide to form a yellow precipitate. Write;

(i) the structural formula of ***Y***

(ii) equation and outline mechanism for the reaction between ***Y*** and 2,4-dinitrophenylhydrazine.

9. $0.3g$ of an organic compound ***Y*** on complete combustion gave 0.88g of carbon dioxide gas and 0.18g of water. 0.53g of ***Y*** in 22g of ethanoic acid lowered the freezing point of ethanoic acid by 0.78K. ($k_f for\ ethanoic\ acid\ is$ $3.89Kmol^{-1}$)

(a) (i) Calculate the empirical formula of ***Y***.

(ii) Determine the molecular mass of ***Y*** and write the possible structural formula of ***Y***.

(b) ***Y*** burns with a yellow sooty flame, gives a yellow precipitate with 2,4-dinitrophenylhydrazine but does not form silvery deposits with ammoniacal silver nitrate solution.

(i) Identify ***Y***

(ii) Write an equation and suggest a possible mechanism between ***Y*** and 2,4-dinitrophenylhydrazine in acidic media.

(c) Write equations indicating conditions to show how you would obtain phenylethyne from ***Y***.

10. (a) Define the term freezing point depression constant of a solvent.

(b) In an experiment, a 5 per cent solution of glucose, $C_6H_{12}O_6$ in water found give the same freezing point depression as a 3.3 percent aqueous solution of $C_nH_{2n}O_n$.

(i) Determine the molecular formula of $C_nH_{2n}O_n$.

(ii) The compound in b (i) above forms a crystalline white precipitate with saturated sodium hydrogen sulphite solution but no observable change with ammoniacal silver nitrate solution. It also reacts with ethanoic acid in the presence of concentrated sulphuric acid to give a product with a sweet fruity smell. Write the structural formula and name of $C_nH_{2n}O_n$.

11. (a) Describe an experiment to determine the relative molecular mass of naphthalene in benzene. (Include a well labelled diagram to illustrate your answer)

(b) The freezing point of pure benzene is $5.481°C$. A solution containing 0.321g of naphthalene, $C_{10}H_8$ in 25g of benzene freezes at $4.971°C$. A solution containing 0.305g of benzoic acid in 25g of the same solvent freezes at $5.226°C$

(i) Calculate the molar freezing point depression constant for benzene.

(ii) Hence calculate the relative molecular mass of benzoic acid in benzene.

Also revisit questions 15, 18 and 19 under empirical and molecular formulae in matter

Graphical representation of freezing point depression

The depression in freezing point is proportional to the lowering in vapour pressure

$$\Delta T \propto \Delta p$$

Since the lowering in vapour pressure is directly proportional to the concentration of solute and inversely proportional to relative molecular mass of the solute;

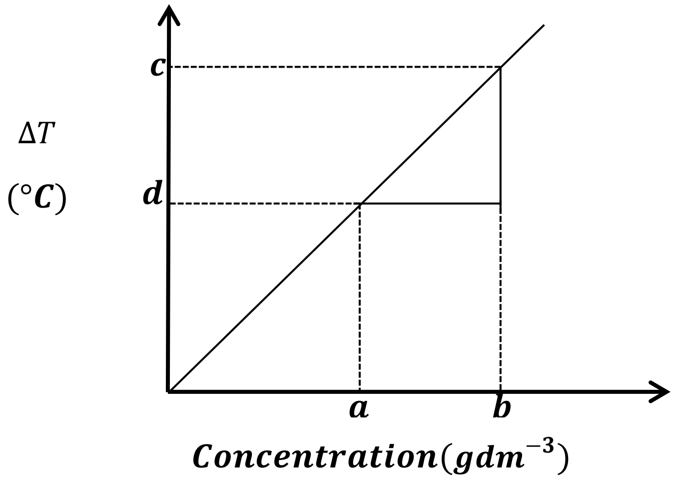
$\Delta p \propto \frac{C}{M_r}$, where C is concentration in grams of solute per litre of solvent

This implies that $\Delta T \propto \frac{C}{M_r}$

$$\Delta T = K_f \frac{C}{M_r}$$

$\boldsymbol{\Delta T = \frac{K_f}{M_r} C}$ where the constant K_f is the freezing point constant

A graph of boiling point elevation , ΔT against concentration can be plotted



A graph of depression in freezing point (ΔT) against $concentration(gdm^{-3})$ of solute in a solvent is a straight line through the origin.

The slope of the graph gives the value $\frac{K_f}{M_r}$

$$Slope = \frac{\boldsymbol{c-d}}{\boldsymbol{b-a}} = \frac{K_f}{M_r}$$

If K_f of the solvent is known, the relative molecular mass of the solute can be calculated.

The data you are usually given may require you to calculate ΔT first before graph plotting.

From the expression; $\Delta T = \frac{K_f}{M_r} C$

$$T^0_{f(water)} - T_{f(solution)} = \frac{K_f}{M_r} C$$

$$T_{f(solution)} = -\frac{K_f}{M_r} C \ - T^0_{f(solvent\ )}$$

A graph of freezing point of solution, $T_{f(solution)}$ when plotted against concentration will be a straight line with a negative slope. The $\boldsymbol{slope = -\frac{K_f}{M_r}}$ from which molar mass of the solute can be obtained if K_f is known. The graph has an intercept on the $T_{f(solution)}$ axis. The intercept gives the freezing point of pure solvent, $T^0_{f(solvent\ )}$.

Questions

1. The table below shows the freezing points of various concentrations of a non-volatile solute $\boldsymbol{Q}$ in water at 760mmHg.

Concentration of Q (gdm^{-3})	0	30	60	90	120	150
Freezing point$(°C)$	0	-0.16	-0.32	-0.49	-0.65	-0.81

   (a) Plot a graph of freezing point depression against concentration of $\boldsymbol{Q}$

   (b) Determine the :

   (i) slope of the graph you have drawn in (a).

   (ii) relative molecular mass of $\boldsymbol{Q}$. (K_f *of water is* $1.86°Ckg^{-1}mol^{-1}$)

2. (a) State what is meant by the following terms

   (i) Colligative property

   (ii) Freezing point constant of a substance

   (b) (i) Describe an experiment to determine the molecular mass of naphthalene using camphor as a solvent. (Diagram not required)

   (ii) State three limitations of the method in (b)(i) above.

   (c) The freezing points of solutions of various concentrations of a solute $\boldsymbol{X}$ in solvent $\boldsymbol{Y}$ at 1.0 atm are given below.

Concentration (gdm^{-3})	20	40	60	80	100	120	140
Freezing point$(°C)$	-0.11	-0.22	-0.32	-0.43	-0.54	-0.65	-0.76

   (i) Plot a graph of freezing point against concentration

   (ii) Use your graph to determine the freezing point of $\boldsymbol{Y}$

   (iii) Determine the relative molecular mass of $\boldsymbol{X}$. (K_f *of Y is* $1.86°Ckg^{-1}mol^{-1}$)

   (d) Ethanoic acid has a freezing point of $16.63°C$. On addition of 2.5g of an organic solute to 40g of the acid, the freezing point was lowered by $15.48°C$. Calculate the molecular mass of the solute. (K_f *of ethanoic acid is* $3.9°Ckg^{-1}mol^{-1}$)

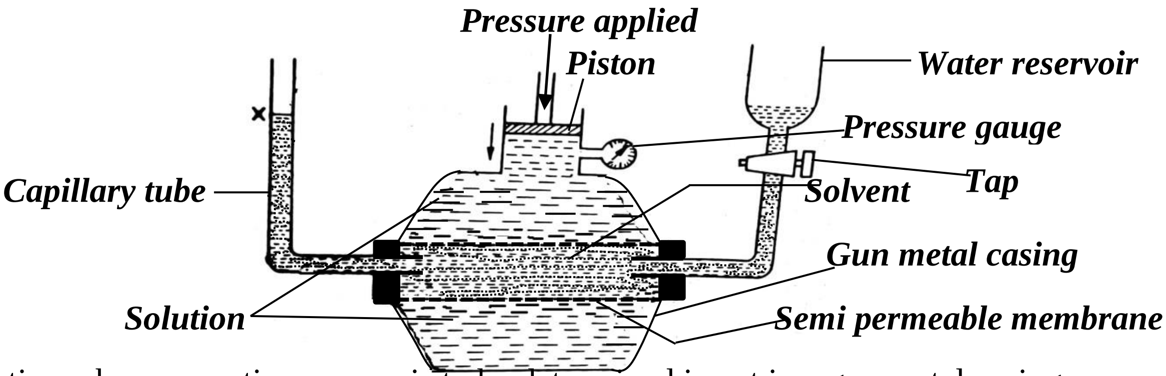
Osmotic pressure, π

Osmosis is the movement of solvent molecules from a dilute solution to a more concentrated solution through a semi-permeable membrane.

If two solutions of different concentrations are separated by a semi-permeable membrane, the solvent molecules from the dilute solution will pass through the semi-permeable membrane to the concentrated solution so that the two solutions have equal concentrations. The osmosis can be stopped by applying pressure on the concentrated solution. This pressure is called **osmotic pressure, π**.

Osmotic pressure is the minimum pressure required to prevent the movement of solvent molecules from a dilute solution to a more concentrated solution when the solution is separated from pure solvent by a semi-permeable membrane.

Experiment to determine osmotic pressure of a solution
(Using the Berkeley and Hartley's method)



A solution whose osmotic pressure is to be determined is put in a gun metal casing
The solution is separated from the solvent in a cylindrical porous tube by a semi-permeable membrane.
External pressure is applied by pushing down the piston until the level of the solvent in the capillary tube is just stationary.
This applied pressure is the osmotic pressure of the solution and is read off directly from the pressure gauge.

Suitability of osmotic pressure in determining molecular mass of non-volatile large molecules e.g. proteins or polymers or plastics

Osmotic pressure is a better method to determine relative molecular mass of large molecules than ebullioscopic and cryoscopic methods because;

Polymers have ***high relative molecular masses*** *and in dilute solutions, the* ***give few dissolved particles.*** *Relative molecular mass is* ***inversely proportional*** *to either freezing point depression or boiling point elevation. The freezing point depression or boiling point depressions caused by the few dissolved polymer particles in dilute* ***solutions are very small and cannot be measured by ordinary thermometers****. However, dilute solutions of polymers have* ***reasonable and accurately measurable osmotic pressures at room temperature****.*
In addition, the ebullioscopic method is not suitable because ***polymers tend to fragment and decompose at high temperatures****.*

In general, the advantages of the osmotic pressure are;

1. Osmotic pressure of a solution containing few particles is appreciable and can be measured accurately than its elevation in boiling point or depression in freezing point
2. Osmotic pressure can be measured at room temperature hence more suitable for substances that are not stable at higher temperatures.

Determination of relative molecular mass by osmotic pressure measurement

If the osmotic pressure of a solution containing $m\ g$ of a solute in $V\ cm^3$ of solution is measured at a temperature, T , the number of moles of solute, n can be determined from the expression;

$$\pi V = nRT$$

$$where\ \pi\ is\ the\ osmotic\ pressure, R\ is\ the\ molar\ gas\ constant, T\ is\ the\ absolute\ temperature$$

Since $n = \frac{m}{M_r}$ where M_r is the molar mass of the solute.

Then;

$$\pi V = \frac{m}{M_r} RT$$

$$\boldsymbol{M_r = \frac{mRT}{\pi V}}$$

The molar gas constant, R, is commonly used as $8.31 JK^{-1}mol^{-1}$ when the units of pressure, volume and temperature are $pascals(Pa)/Nm^{-2}, m^3$ and Kelvin respectively.

Recall that;

$$1\ Nm^{-2} = 1\ Pa$$

$$1\ atm = 101325\ Pa$$

$$760\ mmHg = 101325 Pa$$

$$therefore\ 720\ mmHg = \left(\frac{720}{760} \times 101325\right) Pa$$

$$1\ kNm^{-2} = 1\ kPa = 1000\ Nm^{-2}$$

$$1\ cm^3 = 10^{-6} m^3$$

$$1\ litre/dm^3 = 1000\ cm^3 = 10^{-3} m^3$$

Calculations involving osmotic pressures and molar masses

Examples

1. **Calculate the osmotic pressure of a solution containing 4.0g of a non-volatile solute per litre of solution at $27°C$. The relative molecular mass of the solute is 40.**

$$\pi = ? \qquad m = 4.0g$$
$$T = (27 + 273) = \mathbf{300K}$$
$$V = 1000cm^3 = \mathbf{10^{-3}m^3}$$
$$R = 8.31JK^{-1}mol^{-1}$$
$$From\ \pi V = nRT$$
$$\pi V = \frac{m}{M_r}RT$$

$$\pi = \frac{m}{M_r}\frac{RT}{V}$$
$$\pi = \frac{4.0 \times 8.31 \times 300}{40 \times 10^{-3}}$$
$$\boldsymbol{\pi = 249300\ Pa}$$

2. **A solution containing 1.5% of a polymer was found to have an osmotic pressure of $\mathbf{3.6 \times 10^{-4}}$ atmospheres at $\mathbf{25°C}$. Calculate the molecular mass of the polymer.**

For osmotic pressure ONLY; 1.5% means 1.5g in a volume of 100cm^3

$$m = 1.5g$$
$$V = 100cm^3 = \mathbf{100 \times 10^{-6}m^3}$$
$$\pi = 3.6 \times 10^{-4} \times 101325\ Nm^{-2}$$
$$T = (25 + 273) = \mathbf{298K}$$
$$R = 8.31JK^{-1}mol^{-1}$$
$$From\ \pi V = nRT$$

$$\pi V = \frac{m}{M_r}RT$$
$$M_r = \frac{mRT}{\pi V}$$
$$M_r = \frac{1.5 \times 8.31 \times 298}{3.6 \times 10^{-4} \times 101325 \times 100 \times 10^{-6}}$$
$$\boldsymbol{M_r = 1018332.1\ g}$$

The molecular mass of the polymer is 1,018,332.1g

3. **The osmotic pressure of an aqueous solution of a non-electrolyte containing $\mathbf{5.43gdm^{-3}}$ of solution is $\mathbf{7.093\ x\ 10^4 Nm^{-2}}$ at $\mathbf{25°C}$. Calculate the freezing point of solution. ($\boldsymbol{Cryscopic\ constant\ of\ water\ is\ 1.86°C\ per\ 1000g\ mol^{-1}}$)**

$$m = 5.43g$$
$$V = 1\ dm^3 = \mathbf{10^{-3}m^3}$$
$$\pi = 7.093 \times 10^4\ Nm^{-2}$$
$$T = (25 + 273) = \mathbf{298K}$$
$$R = 8.31JK^{-1}mol^{-1}$$
$$From\ \pi V = nRT$$

$$\pi V = \frac{m}{M_r}RT$$
$$M_r = \frac{mRT}{\pi V}$$
$$M_r = \frac{5.43 \times 8.31 \times 298}{7.093 \times 10^4 \times 10^{-3}}$$
$$\boldsymbol{M_r = 189.58\ g}$$

The molar mass of the polymer is 189.58g

$$Molar\ mass\ of non - electrolyte\ solute = 189.58g$$

Assuming density of solution is $1gcm^3$. The volume of water used is $1000cm^3$ and its mass is 1000g.

$$189.58g\ of\ solute\ \ lower\ freezing\ point\ by\ 1.86°C$$
$$5.43g\ of solute\ \ lower\ freezing\ point\ by\ \left(\frac{5.43 \times 1.86}{189.58}\right)°C$$

$$\Delta T_f = 0.053\,°C$$

$$Depression\ of\ freezing\ point;$$

$$\Delta T_f = T^0_{f(solvent)} - T_{f(solution)}$$

$$T_{f(solution)} = 0 - 0.053$$

$$\boldsymbol{T_{f(solution)} = -0.053°C}$$

4. **The osmotic pressure of a solution containing 1.4g of a polymer X per 100 cm^3 of a solution is $\mathbf{1200\ Nm^{-2}}$ at $\mathbf{25°C}$.**
   (a) Calculate the relative molecular mass of X
   (b) Determine the number of monomers in X
   ($\boldsymbol{The\ molecular\ mass\ of\ the\ monomer\ of\ X\ is\ 28}$)

(a) $m = 1.4g$

$$V = \mathbf{100 \times 10^{-6} m^3}$$

$$\pi = 1200\ Nm^{-2}$$

$$T = (25 + 273) = \mathbf{298K}$$

$$R = 8.31JK^{-1}mol^{-1}$$

$$From\ \pi V = nRT$$

$$\pi V = \frac{m}{M_r}RT$$

$$M_r = \frac{mRT}{\pi V}$$

$$M_r = \frac{1.4 \times 8.31 \times 298}{1200 \times 100 \times 10^{-6}}$$

$$\boldsymbol{M_r = 28,891.1\ g}$$

The relative molecular mass of the polymer is 28,891.1g

(b) $number\ of\ monomers, n = \frac{molar\ mass\ of\ polymer}{molar\ mass\ of\ monomer} = \frac{28891.1}{28} = 1031.8 \approx \mathbf{1032}$

Note that number of monomers should never be a decimal but a whole number.

Questions

1. (a) Define the term **osmotic pressure**.
   (b) At $25°C$, a 1.24% solution of a polymer has an osmotic pressure of 3.1×10^{-3} atmospheres. Calculate the formula mass of the polymer.
   (c) Explain why in the determination of molecular mass of polymers, osmotic pressure is used instead of ebullioscopic and cryoscopic methods.
2. A solution containing $1.00g$ of polyphenylethene in 100 cm^3 of benzene is found to have an osmotic pressure of $59Pa$ at $27°C$. Calculate the average relative molecular mass of polyphenylethene.
3. The osmotic pressure of an aqueous solution of a non-electrolyte containing $8.15g$ per $1.5dm^3$ of solution is $7.093\ x\ 10^4 Nm^{-2}$ at $25°C$. Calculate the freezing point of solution.
   ($cryscopic\ constant\ of\ water\ is\ 1.86°C\ per\ 1000g\ mol^{-1}$)
4. (a) Define the term Osmotic pressure.

(b) A polysaccharide has the formula$(C_{12}H_{22}O_{11})_n$. A solution containing $5.00gdm^{-3}$ of the sugar has an osmotic pressure of $7.12\,x\,10^2Nm^{-2}$ at $20°C$. Find the value of n.

(c) State any two assumptions made in (b) above.

5. A solution containing 20g of a polymer ***X*** in one litre of solvent exerts an osmotic pressure 1.4 $mmHg$ at $25°C$.
   (i) Calculate the molecular formula of ***X***
   (ii) The molecular formula of the monomer of ***X*** is $CH_2 = CHCN$. Determine the number of monomer units in ***X***
   (iii) Explain why the freezing point depression method is not suitable for determining the molecular formula of ***X***.
6. A solution of 42.0g of mannitol in $1\,dm^3$ of water has an osmotic pressure of $5.624 \times 10^5\ Pa$ at $20°C$. Calculate the relative molecular mass of mannitol.
7. A 7% aqueous solution of compound A has an osmotic pressure of $7067.9mmHg$ at $18°C$. Calculate the relative molecular mass of A.
8. A 3.42% solution of substance ***X*** has the same osmotic pressure as a 5.96% solution of substance ***Y***. Calculate the relative molecular mass of ***Y***. (Relative molecular mass of ***X*** is 342)
9. (a) Define the terms;
   (i) osmosis
   (ii) Osmotic pressure
   (b) State conditions under which osmotic pressure laws are valid.
   (c) (i) Describe a method that can be used to determine the osmotic pressure of a sucrose solution.
   (ii) The osmotic pressure of a solution containing 1.4% of a polymer is $1.184\,x\,10^{-2}atm$ at $25°C$. Determine the relative formula mass of the polymer.
   (iii) Briefly explain why osmotic pressure method is the preferred method to determine the relative formula mass of polymers.

Determining relative molecular mass from osmotic-pressure- concentration graphs

From $\pi V = nRT$

$$\pi = \frac{nRT}{V} \text{ but } n = \frac{mass}{RFM} = \frac{m}{RFM}$$

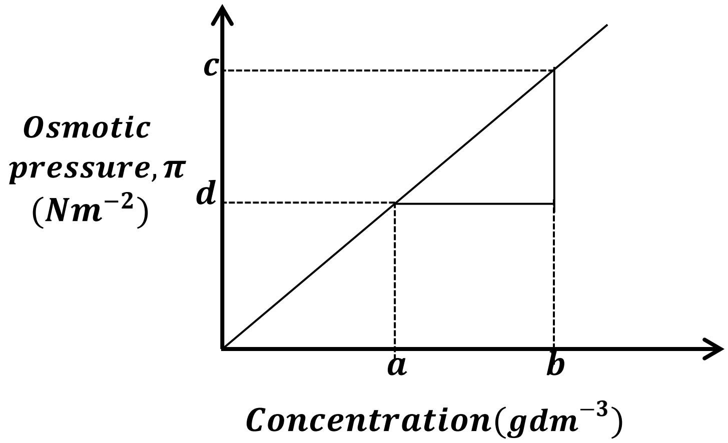
$$\pi = \frac{mRT}{RFM \times V}$$

$$\pi = \left(\frac{m}{V}\right)\frac{RT}{RFM}$$

$$\text{but } \left(\frac{m}{V}\right) = concentration(gdm^{-3}), C$$

$$\boldsymbol{\pi = \frac{RT}{RFM}C}$$

A graph of osmotic pressure, $\boldsymbol{\pi}$ against concentration$(\boldsymbol{gdm^{-3}})$ can be plotted.



A graph of osmotic pressure, $\boldsymbol{\pi}$ against $concentration(gdm^{-3})$ of solute in a solvent is a straight line through the origin.

The slope of the graph gives the value $\frac{RT}{RFM}$

$$Slope = \frac{\boldsymbol{c-d}}{\boldsymbol{b-a}} = \frac{RT}{RFM}$$

The expression $Slope = \frac{RT}{RFM}$ is used to calculate the relative molecular mass of the solute where $R = 8.31JK^{-1}mol^{-1}$ and T given in the question.

Note that if the values of osmotic pressure given are in atm or mmHg, they should be converted as discussed earlier to $\boldsymbol{Nm^{-2}}$ while computing the slope and then use R as stated with T converted to Kelvin.

Questions

1. The osmotic pressures of various concentrations of solute $\boldsymbol{X}$ in methylbenzene at $25°C$ are given in the table below.

Concentration of the solution($\boldsymbol{gdm^{-3}}$)	1.0	2.0	3.0	4.0	5.0	6.0
Osmotic pressure($\boldsymbol{Nm^{-2}}$)	23	37	53	75	92	109

(a) Plot a graph of osmotic pressure against concentration

(b) Use your graph to determine the relative molecular mass of $\boldsymbol{X}$.

2. (a) Define the terms
    - (i) Colligative property
    - (ii) Osmotic pressure

   (b) (i) Describe an experiment to determine the molecular mass of mannitol by osmotic pressure method.
   (ii) State three limitations on this method

   (c) The table below shows the osmotic pressure of a solution of mannitol of various concentrations at $25°C$.

Concentration of the solution(gdm^{-3})	1.5	3.0	4.5	6.0	7.5	9.0	10.5
Osmotic pressure of the solution(atm)	0.20	0.40	0.60	0.81	1.05	1.20	1.40

   - (i) Plot a graph of osmotic pressure against concentration of the solution
   - (ii) Explain the shape of the graph
   - (iii) Use the graph to determine the relative molecular mass of mannitol.

Miscellaneous questions

1. (a) Define the term **colligative property**.
   (b) State four colligative properties of a solution.
   (c) (i) Define the term mole fraction.
   (ii) Calculate the mole fraction of potassium chloride in an aqueous solution containing $10g$ of potassium chloride per $100g$ of water. ($K = 39, Cl = 35.5$)
2. (a) Define the terms;
   - (i) Colligative property
   - (ii) Boiling point constant

   (b) Describe an experiment that you would carry out to determine the relative molecular mass of a compound using the boiling point elevation method. Use a diagram to illustrate your answer.
   (c) Explain the effect of association of the solute on the value of the relative molecular mass determined by boiling point method.
   (d) (i) State the laws of osmotic pressure.
   (ii) State the conditions under which these laws are valid.
   (e) The osmotic pressure of a 1.24% solution of polyvinylchloride is $2.356 \times 10^{-2}\ mmHg$ at $25°C$. Calculate the;
   - (i) relative molecular mass of polyvinylchloride
   - (ii) number of monomer units in polyvinylchloride.

3. Explain the following observations;

(a) When propanone is mixed with tetrachloromethane, a warm miscible mixture was formed whose volume was lower than the sum of the volumes of the individual components.

(b) The boiling points of water and bromobenzene are $100°C$ and $156°C$ respectively. However a mixture of water and bromobenzene boils below $100°C$ at atmospheric pressure.

(c) A 0.01M solution of sodium chloride has the same freezing point depression as a 0.02M aqueous solution of glucose

(d) An aqueous solution of ethanol boils at $78.2°C$ whereas an aqueous solution of sodium chloride boils at $106°C$ at $760\ mmHg$.

(e) When steam at $100°C$ is blown into an aqueous solution of a solid at $100°C$, it raises the temperature of the solution above $100°C$.

(f) Boiling point elevation method is not suitable for measuring relative molecular mass of a plastic.

(g) The osmotic pressure method cannot be used to measure the relative molecular mass of sulphuric acid in solution

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.

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

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

$$H_2C = CH_2(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O\ (l)$$

(ii) Burning magnesium in air to form magnesium oxide

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

(iii) Alkaline hydrolysis of an ethylethanoate to form ethanoate ions and ethanol

$$CH_3COOC_2H_5\ (aq) + \bar{O}H(aq) \longrightarrow CH_3CO\bar{O}(aq) + CH_3CH_2OH\ (aq)$$

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.

$$H_2(g) + I_2\ (g) \rightleftharpoons 2HI(g)$$

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 occuring.

Types of chemical equilibria

There are two types equilibrium systems namely;

(i) Homogeneous equilibrium systems
(i) 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;

(i) the reaction between ethanol and ethanoic acid to form ethyl ethanoate /diethyl ether (esterification)

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$$

(ii) the reaction between hydrogen gas and gaseous iodine to form hydrogen iodide

$$H_2(g) + I_2\ (g) \rightleftharpoons 2HI(g)$$

(iii) Dissociation of dinitrogen tetroxide to form nitrogen dioxide.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

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.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

(ii) Reaction between iron and steam to form triiron tetraoxide and hydrogen

$$3Fe(s) + 4\,H_2O\ (g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

(iii) Reaction between bismuth chloride and water to form bismuth oxychloride and hydrochloric acid

$$BiCl_3(aq) + H_2O\ (l) \rightleftharpoons BiOCl(s) + 2HCl(aq)$$

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;

$$wA + xB \rightleftharpoons yC + zD$$

$$\frac{[C]^y[D]^z}{[A]^w[B]^x} = \boldsymbol{a\ constant\ at\ a\ given\ temperature} = \boldsymbol{K_c}$$

Where **[ ]** *represents molar concentration at equilibrium and*

K_c is the <u>concentration equilibrium constant</u>

The equilibrium law/ law of mass action therefore states that if a <u>reversible reaction</u> is allowed to <u>reach equilibrium</u> at a <u>particular temperature</u>, 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 <u>a constant</u>

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 $\boldsymbol{K_p}$

For example;

$$aX(g) + bY(g) \rightleftharpoons cZ(g)$$

$$\boldsymbol{K_p} = \frac{(\boldsymbol{p_Z})^C}{(\boldsymbol{p_X})^a(\boldsymbol{p_Y})^b}$$

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 $\boldsymbol{K_c}$ should be written.
3. If **total pressure** at equilibrium is given, then expression for $\boldsymbol{K_p}$ should be written.
4. Solids **do not** appear in the equilibrium constant expression since their concentration is assumed to be constant.
5. For a $\boldsymbol{K_p}$ 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 $\boldsymbol{K_c}$**,** strictly square brackets must be used.
9. Sometimes the question may specify for you whether to write a $\boldsymbol{K_c}$ or $\boldsymbol{K_p}$ 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 ($\boldsymbol{K_c}$)
2. The reaction between hydrogen gas and gaseous iodine.(*both* $\boldsymbol{K_c}$*and* $\boldsymbol{K_p}$)
3. Dissociation of dinitrogen tetroxide to form nitrogen dioxide.(*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)
4. Reaction between iodine solution and potassium iodide.($\boldsymbol{K_c}$**)**
5. Thermal dissociation of calcium carbonate.(*both* $\boldsymbol{K_c}$*and* $\boldsymbol{K_p}$)
6. Reaction between iron and steam to form triiron tetraoxide and hydrogen .
(*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)
7. Hydrolysis of bismuth(III) chloride.**(**$\boldsymbol{K_c}$**)**
8. Reaction between hydrogen and nitrogen.(*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)
9. Hydrolysis of ethylethanoate using dilute hydrochloric acid.($\boldsymbol{K_c}$**)**
10. Reaction of phosphorus trichloride and chlorine.(*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)
11. Reaction between nitrogen and oxygen.(*both* $\boldsymbol{K_c}$*and* $\boldsymbol{K_p}$)
12. Conversion of Sulphur dioxide to Sulphur trioxide.(*both* $\boldsymbol{K_c}$*and* $\boldsymbol{K_p}$)
13. Reaction between carbon monoxide and hydrogen to form gaseous methanol.(*both* $\boldsymbol{k_c}$ *and* $\boldsymbol{K_p}$)
14. Dissociation of hydrogen iodide.(*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)
15. Dissociation of phosphorus(V) chloride to phosphorus(III) chloride and chlorine.(*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)
16. Dissociation of Sulphur trioxide.(*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)
17. Reaction between carbon disulphide and hydrogen to form methane and hydrogen sulphide. .(*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)
18. Reaction between ammonia and oxygen to form nitrogen monoxide and water. (*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)
19. Redox reaction between iron metal and chromium(III) ions. ($\boldsymbol{K_c}$)
20. Hydrogenation of nitrogen dioxide to form ammonia and water.(*both* $\boldsymbol{K_c}$ *and* $\boldsymbol{K_p}$)

The relationship between K_p and K_c

k_p is related to k_c by the expression;

$$\boldsymbol{k_p = K_c(RT)^{\Delta n}}$$

where $\boldsymbol{K_p}$ *is the pressure equilibrium constant*

$\boldsymbol{K_c}$ *is the concentration equilibrium constant*

$\boldsymbol{R}$ *is the molar gas constant* $(8.314 Jmol^{-1}K^{-1})$

$\boldsymbol{T}$ *is the absolute temperature(K)*

$\Delta\boldsymbol{n}$ *is the difference between total moles of gaseous products and total moles of gaseous reactants*

Derivation;

Consider a reversible reaction;

$$wA + xB \rightleftharpoons yC + zD$$

$$\boldsymbol{K_c} = \frac{[C]^y[D]^z}{[A]^w[B]^x} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots .(i)$$

If the reactants and products are gaseous,

$$\boldsymbol{K_p} = \frac{(p_c)^y(p_D)^z}{(p_A)^w(p_B)^x} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots ..(ii)$$

If the gases are ideal, then according to the ideal gas equation

$$pV = nRT \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (iii)$$

$$p = \frac{nRT}{V} \; but \; \frac{n}{V} = C \; (concentration\,)$$

$$pV = CRT$$

p is therefore proportional to C

From equation (iii), $p_A = [A]RT \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots *_1$

$$p_B = [B]RT \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots .*_2$$

$$p_C = [C]RT \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots ..*_3$$

$$p_D = [D]RT \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots ..*_4$$

Substituting for p_A , p_B, p_C and p_D in equation (ii) gives;

$$\boldsymbol{K_p} = \frac{([C]RT)^y([D]RT)^z}{([A]RT)^w([B]RT)^x}$$

$$\boldsymbol{K_p} = \left(\frac{[C]^y[D]^z}{[A]^w[B]^x}\right)\frac{(RT)^y(RT)^z}{(RT)^w(RT)^x}$$

Since $\boldsymbol{K_c} = \frac{[C]^y[D]^z}{[A]^w[B]^x}$, *then* $\boldsymbol{K_p}$ *becomes*;

$$\boldsymbol{K_p} = \boldsymbol{K_c}\frac{(RT)^{(y+z)}}{(RT)^{(w+x)}}$$

$$\boldsymbol{K_p} = \boldsymbol{K_c}(\boldsymbol{RT})^{((y+z)-(w+x))}$$

$$(y+z)-(w+x)=\Delta n$$

$$\boldsymbol{K_p = K_c(RT)^{\Delta n}}$$

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***

$$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O\ (l)$$

*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	$\boldsymbol{a-x}$	$\boldsymbol{b-x}$	$\boldsymbol{x}$	$\boldsymbol{x}$
concentration	$\frac{a-x}{v}$	$\frac{b-x}{v}$	$\frac{x}{v}$	$\frac{x}{v}$

$$\boldsymbol{K_c} = \frac{[CH_3COOH][CH_3CH_2OH]}{[CH_3COOCH_2CH_3][H_2O]}$$

$$\boldsymbol{K_c} = \frac{({}^{x}/_{v})({}^{x}/_{v})}{\left(\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)\right)}$$

$$\boldsymbol{K_c} = \frac{\boldsymbol{x^2}}{\boldsymbol{(a-x)(b-x)}}$$

(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***

$$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O\ (l)$$

*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

moles of ethanoic acid at equilibrium=x

moles of ethanoic acid converted to ester and water =(a-x)

since mole ratio of $CH_3COOH : CH_3COOCH_2CH_3 : H_2O = 1:1:1$

(a-x) moles of CH_3COOH *form (a-x) moles of* H_2O *and (a-x) moles of* $CH_3COOCH_2CH_3$ *at equilibrium.*

Since mole ratio of $CH_3COOH : CH_3CH_2OH = 1:1$

Moles of ethanol that react=(a-x)

Moles of ethanol at equilibrium=b-(a-x) =(b-a+x)

	$\boldsymbol{CH_3COOH(l)}$	$+ \boldsymbol{CH_3CH_2OH(l)}$	$\rightleftharpoons \boldsymbol{CH_3COOCH_2CH_3\ (l)}$	$+ \boldsymbol{H_2O\ (l)}$
Initial moles	*a*	*b*	*0*	*0*
Moles reacted/ formed	$a-x$	$a-x$	$a-x$	$a-x$
Moles at equilibrium	$\boldsymbol{x}$	$\boldsymbol{b-a+x}$	$\boldsymbol{a-x}$	$\boldsymbol{a-x}$
Concentration	$\frac{x}{v}$	$\frac{b-a+x}{v}$	$\frac{a-x}{v}$	$\frac{a-x}{v}$

$$\boldsymbol{K_c} = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$

$$\boldsymbol{K_c} = \frac{\left(\frac{a-x}{v}\right)\left(\frac{a-x}{v}\right)}{\left(\left(\frac{x}{v}\right)\left(\frac{b-a+x}{v}\right)\right)}$$

$$\boldsymbol{K_c} = \frac{\boldsymbol{(a-x)^2}}{\boldsymbol{x(b-a+x)}}$$

(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 dm^3)** and kept in a **thermostat at a temperature of** 450℃ 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***

$$I_2(aq) \quad + \quad 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) \quad + \quad S_4O_6^{2-}(aq)$$

*The **amount of iodine present at equilibrium is obtained**.*

Treatment of results

Total volume of the bulb= v dm^3

Number of moles of hydrogen iodide heated= c moles

Degree of dissociation of hydrogen iodide= α

	$\boldsymbol{2HI(g)}$	$\rightleftharpoons \boldsymbol{H_2(g)}$ +	$\boldsymbol{I_2\ (g)}$
Initial moles	n	*0*	*0*
Moles dissociated/formed	$n\alpha$	$\frac{n\alpha}{2}$	$\frac{n\alpha}{2}$
Moles at equilibrium	$\boldsymbol{n - n\alpha}$	$\boldsymbol{\frac{n\alpha}{2}}$	$\boldsymbol{\frac{n\alpha}{2}}$
Concentration at equilibrium	$\frac{n(1-\alpha)}{v}$	$\frac{n\alpha}{2v}$	$\frac{n\alpha}{2v}$

$$\boldsymbol{K_c} = \frac{[H_2][I_2]}{[HI]^2}$$

$$\boldsymbol{K_c} = \frac{\left(\frac{n\alpha}{2v}\right)^2}{\left(\frac{n(1-\alpha)}{v}\right)^2}$$

$$\boldsymbol{K_c} = \frac{\boldsymbol{\alpha^2}}{\boldsymbol{4(1-\alpha)^2}}$$

(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 dm^3)****, kept in a* ***thermostat at a temperature of*** **450**℃ *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***

$$I_2(aq) \quad + \quad 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) \quad + \quad S_4O_6^{2-}(aq)$$

The ***amount of iodine present at equilibrium is obtained****.*

Treatment of results

Total volume of the bulb= v dm^3

Let number of moles of iodine converted to hydrogen iodide= x moles

Moles of hydrogen iodide formed = 2x moles

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$
Initial moles	a	b	0
Moles reacted/formed	x	x	$2x$
Moles at equilibrium	$\boldsymbol{a-x}$	$\boldsymbol{b-x}$	$\boldsymbol{2x}$
Concentration at equilibrium	$\frac{(a-x)}{v}$	$\frac{b-x}{v}$	$\frac{2x}{v}$

$$\boldsymbol{K_c} = \frac{[HI]^2}{[H_2][I_2]}$$

$$\boldsymbol{K_c} = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)}$$

$$\boldsymbol{K_c} = \frac{4x^2}{(a-x)(b-x)}$$

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)

$$Molar\ mass\ of\ \boldsymbol{CH_3COOH} = (2\times12)+(2\times16)+(4\times1) = 60g$$

$$Molar\ mass\ of\ \boldsymbol{CH_3CH_2OH} = (2\times12)+(6\times1)+(1\times16) = 46g$$

$$Moles\ of\ \boldsymbol{CH_3COOH} = \frac{60}{60} = 1.0\ moles$$

$$Moles\ of\ \boldsymbol{CH_3CH_2OH} = \frac{46}{46} = 1.0\ moles$$

$$Molar\ mass\ of\ \boldsymbol{H_2O} = 2+16 = 18g$$

$$Molar\ mass\ of\ \boldsymbol{CH_3COOCH_2CH_3} = (4\times12)+(8\times1)+(2\times16) = 88g$$

$$Moles\ of\ \boldsymbol{H_2O}\ at\ equilibrium = \frac{12}{18} = 0.667\ moles$$

$$Moles\ of\ \boldsymbol{CH_3COOCH_2CH_3}\ at\ equilibrium = \frac{58.7}{88} = 0.6670\ moles$$

	$\boldsymbol{CH_3COOH(l)}$	$+\ \boldsymbol{CH_3CH_2OH(l)}$	$\rightleftharpoons \boldsymbol{CH_3COOCH_2CH_3\ (l)}$	$+\ \boldsymbol{H_2O\ (l)}$
Initial moles	1.0	1.0	*0*	*0*
Moles reacted/ formed	0.667	0.667	0.667	0.667
Moles at equilibrium	$\boldsymbol{1-0.667}$ $\boldsymbol{=0.333}$	$\boldsymbol{1-0.667}$ $\boldsymbol{=0.333}$	$\boldsymbol{0.667}$	$\boldsymbol{0.667}$

$$K_c = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$

$$K_c = \frac{(0.667)^2}{(0.333)^3}$$

$$\boldsymbol{K_c = 4.01}$$

(b)

$$Moles\ of\ \boldsymbol{CH_3COOH} = \frac{90}{60} = 1.5\ moles$$

$$Moles\ of\ \boldsymbol{CH_3CH_2OH} = \frac{92}{46} = 2.0\ moles$$

$$\boldsymbol{CH_3COOH(l)} + \boldsymbol{CH_3CH_2OH(l)} \rightleftharpoons \boldsymbol{CH_3COOCH_2CH_3\ (l)} + \boldsymbol{H_2O\ (l)}$$

Initial moles	1.5	2.0	0	0
Moles reacted/ formed	x	x	x	x
Moles at equilibrium	$\mathbf{1.5 - x}$	$\mathbf{2.0 - x}$	$\boldsymbol{x}$	$\boldsymbol{x}$

$$K_c = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$

$$4.01 = \frac{x^2}{(1.5 - x)(2.0 - x)}$$

$$3.01x^2 - 14.035x + 12.03 = 0$$

$$x = \frac{-(-14.035) \pm \sqrt{(-14.035)^2 - (4 \times 3.01 \times 12.03)}}{2 \times 3.01}$$

$$x = 3.48\ or\ 1.14$$

$But\ x\ cannot\ be\ 3.48\ since\ number\ of\ reacted\ moles\ cannot\ be\ greater\ than\ original\ moles$

$$\boldsymbol{x = 1.14}$$

$$Moles\ of\ \boldsymbol{CH_3COOCH_2CH_3}\ at\ equilibrium = x = 1.14\ moles$$

$$\boldsymbol{Mass\ of\ CH_3COOCH_2CH_3\ at\ equilibrium} = (\mathbf{1.14 \times 88}) = \mathbf{100.32}\boldsymbol{g}$$

2. **A 10.0$\boldsymbol{cm^3}$ 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

$$\boldsymbol{CH_3COOH(l)} + \boldsymbol{CH_3CH_2OH(l)} \rightleftharpoons \boldsymbol{CH_3COOCH_2CH_3\ (l)} + \boldsymbol{H_2O\ (l)})$$

Initial moles	0.0525	0.0515	0.0314	0.0167
Moles reacted/ formed	$0.0525 - 0.0255$ $= \mathbf{0.027}$	0.027	0.027	0.027
Moles at equilibrium	$\mathbf{0.0255}$	$\mathbf{0.0515 - 0.027}$ $= \mathbf{0.0245}$	$\mathbf{0.0314 + 0.027}$ $= \mathbf{0.0584}$	$\mathbf{0.0167 + 0.02}$ $= \mathbf{0.0437}$

$$K_c = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$

$$K_c = \frac{0.0437 \times 0.0584}{0.0255 \times 0.0245}$$

$$\boldsymbol{K_c = 4.08}$$

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$\boldsymbol{cm^3}$ of 0.2 M sodium hydroxide for complete neutralisation. Calculate the equilibrium constant, $\boldsymbol{K_c}$ for the reaction.**

$$Moles\ of NaOH\ that\ reacted\ with\ CH_3COOH\ present\ at\ equilibrium$$
$$= \left(\frac{289 \times 0.2}{1000}\right) = 0.0578\ moles$$
$$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)$$
$$Mole\ ratio\ of CH_3COOH: NaOH = 1:1$$
$$Moles\ of\ CH_3COOH\ present\ at\ equilibrium = (0.0578 \times 1) = 0.0578\ moles$$

	$CH_3COOH(l)$	$+\ CH_3CH_2OH(l)$	$\rightleftharpoons CH_3COOCH_2CH_3\ (l)$	$+\ H_2O\ (l)$
Initial moles	1.0	5.0	*0*	*0*
Moles reacted/ formed	$1 - 0.0578$ $= 0.9422$	0.9422	0.9422	0.9422
Moles at equilibrium	$\mathbf{0.0578}$	$5 - 0.9422$ $= \mathbf{4.0578}$	$\mathbf{0.9422}$	$\mathbf{0.9422}$

$$K_c = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$
$$K_c = \frac{(0.9422)^2}{(0.0578 \times 4.0578)}$$
$$\boldsymbol{K_c = 3.79}$$

(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.

$(\boldsymbol{a})$	$\boldsymbol{H_2(g)}$	$+\ \boldsymbol{I_2\ (g)}$	$\rightleftharpoons\ \boldsymbol{2HI(g)}$
Initial moles	3	1	*0*
Moles reacted/formed	x	x	$2x$
Moles at equilibrium	$\mathbf{3 - x}$	$\mathbf{1 - x}$	$\mathbf{2x}$

Taking volume of vessel to be one litre;

$$\boldsymbol{K_c} = \frac{[HI]^2}{[H_2][I_2]}$$

$$\mathbf{50} = \frac{(2x)^2}{(3-x)(1-x)}$$

$$46x^2 - 200x + 150 = 0$$

$$x = \frac{-(-200) \pm \sqrt{(-200)^2 - (4 \times 46 \times 150)}}{2 \times 46}$$

$$x_1 = 3.384 \quad and\ x_2 = 0.964$$

but x cannot be 3.384, because it gives a negative value for moles of hydrogen and iodine at equilibrium

$$therefore\ \boldsymbol{x = 0.964}$$

Moles of hydrogen iodide at equilibrium

$$= \boldsymbol{2x = 2 \times 0.964 = 1.938\ moles}$$

(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****.*

$$I_2(aq) \quad + \quad 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) \quad + \quad S_4O_6^{2-}(aq)$$

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 ^{o}C. When equilibrium was attained, the tube was rapidly cooled and found to contain 30.8 moles of hydrogen iodide.

(i) Give a reason why the tube was rapidly cooled.

(ii) 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 <u>to stop the reaction</u> *and* ***<u>fix the equilibrium</u>*** *such that the* ***equilibrium <u>does not adjust itself</u> to the <u>equilibrium value at a lower temperature</u>****.*

$(\boldsymbol{ii})$	$\boldsymbol{H_2(g)}$	+	$\boldsymbol{I_2(g)}$	$\rightleftharpoons$	$\boldsymbol{2HI(g)}$
Initial moles	25		18		0
Moles reacted/formed	x		x		$2x$
Moles at equilibrium	$\boldsymbol{25 - x}$		$\boldsymbol{18 - x}$		$\boldsymbol{30.8}$

$$2x = 30.8, \quad x = 15.4$$

$$[HI] = 30.8$$
$$[H_2] = 25 - 15.4 = 9.6$$
$$[I_2] = 18 - 15.4 = 2.6$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$K_c = \frac{(30.8)^2}{9.6 \times 2.6}$$

$$\boldsymbol{K_c = 38}$$

Note that $\boldsymbol{K_c}$ for the dissociation of HI is the reciprocal of $\boldsymbol{K_c}$ for reaction between hydrogen and iodine to form HI

For dissociation of hydrogen iodide,

	$2HI(g) \rightleftharpoons$	$H_2(g) +$	$I_2(g)$
Initial moles	c	0	0
Moles dissociated/formed	$c\alpha$	$\frac{c\alpha}{2}$	$\frac{c\alpha}{2}$
Moles at equilibrium	$\boldsymbol{c - c\alpha}$	$\boldsymbol{\frac{c\alpha}{2}}$	$\boldsymbol{\frac{c\alpha}{2}}$
Concentration at equilibrium	$\frac{c(1-\alpha)}{v}$	$\frac{c\alpha}{2v}$	$\frac{c\alpha}{2v}$

$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

$$K_c = \frac{\left(\frac{c\alpha}{2v}\right)^2}{\left(\frac{c(1-\alpha)}{v}\right)^2}$$

$$\boldsymbol{K_c = \frac{\alpha^2}{4(1-\alpha)^2}}$$

$$\textbf{But } \boldsymbol{K_c} \textbf{ for dissociation of } \boldsymbol{HI = \frac{1}{38}}$$

$$\frac{1}{38} = \frac{\alpha^2}{4(1-\alpha)^2}$$

$$4 - 8\alpha + 4\alpha^2 = 38\alpha^2$$

$$34\alpha^2 + 8\alpha - 4 = 0$$

$$\alpha = \frac{-(8) \pm \sqrt{(8)^2 - (4 \times 34 \times 4)}}{2 \times 34}$$

$$\alpha = -0.48 \ \ or \ 0.24$$

$$But\ \alpha\ cannot\ be\ negative$$

$$Therefore\ \ \boldsymbol{\alpha = \ 0.24}$$

---

3. When stoichiometric amounts of hydrogen and iodine were allowed to reach equilibrium in a 1 litre vessel at 450 °C and $\boldsymbol{1.01 \times 10^5 Nm^{-2}}$, 1.56 moles of hydrogen iodide were formed at equilibrium. Calculate the equilibrium constant , $\boldsymbol{K_p}$.

Note that stoichiometric amounts mean amounts of moles as shown by the balanced equation

	$H_2(g)$ +	$I_2(g) \rightleftharpoons$	$2HI(g)$
Initial moles	1	1	0
Moles reacted/formed	x	x	$2x$
Moles at equilibrium	$\boldsymbol{1 - x}$	$\boldsymbol{1 - x}$	$\boldsymbol{1.56}$

$$2x = 1.56, \quad x = 0.78$$

$$Total\ moles\ at\ equilibrium$$

$$= 1 - x + 1 - x + 2x = 2$$

$$p_{H_2} = \left(\frac{1 - 0.78}{2}\right) \times 1.01 \times 10^5$$

$$= \boldsymbol{1.111 \times 10^4 Nm^{-2}}$$

$$p_{I_2} = \left(\frac{1 - 0.78}{2}\right) \times 1.01 \times 10^5$$

$$= \boldsymbol{1.111 \times 10^4 Nm^{-2}}$$

$$p_{HI} = \left(\frac{1.56}{2}\right) \times 1.01 \times 10^5$$

$$= \boldsymbol{7.878 \times 10^4 Nm^{-2}}$$

$$K_p = \frac{(p_{HI})^2}{p_{H_2} \times p_{I_2}} = \frac{(7.878 \times 10^4)^2}{(1.111 \times 10^4)^2}$$

$$\boldsymbol{K_p = 50.28}$$

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 ^{o}C. Calculate the mass of hydrogen iodide present in the equilibrium mixture at that temperature.**

	$\boldsymbol{H_2(g)}$	+	$\boldsymbol{I_2\,(g)}$	$\rightleftharpoons$	$\boldsymbol{2HI(g)}$
Initial moles	1		$\frac{1}{3}$		*0*
Moles reacted/formed	x		x		$2x$
Moles at equilibrium	$\boldsymbol{1-x}$		$\boldsymbol{\frac{1}{3}-x}$		$\boldsymbol{2x}$

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$\boldsymbol{K_c\ for\ \ the\ reaction} = \frac{\boldsymbol{1}}{\boldsymbol{K_c\ \ for\ dissociation\ of\ HI}}$$

$$\frac{1}{0.02} = \frac{(2x)^2}{(1-x)\left(\frac{1}{3}-x\right)}$$

$$69x^2 - 100x + 25 = 0$$

$$x = \frac{-(-100) \pm \sqrt{(-100)^2 - (4 \times 69 \times 25)}}{2 \times 69}$$

$$x = 0.321\ or\ 1.128$$

$But\ x\ cannot\ be\ 1.128\ since\ it\ gives$
$negative\ values\ of\ \ (1-x)\ and \left(\frac{1}{3}-x\right)$

$$Therefore\ \boldsymbol{x = 0.321}$$

$$Moles\ of\ HI\ at\ equilibrium = 2x$$
$$= 2 \times 0.321 = 0.642$$

$$Molar\ mass\ of\ HI = (1 + 127)$$
$$= 128g$$

$$\boldsymbol{Mass\ of\ HI\ present\ at\ equilibriun}$$
$$= \boldsymbol{(128 \times 0.642) = 82.176g}$$

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 ^{o}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) $Molar\ mass\ of \boldsymbol{H_2} = (2 \times 1) = 2g$

$$Molar\ mass\ of \boldsymbol{I_2}\ = (2 \times 127) = 254g$$
$$Mole\ ratio\ of\ H_2{:}\,HI = 1{:}\,2$$
$$Moles\ of\ HI = (2 \times 0.5) = 1\ mole$$
$$K_c = 50$$
$$R = 8.314Jmol^{-1}K^{-1}$$
$$V = 10 \times 10^{-3}m^3$$

$$Moles\ of \boldsymbol{H_2} = \frac{1}{2} = 0.5\ moles$$
$$Moles\ of \boldsymbol{I_2} = \frac{127}{254} = 0.5\ moles$$
$$T = (450 + 273) = 723K$$
$$\Delta n = 1 - (0.5 + 0.5) = 0$$
$$K_p = K_c(RT)^{\Delta n}$$
$$\boldsymbol{K_p = 50(8.314 \times 723)^0 = 50}$$

	$\boldsymbol{H_2(g)}$	+	$\boldsymbol{I_2\,(g)}$	$\rightleftharpoons$	$\boldsymbol{2HI(g)}$
Initial moles	0.5		0.5		*0*
Moles reacted/formed	x		x		$2x$
Moles at equilibrium	$\boldsymbol{0.5-x}$		$\boldsymbol{0.5-x}$		$\boldsymbol{2x}$

(ii) Total moles equilibrium mixture,

$$n = 0.5 - x + 0.5 - x + 2x = 1$$

$$\boldsymbol{pV = nRT}$$

$$p = \frac{1 \times 8.314 \times 723}{10 \times 10^{-3}}$$

$$\boldsymbol{p = 6011022.2\ Nm^{-2}}$$

(iii)

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$50 = \frac{(2x)^2}{(0.5-x)^2}$$

$$92x^2 - 100x + 25 = 0$$

$$x = \frac{-(-100) \pm \sqrt{(-100)^2 - (4 \times 92 \times 25)}}{2 \times 92}$$

$$x = 0.390\ or\ 0.697$$

But x cannot be 0.697 since it gives negative values of $(0.5 - x)$

$$Therefore\ \boldsymbol{x = 0.390}$$

Partial pressure of hydrogen

$$= \left(\frac{0.5 - x}{1}\right) \times 6011022.2$$

$$= \left(\frac{0.5 - 0.390}{1}\right) \times 6011022.2$$

$$\boldsymbol{p_{H_2} = 661212.442\ Nm^{-2}}$$

6. 3.20g of hydrogen iodide were heated at 450 °C in a glass bulb of volume 800cm^3. 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 cm^3 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****.*

$$\boldsymbol{I_2\,(aq) + I^-(aq) \longrightarrow I_3^-(aq)}$$

(ii)

$$Molar\ mass\ of\ HI = (1 + 127) = 128g$$

$$Moles\ of\ HI = \frac{3.20}{128} = 0.025\ moles$$

$$Moles\ of\ Na_2S_2O_3 that\ reacted\ with\ I_2 = \left(\frac{0.2 \times 36.0}{1000}\right) = 0.0072\ moles$$

$$I_2(aq) \quad + \quad 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) \quad + \quad S_4O_6^{2-}(aq)$$

$$Mole\ ratio\ of\ S_2O_3^{2-} : I_2 = 2:1$$

$$Moles\ of\ \ I_2 = \left(\frac{1}{2} \times 0.0072\right) = 0.0036\ moles$$

	$\boldsymbol{2HI(g)}$ $\rightleftharpoons$	$\boldsymbol{H_2(g)}$ +	$\boldsymbol{I_2\,(g)}$
Initial moles	0.025	0	0
Moles dissociated/formed	0.025α	$\frac{0.025\alpha}{2}$	$\frac{0.025\alpha}{2}$
Moles at equilibrium	$\boldsymbol{0.025 - 0.025\alpha}$	$\boldsymbol{\frac{0.025\alpha}{2}}$	$\boldsymbol{\frac{0.025\alpha}{2}}$

$$\frac{\mathbf{0.025\alpha}}{\mathbf{2}} = \mathbf{0.0036}$$

$$\boldsymbol{\alpha} = \mathbf{0.288}$$

$$moles\ of\ HI\ at\ equilibrium$$

$$= 0.025(1 - 0.288) = 0.0178$$

$$[HI] = \left(\frac{0.0178 \times 1000}{800}\right) = 0.02225M$$

Note: The volume was given in cm^3. Multiplying moles in $800cm^3$ by 1000 converts the concentration to moles per litre

$$[H_2] = \left(\frac{0.0036 \times 1000}{800}\right) = 0.0045M$$

$$[HI] = \left(\frac{0.0036 \times 1000}{800}\right) = 0.0045M$$

$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

$$K_c = \frac{(0.0045)^2}{(0.02225)^2}$$

$$\boldsymbol{K_c} = \mathbf{0.04}$$

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**

	$\mathbf{2HI(g)}$	$\rightleftharpoons$	$\mathbf{H_2(g)}$ +	$\mathbf{I_2\ (g)}$
Initial moles	0.5		*0*	*0*
Moles dissociated/formed	0.5α		$\frac{0.5\alpha}{2}$	$\frac{0.5\alpha}{2}$
Moles at equilibrium	$\mathbf{0.5 - 0.5\alpha}$		$\frac{\mathbf{0.5\alpha}}{\mathbf{2}}$	$\frac{\mathbf{0.5\alpha}}{\mathbf{2}}$

$$\boldsymbol{\alpha} = \frac{\mathbf{25}}{\mathbf{100}} = \mathbf{0.25}$$

$$Total\ moles\ at\ equilibrium$$

$$= 0.5 - 0.5\alpha + \frac{0.5\alpha}{2} + \frac{0.5\alpha}{2} = 0.5$$

$$moles\ of\ HI\ at\ equilibrium$$

$$= 0.5(1 - 0.25) = 0.375$$

$$moles\ of\ H_2\ at\ equilibrium = \frac{0.5}{2} \times 0.25$$

$$= 0.0625$$

$$moles\ of\ I_2\ at\ equilibrium = 0.0625$$

$$Let\ the\ total\ pressure\ at\ equilibrium\ be\ P$$

$$p_{HI} = \left(\frac{0.375}{0.5}\right)P$$

$$p_{H_2} = \left(\frac{0.0625}{0.5}\right)P$$

$$p_{I_2} = \left(\frac{0.0625}{0.5}\right)P$$

$$K_p = \frac{p_{H_2} \times p_{I_2}}{(p_{HI})^2}$$

$$K_p = \frac{\left(\left(\frac{0.0625}{0.5}\right)P\right)^2}{\left(\left(\frac{0.375}{0.5}\right)P\right)^2} = \frac{0.015625P^2}{0.5625P^2}$$

$$\boldsymbol{K_p} = \mathbf{0.0278}$$

(c) Equilibria involving hydrogen, nitrogen and ammonia.

Examples

1. **Nitrogen reacts with hydrogen according to the following equation**

$$\boldsymbol{N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)}$$

   (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) $\boldsymbol{K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}}$

$(b)(i)$	$N_2(g)$	+	$3H_2(g) \rightleftharpoons$	$2NH_3(g)$
Initial moles	1		3	0
Moles dissociated/formed	x		$3x$	$2x$
Moles at equilibrium	$\mathbf{1-x}$		$\mathbf{3-3x}$	$\mathbf{2x}$

$$\boldsymbol{2x = 0.8.\ Therefore\ x = 0.4}$$

$$moles\ of\ H_2\ at\ equilibrium = 3(1-0.4) = 1.8$$

$$moles\ of\ N_2\ at\ equilibrium = (1-0.4) = 0.6$$

$$moles\ of\ NH_3\ at\ equilibrium = (2\times 0.4) = 0.8$$

$$[N_2] = \left(\frac{0.6}{2}\right) = 0.3M$$

$$[H_2] = \left(\frac{1.8}{2}\right) = 0.9M$$

$$[NH_3] = \left(\frac{0.8}{2}\right) = 0.4M$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$K_c = \frac{(0.4)^2}{0.3\times(0.9)^3}\ \frac{mol^2dm^{-6}}{moldm^{-3}\times mol^3dm^{-9}}$$

$$\boldsymbol{K_c = 0.732\ mol^{-2}dm^6}$$

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.**

	$N_2(g)$	+	$3H_2(g) \rightleftharpoons$	$2NH_3(g)$
Initial moles	0.8		0.9	0
Moles dissociated/formed	x		$3x$	$2x$
Moles at equilibrium	$\mathbf{0.8-x}$		$\mathbf{0.9-3x}$	$\mathbf{2x}$

$$Total\ moles\ at\ equilibrium = 0.8 - x + 0.9 - 3x + 2x = \mathbf{1.7 - 2x}$$

$$\boldsymbol{But\ \left(\frac{0.9-3x}{1.7-2x}\right)\times 100 = 20}$$

$$0.9 - 3x = 0.2(1.7-2x)$$

$$x = 0.215$$

$$moles\ of\ H_2\ at\ equilibrium = 0.9 - (3\times 0.215) = 0.255$$

$$moles\ of\ N_2\ at\ equilibrium = (0.8 - 0.215) = 0.585$$

$$moles\ of\ NH_3\ at\ equilibrium = (2\times 0.215) = 0.430$$

$$[N_2] = \left(\frac{0.585\times 1000}{1500}\right) = 0.39M$$

$$[H_2] = \left(\frac{0.255\times 1000}{1500}\right) = 0.17M$$

$$[NH_3] = \left(\frac{0.430\times 1000}{1500}\right) = 0.287M$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$K_c = \frac{(0.287)^2}{0.39\times(0.17)^3}\ \frac{mol^2dm^{-6}}{moldm^{-3}\times mol^3dm^{-9}}$$

$$\boldsymbol{K_c = 42.99\ mol^{-2}dm^6}$$

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

$(\boldsymbol{i})$	$\boldsymbol{N_2(g)}$	$+$	$\boldsymbol{3H_2(g)}$	$\rightleftharpoons$	$\boldsymbol{2NH_3(g)}$
Initial moles	1		3		0
Moles dissociated/formed	x		$3x$		$2x$
Moles at equilibrium	$\boldsymbol{1-x}$		$\boldsymbol{3-3x}$		$\boldsymbol{2x}$

$$\text{Total moles at equilibrium}$$
$$= 1 - x + 3 - 3x + 2x = \boldsymbol{4 - 2x}$$
$$\boldsymbol{But}\ \left(\frac{\boldsymbol{2x}}{\boldsymbol{4-2x}}\right) \times \boldsymbol{100 = 25}$$
$$2x = 1 - 0.5x$$
$$x = 0.4$$
$$moles\ of\ H_2\ at\ equilibrium = 3(1-0.4)$$
$$= 1.8\ moles$$

(ii) $moles\ of\ N_2\ at\ equilibrium = (1-0.4) = 0.6\ moles$

$$moles\ of\ NH_3\ at\ equilibrium = (2 \times 0.4)$$
$$= 0.8\ moles$$

$$\text{Total moles at equilibrium}$$
$$= 4 - 2(0.4) = 3.2$$
$$p_{N_2} = \left(\frac{0.6}{3.2} \times 100\right) = 18.75\ atm$$
$$p_{H_2} = \left(\frac{1.8}{3.2} \times 100\right) = 56.25\ atm$$
$$p_{NH_3} = \left(\frac{0.8}{3.2} \times 100\right) = 25\ atm$$
$$K_p = \frac{\left(p_{NH_3}\right)^2}{p_{N_2} \times \left(p_{H_2}\right)^3}$$
$$K_p = \frac{25^2}{18.75 \times 56.25^3}\ \frac{atm^2}{atm \times atm^3}$$
$$\boldsymbol{K_p = 1.87 \times 10^{-4} atm^{-2}}$$

---

4. **Ammonia dissociates according to the following equation**

$$\boldsymbol{2NH_3(g) \rightleftharpoons 3H_2(g) + N_2(g)}$$

Calculate the equilibrium constant, K_C for the reaction given 3.0 moles of ammonia were found to be 15% dissociated.

	$\boldsymbol{2NH_3(g)}$	$\rightleftharpoons$	$\boldsymbol{N_2(g)}$	$+$	$\boldsymbol{3H_2(g)}$
Initial moles	3.0		0		0
Moles dissociated/formed	3α		$\frac{3\alpha}{2}$		$3\left(\frac{3\alpha}{2}\right)$
Moles at equilibrium	$\boldsymbol{3-3\alpha}$		$\boldsymbol{\frac{3\alpha}{2}}$		$\boldsymbol{\frac{9\alpha}{2}}$

$$\boldsymbol{But\ \alpha = \frac{15}{100} = 0.15}$$
$$moles\ of\ H_2\ at\ equilibrium = \frac{9 \times 0.15}{2}$$
$$= 0.675\ moles$$

$$\text{Assuming volume is one litre}$$
$$[N_2] = 0.255M$$
$$[H_2] = 0.675M$$
$$[NH_3] = 2.55M$$
$$K_c = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

$$moles\ of\ N_2\ at\ equilibrium = \frac{3 \times 0.15}{2}$$
$$= 0.225\ moles$$
$$moles\ of\ NH_3\ at\ equilibrium$$
$$= 3(1 - 0.15) = 2.55\ moles$$

$$K_c = \frac{0.255 \times (0.675)^3}{(2.55)^2}\ \frac{moldm^{-3} \times mol^3dm^{-9}}{mol^2dm^{-6}}$$
$$\mathbf{K_c = 0.012\ mol^2dm^{-6}}$$

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.**

	$\mathbf{2NH_3(g)} \rightleftharpoons$	$\mathbf{N_2(g)}$	$+$	$\mathbf{3H_2(g)}$
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	$\mathbf{1.75 - 1.75\alpha}$	$\mathbf{\frac{1.75\alpha}{2}}$		$\mathbf{\frac{5.25\alpha}{2}}$

$$Total\ moles\ at\ equilibrium$$
$$= 1.75 - 1.75\alpha + 0.875\alpha + 2.625\alpha$$
$$= \mathbf{1.75 + 1.75\alpha}$$
$$\mathbf{But\ \frac{2.625\alpha}{1.75 + 1.75\alpha} \times 100 = 42.9}$$
$$1.87425\alpha = 0.75075$$
$$\boldsymbol{\alpha = 0.4}$$
$$moles\ of\ H_2\ at\ equilibrium$$
$$= (2.625 \times 0.4)$$
$$= 1.05\ moles$$
$$moles\ of\ N_2\ at\ equilibrium$$
$$= (0.875 \times 0.4) = 0.35\ moles$$

$$moles\ of\ NH_3\ at\ equilibrium$$
$$= 1.75(1 - 0.4)$$
$$= 1.05\ moles$$
$$Since\ volume\ is\ one\ litre$$
$$[N_2] = 0.35M \quad [H_2] = 1.05M$$
$$[NH_3] = 1.05M$$
$$K_c = \frac{[N_2][H_2]^3}{[NH_3]^2}$$
$$K_c = \frac{0.35 \times (1.05)^3}{(1.05)^2}\ \frac{moldm^{-3} \times mol^3dm^{-9}}{mol^2dm^{-6}}$$
$$\mathbf{K_c = 0.3675\ mol^2dm^{-6}}$$

(d) Equilibria involving phosphorus, chlorine and phosphorus(V) chloride

Examples

1. **Phosphorus(V) chloride dissociates at high temperatures according to the equation**

$$\mathbf{PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)}$$

83.4 g of phosphorus(V) chloride were placed in a vessel of 9.23dm^3.At equilibrium at a certain temperature, 11.1g of chlorine were formed at a total pressure of $250kPa$.

(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)

$$Molar\ mass\ of\ PCl_5 = 31 + (5 \times 35.4) = 208$$

$$moles\ of\ PCl_5\ before\ equilibrium = \frac{83.4}{208} = 0.401$$

$$Molar\ mass\ of\ Cl_2 = (35.4 \times 2) = 70.8$$

$$\boldsymbol{moles\ of\ chlorine\ at\ equilibrium = \frac{11.1}{70.8} = 0.15678\ moles}$$

$$Molar\ concetration\ of\ Cl_2 = \frac{0.1186}{9.0} = 0.0132M$$

	$\boldsymbol{PCl_5(g)}$	$\rightleftharpoons$	$\boldsymbol{PCl_3(g)}$	+	$\boldsymbol{Cl_2(g)}$
Initial moles	0.401		0		0
Moles dissociated/formed	0.401α		0.401α		0.401α
Moles at equilibrium	$\boldsymbol{0.401(1-\alpha)}$		$\boldsymbol{0.401\alpha}$		$\boldsymbol{0.401\alpha}$

$$\boldsymbol{But\quad 0.401\alpha = 0.15678}$$

$$\boldsymbol{\alpha = 0.391}$$

$$moles\ of\ PCl_5\ at\ equilibrium$$
$$= 0.401(1 - 0.391)$$
$$= 0.24421\ moles$$

$$moles\ of\ Cl_2\ at\ equilibrium$$
$$= 0.15679\ moles$$

(b) $moles\ of\ PCl_3\ at\ equilibrium =$
$(0.401 \times 0.391) = 0.15679\ moles$

$$Since\ volume\ is\ 9.23\ litres$$

$$[PCl_5] = \left(\frac{0.24421}{9.23}\right) = 0.0265M$$

$$[Cl_2] = \left(\frac{0.15679}{9.23}\right) = 0.0170M$$

$$[PCl_3] = 0.0170M$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$K_c = \frac{0.0170 \times 0.0170}{0.0265}\ \frac{mol^2dm^{-6}}{moldm^{-3}}$$

$$\boldsymbol{K_c = 0.011moldm^{-3}}$$

(c) $Total\ moles\ at\ equilibrium$
$= 0.24421 + 0.15679 + 0.15679$
$= 0.55779$

$$p_{PCl_5} = \left(\frac{0.24421}{0.55779} \times 250\right) = 109.45kPa$$

$$p_{PCl_3} = \left(\frac{0.15679}{0.55779} \times 250\right) = 70.27kPa$$

$$p_{Cl_2} = \left(\frac{0.15679}{0.55779} \times 250\right) = 70.27kPa$$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$$

$$K_p = \frac{70.27 \times 70.27}{109.45}\frac{kPa^2}{kPa}$$

$$\boldsymbol{K_p = 45.13\ kPa}$$

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.

(a) (i) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(ii) $Cl_2(g) + 2I^-(aq) \longrightarrow I_2(aq) + 2Cl^-(aq)$

(b) ***(i) Bulb was rapidly broken <u>to stop the reaction</u>*** *and* ***<u>fix the equilibrium</u> such that the equilibrium <u>does not adjust itself</u> to the <u>equilibrium value at a lower temperature</u>***.

(ii) Bulb is broken under potassium iodide to <u>dissolve and oxidise chlorine present at equilibrium to chloride ions</u> as the <u>potassium iodide is reduced to iodine</u>.

(c) (i)	$\boldsymbol{PCl_5(g)} \rightleftharpoons$	$\boldsymbol{PCl_3(g)}$ +	$\boldsymbol{Cl_2(g)}$
Initial moles	1	0	0
Moles dissociated/formed	α	α	α
Moles at equilibrium	$(\boldsymbol{1-\alpha})$	$\boldsymbol{\alpha}$	$\boldsymbol{\alpha}$

$\boldsymbol{Total\ moles\ at\ equilibrium}$

$= 1 - \alpha + \alpha + \alpha = (\boldsymbol{1+\alpha})$

$$\boldsymbol{But}\quad \frac{\boldsymbol{\alpha}}{\boldsymbol{1+\alpha}} \times \boldsymbol{100 = 40.70}$$

$moles\ of\ PCl_5\ at\ equilibrium$

$= (1 - 0.686) = 0.314\ moles$

$moles\ of\ Cl_2\ at\ equilibrium = 0.686\ moles$

$moles\ of\ PCl_3\ at\ equilibrium$

$= 0.686\ moles$

$Since\ volume\ is\ 1\ litre$

$[PCl_5] = 0.314M$

$$\boldsymbol{0.593\alpha = 0.407}$$

$$\boldsymbol{\alpha = 0.686}$$

$[Cl_2] = 0.686M$

$[PCl_3] = 0.686M$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$K_c = \frac{0.686 \times 0.686}{0.314}\ \frac{mol^2dm^{-6}}{moldm^{-3}}$$

$$\boldsymbol{K_c = 1.499\ moldm^{-3}}$$

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 cm^3 of 0.1M sodium thiosulphate solution. Calculate the equilibrium constant, K_c, for the reaction.

$$Molar\ mass\ of\ PCl_5 = 31 + (5 \times 35.4) = 208$$

$$moles\ of\ PCl_5\ before\ equilibrium = \frac{2.085}{208} = 0.01$$

$$Moles\ of\ Na_2S_2O_3 that\ reacted\ with\ I_2 = \left(\frac{40 \times 0.1}{1000}\right) = 0.004\ moles$$

$$I_2(aq) \quad + \quad 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) \quad + \quad S_4O_6^{2-}(aq)$$

$$Mole\ ratio\ of\ S_2O_3^{2-} : I_2 = 2:1$$

$$Moles\ of\ \ I_2\ that\ were\ formed\ from\ KI = \left(\frac{1}{2} \times 0.004\right) = 0.002\ moles$$

$$From\ \ Cl_2(g) + 2I^-(aq) \longrightarrow I_2(aq) + 2Cl^-(aq)$$

$$1\ mole\ of\ I_2\ is\ formed\ from\ 1\ mole\ of\ \ Cl_2$$

$$Therefore\ moles\ of\ \ Cl_2\ at\ equilibrium = 0.002\ moles$$

	$\boldsymbol{PCl_5(g)}$	$\rightleftharpoons$	$\boldsymbol{PCl_3(g)}$	+	$\boldsymbol{Cl_2(g)}$
Initial moles	1		0		0
Moles dissociated/formed	0.002		0.002		0.002
Moles at equilibrium	$(\mathbf{1 - 0.002})$		0.002		$\mathbf{0.002}$

$$moles\ of\ PCl_5\ at\ equilibrium = (1 - 0.002)$$
$$= 0.998\ moles$$

$$moles\ of\ Cl_2\ at\ equilibrium = 0.002\ moles$$

$$moles\ of\ PCl_3\ at\ equilibrium$$
$$= 0.002\ moles$$

$$Since\ volume\ is\ 1\ litre$$
$$[PCl_5] = 0.998\ M$$

$$[Cl_2] = 0.002M$$
$$[PCl_3] = 0.002M$$
$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$
$$K_c = \frac{0.002 \times 0.002}{0.998}\ \frac{mol^2dm^{-6}}{moldm^{-3}}$$
$$\boldsymbol{K_c = 4.01 \times 10^{-6}\ moldm^{-3}}$$

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4. 2.00 g of phosphorus(V) chloride were allowed to reach equilibrium at 200°C in a 1 $\boldsymbol{dm^3}$ capacity vessel. If the equilibrium constant of the above reaction is $\boldsymbol{0.008\ moldm^{-3}}$ at this temperature and in the conditions stated. Calculate the percentage dissociation of phosphorus pentachloride at equilibrium.

$$Molar\ mass\ of\ PCl_5 = 31 + (5 \times 35.4) = 208g$$

$$moles\ of\ PCl_5\ before\ equilibrium = \frac{2.00}{208} = 0.009615$$

	$\boldsymbol{PCl_5(g)}$	$\rightleftharpoons$	$\boldsymbol{PCl_3(g)}$	+	$\boldsymbol{Cl_2(g)}$
Initial moles	0.009615		0		0
Moles dissociated/formed	0.009615α		0.009615α		0.009615α
Moles at equilibrium	$\boldsymbol{0.009615(1 - \alpha)}$		$\boldsymbol{0.009615\alpha}$		$\boldsymbol{0.009615\alpha}$

$$\text{Since volume is 1 litre}$$
$$[PCl_5] = (0.009615(1-\alpha))\ M$$
$$[Cl_2] = (0.009615\alpha)M$$
$$[PCl_3] = (0.009615\alpha)M$$
$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$
$$0.008 = \frac{(0.009615\alpha)^{\mathbf{2}}}{0.009615(1-\alpha)}$$
$$9.244\alpha^2 + 7.962\alpha - 7.962 = 0$$

$$\alpha = \frac{-(7.962) \pm \sqrt{(7.962)^2 - (4 \times 9.244 \times -7.962)}}{2 \times 9.244}$$
$$\alpha = -1.454 \text{ or } 0.592$$
$$\text{But } \alpha \text{ cannot be negative.}$$
$$\text{Therefore } \boldsymbol{\alpha = 0.592}$$
$$\textbf{Percentage dissociation of } \boldsymbol{PCl_5}$$
$$\boldsymbol{= 0.592 \times 100 = 59.2\%}$$

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**.

	$\boldsymbol{PCl_5(g)} \rightleftharpoons$	$\boldsymbol{PCl_3(g)}$ +	$\boldsymbol{Cl_2(g)}$
Initial moles	3.6	0	0
Moles dissociated/formed	3.6α	3.6α	3.6α
Moles at equilibrium	$\boldsymbol{3.6(1-\alpha)}$	$\boldsymbol{3.6\alpha}$	$\boldsymbol{3.6\alpha}$

$$\text{But } \alpha = \frac{38}{100} = 0.38$$

$$\text{Moles of } PCl_5 \text{ at equilibrium}$$
$$= 3.6(1-0.38)$$
$$= 2.232 \text{ moles}$$

$$\text{moles of } Cl_2 \text{ at equilibrium} = (3.6 \times 0.38)$$
$$= 1.368 \text{ moles}$$
$$\text{moles of } PCl_3 \text{ at equilibrium} = 1.368 \text{ moles}$$

$$\text{Since volume is 2 litres}$$
$$[PCl_5] = \left(\frac{2.232}{2}\right) = 1.116\ M$$
$$[Cl_2] = \left(\frac{1.368}{2}\right) = 0.684M$$
$$[PCl_3] = 0.684M$$
$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$
$$K_c = \frac{(0.684)^{\mathbf{2}}}{1.116}\ \frac{mol^2dm^{-6}}{moldm^{-3}}$$
$$\boldsymbol{K_c = 0.419\ moldm^{-3}}$$

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. ($\boldsymbol{The\ equilibrium\ constant\ is\ 0.02moldm^{-3}}$).**

	$\boldsymbol{PCl_5(g)} \rightleftharpoons$	$\boldsymbol{PCl_3(g)}$ +	$\boldsymbol{Cl_2(g)}$
Initial moles	0.4	0	0
Moles dissociated/formed	0.4α	0.4α	0.4α
Moles at equilibrium	$\boldsymbol{0.4(1-\alpha)}$	$\boldsymbol{0.4\alpha}$	$\boldsymbol{0.4\alpha}$

$$\text{Since volume is 1 litre}$$
$$[PCl_5] = (0.4(1-\alpha))\ M$$
$$[Cl_2] = \quad (0.4\alpha)M$$
$$[PCl_3] = (0.4\alpha)M$$
$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$
$$0.02 = \frac{(0.4\alpha)^2}{0.4(1-\alpha)}$$
$$\alpha^2 + 0.05\alpha - 0.05 = 0$$

$$\alpha = \frac{-(0.05) \pm \sqrt{(0.05)^2 - (4 \times 1 \times -0.05)}}{2 \times 1}$$
$$\alpha = -0.25 \text{ or } 0.2$$
$$\text{But } \alpha \text{ cannot be negative.}$$
$$\text{Therefore } \boldsymbol{\alpha = 0.2}$$
$$\text{Total moles at equilibrium}$$
$$= 0.4(1-0.2) + 0.4(0.2) + 0.4(0.2) = 0.48$$
$$\text{Percentage of chlorine}$$
$$= \boldsymbol{\left(\frac{0.4 \times 0.2}{0.48}\right) \times 100 = 16.67\%}$$

(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.**

$$\boldsymbol{2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)}$$

$$p_{Total} = 1.0\ atm$$
$$p_{SO_2} = 0.27\ atm$$
$$p_{O_2} = 0.41\ atm$$
$$p_{SO_3} = 1.0 - (0.27 + 0.41) = 0.32$$

$$K_p = \frac{\left(p_{SO_3}\right)^2}{\left(p_{SO_2}\right)^2 \times p_{O_2}}$$
$$K_p = \frac{0.32^2}{0.27^2 \times 0.41}\ \frac{atm^2}{atm^2 \times atm}$$
$$\boldsymbol{K_p = 3.426\ atm^{-1}}$$

---

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.**

	$\boldsymbol{2SO_2(g)}$	+ $\boldsymbol{O_2(g)}$	$\rightleftharpoons$ $\boldsymbol{2SO_3(g)}$
Initial moles	0.425	0.294	0
Moles reacted/formed	$2x$	x	$2x$
Moles at equilibrium	$\boldsymbol{(0.425-2x)}$	$\boldsymbol{(0.294-x)}$	$\boldsymbol{2x}$

$$\text{Total moles at equilibrium}$$
$$= 0.425 - 2x + 0.294 - x + 2x = (0.719 - x)$$
$$\text{Moles of } O_2 \text{ that reacted} = x$$
$$x = \frac{52}{100} \times 0.294 = 0.15288$$

$$\text{Since volume is 1.6 litres,}$$
$$[O_2] = \left(\frac{0.14112}{1.6}\right) = 0.0882M$$
$$[SO_2] = \left(\frac{0.11924}{1.6}\right) = 0.0745M$$
$$[SO_3] = \left(\frac{0.30576}{1.6}\right) = 0.1911M$$

$Moles\ of\ O_2\ at\ equilibrium = 0.294 - 0.15288$
$= 0.14112$
$Moles\ of\ SO_2\ at\ equilibrium$
$= 0.425 - 2(0.15288) = 0.11924$
$Moles\ of\ SO_3\ at\ equilibrium$
$= 2(0.15288) = 0.30576$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

$$K_c = \frac{(0.1911)^2}{(0.0745)^2 \times 0.0882}\ \frac{mol^2dm^{-6}}{mol^3dm^{-9}}$$

$$\boldsymbol{K_c = 74.6\ mol^{-1}dm^3}$$

---

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) $$\boldsymbol{2SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)}$$

(ii) $K_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$

	$2SO_3(g)$	$2\,SO_2(g)$	$O_2(g)$
Initial moles	1	0	0
Moles dissociated/formed	α	α	$\frac{\alpha}{2}$
Moles at equilibrium	$\boldsymbol{1-\alpha}$	$\boldsymbol{\alpha}$	$\boldsymbol{\frac{\alpha}{2}}$

$Total\ moles\ at\ equilibrium$
$= 1 - \alpha + 2\alpha + \alpha = \boldsymbol{1 + 0.5\alpha}$
$\boldsymbol{But\ 1 - \alpha = 0.35}$
$\boldsymbol{\alpha = 0.65}$
$Moles\ of\ O_2\ at\ equilibrium$
$= \frac{0.65}{2} = 0.325$
$Moles\ of\ SO_2\ at\ equilibrium = 0.65$
$Moles\ of\ SO_3\ at\ equilibri\ = 0.35$

$Since\ volume\ is\ one\ litre$
$[O_2] = 0.325M \quad [SO_2] = 0.65M$
$[SO_3] = 0.35M$

$$K_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$$

$$K_c = \frac{0.65^2 \times 0.325}{(0.35)^2}\ \frac{mol^3dm^{-9}}{mol^2dm^{-6}}$$

$$\boldsymbol{K_c = 1.12\ moldm^{-3}}$$

(f) Examples involving other equilibria systems

1. Dinitrogen tetroxide and nitrogen dioxide exist in the following equilibrium.

$$\boldsymbol{N_2O_4(g) \rightleftharpoons 2\,NO_2(g)}$$

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)

$$Molar\ mass\ of\ N_2O_4 = (2 \times 14) + (4 \times 16) = 92g$$

$$Initial\ moles\ of\ N_2O_4 = \frac{11.04}{92} = 0.12\ moles$$

$$Molar\ mass\ of\ NO_2 = (1 \times 14) + (2 \times 16) = 46g$$

$$\boldsymbol{Moles\ of\ NO_2\ at\ equilibrium = \frac{5.52}{46} = 0.12\ moles}$$

$$\boldsymbol{N_2O_4(g) \rightleftharpoons 2NO_2(g)}$$

Initial moles	0.12	0
Moles dissociated/formed	0.12α	$2(0.12\alpha)$
Moles at equilibrium	$\boldsymbol{0.12(1-\alpha)}$	$\boldsymbol{0.24\alpha}$

$$\boldsymbol{But\ \ 0.24\alpha = 0.12}$$

$$\boldsymbol{\alpha = 0.5}$$

$$\boldsymbol{Moles\ of\ NO_2\ at\ equilibrium = 0.12\ moles}$$

$$\boldsymbol{Moles\ of\ N_2O_4\ at\ equilibrium}$$

$$\boldsymbol{= 0.12(1-0.5) = 0.06\ \ moles}$$

(b) $[N_2O_4] = \frac{0.06}{4.8} = 0.0125M$

$$[NO_2] = \frac{0.12}{4.8} = 0.025\ M$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_c = \frac{(0.025)^2}{0.0125}\ \frac{mol^2dm^{-6}}{moldm^{-3}}$$

$$\boldsymbol{K_c = 0.05\ moldm^{-3}}$$

(c) $Total\ moles\ \ at\ equilibrium$

$$= 0.12 + 0.06 = 0.18\ moles$$

$$p_{N_2O_4} = \frac{0.06}{0.18} \times 100 = 33.333\ kPa$$

$$p_{NO_2} = \frac{0.12}{0.18} \times 100 = 66.667\ kPa$$

$$K_p = \frac{\left(p_{NO_2}\right)^2}{p_{N_2O_4}}$$

$$K_p = \frac{(66.667)^2}{33.333}\ \frac{(kPa)^2}{kPa}$$

$$\boldsymbol{K_p = 133.336\ kPa}$$

---

2. **For the following gas equilibrium, $\boldsymbol{N_2O_4(g) \rightleftharpoons 2\ NO_2(g)}$ at 333K, the equilibrium constant, $\boldsymbol{K_p}$ is 1.33 atmospheres. Calculate the degree of dissociation of one mole of dinitrogen tetraoxide at 333K if the total pressure of the system is 2 atmospheres.**

$$\boldsymbol{N_2O_4(g) \rightleftharpoons 2NO_2(g)}$$

Initial moles	1	0
Moles dissociated/formed	α	2α
Moles at equilibrium	$\boldsymbol{(1-\alpha)}$	$\boldsymbol{2\alpha}$

$$\textit{Total moles at equilibrium} = 1-\alpha+2\alpha = (\mathbf{1}+\boldsymbol{\alpha})$$

$$p_{N_2O_4} = \frac{1-\alpha}{1+\alpha}\times 2 = \frac{2(1-\alpha)}{1+\alpha}\ atm$$

$$p_{NO_2} = \frac{2\alpha}{1+\alpha}\times 2 = \frac{4\alpha}{1+\alpha}\ atm$$

$$K_p = \frac{\left(p_{NO_2}\right)^2}{p_{N_2O_4}} = 1.33$$

$$\frac{\left(\frac{4\alpha}{1+\alpha}\right)^2}{\frac{2(1-\alpha)}{1+\alpha}} = 1.33$$

$$\left(\frac{16\alpha^2}{(1+\alpha)^2}\right)\times\left(\frac{1+\alpha}{2(1-\alpha)}\right) = 1.33$$

$$\frac{16\alpha^2}{2(1+\alpha)(1-\alpha)} = 1.33$$

$$16\alpha^2 = 2.66(1-\alpha^2)$$

$$16\alpha^2 + 2.66\alpha^2 = 2.66$$

$$18.66\alpha^2 = 2.66$$

$$\alpha^2 = 0.142551$$

$$\boldsymbol{\alpha = 0.378}$$

$$\textbf{\textit{The degree of dissociation of }} \boldsymbol{N_2O_4} \textbf{\textit{ is }} \mathbf{0.378}$$

3. **When heated, carbon dioxide dissociates according to the equation:**

$$\boldsymbol{2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)}$$

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.

	$\boldsymbol{2CO_2(g)}$	$\rightleftharpoons$ $\boldsymbol{2CO(g)}$	+ $\boldsymbol{O_2(g)}$
Initial moles	n	0	0
Moles dissociated/formed	$n\alpha$	$n\alpha$	$\frac{n\alpha}{2}$
Moles at equilibrium	$\boldsymbol{n(1-\alpha)}$	$\boldsymbol{n\alpha}$	$\boldsymbol{\frac{n\alpha}{2}}$

$$\textit{But}\quad \boldsymbol{\frac{n(1-\alpha)}{n}\times 100 = 60}$$

$$\boldsymbol{1-\alpha = 0.6}$$

$$\boldsymbol{\alpha = 0.4}$$

$$\textbf{\textit{Total moles at equilibrium}}$$

$$\boldsymbol{= n(1-\alpha) + n\alpha + \frac{n\alpha}{2}}$$

$$\boldsymbol{= n(1-\alpha+\alpha+\tfrac{\alpha}{2})}$$

$$\boldsymbol{= n\left(1+\tfrac{\alpha}{2}\right) = 1.2n}$$

$$p_{CO_2} = \frac{0.6n}{1.2n}\times 1 = 0.5\ atm$$

$$p_{CO} = \frac{0.4n}{1.2n}\times 1 = 0.333\ atm$$

$$p_{O_2} = \frac{0.2n}{1.2n}\times 1 = 0.167\ atm$$

$$K_p = \frac{(p_{CO})^2\times p_{O_2}}{\left(p_{CO_2}\right)^2}$$

$$K_p = \frac{(0.333)^2\times 0.167}{(0.5)^2}\ \frac{atm^3}{atm^2}$$

$$\boldsymbol{K_p = 0.0741\ atm}$$

4. **Nitrogen monoxide reacts with oxygen according to the reaction:**

$$\boldsymbol{2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)}$$

At equilibrium, the equilibrium constant is $\boldsymbol{375\ mol^{-1}l}$ at a given temperature in a container of volume, $\boldsymbol{755cm^3}$. The equilibrium mixture was found to contain

0.0148 moles of oxygen. Calculate the ratio of $[NO]$ to $[NO_2]$ in the equilibrium mixture.

	$2NO(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2NO_2(g)$
Moles at equilibrium	?		$\mathbf{0.0148}$		***?***

$$\text{Since volume is } 755\ cm^3,$$

$$[O_2] = \left(\frac{0.0148 \times 1000}{755}\right) = 0.0196M$$

$$[NO] = ? \quad [NO_2] = ?$$

$$K_c = \frac{[NO_2]^2}{[NO]^2[O_2]} = 375$$

$$\frac{[NO_2]^2}{[NO]^2} = 375[O_2]$$

$$\frac{[NO_2]^2}{[NO]^2} = 375 \times 0.0196$$

$$\frac{[NO_2]}{[NO]} = \sqrt{375 \times 0.0196}$$

$$\frac{[NO_2]}{[NO]} = 2.711$$

$$\boldsymbol{\frac{[NO]}{[NO_2]} = \frac{1}{2.711} = 0.3689}$$

5. **For the equilibrium system below:**

$$\boldsymbol{CO\ (g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)}$$

   (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.

	$CO(g)$	+	$H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$H_2(g)$
Initial moles	1		1		0		0
Moles reacted/formed	x		x		x		x
Moles at equilibrium	$\mathbf{1-x}$		$\mathbf{1-x}$		$\boldsymbol{x}$		$\boldsymbol{x}$

$$\textbf{Total moles at equilibrium}$$

$$\boldsymbol{= 1 - x + 1 - x + x + x = 2}$$

$$\textbf{But } \frac{x}{2} \times \mathbf{100 = 33.3}$$

$$\boldsymbol{x = 0.666}$$

Let the total pressure be P

$$p_{CO} = \frac{1 - 0.666}{2}P = 0.167\ units$$

$$p_{H_2O} = \frac{1 - 0.666}{2}P = 0.167\ units$$

$$p_{CO_2} = \frac{0.666}{2}P = 0.333\ units$$

$$p_{H_2} = \frac{0.666}{2}P = 0.333\ units$$

$$K_p = \frac{p_{CO_2} \times p_{H_2}}{p_{CO} \times p_{H_2O}}$$

$$K_p = \frac{(0.333)^2}{(0.167)^2}$$

$$\boldsymbol{K_p = 3.976}$$

6. **Methane reacts with steam according to the equation**

$$CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$$

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	$\mathbf{0.18 - x}$	$\mathbf{0.22 - 2x}$		$\mathbf{x}$	$\mathbf{4x}$

$$\textbf{But number of moles of } CO_2 \textbf{ at equilibrium} = 0.1$$

$$\textbf{Therefore } x = 0.1$$

$$Moles\ of\ CH_4\ at\ equilibrium = 0.18 - 0.1 = 0.08$$

$$Moles\ of\ H_2O\ at\ equilibrium = 0.22 - 2(0.1) = 0.02$$

$$Moles\ of\ CO_2\ at\ equilibrium = 0.1$$

$$Moles\ of\ H_2\ at\ equilibrium = 4(0.1) = 0.4$$

Since volume is 5 litres,

$$[CH_4] = \left(\frac{0.08}{5}\right) = 0.016M$$

$$[H_2O] = \left(\frac{0.02}{5}\right) = 0.004M$$

$$[CO_2] = \left(\frac{0.1}{5}\right) = 0.02M$$

$$[H_2] = \left(\frac{0.4}{5}\right) = 0.08M$$

$$K_c = \frac{[CO_2][H_2]}{[CH_4]\,[H_2O]}$$

$$K_c = \frac{0.02 \times 0.08}{0.016 \times 0.004}$$

$$\mathbf{K_c = 25}$$

7. **Sulphoryl dichloride dissociates when heated according to the following equation: $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$**

When 67.5g of Sulphoryl 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) $$Molar\ mass\ of\ SO_2Cl_2 = 32 + (2 \times 16) + (2 \times 35.4) = 134.8g$$

$$Initial\ moles\ of\ SO_2Cl_2 = \frac{67.5}{134.8} = 0.5$$

	$SO_2Cl_2(g)$	$\rightleftharpoons$	$SO_2(g)$	$+\ Cl_2(g)$
Initial moles	0.5		0	0
Moles dissociated/formed	0.5α		0.5α	0.5α
Moles at equilibrium	$\mathbf{0.5(1-\alpha)}$		$\mathbf{0.5\alpha}$	$\mathbf{0.5\alpha}$

$$\boldsymbol{But\ \alpha = \frac{45}{100} = 0.45}$$

$\boldsymbol{Moles\ of\ SO_2Cl_2\ at\ equilibrium}$

$$\boldsymbol{= 0.5(1 - 0.45) = 0.275}$$

$\boldsymbol{Moles\ of\ SO_2\ at\ equilibrium}$

$$\boldsymbol{= (0.5 \times 0.45) = 0.225}$$

$\boldsymbol{Moles\ of\ Cl_2\ at\ equilibrium = 0.225}$

(iii) $Since\ volume\ is\ 1\ litre$

$$[SO_2Cl_2] = 0.275\ M$$

$$[SO_2] = \quad 0.225\ M$$

$$[Cl_2] = 0.225\ M$$

$$K_c = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]} = \frac{(0.225)^2}{0.275} = \boldsymbol{0.184\ moldm^{-3}}$$

8. The equilibrium constant, K_p for the reaction below at 250℃ is $1.08 \times 10^{-1} atm^2$:

$$\boldsymbol{NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)}$$

Calculate the:

(i) total pressure of the system at equilibrium.

(ii) degree of dissociation of ammonium hydrogen sulphide

	$\boldsymbol{NH_4HS(s)}$ $\rightleftharpoons$	$\boldsymbol{NH_3(g)}$ +	$\boldsymbol{H_2S(g)}$
Initial moles	n	0	0
Moles dissociated/formed	$n\alpha$	$n\alpha$	$n\alpha$
Moles at equilibrium	$\boldsymbol{n(1-\alpha)}$	$\boldsymbol{n\alpha}$	$\boldsymbol{n\alpha}$

$\boldsymbol{Total\ moles\ at\ equilibrium}$

$$\boldsymbol{= n(1 - \alpha) + n\alpha + n\alpha}$$

$$\boldsymbol{= n(1 - \alpha + \alpha + \alpha)}$$

$$\boldsymbol{= n(1 + \alpha)}$$

Let the total pressure at equilibrium be P

$$p_{NH_3} = p_{H_2S} = \frac{n\alpha}{n(1+\alpha)}P = \frac{\alpha}{(1+\alpha)}P$$

$$K_p = p_{NH_3} \times p_{H_2S}$$

$$Since\ p_{NH_3} = p_{H_2S};$$

$$K_p = \left(p_{NH_3}\right)^2$$

$$1.08 \times 10^{-1} = \left(p_{NH_3}\right)^2$$

$$p_{NH_3} = \sqrt{1.08 \times 10^{-1}}$$

$$p_{NH_3} = 0.3286\ atm$$

$$P = p_{NH_3} + p_{H_2S}$$

$$= 2(0.3286) = \boldsymbol{0.6572\ atm}$$

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 50ºC. 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℃. 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℃. 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℃. 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℃ 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℃. 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 100ºC, the percentage of esterification was 54%
   (i) Write equation for the esterification reaction.
   (ii) Calculate the value of the concentration equilibrium constant, K_c.
   (iii) 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:
   (i) equilibrium constant
   (ii) 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 450ºC. At equilibrium, 0.2 mole of iodine had reacted.
    (i) Write an expression for the equilibrium constant, K_c, for the reaction
    (ii) Calculate the value of K_C, at 450ºC.
11. Hydrogen reacts with iodine according to the equation

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

   (a) Calculate the equilibrium concentration of each of the following when:
      (i) 0.2 mole of iodine and 0.3 moles of hydrogen are reacted in a one litre vessel.
      (ii) 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:
       (i) equilibrium constant
       (ii) 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 ;

   (i) Number of moles of hydrogen iodide in 1.54g
   (ii) Number of moles of iodine formed

(iii) Value of $\boldsymbol{K_c}$ 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 460ºC 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 ºC until equilibrium was attained and 36 moles of hydrogen iodide was obtained. Calculate the degree of dissociation of hydrogen iodide at 460ºC
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;

$$3H_2(g) + \quad N_2(g) \rightleftharpoons 2NH_3(g)$$

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, $\boldsymbol{K_c}$.
19. When 1.65 moles of hydrogen and 0.6 moles of nitrogen were heated to 150ºC in a 1.5 litre closed vessel, equilibrium was attained when 0.9 moles of ammonia were formed. Calculate the value of equilibrium constant, $\boldsymbol{K_c}$ for the reaction.
20. Nitrogen and hydrogen are mixed in a ratio 1:3. At equilibrium at 600^{O}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,

$$3H_2(g) + \quad N_2(g) \rightleftharpoons 2NH_3(g)$$

Calculate the molar percentage of ammonia in the equilibrium mixture formed at 400^{o}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, $\boldsymbol{K_p}$of the reaction.

(ii) Given that the value of $\boldsymbol{K_p}$ 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, $\boldsymbol{K_p}$ for the reaction in (a) above is $1.5 \times 10^{-5} atm^{-2}$ at 500℃ . 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 ^{o}C, the equilibrium concentration of hydrogen is *0.250* $moll^{-1}$ and that of nitrogen is *2.7* $moll^{-1}$ Calculate the equilibrium concentration of ammonia at the same temperature given that $K_c = 6 \times 10^{-2} mol^{-2} l^2$ at 500 ^{o}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

26. At a certain temperature, the equilibrium constant for the reaction between nitrogen and hydrogen, $\boldsymbol{K_p}$, is $4.82 \times 10^{-2} atm^{-2}$ and the partial pressures of nitrogen and hydrogen are 30 and 120 atm respectively.
    (i) Write the expression for the equilibrium constant, $\boldsymbol{K_p}$.
    (ii) 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:
    (i) amount of phosphorus(V) chloride and phosphorus(III) chloride at equilibrium in moles per litre.
    (ii) equilibrium constant, $\boldsymbol{K_c}$, for the reaction and state its units.
28. (a) When 2.6 mole of phosphorus(V) chloride was heated in a $1.5dm^3$vessel, equilibrium was established when 1.04 mole of phosphorus(III) chloride was formed. Calculate the value of equilibrium constant, $\boldsymbol{K_c}$.
    (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, $\boldsymbol{K_c}$.
29. **75.06g** of phosphorus(V) chloride were heated to 200ºC in a vessel of volume $1000cm^3$ at a pressure of 170kPa. Calculate the;
    (a) degree of dissociation of phosphorus(V) chloride
    (b) value of equilibrium constant, $\boldsymbol{K_p}$, at 200ºC
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.
    (a) Calculate the equilibrium constant, $\boldsymbol{K_p}$.
    (b) 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 $1.5dm^3$ vessel and at equilibrium, it was found to contain 23.53% phosphorus trichloride.

(a) Write equation for the dissociation of phosphorus pentachloride
(b) Write the expression for the equilibrium constants, $\boldsymbol{K_c}$, and $\boldsymbol{K_p}$, for the reaction.
(c) Determine the value of equilibrium constant, $\boldsymbol{K_c}$.

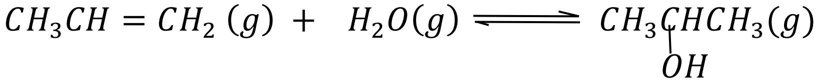
32. (a) 2.6 mole of phosphorus pentachloride was heated in a 500 cm^3 closed vessel. At equilibrium, it was found to contain 1.04 mole of phosphorus trichloride. Determine the value of equilibrium constant, $\boldsymbol{K_c}$.
    (b) 3.0 mole of phosphorus pentachloride was heated in a 750 cm^3vessel until equilibrium was established. The vessel contained 1.14 moles of chlorine. Determine the value of equilibrium constant, $\boldsymbol{K_c}$.

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. $(The\ equilibrium\ constant\ is\ 0.043\ moldm^{-3})$
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℃ 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:
    $$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
    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 1litre vessel to equilibrium, the equilibrium mixture contained 18.75% sulphur dioxide. Calculate the equilibrium constant value, K_p.
37. Dinitrogen tetraoxide dissociates at 40 ^{o}C and 1 atm according to the following equation.
    $$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \qquad \Delta H = +57kJmol^{-1}$$
    (i) Write an equation for the equilibrium constant , $\boldsymbol{K_p}$.
    (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 $\boldsymbol{K_p}$ at 40 ^{o}C for the reaction.
38. (a) At 40℃ 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℃. 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.



$$CH_3CH = CH_2\,(g) + H_2O(g) \rightleftharpoons CH_3\underset{\underset{OH}{|}}{C}HCH_3(g)$$

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 $\boldsymbol{K_p}$ at this temperature and state its units.

41. Nitrogen monoxide combines with oxygen according to the equation

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

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 $\boldsymbol{K_c}$.

42. Carbon monoxide reacts with steam according to the reaction;

$$CO\,(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

When 6.5 cm^3 of carbon monoxide were heated with 4.8 cm^3 of steam at 45℃ 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, $\boldsymbol{K_c}$.

43. At 700℃, 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:

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

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, $\boldsymbol{K_c}$.

45. Ammonium hydrogen sulphide was allowed to dissociated 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

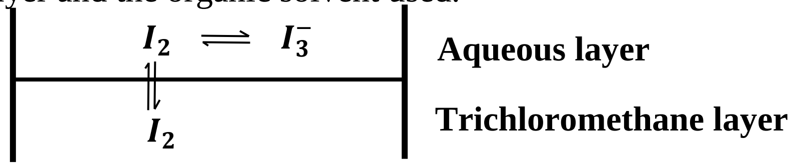
Iodine reacts with potassium iodide to form potassium triiodide according to the equation;

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

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 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;

$$K_D = \frac{[I_2]\ in\ free\ aqueous\ layer}{[I_2]\ free\ in\ organic\ layer}$$

$$[I_2]_{total}\ in\ aqueous\ layer = [I_2]_{free(aqueous\ layer)} + [I_3^-]$$

The total concentration of iodine in the aqueous layer, $[I_2]_{total}$ is obtained by titrating a portion of a known volume of it with standard sodium thiosulphate solution.

$$[I_2]_{total}\ in\ aqueous\ layer = [I_2]_{free(aqueous\ layer)} + [I_3^-]$$

Since $[I_2]_{free(aqueous\ layer)}$ 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.

$$[I^-]_{total} = [I^-]_{aqueous} + [I_3^-]$$

Since $[I_3^-]$ is known, then$[I^-]_{aqueous}$ 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:

$$\boldsymbol{I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)}$$

$$Molar\ mass\ of\ KI = 39 + 127 = 166g$$

$$Moles\ of\ Na_2S_2O_3\ that\ reacted\ with\ I_2\ in\ benzene\ layer = \left(\frac{5.1 \times 0.1}{1000}\right) = 0.00051\ moles$$

$$I_2(aq)\ +\ 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

$$Mole\ ratio\ of S_2O_3^{2-}: I_2 = 2:1$$

$$Moles\ of\ I_2\ in\ 10\ cm^3\ of\ benzene\ layer = \frac{1}{2} \times 0.00051 = 0.000255\ moles$$

$$10\ cm^3\ of\ benzene\ layer\ contain\ 0.000255\ moles\ of\ I_2$$

$$1000\ cm^3\ of\ benzene\ layer\ contain\ \left(\frac{1000 \times 0.000255}{10}\right) moles\ of\ I_2$$

$$[I_2]\ in\ benzene\ layer = 0.0255M$$

$$K_D = \frac{[I_2]\ free\ in\ benzene}{[I_2]\ free\ in\ aqueous\ layer} = 130$$

$$[I_2]\ free\ in\ aqueous\ layer = \frac{0.0255}{130} = 0.000196M$$

$$Moles\ of\ Na_2S_2O_3\ that\ reacted\ with\ free\ I_2\ in\ aqueous\ layer = \left(\frac{2.9 \times 0.1}{1000}\right) = 0.00029\ moles$$

$$Mole\ ratio\ of S_2O_3^{2-}: I_2 = 2:1$$

$$Moles\ of\ total\ \ I_2\ in\ 50\ cm^3\ of\ aqueous\ layer = \frac{1}{2} \times 0.00029 = 0.000145\ moles$$

$$50\ cm^3\ of\ aqueous\ layer\ contain\ 0.000145\ moles\ of\ total\ I_2$$

$$1000\ cm^3\ of aqueous\ layer\ contain\ \left(\frac{1000 \times 0.000145}{50}\right) moles\ of\ total\ I_2$$

$$[I_2]\ \ total\ in\ aqueous\ layer = 0.0029M$$

$$[I_2]\ \ total\ in\ aqueous\ layer = [I_2]\ free + [I_3^-]$$

$$[I_2]\ free + [I_3^-] = 0.0029$$

$$[I_3^-] = 0.0029 - 0.000196 = 0.0027$$

$$Moles\ of\ KI\ in\ 500cm^3 = \frac{4}{166} = 0.0241\ moles$$

$$Molar\ concentration\ of\ KI\ solution = \left(\frac{1000 \times 0.0241}{500}\right) = 0.0482\ M$$

$$[I^-]_{total} = [I^-]_{aqueous} + [I_3^-]$$

$$[I^-]_{aqueous} = 0.0482 - 0.0027 = 0.0455$$

$$K_c = \frac{[I_3^-]}{[I_2][I^-]} = \frac{0.0027}{0.000196 \times 0.0455} = \mathbf{302.8 mol^{-1} dm^3}$$

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: $I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$ is 730. Calculate the concentration of:
   (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 $\Delta \boldsymbol{n} = \mathbf{0}$ ($\boldsymbol{where\ total\ number\ of\ moles\ of\ products - total\ number\ of\ moles\ of\ reactants\ is\ zero}$)	

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, $\boldsymbol{K_c}$ ***or*** $\boldsymbol{K_p}$ 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;

$$\boldsymbol{Q} = \frac{[C]^y[D]^z}{[A]^w[B]^x}$$

- At equilibrium, $\boldsymbol{K_c = Q}$ **,** and this is defined as the **equilibrium condition.**
- If $\boldsymbol{K_c < Q}$, the backward reaction is favoured, the reaction moves from right to left, until equilibrium is established.
- If $\boldsymbol{K_c > Q}$, 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:**

$$\boldsymbol{CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)}$$

If $\boldsymbol{K_c = 0.64}$ 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 ?

$$[CO] = \frac{0.01}{4} = 0.0025M$$

$$[H_2O] = \frac{0.01}{4} = 0.0025M$$

$$[CO_2] = \frac{0.008}{4} = 0.002M$$

$$[H_2] = \frac{0.012}{4} = 0.003M$$

$$Q = \frac{[CO_2] \times [H_2]}{[CO] \times [H_2O]}$$

$$Q = \frac{0.002 \times 0.003}{0.0025 \times 0.0025}$$

$$\boldsymbol{Q = 0.96}$$

Since $\boldsymbol{Q > K_c}$**, the reaction proceeds from right to left, until equilibrium is established.**

2. **Consider the following reversible reaction; $\boldsymbol{2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)}$. At a certain temperature, the partial pressure were measured and found to be $\boldsymbol{0.57 atm}$ for sulphur trioxide, $\boldsymbol{0.4\ atm}$ for sulphur dioxide and $\boldsymbol{0.16\ atm}$ for oxygen. Predict the direction in which the reaction should proceed in order to attain equilibrium.**

$$\boldsymbol{(K_p = 3.4\ atm^{-1})}$$

$p_{SO_3} = 0.57\ atm$ $p_{SO_2} = 0.4\ atm$ $p_{O_2} = 0.16\ atm$ $Q = \frac{(p_{SO_3})^2}{(p_{SO_2})^2 \times p_{O_2}}$	$Q = \frac{0.57^2}{0.4^2 \times 0.16}$ $\boldsymbol{Q = 12.69\ atm^{-1}}$ ***Since*** $\boldsymbol{Q > K_p}$**, the reaction proceeds from right to left, until equilibrium is established.**

Questions

1. For the reaction: $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, the equilibrium constant, $\boldsymbol{K_c}$, 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: $[N_2] = 0.05\ mol\ l^{-1}$, $[O_2] = 0.02\ mol\ l^{-1}$, and $[NO] = 0.30\ mol\ l^{-1}$.
2. For the reaction: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the equilibrium constant, $\boldsymbol{K_c}$, 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 $0.10\ mol\ l^{-1}$
3. 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.
   (a) Write:
      (i) equation for the decomposition of Sulphur trioxide
      (ii) an expression for the equilibrium constant, $\boldsymbol{K_c}$
   (b) Calculate the value of $\boldsymbol{K_c}$.
   (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 $\boldsymbol{K_c}$ value for the reaction.
   (d) Using your answers in (b) and (c) above, state how the position of the equilibrium was affected.

L*é* CHATELIER'S PRINCIPLE AND THE EFFECTS OF VARIOUS FACTORS ON THE EQUILIBRIUM OF REVERSIBLE CHEMICAL REACTIONS

L*é* 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.

<u>or</u>

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**

$$N_2(g) \ + \ 3H_2(g) \rightleftharpoons 2NH_3(g)$$

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 $\boldsymbol{1\ volume\ of}\ N_2 + \boldsymbol{3\ volumes\ of}\ \ H_2\ (\boldsymbol{a\ total\ of\ 4\ volumes})\boldsymbol{produce\ 2\ volumes\ of\ ammonia}$

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**

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

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;**

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

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 ($\Delta H\ is\ positive$) or exothermic ($\Delta H\ is\ negative$).

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

1. **Ammonia is formed from nitrogen and hydrogen at 25°C and 10 atm.**

$$N_2(g) \quad + \quad 3H_2(g) \rightleftharpoons 2NH_3(g)\ ,\ \Delta H^{\theta} = -92kJmol^{-1}$$

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

$$N_2(g) \quad + \quad O_2(g) \rightleftharpoons 2NO(g)\,;\ \Delta H^{\theta} = +180\ kJmol^{-1}$$

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:

$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$$

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.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -ve$$

   (a) State what would be 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 in increased

2. The reaction between nitrogen and hydrogen at 25℃ and 10 atm takes place according to the following equation.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H^{\theta} = -92\ kJmol^{-1}$$

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℃ 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

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

   (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, $\boldsymbol{K_c}$.
      (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.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

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.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

   (i) Write the expression for the equilibrium constant, $\boldsymbol{K_c}$.

   (ii) When 1 mole of phosphorus(V) chloride was heated in a closed vessel at 350℃, the equilibrium mixture was found to contain 38.4% of chlorine. Calculate the equilibrium constant at 350℃.

   (iii) The equilibrium constant at 250℃ was found to b 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℃. Give a reason for your answer.

6. When heated at 1atm, carbon dioxide decomposes according to the equation:

$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$$

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, $\boldsymbol{K_p}$.

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.

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOC_2H_5\,(l) + H_2O\,(l) \quad \Delta H = -ve$$

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;

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

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:

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

(a) At a temperature of 375℃ 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, $\boldsymbol{K_p}$.

(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:

$$NH_4CONH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g) \qquad + \Delta H^0(kJmol^{-1})$$

(a) Write the expression for the equilibrium constant ($\boldsymbol{K_p}$)

(b) At equilibrium, the total pressure of the system is 0.36 atm. at 40℃. Calculate the value of $\boldsymbol{K_p}$ for the reaction at 40℃ and indicate its units.

(c) State what happens to the $\boldsymbol{K_p}$ calculated in (a) if :

(i) more solid ammonium carbamate is added to the equilibrium mixture.

(ii) the temperature is increased to 80℃.

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**

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)\,;\ \Delta H^{\theta}(298K) = -92.4\,kJmol^{-1}$$

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**.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H^{\theta}(298K) = -197.6\,kJmol^{-1}$$

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

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

or by roasting iron pyrites in air

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

or roasting zinc blende in air

$$2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$$

or roasting copper pyrites

$$2CuFeS_2(s) + 4O_2(g) \longrightarrow Cu_2S(s) + 3SO_2(g) + 2FeO(s)$$

(b) Iron pyrites are roasted in air to form iron(III) oxide and sulphur dioxide.

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

*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.***

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

*The sulphur trioxide is **dissolved in concentrated sulphuric acid** to form a fuming liquid called **oleum**.*

$$H_2SO_4(aq) + SO_3(g) \longrightarrow H_2S_2O_7(l)$$

*The oleum is carefully **diluted with a correct amount of water** to form 98% concentrated sulphuric acid.*

$$H_2S_2O_7(l) + H_2O\ (l) \longrightarrow 2H_2SO_4(aq)$$

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.

$$Ca_3(PO_4)_2(s) + 2H_2SO_4(aq) \longrightarrow Ca(H_2PO_4)_2(s) + 2CaSO_4(s)$$

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.

$$Ca_3(PO_4)_2(s) + 4H_3PO_4(aq) \longrightarrow 3Ca(H_2PO_4)_2(s)$$

Details of these process for conversion of ammonia formed by Haber process to nitric acid are discussed in DEMISTYFYING 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, $\boldsymbol{K_p}$ 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℃.
   (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℃ 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.

CHAPTER SEVEN

IONIC EQUILIBRIA

ACIDS, BASES AND SALTS

Acids and bases

Acids are characterized by a sour taste and their effect on litmus and changing colour of indicators. They react with bases and also some other compounds to form salts. They liberate carbon dioxide from carbonates and hydrogen when reacted with metals.

Bases are characterized by a soapy feel and detergent power. They react with acids to form a salt and water.

There have been many attempts to define acids and bases. Early definitions considered acids as substances that provide hydrogen ions when dissolved in water and bases as substances that react with hydrogen ions to form a salt and water.

The concept of acids and bases according to various theories

Acids and bases have been defined according three theories which include the **Arrhenius theory**, **Bronsted-Lowry theory** and the **Lewis theory**.

1. **Acids and bases according to the Arrhenius theory**.

According to this theory;

- ***An acid is a substance that on dissolving in water dissociates to produce hydrogen ions***

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$
$$HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$$
$$H_2SO_4(aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$$

- ***A base is a substance which on dissolving in water dissociates to produce hydroxyl ions***.

$$NaOH(aq) \longrightarrow Na^+(aq) + \bar{O}H(aq)$$
$$KOH(aq) \longrightarrow K^+(aq) + \bar{O}H(aq)$$

Considering the reactions above when a base is reacted with an acid, a **neutralisation reaction** occurs.

$$H^+(aq) + \bar{O}H(aq) \longrightarrow H_2O(l)$$

Arrhenius theory however didn't explain bases which do not contain hydroxyl ions for example basic oxides, carbonates, and ammonia. Ammonia neutralises acids by accepting hydrogen ions rather than providing hydroxide ions because undissociated ammonium hydroxide is hypothesized.

$$NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$$

The Arrhenius theory definitions of acids and bases only applied to aqueous solution. It could not explain acid-base reactions other solvents unlike water.

2. Acids and bases according to Bronsted-Lowry theory

The Bronsted-Lowry theory catered for some of the setbacks of the Arrhenius theory

According to this theory;

- ***An acid is a substance that donates protons to a base***

(i) $HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$

(ii) $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$

H_3O^+ is a hydrated proton and is called the **oxonium ion, hydroxonium ion or hydronium ion**, and is also referred to as the hydrogen ion.

$$H^+(aq) + H_2O(l) \longrightarrow H_3O^+(aq)$$

- ***A base is a substance that accepts protons from an acid***

(iii) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$

(iv) $CH_3CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2NH_3^+(aq) + \bar{O}H(aq)$

(v) $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + \bar{O}H(aq)$

Note: In reaction(i), water accepts a proton from hydrochloric acid to form the oxonium ion. Water behaves as a proton- acceptor(base)

In reaction(iv), water donates a proton to ethylamine to form the ethylammonium ion. Water behaves as a proton- donor(acid)

Also note that strong acids and bases completely ionise in solution whereas weak acids and bases partly ionise in solution.

3. Acids and bases according to Lewis theory

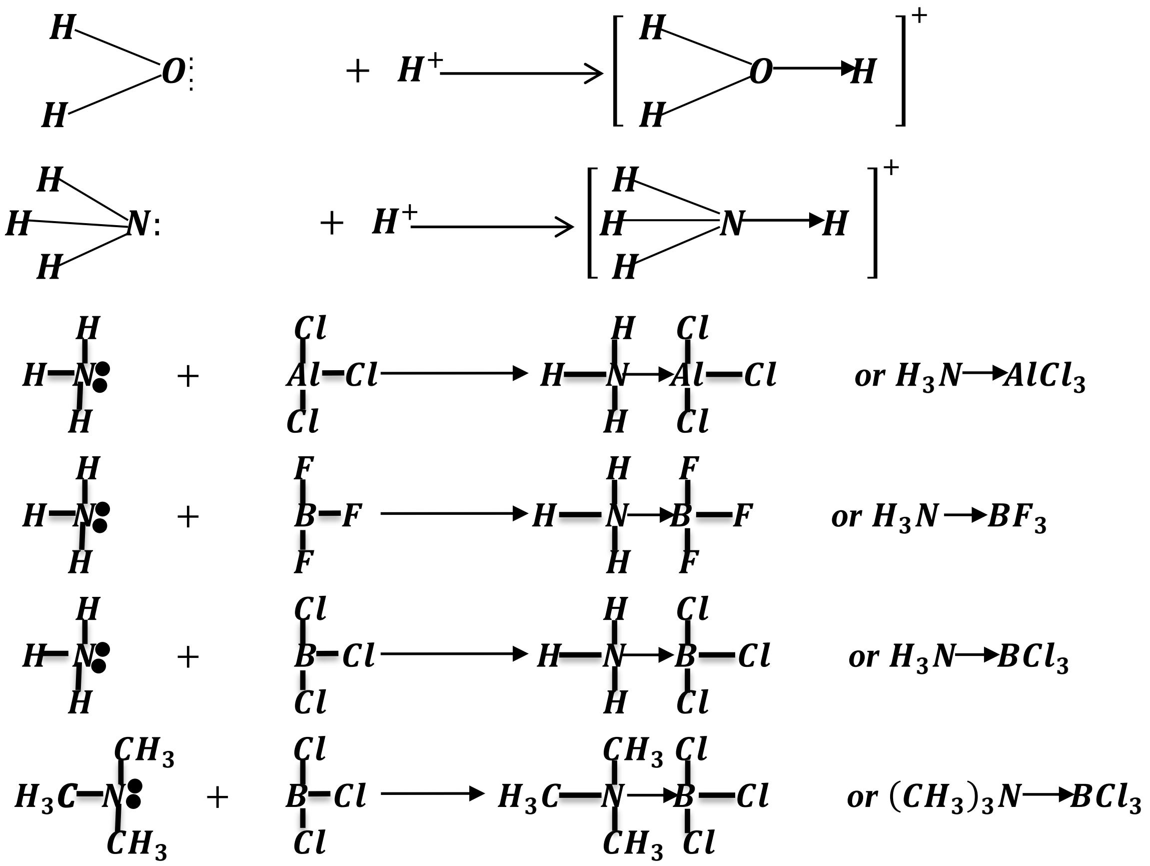
The Bronsted-Lowry theory of acids is based on protolysis. The Bronsted-Lowry acids must therefore contain hydrogen according to the theory. However, there are substances also react as acids and change the color of indicators even in dry state but they do not contain hydrogen. The Lewis theory catered for this shortcoming.

According to the Lewis theory;

- ***An acid is any substance that can accept a lone pair of electrons.***
- ***A base is any substance that can donate a lone pair of electrons.***

Examples of Lewis acids and bases include

Lewis acids	Lewis bases
Aluminium chloride, Iron(III) chloride, Boron trifluoride, Boron trichloride and Beryllium chloride	Water, ammonia, triethylamine, trimethylamine and alcohols
Hydrogen ion, aluminium ion, iron(III) ion and copper(II) ion	Hydroxyl ion, chloride ion and cyanide ion
Silicon(IV) chloride and phosphorus(V) chloride	Ethene and ethyne



or $H_3N \rightarrow AlCl_3$

or $H_3N \rightarrow BF_3$

or $H_3N \rightarrow BCl_3$

or $(CH_3)_3N \rightarrow BCl_3$

Conjugate acid and bases

Benzoic acid ionises in its aqueous solution according to the equation;

$$C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons C_6H_5COO^-(aq) + H_3O^+(aq)$$

In the equilibrium above, the benzoate ion($C_6H_5COO^-$) is a conjugate base of benzoic acid. Benzoic acid is a conjugate acid of the benzoate ion and the two form a **conjugate acid-base pair**.

The conjugate base is formed when an acid loses a proton and when the conjugate base gains a proton, it forms its conjugate acid.

Acids and bases can therefore be neutral molecules, positive ions or negative ions.

Examples of conjugate acid-base pairs include;

Conjugate acid	Conjugate base
$\boldsymbol{HCl}$	Cl^-
$\boldsymbol{HNO_3}$	NO_3^-
$\boldsymbol{H_2SO_4}$	HSO_4^-
$\boldsymbol{HSO_4^-}$	SO_4^{2-}
$\boldsymbol{H_2S}$	HS^-
$\boldsymbol{HS^-}$	S^{2-}
$\boldsymbol{NH_4^+}$	NH_3
$\boldsymbol{C_6H_5NH_3^+}$	$C_6H_5NH_2$

Try to write equations showing how the conjugate base is formed from the conjugate acid for each of the above conjugate acid-base pairs.

Classification of strong acids and bases, weak acids and bases

A strong acid is an acid which ionises completely in its aqueous solution and easily releases protons

A weak acid an acid which partly ionises in its aqueous solution and does not easily release protons

Examples include;

Strong acid	Weak acid
Hydrochloric acid	Ethanoic acid
Hydrobromic acid	Methanoic acid
Hydroiodic acid	Hydrocyanic acid
Nitric acid	Hydrofluoric acid
Sulphuric acid	Butanoic acid
Chloric(VII) acid	Carbonic acid

A strong base is a base which ionises completely in its aqueous solution and easily accepts protons

A weak base is a base which partly ionises in its aqueous solution and does not easily accept protons

Examples include;

Strong bases	Weak bases
Potassium hydroxide	Aqueous ammonia
Sodium hydroxide	Aqueous methylamine
Barium hydroxide	Aqueous phenylamine
Lithium hydroxide	Aqueous triethylamine

Relative strength of Bronsted-Lowry acids and bases

The strength of different acids in an aqueous solution under similar conditions can be compared using their ***degrees of dissociation($\propto$)*** and acid ***dissociation constants(K_a), (for weak acids)*** at the same dilution and temperature.

(a) Using degrees of dissociation

- The higher the degree of dissociation at a given temperature and dilution, the stronger the acid
- The degree of dissociation of an acid increases with dilution and all acids become equally stronger and infinite dilution because they become completely dissociated.
- The degree of dissociation for an acid that ionises endothermically increases with increase in temperature hence the acid releases more hydrogen ions as the temperature increases, becoming stronger with increase in temperature.
- The degree of dissociation for an acid that ionises exothermically decreases with increase in temperature hence the acid releases fewer hydrogen ions as the temperature increases, becoming weaker with increase in temperature.

Acid	**Degree of dissociation**	
	for a $1M$ solution	**for a $0.1M$ solution**
HNO_3	0.82	0.96
HCl	0.79	0.92
$\frac{1}{2}H_2SO_4$	0.51	0.65
CH_3COOH	0.004	0.013

(b) Using acid dissociation constants ($K_a values$)

The strengths of weak acids are compared using more conveniently by use of their dissociation constants.

The higher the acid dissociation constant, the stronger the acid. The strength can then be explained by use of other terms like **electronegativity of bonded atoms**, **inductive effect** and **number of oxygen atom (for oxo-acids of chlorine)** in **relation to polarity of the oxygen-hydrogen bond** hence the **bond strength**.

N.B. Inductive effect is the ability of an atom or group of atoms to donate electrons towards a neighbouring atom or ability to withdraw electrons from the neighbouring atom.

An atom or group of atoms that donate electrons to a neighbouring atom have positive inductive effect. These include all **alkyl groups**.

An atom or group of atoms that withdraws electrons from a neighbouring atom have negative inductive effect. These include all **halogen atoms,** $-NO_2, -NH_2,$
$-C \equiv N, -SO_3H$.

The nature of the groups attached to the carboxyl group has a great effect on the acid strength therefore due to inductive effect.

Electron withdrawing groups make carboxylic acid stronger by making the oxygen-hydrogen bond becomes more polar and weak hence release of hydrogen ions in aqueous solution.

Electron donating groups makes carboxylic acid weaker by making the oxygen-hydrogen bond less polar and strong hence release of few hydrogen ions in aqueous solution.

Examples

1. **The table below shows acid dissociation constants, K_a, of group VII hydrides.**

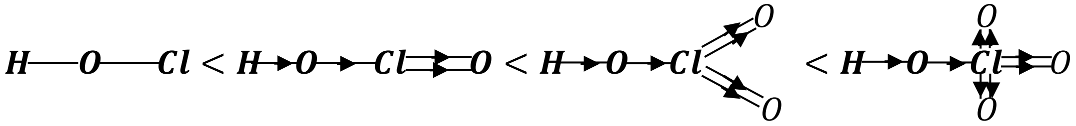
Hydride	***HF***	***HCl***	***HBr***	***HI***
K_a $(moldm^{-3})$at 25 ^{O}C	6.6×10^{-4}	1.3×10^{6}	1.0×10^{9}	3.2×10^{9}

Explain the trend in K_a values of the hydrides.

The K_a values increase in the order $HF < HCl < HBr < HI$ indicating that ***acid strength increases in the same order****. The* ***strength of an acid depends on how easily it releases protons****. This is because* ***atomic radius of the halogen atoms increases from fluorine to iodine****. This makes the* ***hydrogen-halogen bond length longer****,* ***reducing the bond strength from the hydrogen-fluorine bond to hydrogen-iodine bond****, releasing many hydrogen ions in solution.*

Hydrofluoric acid is the weakest acid because the fluorine atom has the ***highest electronegativity*** *due to a* ***very small atomic radius****. Therefore the hydrogen- fluorine bond is* ***highly polar*** *and* ***very strong*** *making the acid to dissociate to a* ***considerably smaller extent****.*

2. **The acid strength of the oxo-acids of chlorine increases in the order $HOCl < HClO_2 < HClO_3 < HClO_4$. Explain this observation.**



The ***strength of an acid depends on how easily it releases protons****. The acid strength increases depending on* ***the number of oxygen atoms that exert a negative inductive effect*** *in each molecule of the acid,* ***increasing the polarity of the oxygen-hydrogen bond****. This is because oxygen is* ***more electronegative than chlorine****. In chloric(VII) acid, 3 oxygen atoms exert a negative inductive effect on the O-H bond making it very weak and breaks to release very many hydrogen ions making it stronger than chloric(V) acid in which two oxygen atoms exert a negative inductive effect making the O-H bond weaker than in chloric(III) acid in which only one oxygen atom has a negative inductive* *effect. Chloric(I) acid has the* ***strongest oxygen-hydrogen bond*** *because* ***no oxygen atom has a negative inductive effect*** *in it.*

3. **The table below shows acid dissociation constants, K_a for some acids at a particular temperature.**

Acid	$HCOOH$	CH_3COOH	CH_3CH_2COOH
K_a $(moldm^{-3})$	1.77×10^{-4}	1.70×10^{-5}	1.3×10^{-5}

State and explain the trend in acid strength of the acids.

Acid strength decreases in the order $HCOOH > CH_3COOH > CH_3CH_2COOH$

The ***strength of an acid depends on how easily it releases a proton****. Methanoic acid has* ***a hydrogen atom instead of an alkyl group*** *attached to the carboxyl group, which has* ***no inductive effect*** *hence the* ***oxygen-hydrogen bond in it is the weakest****, easily breaks to release many hydrogen ions. The alkyl groups in ethanoic acid and propanoic acid have* ***a positive inductive effect*** *which* ***decreases the polarity of the oxygen-hydrogen bond****, making it not easy break. The* ***strength of the oxygen-hydrogen bond increases as the positive inductive effect increases with the increase in number of carbon atoms in the alkyl groups*** *attached to the carboxyl group.*

4. **The table below shows acid dissociation constants, K_a for some acids at a particular temperature.**

Acid	CH_3COOH	$ClCH_2COOH$	$Cl_2CHCOOH$	Cl_3CCOOH
K_a $(moldm^{-3})$	1.7×10^{-5}	1.4×10^{-3}	5.1×10^{-3}	2.2×10^{-1}

State and explain the trend in acid strength of the acids.

Acid strength increases in the order

$$CH_3COOH < ClCH_2COOH < Cl_2CHCOOH < Cl_3CCOOH$$

The ***strength of an acid depends on how easily it releases a proton****. Ethanoic acid has* ***a methyl group*** *attached to the carboxyl group, which has* ***a positive inductive effect*** *hence the* ***oxygen-hydrogen bond in it has lowest polarity****,* ***making it the strongest*** *hence does not easily break to release hydrogen ions. The chlorine atoms in chloroethanoic acid, dichloroethanoic acid and trichloroethanoic acid are* ***more electronegative than carbon*** *and have* ***a negative inductive effect*** *which* ***increases the polarity of the oxygen-hydrogen bond****, making it weak and easy to break. The* ***strength of the oxygen-hydrogen bond decreases as the negative inductive effect increases with the increase in number of chlorine atoms in the chain*** *attached to the carboxyl group.*

5. **The table below shows acid dissociation constants, K_a for some acids at a particular temperature.**

Acid	K_a $(moldm^{-3})$
CH_3COOH	1.7×10^{-5}
FCH_2COOH	2.0×10^{-3}
$ClCH_2COOH$	1.6×10^{-3}
$BrCH_2COOH$	1.4×10^{-3}
ICH_2COOH	7.3×10^{-4}

State and explain the acid strengths of the acids.

Ethanoic acid is the weakest acid among all the acids. For the other acids, acid strength decreases in the order $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$

*The **strength of an acid depends on how easily it releases a proton**. Ethanoic acid has **a methyl group** attached to the carboxyl group, which has **a positive inductive effect** hence the **oxygen-hydrogen bond in it has lowest polarity**, **making it the strongest** hence does not easily break to release hydrogen ions. For the halogen substituted acids, the halogen atoms are **more electronegative than carbon** and have **a negative inductive effect**. However, the **negative inductive effect decreases with the decrease in electronegativity from fluorine to iodine, decreasing the polarity of the oxygen-hydrogen bond**, making it stronger and not easily broken from fluoroethanoic acid to iodoethanoic acid.*

The strength of different bases in an aqueous solution under similar conditions can also be compared using their ***degrees of dissociation($\propto$)*** and ***base dissociation constants(K_b), (for weak bases)*** at the same dilution and temperature.

(a) Using degrees of dissociation

The higher the degree of dissociation at a given temperature and dilution, the stronger the base

Base	Degree of dissociation
KOH	0.95
$NaOH$	0.93
$\frac{1}{2}Ba(OH)_2$	0.90

(b) Using acid dissociation constants (K_b $values$)

The strengths of weak bases are compared using more conveniently by use of their base dissociation constants.

The higher the base dissociation constant, the stronger the base.

Electron withdrawing groups make bases weaker by making the lone pair of electrons less available to accept protons.

Electron donating groups makes bases stronger by making the lone pair of electrons readily available to accept protons.

Example

1. **The table below shows the base dissociation constants of different bases in aqueous solutions.**

Base	Base dissociation constant, K_b ($moldm^{-3}$)
$C_6H_5NH_2$	3.5×10^{-10}
NH_3	1.8×10^{-5}
$(CH_3)_3N$	6.0×10^{-5}
CH_3NH_2	4.4×10^{-4}
$CH_3CH_2NH_2$	4.7×10^{-4}
$(CH_3)_2NH$	5.1×10^{-4}
$(CH_3CH_2)_3N$	5.5×10^{-4}
$(CH_3CH_2)_2NH$	9.5×10^{-4}

(a) Compare and explain the basic strength of ammonia, methylamine and ethylamine

Basic strength increases in the order; $NH_3 < CH_3NH_2 < CH_3CH_2NH_2$

The basic strength of amines depends on the ***availability of lone pair of electrons on the nitrogen atom****. Ammonia is the* ***weakest base*** *because the* ***hydrogen atoms*** *attached to the nitrogen atom,* ***have no inductive effect****. The alkyl groups attached to the nitrogen atom in methylamine and ethylamine have* ***a positive inductive effect*** *which* ***increases the electron density on the nitrogen atom****, making the* ***lone pairs of electrons readily available for protonation****. The* ***positive inductive effect increases with the increase in number of carbon atoms in the alkyl groups*** *attached to the nitrogen atom hence ethylamine is a stronger base than methylamine.*

(b) Compare and explain the basic strength of methylamine, dimethylamine and trimethylamine

Basic strength increases in the order; $(CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$

*The basic strength of amines depends on the **availability of lone pair of electrons on the nitrogen atom**. The **three methyl groups attached to the nitrogen atom in trimethylamine**, **have the greatest positive inductive effect** but **due to steric hindrance to the approach of a proton towards the nitrogen atom and poorest solvation due to lack of nitrogen-hydrogen bonds,** trimethylamine is the **weakest base.** The **methyl groups attached to the nitrogen atom in methylamine and dimethylamine have a positive inductive effect** which **increases the electron density on the nitrogen atom**, making the **lone pairs of electrons readily available for protonation**. Methylamine and dimethylamine also have **nitrogen-hydrogen bonds which increase their solvation. The positive inductive effect and solvation increase with the increase in number of alkyl groups** attached to the nitrogen atom **and number of nitrogen-hydrogen bonds respectively** hence dimethylamine is a stronger base than methylamine.*

(c) Compare and explain the basic strength of ammonia, ethylamine and aniline

Basic strength increases in the order; $C_6H_5NH_2 < NH_3 < CH_3CH_2NH_2$

*The basic strength of amines depends on the **availability of lone pair of electrons on the nitrogen atom**. Aminobenzene is **the weakest base** because the **lone pairs of electrons on the nitrogen atom interact with the delocalised pi- electrons in the benzene ring**. This reduces the electron density on nitrogen atom, making the **lone pair of electrons less available for protonation**. Ammonia is a **stronger base than aminobenzene** because the **hydrogen atoms** attached to the nitrogen atom, **have no inductive effect**. Ammonia also **has more nitrogen-hydrogen bonds** hence **more solvated than aminobenzene**. The **ethyl group attached to the nitrogen atom in ethylamine has a positive inductive effect** which **increases the electron density on the nitrogen atom**, making the **lone pair of electrons readily available for protonation**.*

Note; Amides ($RCONH_2$) are negligibly basic or neutral in aqueous solution compared to aliphatic amines(RNH_2) because the lone pair of electrons on the nitrogen atom in amides is partially involved in bonding to the carbon of the carbonyl group and therefore less available for protonation

2. **Explain why ethylamine is a stronger base than ethanamide, CH_3CONH_2 although both compounds have an amino group**

The ***ethyl group attached to the nitrogen atom in ethylamine has a positive inductive effect*** *which* ***increases the electron density on the nitrogen atom****, making the* ***lone pair of electrons readily available for protonation****. In ethanamide, the* ***lone pair of electrons on the nitrogen atom interacts with the pi-electrons of the carbonyl group*** *therefore* ***less available for protonation****.*

Questions

1. The oxy-acids of chlorine include; $HOCl, HClO_2, HClO_3 \text{ and } HClO_4$.
   (a) Write the name of each oxo-acid.
   (b) Draw the structure and name the shape of each of the acids
   (c) Arrange the acids in order of decreasing acid strength and explain your answer.
2. (a) What do you understand by the term inductive effect?
   (b) The carboxylic acids below have the following values for the acid dissociation constant, K_a

Acid	HCO_2H	CH_3CO_2H	$C_6H_5CO_2H$	FCH_2CO_2H	$BrCH_2CO_2H$
K_a at 25℃ $(moldm^{-3})$	1.77×10^{-4}	1.75×10^{-5}	6.3×10^{-5}	2.6×10^{-3}	1.25×10^{-3}

Explain the observations in the acid dissociation constants

(c) (i) Amines are basic in nature. Explain the role of inductive effect of the alkyl groups on the strength of bases.

(ii) How do you account for the fact that amides though having a $-NH_2$ group are not basic in nature.

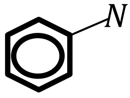
3. Ethylamine, dimethylamine and ammonia are weak bases in aqueous solution.
   (a) (i) Arrange the compounds in order of increasing basic strength

(ii) Suggest why the basic strength is in that order.

(b) (i) Name a reagent that can be used to identify the functional group of the bases.

(ii) State what is observed when each of the bases is separately treated with the named reagent.

4. The basic strength of aminobenzene, ammonia and dimethylamine are in the order.



$NH_2 < NH_3 < (CH_3)_2NH$

Derivation of expressions for acid dissociation constant, K_a and base dissociation constant, K_b

Consider an aqueous solution of a weak binary acid, HX of original concentration $c\ moldm^{-3}$ and with a degree of dissociation, α.

	$\boldsymbol{HX(aq)} \rightleftharpoons$	$\boldsymbol{H^+(aq)}$ +	$\boldsymbol{X^-(aq)}$
Initial concentration	c	0	0
Concentration dissociated/formed	$c\alpha$	$c\alpha$	$c\alpha$
Moles at equilibrium	$\boldsymbol{c(1-\alpha)}$	$\boldsymbol{c\alpha}$	$\boldsymbol{c\alpha}$

$$K_a = \frac{[H^+][X^-]}{[HX]} = \frac{(c\alpha)^2}{c(1-\alpha)} = \frac{c^2\alpha^2}{c(1-\alpha)}$$

$$\boldsymbol{K_a = \frac{c\alpha^2}{(1-\alpha)}}$$

Also considering an aqueous solution of a weak binary base, B of original concentration $c\ moldm^{-3}$ and with a degree of dissociation, α.

The equation for ionisation of the base in water would be;

$$\boldsymbol{B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + \bar{O}H(aq)}$$

$$K_b = \frac{[BH^+][\bar{O}H]}{[B]}$$

The same treatment as the acid will give the expression below. The concentration of water remains constant hence is not included in the equation.

$$\boldsymbol{K_b = \frac{c\alpha^2}{(1-\alpha)}}$$

Calculations involving K_a

The expression for acid dissociation constant, $\boldsymbol{K_a}$ of a weak acid, relating concentration, c in $moldm^{-3}$, and the degree of dissociation, $\boldsymbol{\alpha}$ is given by;

$$\boldsymbol{K_a = \frac{c\alpha^2}{(1-\alpha)}}$$

However, if $\boldsymbol{\alpha}$ is small compared to 1, then $(\boldsymbol{1-\alpha})$ is approximately equal to one, so that; $\boldsymbol{K_a = c\alpha^2}$ and $\boldsymbol{\alpha = \sqrt{\frac{K_a}{C}}}$

Also from the procedure of derivation above, at equilibrium; $\boldsymbol{[H^+] = c\alpha}$

All the derived equations above can be used in calculations involving ionic equilibria of weak acids.

Also note that, in calculations, for the accurate expression $\boldsymbol{K_a = \frac{c\alpha^2}{(1-\alpha)}}$ ***or the approximated one*** $\boldsymbol{K_a = c\alpha^2}$ ***is used depending on the value of*** $\boldsymbol{\alpha}$

This can be known by testing using the approximated expression first.
For example:

Using a 0.1M ethanoic acid; $K_a = 1.8 \times 10^{-5} moldm^{-3}$ $\boldsymbol{\alpha} = \sqrt{\frac{\boldsymbol{K_a}}{\boldsymbol{C}}} = \sqrt{\frac{1.8 \times 10^{-5}}{\mathbf{0.1}}}$ $= \mathbf{0.0134}\ \boldsymbol{or}\ \mathbf{1.34}\%$ **The value of α is small as compared to one so $\boldsymbol{K_a = c\alpha^2}$ can be used in calculations**	**Using a 0.001M ethanoic acid;** $K_a = 1.8 \times 10^{-5} moldm^{-3}$ $\boldsymbol{\alpha} = \sqrt{\frac{\boldsymbol{K_a}}{\boldsymbol{C}}} = \sqrt{\frac{1.8 \times 10^{-5}}{\mathbf{0.001}}}$ $= \mathbf{0.134}\ \boldsymbol{or}\ \mathbf{13.4}\%$ **The value of α is not very small as compared to one so $\boldsymbol{K_a = c\alpha^2}$ cannot be used in calculations but rather $\boldsymbol{K_a = \frac{c\alpha^2}{(1-\alpha)}}$ is used.**

Examples

1. A solution was made by dissolving 1.22g of benzoic acid in 500$\boldsymbol{cm^3}$ of water.

(a) Write the equation for ionisation of benzoic acid in aqueous solution hence the expression for the ionisation constant, $\boldsymbol{K_a}$

(b) Calculate the:

(i) hydrogen ion concentration

(ii) degree of dissociation

$$(\boldsymbol{K_a\ for\ benzoic\ acid\ is}\ \mathbf{6.4 \times 10^{-5}}\boldsymbol{moldm^{-3}})$$

(a) $$C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons C_6H_5COO^-(aq) + H_3O^+(aq)$$

$$K_a = \frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5COOH]}$$

(b) (i) $Molar\ mass\ of\ C_6H_5COOH = (7 \times 12) + (6 \times 1) + (2 \times 16) = 122g$

$$Moles\ of\ C_6H_5COOH\ in\ 500cm^3 = \frac{1.22}{122} = 0.01\ moles$$

$$500cm^3 of\ solution\ contain\ 0.01\ moles\ of\ C_6H_5COOH$$

$$1000cm^3 of\ solution\ contain\ \left(\frac{1000 \times 0.01}{500}\right)\ moles\ of\ C_6H_5COOH$$

$$= 0.02M$$

At equilibrium; $[C_6H_5COO^-] = [H_3O^+]$

$$K_a = \frac{[H_3O^+]^2}{[C_6H_5COOH]}$$

$$[\boldsymbol{H_3O^+}] = \sqrt{\boldsymbol{K_a}[\boldsymbol{C_6H_5COOH}]}$$

$$[H_3O^+] = \sqrt{6.4 \times 10^{-5} \times 0.02}$$

$$= \mathbf{1.131 \times 10^{-3}}\boldsymbol{moldm^{-3}}$$

b(ii) $\boldsymbol{From\ \alpha} = \sqrt{\frac{\boldsymbol{K_a}}{\boldsymbol{C}}}, \boldsymbol{\alpha} = \sqrt{\frac{\mathbf{6.4 \times 10^{-5}}}{\mathbf{0.02}}}$

$$\boldsymbol{\alpha} = \mathbf{0.057}$$

2. **(a) Write the expression for the acid dissociation constant of methanoic acid in aqueous solution.**
   (b) A 0.01M solution of methanoic acid is 14% dissociated at 25℃. Calculate the dissociation constant of methanoic acid at 25℃.

(a)

$$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$$

$$C = 0.01M, \alpha = \frac{14}{100} = 0.14$$

$$K_a = \frac{c\alpha^2}{1-\alpha}$$

$$K_a = \frac{0.01 \times 0.14^2}{1 - 0.14}$$

$$\boldsymbol{K_a = 2.28 \times 10^{-4} moldm^{-3}}$$

Questions

1. (a) (i) Write equation for ionisation of ethanoic acid in water
   (ii) write the expression for the ionisation constant of ethanoic acid
   (b) Calculate the degree of ionisation of a 0.05M solution of ethanoic acid. ($K_a\ for\ ethanoic\ acid\ is\ 1.8 \times 10^{-5} moldm^{-3}$)
2. A solution containing 0.001M of methanoic acid is 1% ionised. Calculate the :
   (i) Hydrogen ion concentration
   (ii) Acid dissociation constant, K_a, for methanoic acid
3. A solution is prepared by adding 0.0005 moles of ethanoic acid to half a litre of water. Calculate the degree of ionisation of ethanoic acid.
   ($K_a\ for\ ethanoic\ acid\ is\ 1.8 \times 10^{-5} moldm^{-3}$)

Calculations involving K_b

The expression for base dissociation constant, $\boldsymbol{K_b}$ of a weak base, relating concentration, c in dm^{-3} , and the degree of dissociation, $\boldsymbol{\alpha}$ is given by;

$$\boldsymbol{K_b = \frac{c\alpha^2}{(1-\alpha)}}$$

However, if $\boldsymbol{\alpha}$ is small compared to 1, then $(\boldsymbol{1-\alpha})$ is approximately equal to one, so that; $\boldsymbol{K_b = c\alpha^2}$ and $\boldsymbol{\alpha = \sqrt{\frac{K_b}{C}}}$

Also from the procedure of derivation above, at equilibrium; $[\boldsymbol{\bar{O}H}] = \boldsymbol{c\alpha}$

All the derived equations above can be used in calculations involving ionic equilibria of weak bases.

Whether to use the accurate or approximated expression of K_b ,in calculations, the same procedure done for weak acids is considered.

Examples

1. **A 0.01M solution of ammonia is 4.0% ionised.**
   (a) Calculate the hydroxide ion concentration
   (b) Determine the base dissociation constant, K_b, for ammonia

(a) $NH_3(aq + H_2O(l) \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$

$$C = 0.01M, \alpha = \frac{4}{100} = 0.04$$

$$[\bar{O}H] = c\alpha = 0.01 \times 0.04$$

$$= 4 \times 10^{-4}\ moldm^{-3}$$

(b) $K_b = \frac{c\alpha^2}{1-\alpha}$

$$K_b = \frac{0.01 \times 0.04^2}{1 - 0.04}$$

$$K_b = 1.67 \times 10^{-5}\ moldm^{-3}$$

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2. **(a) Write the:**
   - **(i) equation for the ionisation of methylamine in water**
   - **(ii) expression for the base dissociation constant, K_b, for methylamine**

   (b) The hydroxyl ion concentration of a 1M methylamine solution is 0.04 $moldm^{-3}$. Calculate the:
   - **(i) degree of dissociation**
   - **(ii) base dissociation constant, K_b, for methylamine.**

(a) (i) $CH_3NH_2(aq + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + \bar{O}H(aq)$

(ii) $K_b = \frac{[CH_3NH_3^+][\bar{O}H]}{[CH_3NH_2]}$

(b) (i) $[CH_3NH_2] = 1M$

$$[\bar{O}H] = c\alpha = 0.04\, moldm^{-3}$$

$$\alpha = \frac{[\bar{O}H]}{c} = \frac{0.04}{1} = 0.04$$

(ii) ***From*** $K_b = \frac{c\alpha^2}{1-\alpha}$

$$K_b = \frac{1 \times 0.04^2}{1 - 0.04}$$

$$K_b = 1.667 \times 10^{-3} moldm^{-3}$$

The auto ionisation (self-ionisation) of water

Pure water is a weak electrolyte due to the slight dissociation into oxonium and hydroxyl ions.

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + \bar{O}H(aq)$$

From the law of mass action;

$$K = \frac{[H_3O^+][\bar{O}H]}{[H_2O]}$$

Since the degree of dissociation of pure water is very small (approximately 18×10^{-10}) or the $[H_2O]$ is so very large compared to $[H_3O^+]$ and $[\bar{O}H]$. Therefore $[H_2O]$ can be taken to be constant such that;

$$K_w = [H_3O^+][\bar{O}H]$$

The constant, K_w is called the ionic product of water. At 25℃, $1dm^3$ of water contains approximately 1.0×10^{-7} $moles$ of both hydrogen ions and hydroxyl ions.

Hence

$$K_w = (1.0 \times 10^{-7})^2 (moldm^{-3})$$

$$\boldsymbol{K_w = 1.0 \times 10^{-14} mol^2 dm^{-6}}$$

Since the dissociation of water is endothermic, the ionic product of water, K_w, increases with increase in temperature. However the value at 25℃ is commonly used since most experiments are carried out at that temperature.

Temperature	**Ionic product of water, $K_w (mol^2 dm^{-6})$**
10℃	2.9×10^{-15}
25℃	1.0×10^{-14}
50℃	5.47×10^{-14}

The concept of pH

The pH is the negative logarithm to the base ten of the hydrogen ion concentration in moles per litre of a solution.

$$pH = -\log_{10}[H_3O^+]$$

Since at 25℃, $1dm^3$ of water contains approximately 1.0×10^{-7} $moles$ of hydrogen ions. The pH of water at 25℃ is given by:

$$pH = -\log_{10}(1.0 \times 10^{-7}) = 7$$

The higher the concentration of hydrogen ions, the lower the pH hence the stronger the acid.

The pH of an aqueous solution of an acid or base depends on the concentration and the degree of ionisation.

Just like pH, pOH is related to the hydroxyl ion concentration by the expression;

$$pOH = -\log_{10}[\bar{O}H]$$

The pK_w is also related to the ionic product of water by:

$$pK_w = -\log_{10} K_w$$

Therefore from the ionic product of water;

$$K_w = [H_3O^+][\bar{O}H]$$

$$-\log_{10} K_w = -\log_{10}([H_3O^+][\bar{O}H])$$

$$-\log_{10} K_w = -\log_{10}[H_3O^+] + (-\log_{10}[\bar{O}H])$$

$$\boldsymbol{pK_w = pH + pOH}$$

$$\text{At } 25°\text{C}, pK_w = -\log_{10}(1.0 \times 10^{-14}) = 14$$

$$\boldsymbol{Therefore\ 14 = pH + pOH}$$

The above equation can be used for aqueous solutions including water at 25℃ .

The pH scale

The pH scale ranges from 1 to 14 depending on the hydrogen ion concentration in the solution. It is summarised below:

$[H_3O^+]$	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	Strong acids			Weak acids				**Neutral**	Weak bases				Strong bases		

Calculations involving $pH, pOH\ and\ pK_w$ for strong acids and bases

(a) For strong acids

Strong acids are completely ionized in aqueous solution.

Therefore their $pH = -\log_{10}[H^+]$

Examples

1. **A solution is formed by dissolving 1120 cm^3 hydrogen chloride gas in 500 cm^3 of water at standard temperature and pressure. Calculate the pH of the solution.**

Hydrogen chloride gas dissolves in water to form hydrochloric acid

$$22400cm^3\ contain\ 1\ mole\ of\ HCl\ at\ stp$$

$$1120cm^3\ contain\ \left(\frac{1 \times 1120}{22400}\right)\ moles\ of\ HCl\ at\ stp$$

$$= 0.05\ mole\ of\ HCl\ at\ stp$$

$$500cm^3\ of\ solution\ contain\ 0.05\ mole\ of\ HCl$$

$$1000cm^3\ of\ solution\ contain\ \left(\frac{1000 \times 0.05}{500}\right) mole\ of\ HCl$$

$$= 0.1M$$

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

$$[HCl] = [H^+] = 0.1M$$

$$pH = -\log_{10}[H^+] = -\log_{10}(0.1) = 1$$

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2. **$25\ cm^3$ of a 0.05M sulphuric acid was added to $750\ cm^3$ of water. Calculate the pH of the resultant solution**.

$$Moles\ of\ H_2SO_4\ in\ 25cm^3\ of\ solution = \left(\frac{25 \times 0.5}{1000}\right) = 0.0125$$

$$Total\ volume\ of\ resultant\ solution = (25 + 750) = 775\ cm^3$$

$$775\ cm^3\ of\ solution\ contain\ 0.0125\ moles\ of\ H_2SO_4$$

$$1000\ cm^3\ of\ solution\ contain\ \left(\frac{1000 \times 0.0125}{775}\right)\ moles\ of\ H_2SO_4$$
$$= 0.0161\ M$$
$$H_2SO_4(aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$$
$$Mole\ ratio\ of\ H_2SO_4 : H^+ = 1:2$$
$$[H^+] = 2[H_2SO_4] = 2 \times 0.0161 = 0.0322M$$
$$pH = -\log_{10}[H^+] = -\log_{10}(0.0322) = 1.5$$

3. **Calculate the mass of hydrogen chloride required per litre to form a solution with $pH = 3$.**

$$pH = -\log_{10}[H^+]$$
$$3 = -\log_{10}[H^+]$$
$$\log_{10}[H^+] = -3$$
$$[H^+] = 10^{-3} = 0.001M$$
$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

$$From\ the\ equation; mole\ ratio\ of H^+ : HCl = 1:1$$
$$[HCl] = [H^+] = 0.001\ M$$
$$Molar\ mass\ of\ HCl = (1 + 35.5) = 36.5g$$
$$Mass\ of\ HCl\ required = (36.5 \times 0.01) = 0.365g$$

4. **Calculate the pH of a solution formed by mixing $80\ cm^3$ of 0.1M sulphuric acid with $120\ cm^3$ of 0.1M potassium hydroxide.**

$$Moles\ of\ H_2SO_4 = \left(\frac{80 \times 0.1}{1000}\right) = 0.008\ moles$$
$$Moles\ of\ KOH = \left(\frac{120 \times 0.1}{1000}\right) = 0.012\ moles$$
$$H_2SO_4(aq) + 2KOH(aq) \longrightarrow K_2SO_4(aq) + 2H_2O(l)$$
$$2\ moles\ of\ KOH\ that\ react\ with\ 1\ mole\ of\ H_2SO_4$$
$$0.012\ moles\ of\ KOH\ react\ with\ \left(\frac{1 \times 0.012}{2}\right)\ moles\ of\ H_2SO_4$$
$$= 0.006\ moles\ of\ H_2SO_4$$
$$Moles\ of\ excess(unreacted)H_2SO_4 = (0.008 - 0.006) = 0.002\ moles$$
$$Total\ volume\ of\ solution = (80 + 120) = 200cm^3$$
$$200cm^3\ of\ solution\ contain\ 0.002\ moles\ of\ H_2SO_4$$
$$1000cm^3\ of\ solution\ contain\ \left(\frac{0.002 \times 1000}{200}\right)\ moles\ of\ H_2SO_4$$
$$\boldsymbol{[H_2SO_4] = 0.01M}$$
$$H_2SO_4(aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$$
$$Mole\ ratio\ of\ H_2SO_4 : H^+ = 1:2$$
$$[H^+] = 2[H_2SO_4] = 2 \times 0.01 = 0.02M$$

$$pH = -\log_{10}[H^+]$$
$$pH = -\log_{10}(0.02) = 1.7$$

Question

1. Calculate the pH of a 0.005M sulphuric acid.
2. A solution has a pH of 5.5. Calculate its hydrogen ion concentration
3. (a) Chloric(VII) acid is a strong acid. State what is meant by the term **strong acid**.
   (b) Calculate the pH of a 0.025 solution of chloric(VII) acid.

4. What is the pH of a $3.6 \times 10^{-5} M$ solution of nitric acid
5. $20.0\ cm^3$ of 0.02M sodium hydroxide was added to $30\ cm^3$ of 0.025M sulphuric acid. Calculate the:
   (i) molar concentration of the hydrogen ions in the initial sulphuric acid
   (ii) concentration of hydrogen ions in the resultant solution
   (iii) the pH of the resultant solution
6. Calculate the pH of a solution obtained by adding $20cm^3$ of 0.1M sodium hydroxide to $25cm^3$ of 0.1M hydrochloric acid.
7. Calculate the pH of a solution formed when $25.0cm^3$ of 0.3M sodium hydroxide are added to $75.0cm^3$ of 0.2M hydrochloric acid at 25℃.

(b) For strong bases

Strong bases are completely ionized in solution to produce hydroxyl ions in the solution but not hydrogen ions. Therefore the hydrogen ion concentration is obtained first using the ionic product expression for water, if $[\bar{O}H]$ is known.

$K_w = [H^+][\bar{O}H]$ $[H^+] = \frac{K_w}{[\bar{O}H]}$ $Then\ pH = -\log_{10}[H^+]$	Or from $pH + pOH = pK_w$ $pOH = -\log_{10}[\bar{O}H]$ $pK_w = -\log_{10} K_w$ $pH = pK_w - pOH$

Examples

1. **Calculate the pH of a solution made by dissolving 1.5g of potassium hydroxide in 250 cm^3 of water at 25℃.**

$$Molar\ mass\ of\ KOH = 39 + 16 + 1 = 56g$$

$$Moles\ of\ KOH = \frac{1.5}{56} = 0.0268\ moles$$

$$250cm^3\ of\ solution\ contain\ 0.0268\ mole\ of\ KOH$$

$$1000cm^3\ of\ solution\ contain\ \left(\frac{1000 \times 0.0268}{250}\right) mole\ of\ KOH$$

$$= 0.1072M$$

$$KOH(aq) \longrightarrow K^+(aq) + \bar{O}H(aq)$$

$$[KOH] = [\bar{O}H] = 0.1072M$$

$$From\ K_w = [H^+][\bar{O}H]$$

$$[H^+] = \frac{K_w}{[\bar{O}H]} = \frac{1 \times 10^{-14}}{0.1072} = 9.328 \times 10^{-14}M$$

$$pH = -\log_{10}[H^+] = -\log_{10}(9.328 \times 10^{-14}) = 13$$

2. **At $0\ ℃$, $K_w = 1.14 \times 10^{-15} mol^2 dm^{-6}$. Calculate the:**

   (i) p^{K_w} **at $0\ ℃$.**

   (ii) **the pH at $0\ ℃$ of a 0.01M solution of sodium hydroxide.**

(i) $pK_w = -\log_{10} K_w = -\log_{10}(1.14 \times 10^{-15}) = 14.94$

(ii)
$$NaOH(aq) \longrightarrow Na^+(aq) + \bar{O}H(aq)$$
$$[NaOH] = [\bar{O}H] = 0.01M$$
$$pOH = -\log_{10}[\bar{O}H] = -\log_{10}(0.01) = 2$$
$$pK_w = pH + pOH$$
$$pH = pK_w - pOH = 14.94 - 2 = 12.94$$

3. **$25\ cm^3$ of a 0.3M sodium hydroxide was added to $225\ cm^3$ of water at $25℃$. Calculate the pH of the solution formed**.

$$Moles\ of\ NaOH\ in\ 25cm^3\ of\ solution = \left(\frac{25 \times 0.3}{1000}\right) = 0.0075$$
$$Total\ volume\ of\ resultant\ solution = (25 + 225) = 250\ cm^3$$
$$250\ cm^3\ of\ solution\ contain\ 0.0075\ moles\ of\ NaOH$$
$$1000\ cm^3\ of\ solution\ contain\ \left(\frac{1000 \times 0.0075}{250}\right)\ moles\ of\ NaOH$$
$$= 0.03\ M$$
$$NaOH(aq) \longrightarrow Na^+(aq) + \bar{O}H(aq)$$
$$Mole\ ratio\ of\ NaOH{:}\ \bar{O}H = 1{:}1$$
$$[NaOH] = [\bar{O}H] = 0.03M$$
$$From\ K_w = [H^+][\bar{O}H]$$
$$[H^+] = \frac{K_w}{[\bar{O}H]} = \frac{1 \times 10^{-14}}{0.03} = 3.333 \times 10^{-13} M$$
$$pH = -\log_{10}[H^+] = -\log_{10}(3.333 \times 10^{-13}) = 12.5$$

4. **Calculate the pH of solution formed by mixing $80\ cm^3$ of 0.1M hydrochloric acid with $120\ cm^3$ of 0.1M potassium hydroxide.**

$$Moles\ of\ HCl = \left(\frac{80 \times 0.1}{1000}\right) = 0.008\ moles$$
$$Moles\ of\ KOH = \left(\frac{120 \times 0.1}{1000}\right) = 0.012\ moles$$
$$HCl(aq) + KOH(aq) \longrightarrow KCl(aq) + H_2O(l)$$
$$Mole\ ratio\ of\ KOH{:}\ HCl = 1{:}1$$
$$Moles\ of\ HCl\ that\ reacted = moles\ of\ KOH\ that\ reacted = 0.008\ moles$$
$$Moles\ of\ excess(unreacted)KOH = (0.012 - 0.008) = 0.004\ moles$$
$$Total\ volume\ of\ solution = (80 + 120) = 200cm^3$$
$$200cm^3\ of\ solution\ contain\ 0.004\ moles\ of\ KOH$$

$$1000cm^3\ of\ solution\ contain\ \left(\frac{0.004\times 1000}{200}\right)\ moles\ of\ KOH$$

$$\boldsymbol{[KOH] = 0.02M}$$

$$KOH(aq)\longrightarrow K^+(aq) + \bar{O}H(aq)$$

$$\boldsymbol{[KOH] = [\bar{O}H] = 0.02M}$$

$$pOH = -\log_{10}[\bar{O}H]$$

$$pOH = -\log_{10}(0.02) = \mathbf{1.699}$$

$$pH = 14 - pOH$$

$$pH = 14 - 1.699 = \mathbf{12.3}$$

Questions

1. Calculate the pH of a solution made by dissolving 4g of sodium hydroxide in one litre of water at 25℃.
2. Calculate the pH of a 0.01M potassium hydroxide solution at 25℃. (The ionic product of water is $1\times 10^{-14}mol^2dm^{-6}$

The relationship between K_a and K_b for an acid-base conjugate

Considering an acid-base conjugate pair of NH_4^+ and NH_3, in aqueous solution, the equilibria involved for the acid, NH_4^+ and its base, NH_3 are:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$$

For the first equilibrium;

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} \dots\dots\dots\dots\dots\dots\dots.(i)$$

For the second equilibrium;

$$K_b = \frac{[NH_4^+][\bar{O}H]}{[NH_3]} \dots\dots\dots\dots\dots\dots.(ii)$$

$$Equation (i) \times Equation\ (ii)\ yields;$$

$$K_a \times K_b = \frac{[NH_3][H_3O^+]}{[NH_4^+]} \times \frac{[NH_4^+][\bar{O}H]}{[NH_3]}$$

$$K_a \times K_b = [H_3O^+]\times[\bar{O}H]$$

$$But\ [H_3O^+]\times[\bar{O}H] = K_w$$

$$Therefore\ \boldsymbol{K_a \times K_b = K_w}$$

Expression of pH for weak acids and bases

Weak acids are not completely dissociated even in very dilute solutions. The expression $\boldsymbol{[H^+] = c\alpha}$ can be used to get the hydrogen ion concentration or the hydrogen ion concentration can be got from the concentration and dissociation constant of the acid.

$$\boldsymbol{Then\ pH = -\log_{10}[H_3O^+]}$$

Weak bases are also not completely dissociated solution. The expressions $[\bar{\boldsymbol{O}}\boldsymbol{H}] = \boldsymbol{c\alpha}$ can be used to get the hydroxyl ion concentration and then the hydrogen ion concentration can be got from the expression for ionic product of water.

$K_w = [H^+][\bar{O}H]$ $[H^+] = \frac{K_w}{[\bar{O}H]}$ $Then\ pH = -\log_{10}[H_3O^+]$	Or from $pH + pOH = pK_w$ $pOH = -\log_{10}[\bar{O}H]$ $pK_w = -\log_{10} K_w$ $pH = pK_w - pOH$

pH calculations for weak acids and weak bases

(a) For weak acids

Examples

1. **Calculate the pH of a $0.01M$ solution of ethanoic acid.**
($K_a = 1.8 \times 10^{-5}\ moldm^{-3}$)

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

At equilibrium; $[CH_3COO^-] = [H_3O^+]$

$$[CH_3COOH] = 0.01M$$

$$K_a = \frac{[H_3O^+]^2}{[CH_3COOH]}$$

$$[H_3O^+]^2 = K_a \times [CH_3COOH]$$

$$[H_3O^+] = \sqrt{1.8 \times 10^{-5} \times 0.01}$$

$$= 4.24 \times 10^{-4}M$$

$$pH = -\log_{10}[H_3O^+]$$

$$pH = -\log_{10}(4.24 \times 10^{-4}) = \mathbf{3.37}$$

2. **Calculate the pH of a solution made by dissolving $2.45g$ of benzoic acid in one litre of solution. ($K_a\ at\ 25℃ = 6.6 \times 10^{-5}\ moldm^{-3}$)**

$$C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons C_6H_5COO^-(aq) + H_3O^+(aq)$$

$$Molar\ mass\ of\ C_6H_5COOH = (7 \times 12) + (6 \times 1) + (2 \times 16) = 122g$$

$$Moles\ of\ C_6H_5COOH\ in\ 1\ litre\ of\ solution = \frac{2.45}{122} = 0.02\ moles$$

$$[\boldsymbol{C_6H_5COOH}] = \mathbf{0.02}\boldsymbol{M}$$

$$K_a = \frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5COOH]}$$

At equilibrium; $[C_6H_5COO^-] = [H_3O^+]$

$$[C_6H_5COOH] = 0.02M$$

$$K_a = \frac{[H_3O^+]^2}{[C_6H_5COOH]}$$

$$[H_3O^+]^2 = K_a \times [C_6H_5COOH]$$

$$[H_3O^+] = \sqrt{6.6 \times 10^{-5} \times 0.02}$$

$$= 1.149 \times 10^{-3}M$$

$$pH = -\log_{10}[H_3O^+]$$

$$pH = -\log_{10}(1.149 \times 10^{-3}) = \mathbf{2.9}$$

3. **The pH of a 0.01M solution of benzoic acid is 3.59. Calculate the:**
   (a) acid dissociation constant
   (b) degree of dissociation

$$C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons C_6H_5COO^-(aq) + H_3O^+(aq)$$

(a) $pH = -\log_{10}[H_3O^+]$

$$3.59 = -\log_{10}[H_3O^+]$$

$$[H_3O^+] = 10^{-3.59} = 2.57 \times 10^{-4}M$$

$$K_a = \frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5COOH]}$$

At equilibrium; $[C_6H_5COO^-] = [H_3O^+]$

$$[C_6H_5COOH] = 0.01M$$

$$K_a = \frac{[H_3O^+]^2}{[C_6H_5COOH]} = \frac{(2.57 \times 10^{-4})^2}{0.01}$$

$$\boldsymbol{K_a = 6.607 \times 10^{-6} moldm^{-3}}$$

(b) From $[H_3O^+] = c\alpha$,

$$\alpha = \frac{[H_3O^+]}{c} = \frac{2.57 \times 10^{-4}}{0.01} = \mathbf{0.026}$$

---

4. **Propanoic acid undergoes dissociation according to the following equation.**

$$\boldsymbol{CH_3CH_2COOH\,(aq) \rightleftharpoons CH_3CH_2COO^-(aq) + H^+(aq)}$$

   (a) Write the expression for the acid dissociation constant, K_a.
   (b) Given that the concentration of propanoic acid is 0.1M and its degree of dissociation is 0.01133. Calculate the;
      (i) pH of propanoic acid,
      (ii) acid dissociation constant, K_a.

(a) $K_a = \frac{[CH_3CH_2COO^-][H^+]}{[CH_3CH_2COOH]}$

(b) (i) From $[H^+] = c\alpha$

$$[H^+] = 0.1 \times 0.01133 = 1.133 \times 10^{-3}M$$

$$pH = -\log_{10}[H^+]$$

$$= -\log_{10}(1.133 \times 10^{-3}) = \mathbf{2.95}$$

At equilibrium; $[CH_3CH_2COO^-] = [H^+]$

$$[CH_3CH_2COOH] = 0.1M$$

$$K_a = \frac{[H^+]^2}{[CH_3CH_2COOH]} = \frac{(1.133 \times 10^{-3})^2}{0.1}$$

$$\boldsymbol{K_a = 1.28 \times 10^{-5} moldm^{-3}}$$

---

5. **Calculate the pH of a solution containing 1 mole of methanoic acid in 10 litres of water. ($pK_a = 3.75$)**

$$HCOOH(aq) + H_2O(l) \rightleftharpoons HCOO^-(aq) + H_3O^+(aq)$$

$$10{,}000cm^3\ of\ solution\ contain\ 1\ mole\ of\ HCOOH$$

$$1000cm^3\ of\ solution\ contain\ \left(\frac{1000 \times 1}{10{,}000}\right) molesof\ HCOOH$$

$$\boldsymbol{[HCOOH] = 0.1M}$$

$$pK_a = -\log_{10} K_a$$

$$3.75 = -\log_{10} K_a$$

$$K_a = 10^{-3.75} = 1.78 \times 10^{-4} moldm^{-3}$$

$$But\ K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$$

At equilibrium; $[HCOO^-] = [H_3O^+]$

$$[HCOOH] = 0.1M$$

$$K_a = \frac{[H_3O^+]^2}{[HCOOH]}$$

$$[H_3O^+]^2 = K_a \times [HCOOH]$$

$$[H_3O^+] = \sqrt{1.78 \times 10^{-4} \times 0.1}$$

$$= 4.217 \times 10^{-3}M$$

$$pH = -\log_{10}[H_3O^+]$$

$$pH = -\log_{10}(4.217 \times 10^{-3}) = \mathbf{2.38}$$

6. **Calculate the mass of dichloroethanoic acid that should be dissolved in $\mathbf{500\ cm^3}$ of water to make a solution of $\boldsymbol{pH = 1.8}$. ($\boldsymbol{K_a = 5.1 \times 10^{-3}\ moldm^{-3}}$)**

$$Cl_2CHCOOH(aq) + H_2O(l) \rightleftharpoons Cl_2CHCOO^-(aq) + H_3O^+(aq)$$

$$pH = -\log_{10}[H_3O^+]$$

$$1.8 = -\log_{10}[H_3O^+]$$

$$[H_3O^+] = 10^{-1.8} = 0.0158M$$

$$K_a = \frac{[Cl_2CHCOO^-][H_3O^+]}{[Cl_2CHCOOH]}$$

At equilibrium; $[Cl_2CHCOO^-] = [H_3O^+]$

$$K_a = \frac{[H_3O^+]^2}{[Cl_2CHCOOH]}$$

$$5.1 \times 10^{-3} = \frac{(0.0158)^2}{[Cl_2CHCOOH]}$$

$$[Cl_2CHCOOH] = \frac{(0.0158)^2}{5.1 \times 10^{-3}}$$

$$\boldsymbol{[Cl_2CHCOOH] = 0.0489M}$$

$Molar\ mass\ of\ Cl_2CHCOOH$

$$= 71 + 24 + 2 + 32 = 129g$$

$Mass\ of\ Cl_2CHCOOH\ per\ litre$

$$= 129 \times 0.0489 = 6.308g$$

$$1000\ cm^3\ contain\ 6.308g$$

$$500\ cm^3\ contain\ \left(\frac{500 \times 6.308}{1000}\right)g$$

$$\boldsymbol{= 3.154g}$$

Questions

1. Calculate the pH of a $0.01M$ solution of butanoic acid. ($K_a = 1.51 \times 10^{-5}\ moldm^{-3}$)
2. Calculate the pH of a 0.01M solution of propanoic acid. ($K_a = 1.45 \times 10^{-5}\ moldm^{-3}$)
3. (a) (i) Write the equation for the ionisation of ethanoic acid in aqueous solution.
    (ii) Write the expression for the acid dissociation constant, K_a of ethanoic acid.
   (b) The pH of a 0.1M aqueous ethanoic acid is 2.9. Calculate the dissociation constant of ethanoic acid.
4. The pH of a solution of ethanoic acid of concentration of $0.1\ moldm^{-3}$ is 2.88. Calculate the acid ionisation constant, K_a
5. Calculate the dissociation constant of a 2M solution of hydrocyanic acid if the pH is 4.55.
6. A 1M solution of iodic(I) acid has a pH of 5.26. Calculate the acid dissociation constant of the acid.
7. The dissociation constant of a 0.5M propanoic acid solution is $1.5 \times 10^{-5}\ moldm^{-3}$. Calculate the:
   (a) degree of dissociation
   (b) hydrogen ion concentration
   (c) pH of the solution
8. (a) (i) Write the equation for the ionisation of an acid $RCOOH$ in water.
    (ii) Write the expression for the ionisation constant.
   (b) The ionisation constant, K_a for $RCOOH$ is $1.8 \times 10^{-5}\ moll^{-1}$. Calculate the:

  - (i) pK_a value of the acid
  - (ii) the percentage ionisation of the acid in a 1M aqueous solution

9. Calculate the pH of 0.5M solution of methanoic acid. ($pK_a = 3.75$)
10. The dissociation constant of a 0.05M solution of a very weak monobasic acid is $2 \times 10^{-5}\ moldm^{-3}$ at 25℃. Calculate the:
    - (a) degree of dissociation
    - (b) hydrogen ion concentration
    - (c) pH of the solution
11. Calculate the mass of benzoic acid that should be dissolved in one litre of water to make a solution of $pH = 6$. ($K_a\ at\ 25℃ = 6.4 \times 10^{-5}\ moldm^{-3}$)

(a) For weak bases

Examples

1. **Calculate the pH of a 0.001M ammonia solution. ($K_b = 1.8 \times 10^{-5}\ moldm^{-3}$)**

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$$

$$K_b = \frac{[NH_4^+][\bar{O}H]}{[NH_3]}$$

At equilibrium; $[\bar{O}H] = [NH_4^+]$

$$[NH_3] = 0.001M$$

$$K_b = \frac{[\bar{O}H]^2}{[NH_3]}$$

$$[\bar{O}H]^2 = K_b \times [NH_3]$$

$$[\bar{O}H] = \sqrt{1.8 \times 10^{-5} \times 0.001}$$

$$= 1.34 \times 10^{-4}M$$

$$pOH = -\log_{10}[\bar{O}H]$$

$$pOH = -\log_{10}(1.34 \times 10^{-4}) = \mathbf{3.87}$$

$$pH = 14 - pOH$$

$$pH = 14 - 3.87 = \mathbf{10.13}$$

2. **(a) Write:**
    - **(i) equation for the ionisation of ethylamine in water**
    - **(ii) the expression for the ionisation constant, K_b of ethylamine.**

   (b) The pH of a 0.01M solution of ethylamine is 11.37.
    - **(i) Calculate the ionisation constant, K_b of ethylamine at 25℃.**

($K_w = 1.0 \times 10^{-14}\ mol^2l^{-2}\ at\ 25$ ℃)

   - **(ii) State the assumptions you have made in b(i) above.**

(a) (i) $CH_3CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2NH_3^+(aq) + \bar{O}H(aq)$

(ii) $K_b = \frac{[CH_3CH_2NH_3^+][\bar{O}H]}{[CH_3CH_2NH_2]}$

(b) (i) $pH = -\log_{10}[H^+]$

$$11.37 = -\log_{10}[H^+]$$

$$[H^+] = 10^{-11.37} = 4.266 \times 10^{-12}M$$

From $K_w = [H^+][\bar{O}H]$

$$[\bar{O}H] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{4.266 \times 10^{-12}}$$

$$= 2.344 \times 10^{-3}M$$

$$K_b = \frac{[\bar{O}H]^2}{[CH_3CH_2NH_2]} = \frac{(2.344 \times 10^{-3})^2}{0.01}$$

$$= \mathbf{5.49 \times 10^{-4} moldm^{-3}}$$

(ii) At equilibrium;

$$[\bar{O}H] = [CH_3CH_2NH_3^+]$$

$$[CH_3CH_2NH_2] \approx 0.01M$$

3. **The pH of a solution of dimethylamine of concentration $\mathbf{0.01\,moldm^{-3}}$ is 7.64 at $\mathbf{25}$℃. Calculate the basic dissociation constant, $\boldsymbol{K_b}$ for dimethylamine.**

$$(\boldsymbol{K_w = 1.0 \times 10^{-14}\ mol^2dm^{-6}})$$

$$(CH_3)_2NH(aq) + H_2O(l) \rightleftharpoons (CH_3)_2NH_2^+(aq) + \bar{O}H(aq)$$

$$pH = -\log_{10}[H^+]$$
$$7.64 = -\log_{10}[H^+]$$
$$[H^+] = 10^{-7.64} = 2.291 \times 10^{-8}M$$
From $K_w = [H^+][\bar{O}H]$
$$[\bar{O}H] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{2.291 \times 10^{-8}}$$
$$= 4.365 \times 10^{-7}M$$

$$K_b = \frac{[(CH_3)_2NH_2^+][\bar{O}H]}{[(CH_3)_2NH]}$$
At equilibrium; $[\bar{O}H] = [(CH_3)_2NH_2^+]$
$$[(CH_3)_2NH] = 0.01M$$
$$K_b = \frac{[\bar{O}H]^2}{[(CH_3)_2NH]}$$
$$K_b = \frac{[\bar{O}H]^2}{[(CH_3)_2NH]} = \frac{(4.365 \times 10^{-7})^2}{0.01}$$
$$= \mathbf{1.91 \times 10^{-11} moldm^{-3}}$$

4. **Calculate the concentration in moles per litre of an aqueous solution of ammonia whose pH is 10.3 ($\boldsymbol{K_b = 1.74 \times 10^{-5}\ moldm^{-3}}$**

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$$

$$pH = -\log_{10}[H^+]$$
$$10.3 = -\log_{10}[H^+]$$
$$[H^+] = 10^{-10.3} = 5.01 \times 10^{-11}M$$
From $K_w = [H^+][\bar{O}H]$
$$[\bar{O}H] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{5.01 \times 10^{-11}} = 2 \times 10^{-3}M$$
$$K_b = \frac{[NH_4^+][\bar{O}H]}{[NH_3]}$$

At equilibrium; $[\bar{O}H] = [NH_4^+]$
$$K_b = \frac{[\bar{O}H]^2}{[NH_3]}$$
$$1.74 \times 10^{-5} = \frac{(2 \times 10^{-3})^2}{[NH_3]}$$
$$[NH_3] = \frac{(2 \times 10^{-3})^2}{1.74 \times 10^{-5}} = \mathbf{0.2299\ M}$$

5. **0.02M methylamine solution is 4% ionized at $\mathbf{25}$℃.**
   - **(a) Write ;**
     - **(i) an equation for the ionization of methylamine in water.**
     - **(ii) an expression for the base ionization constant $\boldsymbol{K_b}$ for methylamine.**
   - **(b) Calculate the:**
     - **(i) pH of the methylamine solution.($\boldsymbol{K_w = 1.0 \times 10^{-14}\ mol^2dm^{-6}\ at\ 25}$℃)**
     - **(ii) base ionization constant, $\boldsymbol{K_b}$ for methylamine**.

(a) (i) $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + \bar{O}H(aq)$

(ii) $K_b = \frac{[CH_3NH_3^+][\bar{O}H]}{[CH_3NH_2]}$

(b) (i) $[\bar{O}H] = c\alpha = 0.02 \times \frac{4}{100}$

$$= 8 \times 10^{-4}M$$

From $K_w = [H^+][\bar{O}H]$

$$[H^+] = \frac{K_w}{[\bar{O}H]} = \frac{1.0 \times 10^{-14}}{8 \times 10^{-4}}$$

$$= 1.25 \times 10^{-11}M$$

$$pH = -\log_{10}[H^+]$$

$$pH = -\log_{10}(1.25 \times 10^{-11})$$

$$= \mathbf{10.9}$$

At equilibrium;

$$[\bar{O}H] = [CH_3NH_3^+]$$

$$[CH_3NH_2] \approx 0.02M$$

(ii) $K_b = \frac{[\bar{O}H]^2}{[CH_3NH_2]}$

$$= \frac{(8 \times 10^{-4})^2}{0.02}$$

$$= \mathbf{3.2 \times 10^{-5} moldm^{-3}}$$

6. **Calculate the pH of a solution made by dissolving 7.2g of aminobenzene in $\mathbf{500\ cm^3}$.**

$$(\boldsymbol{K_b = 3.5 \times 10^{-10}\ moldm^{-3}})$$

$$C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + \bar{O}H(aq)$$

$$Molar\ mass\ of\ C_6H_5NH_2 = (6 \times 12) + (7 \times 1) + (1 \times 14) = 93g$$

$$Moles\ of\ C_6H_5NH_2\ in\ 500\ cm^3\ of\ solution = \frac{7.2}{93} = 0.0774\ moles$$

$$500\ cm^3\ of\ solution\ 0.0774\ moles\ of\ C_6H_5NH_2$$

$$1000\ cm^3\ of\ solution\ \left(\frac{0.0774 \times 1000}{500}\right)\ moles\ of\ C_6H_5NH_2$$

$$= 0.1548\ M$$

$$\mathbf{[C_6H_5NH_2] = 0.1548M}$$

$$K_b = \frac{[C_6H_5NH_3^+][\bar{O}H]}{[C_6H_5NH_2]}$$

At equilibrium; $[\bar{O}H] = [C_6H_5NH_3^+]$

$$[C_6H_5NH_2] = 0.1548\ M$$

$$K_b = \frac{[\bar{O}H]^2}{[C_6H_5NH_2]}$$

$$[\bar{O}H]^2 = K_b \times [C_6H_5NH_2]$$

$$[\bar{O}H] = \sqrt{3.5 \times 10^{-10} \times 0.1548}$$

$$= 7.361 \times 10^{-6}M$$

$$pOH = -\log_{10}[\bar{O}H]$$

$$pOH = -\log_{10}(7.361 \times 10^{-6}) = \mathbf{5.13}$$

$$pH = 14 - pOH$$

$$pH = 14 - 5.13 = \mathbf{8.87}$$

7. **Determine the mass of aminobenzene that should be dissolved in 1 litre of water to form a solution whose pH is 8.3. ($\boldsymbol{K_b = 3.5 \times 10^{-10}\ moldm^{-3}}$)**

$$C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + \bar{O}H(aq)$$

$$pH = -\log_{10}[H^+]$$

$$8.3 = -\log_{10}[H^+]$$

$$[H^+] = 10^{-8.3} = 5.01 \times 10^{-9}M$$

From $K_w = [H^+][\bar{O}H]$

$$[\bar{O}H] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{5.01 \times 10^{-9}}$$

$$= 1.996 \times 10^{-6}M$$

$$K_b = \frac{[C_6H_5NH_3^+][\bar{O}H]}{[C_6H_5NH_2]}$$

At equilibrium; $[\bar{O}H] = [C_6H_5NH_3^+]$

$$K_b = \frac{[\bar{O}H]^2}{[C_6H_5NH_2]}$$

$$3.5 \times 10^{-10} = \frac{(1.996 \times 10^{-6})^2}{[C_6H_5NH_2]}$$

$$[C_6H_5NH_2] = \frac{(1.996 \times 10^{-6})^2}{3.5 \times 10^{-10}} = 0.0114M$$

$$Molar\ mass\ of\ C_6H_5NH_2$$

$$= 72 + 7 + 14 \quad = 93g$$

$$Mass\ of\ C_6H_5NH_2\ in\ 1\ litre$$

$$= (93 \times 0.0114) = \mathbf{1.06g}$$

Questions

1. Determine the pH of 0.01M solution of methylamine.

$$(K_b\ at\ 25℃ = 5.0 \times 10^{-4}\ moldm^{-3})$$

2. (a) Write the:
    - (i) equation for the ionisation of ethylamine in water
    - (ii) expression for the ionisation constant, K_b of ethylamine.

   (b) A solution contains 0.1 mole of ethylamine per litre of solution at 25 ℃.
    - (i) Calculate the pH of the solution. (The ionisation constant of ethylamine is $5.4 \times 10^{-4} moldm^{-3}$ at 25 ℃ , $K_w = 1.0 \times 10^{-15} mol^2 dm^{-6}$)
    - (ii) State the assumptions made in b(i) above.
3. The pH of 0.01M solution of ammonia is 10.6. Calculate the ionisation constant for ammonia. ($K_w = 1.0 \times 10^{-14}\ mol^2 dm^{-6}$)
4. The pH of 0.1M solution of ethylamine is 11.85. Calculate the basic dissociation constant, K_b for ethylamine. ($pK_w = 14$)
5. A solution containing $0.15\ moldm^{-3}$ of ammonia is 1.4% ionised.
    - (a) Write equation for ionisation of ammonia in water.
    - (b) Calculate the:
        - (i) pH of ammonia solution ($K_w = 1.0 \times 10^{-14}\ mol^2 dm^{-6}\ at\ 25℃$)
    - (ii) base association constant, K_b
6. Calculate the pH of a $0.2\ moldm^{-3}$ of ammonia. $(p^{K_b}\ for\ ammonia\ is\ 4.76\ and\ ionic\ product\ for\ water\ at\ 25℃\ is$

$$1.0 \times 10^{-14}\ mol^2 dm^{-6})$$

7. (a) Dimethylamine partially ionises in water to form an alkaline solution.

Write an equation for the ionisation of dimethylamine in water

   (b) The pH of a 0.02M dimethylamine solution at 20℃ was found to be 11.51.
    - (i) Calculate the molar concentration of hydroxide ions in the solution. The ionic product of water at 20℃ is $6.81 \times 10^{-15} mol^2 dm^{-6}$
    - (ii) Deduce the basic ionisation constant, K_b of dimethylamine from your answer in b(i) above.

   (c) Explain why K_b for ammonia at 20℃ is lower than the value calculate in b(ii) above.
8. (a) Explain the order of increasing basicity of the following compounds.

$$C_6H_5NH_2 < NH_3 < CH_3NH_2$$

   (b) When one mole of methylamine is dissolved in water, the hydrogen ion concentration is found to be $2.5 \times 10^{-10}\ moldm^{-3}$
    - (i) Write an equation for the reaction between water and ethylamine
    - (ii) Calculate the base dissociation constant, K_b for methylamine.

9. (a) Ethanoic acid is a weak acid and has a pK_a value of 4.74
   - (i) State what is meant by the term weak acid.
   - (ii) Write an equation for the ionisation of ethanoic acid
   - (iii) Derive an expression relating K_a and the degree of dissociation of ethanoic acid.
   - (iv) Calculate the pH of a 0.75M ethanoic acid solution.

   (b) Ammonia undergoes the following reaction in water.

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$$

   - (i) Write the expression for the ionisation constant, K_b for the reaction.
   - (ii) If the ionisation constant, K_b for ammonia is $1.8 \times 10^{-5}\ moldm^{-3}$. Calculate the pH of a 0.1M solution of aqueous ammonia.

10. (a) State Graham's law of gaseous diffusion.

   (b) Equimolar amounts of an amine, W and oxygen were allowed to diffuse through a porous medium under the same conditions of pressure and temperature. The amine W diffuses 1.19 times as fast as the time taken by oxygen.
   - (i) Determine the molecular mass of W.
   - (ii) Determine the molecular formula of W.

   (c) (i) Write the equation for the reaction that occurs when W was dissolved in water.
   - (ii) Determine the pH of 0.1M aqueous solution of compound W.

(The base dissociation constant of W is $1.85 \times 10^{-5} moldm^{-3}$ and K_w for water at 25 ℃ is $1.0 \times 10^{-14} mol^2 dm^{-6}$)

HYDROLYSIS OF SALTS

Salt

A salt is a substance formed when the replaceable hydrogen of an acid is either wholly or partially replaced by a metal or an equivalent radical such as the ammonium radical.

A salt always consists of oppositely charged ions.

An acid and base react to form a salt and water. The salt formed can may also react with water to form an acid and a base.

Salt hydrolysis

Some salts react with water to form neutral solutions. Other salts react with water to form acidic or alkaline solutions.

Salt hydrolysis is the reaction between a salt and water to form either a basic or acidic solution.

The extent of the hydrolysis of the salt depends on the strengths of the acid and base from which the hydrolysed salt can be formed.

The various types of salts

(a) Salt of a strong acid and strong base.

Salts formed from strong acids and strong bases include: sodium chloride, sodium sulphate, potassium nitrate, potassium iodide and sodium bromide.

Such salts are not hydrolysed and their aqueous solutions are neutral, with a pH of 7

Salt	Strong base	Strong acid	Equation in aqueous solution
$\boldsymbol{NaCl}$	$NaOH$	HCl	$NaCl(aq) \longrightarrow Na^+(aq) + Cl^-(aq)$
$\boldsymbol{Na_2SO_4}$	$NaOH$	H_2SO_4	$Na_2SO_4(aq) \longrightarrow 2Na^+(aq) + SO_4^{2-}(aq)$
$\boldsymbol{KNO_3}$	KOH	HNO_3	$KNO_3(aq) \longrightarrow K^+(aq) + NO_3^-(aq)$
$\boldsymbol{KI}$	KOH	HI	$KI(aq) \longrightarrow K^+(aq) + I^-(aq)$
$\boldsymbol{NaBr}$	$NaOH$	HBr	$NaBr(aq) \longrightarrow Na^+(aq) + Br^-(aq)$

Considering sodium chloride in water;

The sodium chloride dissociates to form sodium ions and chloride ions.

$$NaCl(aq) \longrightarrow Na^+(aq) + Cl^-(aq)$$

In the solution therefore, there are sodium ions and chloride ions from sodium chloride, then hydroxyl ions and hydrogen ions from water. However, since sodium hydroxide and hydrochloric acid are fully ionised in solution, there is no tendency for reaction between sodium ions and hydroxyl ions to form sodium hydroxide or hydrogen ions and chloride ions to form hydrochloric acid. The concentrations of hydrogen ions and hydroxyl ions remain as they are in pure water mantaining the pH of the solution neutral.

(b) Salt of a strong acid and weak base.

Examples include ammonium chloride, ammonium nitrate, ammonium sulphate.

Phenylammonium chloride, methylammonium chloride, ethylammonium sulphate, methylammonium nitrate.

They undergo **cation hydrolysis** to form acidic solutions.

Salt	Weak base	Strong acid	Equation for hydrolysis in aqueous solution
$\boldsymbol{NH_4Cl}$	$NH_3(aq)$	HCl	$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
$\boldsymbol{(NH_4)_2SO_4}$	$NH_3(aq)$	H_2SO_4	$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
$\boldsymbol{C_6H_5NH_3^+Cl^-}$	$C_6H_5NH_2$	HCl	$C_6H_5NH_3^+(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_2(aq) + H_3O^+(aq)$
$\boldsymbol{CH_3NH_3^+Cl^-}$	CH_3NH_2	HCl	$CH_3NH_3^+(aq) + H_2O(l) \rightleftharpoons CH_3NH_2(aq) + H_3O^+(aq)$
$\boldsymbol{(CH_3CH_2NH_3^+)_2SO_4^{2-}}$	$CH_3CH_2NH_2$	H_2SO_4	$CH_3CH_2NH_3^+(aq) + H_2O(l) \rightleftharpoons CH_3CH_2NH_2(aq) + H_3O^+(aq)$
$\boldsymbol{CH_3NH_3^+NO_3^-}$	CH_3NH_2	HNO_3	$CH_3NH_3^+(aq) + H_2O(l) \rightleftharpoons CH_3NH_2(aq) + H_3O^+(aq)$

Aluminium salts, Chromium(III) salts and iron(III) salts, copper(II) salts and zinc salts of strong acids also undergo **cation hydrolysis**.

The cations in each of the salts above have ***small ionic radii*** and ***high charges*** hence a ***high charge density*** and ***high polarising power***. They therefore undergo ***cation hydrolysis*** to produce ***hydrogen ions***, making their ***solutions acidic*** and exist as $Al(H_2O)_6^{3+}$, $Cr(H_2O)_6^{3+}$, $Fe(H_2O)_6^{3+}$, $Cu(H_2O)_4^{2+}$ and $Zn(H_2O)_4^{2+}$ respectively.

The dissociation of the takes place in stages but the **first stage** being as shown below for each of the solutions:

$$Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Al(H_2O)_5(OH)^{2+}(aq) + H_3O^+(aq)$$
$$Cr(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Cr(H_2O)_5(OH)^{2+}(aq) + H_3O^+(aq)$$
$$Fe(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Fe(H_2O)_5(OH)^{2+}(aq) + H_3O^+(aq)$$
$$Cu(H_2O)_4^{2+}(aq) + H_2O(l) \rightleftharpoons Cu(H_2O)_3(OH)^{+}(aq) + H_3O^+(aq)$$
$$Zn(H_2O)_4^{2+}(aq) + H_2O(l) \rightleftharpoons Zn(H_2O)_3(OH)^{+}(aq) + H_3O^+(aq)$$

The final dissociation results into formation of insoluble hydrated hydroxides of each of the metal and the hydrogen ions can react with basic anions.

$$Al(H_2O)_6^{3+}(aq) + 3H_2O(l) \longrightarrow Al(H_2O)_3(OH)_3(s) + 3H_3O^+(aq)$$
$$Cr(H_2O)_6^{3+}(aq) + 3H_2O(l) \longrightarrow Cr(H_2O)_3(OH)_3(s) + 3H_3O^+(aq)$$
$$Fe(H_2O)_6^{3+}(aq) + 3H_2O(l) \longrightarrow Fe(H_2O)_3(OH)_3(s) + 3H_3O^+(aq)$$
$$Cu(H_2O)_4^{2+}(aq) + 2H_2O(l) \longrightarrow Cu(H_2O)_2(OH)_2(s) + 2H_3O^+(aq)$$
$$Zn(H_2O)_4^{2+}(aq) + 2H_2O(l) \longrightarrow Zn(H_2O)_2(OH)_2(s) + 2H_3O^+(aq)$$

To a solution of any of the above salts, including those shown in the table above, if added a basic substance, a reaction occurs. For example: The solutions evolve:

- ***Carbon dioxide from carbonates and hydrogen carbonates***
- ***Sulphur dioxide from sulphites and sulphites***
- ***Hydrogen sulphide from sulphides***
- ***Hydrogen gas with magnesium***.

Details about these reactions and a variety of ways in which they can be written can be seen in Demystifying Inorganic Chemistry by the same author.

(c) Salt of a weak acid and strong base.

Examples include sodium methanoate, sodium ethanoate, sodium sulphide, potassium cyanide, potassium sulphite, sodium carbonate, sodium hydrogencarbonate, potassium nitrite

They undergo **anion hydrolysis** to form alkaline solutions.

Salt	Weak acid	Strong base	Equation for hydrolysis in aqueous solution
$\boldsymbol{HCOONa}$	$HCOOH$	$NaOH$	$HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + \bar{O}H(aq)$
$\boldsymbol{CH_3COOK}$	CH_3COOH	KOH	$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + \bar{O}H(aq)$
$\boldsymbol{C_6H_5COONa}$	C_6H_5COOH	$NaOH$	$C_6H_5COO^-(aq) + H_2O(l) \rightleftharpoons C_6H_5COOH(aq) + \bar{O}H(aq)$
$\boldsymbol{Na_2S}$	H_2S	$NaOH$	$S^{2-}(aq) + 2H_2O(l) \rightleftharpoons H_2S(aq) + 2\bar{O}H(aq)$
$\boldsymbol{KCN}$	HCN	KOH	$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + \bar{O}H(aq)$
$\boldsymbol{K_2SO_3}$	H_2SO_3	KOH	$SO_3^{2-}(aq) + 2H_2O(l) \rightleftharpoons H_2SO_3(aq) + 2\bar{O}H(aq)$
$\boldsymbol{Na_2CO_3}$	H_2CO_3	$NaOH$	$CO_3^{2-}(aq) + 2H_2O(l) \rightleftharpoons H_2CO_3(aq) + 2\bar{O}H(aq)$
$\boldsymbol{NaHCO_3}$	H_2CO_3	$NaOH$	$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + \bar{O}H(aq)$
$\boldsymbol{KNO_2}$	HNO_2	KOH	$NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + \bar{O}H(aq)$

To a solution of any of the above salts, if added a solution of a cation that forms an insoluble hydroxide, the hydroxide is precipitated. Similarly if the solutions of the salts are warmed with an ammonium salt, ammonia gas is evolved.

Prediction and explaining pH of a salt solution, and hydrolysis basing on its composition

Examples

(a) ***An aqueous solution of potassium nitrate is neutral to litmus whereas an aqueous solution of potassium nitrite turns red litmus paper blue.***

Potassium nitrate is **a salt of a strong acid and a strong base**. It **does not therefore undergo hydrolysis**.

Potassium nitrite is a **salt of a weak acid and a strong base**. It therefore **undergoes anion hydrolysis** to form **hydroxyl ions that make the solution alkaline**.

$$NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + \bar{O}H(aq)$$

(b) ***An aqueous solution of sodium sulphite is alkaline whereas that of sodium hydrogen sulphite is acidic***.

Sodium sulphite is **a salt of a weak acid and a strong base**. It therefore **undergoes hydrolysis** to form **hydroxyl ions that make the solution alkaline**.

$$SO_3^{2-}(aq) + 2H_2O(l) \rightleftharpoons H_2SO_3(aq) + 2\bar{O}H(aq)$$

Sodium hydrogensulphite is also a **salt of a weak acid and a strong base**. It therefore also **undergoes anion hydrolysis** to form hydroxyl ions.

$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons H_2SO_3(aq) + \bar{O}H(aq)$$

However, the hydrogensulphite ion **is a strong acid which dissociates to form hydrogen ions more than it is hydrolysed,** forming an **acidic solution**.

$$HSO_3^-(aq) \longrightarrow SO_3^{2-}(aq) + H^+(aq)$$

(c) Ammonium nitrate solution gives effervescence with magnesium ribbon whereas sodium benzoate solution gives a green precipitate that dissolves in excess with aqueous chromium(III) sulphate solution.

Ammonium nitrate is **a salt of a weak base and a strong acid**. It therefore **undergoes cation hydrolysis** to form **hydrogen ions that make the solution acidic**.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

The **hydrogen ions react with magnesium** to form **hydrogen gas**.

$$Mg(s) + 2H_3O^+(aq) \longrightarrow Mg^{2+}(aq) + H_2(g) + 2H_2O(l)$$

Sodium benzoate is also a **salt of a weak acid and a strong base**. It therefore also **undergoes anion hydrolysis** to form **hydroxyl ions**.

$$C_6H_5COO^-(aq) + H_2O(l) \rightleftharpoons C_6H_5COOH(aq) + \bar{O}H(aq)$$

The **hydroxyl ions react with chromium(III) ions** to form **insoluble chromium(III) hydroxide**.

$$Cr^{3+}(aq) + 3\bar{O}H(aq) \longrightarrow Cr(OH)_3(s)$$

Chromium(III) hydroxide is **amphoteric**, hence **reacts with excess hydroxyl ions** to form a **soluble complex** of **tetrahydroxochromate(III) ions**.

$$Cr(OH)_3(s) + \bar{O}H(aq) \longrightarrow Cr(OH)_4^-(aq)$$

Note; You may be required to write one equation for the reactions leading to formation of hydrogen or precipitation of the hydroxide. This can be done by adding up two equations to get the general equations as shown below:

$$2NH_4^+(aq) + Mg(s) \longrightarrow Mg^{2+}(aq) + H_2(g) + 2NH_3(aq)$$

The equation above is got by eliminating hydrogen ions. This done by multiplying the first equation by 2.

$$3C_6H_5COO^-(aq) + 3H_2O(l) + Cr^{3+}(aq) \longrightarrow 3C_6H_5COOH(aq) + Cr(OH)_3(s)$$

The above equation is obtained by multiplying the first equation by 3 to eliminate hyroxyl ions.

(d) When a concentrated solution of sodium carbonate is added to an aqueous solution of chromium(III) sulphate, a green precipitate is formed with effervescence.

The chromium(III) ion in chromium(III) sulphate has a **small ionic radii** and a **high charge** hence a **high charge density** and **high polarising power**. It therefore exists as **hexaaquachromium(III) ion** in solution and undergoes **cation hydrolysis** to produce **hydrogen ions**, making the **solution acidic.** The **hydrogen ions react with sodium carbonate** to form **carbon dioxide gas** and **insoluble hydrated chromium(III) hydroxide**.

~~$Cr(H_2O)_6^{3+}(aq) + 3H_2O(l) \longrightarrow Cr(H_2O)_3(OH)_3(s) + 3H_3O^+(aq) \quad \times 2$~~

~~$2H_3O^+(aq) + CO_3^{2-}(aq) \longrightarrow CO_2(g) + 3H_2O(l) \quad \times 3$~~

$$2Cr(H_2O)_6^{3+}(aq) + 3CO_3^{2-}(aq) \longrightarrow 2Cr(H_2O)_3(OH)_3(s) + 3CO_2(g) + 3H_2O(l)$$

(e) **When magnesium ribbon is added to aluminium chloride solution, bubbles of a colourless gas and a brown solid is formed**.

The aluminium(III) ion in aluminium chloride has a **small ionic radii** and a **high charge** hence a **high charge density** and **high polarising power**. It therefore exists as **hexaaquaaluminium(III) ion** in solution and undergoes **cation hydrolysis** to produce **hydrogen ions**, making the **solution acidic.** The **hydrogen ions react with magnesium** to form **hydrogen gas** and **insoluble hydrated aluminium hydroxide**.

~~$Al(H_2O)_6^{3+}(aq) + 3H_2O(l) \longrightarrow Al(H_2O)_3(OH)_3(s) + 3H_3O^+(aq) \quad \times 2$~~

~~$Mg(s) + 2H_3O^+(aq) \longrightarrow Mg^{2+}(aq) + H_2(g) + 2H_2O(l) \quad \times 3$~~

$$2Al(H_2O)_6^{3+}(aq) + 3Mg(s) \longrightarrow 2Al(H_2O)_3(OH)_3(s) + 3Mg^{2+}(aq) + 3H_2(g)$$

(f) **When ammonium sulphide is added to a solution of iron(III) sulphate, effervescence occurs and a brown precipitate formed**.

The iron(III) ion in iron(III) sulphate has a **small ionic radii** and a **high charge** hence a **high charge density** and **high polarising power**. It therefore exists as **hexaaquairon(III) ion** in solution and undergoes **cation hydrolysis** to produce **hydrogen ions**, making the **solution acidic.** The **hydrogen ions react with sulphide ions** to form **hydrogen sulphide gas** and **insoluble hydrated iron(III) hydroxide**.

~~$Fe(H_2O)_6^{3+}(aq) + 3H_2O(l) \longrightarrow Fe(H_2O)_3(OH)_3(s) + 3H_3O^+(aq) \quad \times 2$~~

~~$S^{2-}(aq) + 2H_3O^+(aq) \longrightarrow H_2S(g) + 2H_2O(l) \quad \times 3$~~

$$2Fe(H_2O)_6^{3+}(aq) + 3S^{2-}(aq) \longrightarrow 2Fe(H_2O)_3(OH)_3(s) + 3H_2S(g)$$

(g) **When sodium sulphite is added to phenylammonium chloride solution, bubbles of a colourless gas are observed whereas phenylamine solution forms a green precipitate soluble in excess with nickel(II) sulphate solution**.

Phenylammonium chloride is **a salt of a weak base and a strong acid**. It therefore **undergoes cation hydrolysis** to form **hydrogen ions that make the solution acidic**.

$$C_6H_5NH_3^+(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_2(aq) + H_3O^+(aq)$$

The **hydrogen ions react with sodium sulphite to form** to form **sulphur dioxide gas**.

$$2H_3O^+(aq) + SO_3^{2-}(aq) \longrightarrow SO_2(g) + 3H_2O(l)$$

or general equation: $2C_6H_5NH_3^+(aq) + SO_3^{2-}(aq) \longrightarrow 2C_6H_5NH_2(aq) + SO_2(g) + H_2O(l)$

Phenylamine is a weak base hence ionises partially to form hydroxide ions.

$$C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + \bar{O}H(aq)$$

The **hydroxide ions react with nickel(II) ions** to form **insoluble nickel(II) hydroxide**.

$$Ni^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Ni(OH)_2(s)$$

Nickel(II) hydroxide **reacts with excess phenylamine solution** to form a **soluble complex** of **hexaphenylaminenickel(II) ions**.

$$Ni(OH)_2(s) + 6C_6H_5NH_2(aq) \longrightarrow Ni(C_6H_5NH_2)_6^{2+}(aq) + 2\bar{O}H(aq)$$

Questions

Explain the following observations

(a) An aqueous solution of sodium sulphate is neutral to litmus whereas an aqueous solution of sodium sulphite turns red litmus paper blue.

(b) When potassium methanoate was added to copper(II) sulphate, a blue precipitate was formed.

(c) When ammonium sulphate solution was mixed with some sodium sulphite solution and the mixture warmed, there was effervescence of a colourless gas that turns moist red litmus paper blue.

(d) An aqueous solution of aluminium chloride is acidic

(e) When sodium carbonate solution is added to aqueous aluminium sulphate, bubbles of a colourless gas and a white precipitate are observed.

(f) When sodium sulphite is added to a solution of iron(III) chloride, a brown precipitate and bubbles of a colourless gas are observed.

The hydrolysis constant, K_h

Derivation for an expression for K_h

Consider a solution of a salt of a strong acid and weak base for example methylammonium chloride. If the concentration of the solution is $c\ moldm^{-3}$ and the degree of hydrolysis of the salt is α .

$$\boldsymbol{CH_3NH_3^+(aq) + H_2O(l) \rightleftharpoons CH_3NH_2(aq) + H_3O^+(aq)}$$

	$CH_3NH_3^+(aq)$	$H_2O(l)$	$CH_3NH_2(aq)$	$H_3O^+(aq)$
Initial concentration	c		0	0
Concentration dissociated/formed	$c\alpha$		$c\alpha$	$c\alpha$
Moles at equilibrium	$\boldsymbol{c(1-\alpha)}$		$\boldsymbol{c\alpha}$	$\boldsymbol{c\alpha}$

The hydrolysis constant, K_h is given by:

$$K_h = \frac{[CH_3NH_2][H_3O^+]}{[CH_3NH_3^+]} = \frac{(\boldsymbol{c\alpha})^2}{\boldsymbol{c(1-\alpha)}} = \frac{\boldsymbol{c^2\alpha^2}}{\boldsymbol{c(1-\alpha)}}$$

$$\boldsymbol{K_h = \frac{c\alpha^2}{(1-\alpha)}}$$

$\boldsymbol{K_h \approx c\alpha^2}$ ***if α is small compared with 1***

Also from the ionisation of methylamine,

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + \bar{O}H(aq)$$

$$K_b = \frac{[CH_3NH_3^+][\bar{O}H]}{[CH_3NH_2]}$$

$$K_b \times K_h = \frac{[CH_3NH_3^+][\bar{O}H]}{[CH_3NH_2]} \times \frac{[CH_3NH_2][H_3O^+]}{[CH_3NH_3^+]} = [\bar{O}H] \times [H_3O^+]$$

$$K_b \times K_h = K_w$$

$$K_h = \frac{K_w}{K_b}$$

Also considering a solution of a salt of a weak acid and strong base for example potassium ethanoate. If the concentration of the solution is $c\ moldm^{-3}$ and the degree of hydrolysis of the salt is α .

$$\boldsymbol{CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + \bar{O}H(aq)}$$

Initial concentration	c	0	0
Concentration dissociated/formed	$c\alpha$	$c\alpha$	$c\alpha$
Moles at equilibrium	$\boldsymbol{c(1-\alpha)}$	$\boldsymbol{c\alpha}$	$\boldsymbol{c\alpha}$

The hydrolysis constant, K_h is given by: $K_h = \frac{[CH_3COOH][\bar{O}H]}{[CH_3COO^-]} = \frac{(\boldsymbol{c\alpha})^2}{\boldsymbol{c(1-\alpha)}}$	$\boldsymbol{K_h = \frac{c\alpha^2}{(1-\alpha)}}$ $\boldsymbol{K_h \approx c\alpha^2}$ ***if*** $\boldsymbol{\alpha}$ ***is small compared with 1***

Also from the ionisation of ethanoic acid,

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

$$K_a \times K_h = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \times \frac{[CH_3COOH][\bar{O}H]}{[CH_3COO^-]} = [H_3O^+] \times [\bar{O}H]$$

$$K_a \times K_h = K_w$$

$$K_h = \frac{K_w}{K_a}$$

Calculations involving $pH\ and\ K_h$ of salt solutions

Examples

1. **Ammonium chloride undergoes hydrolysis when dissolved in water**
   - **(a) Write the equation for the hydrolysis of ammonium chloride in water**
   - **(b) Calculate the:**
     - **(i)** $\boldsymbol{pH}$ **of a 0.1M solution of ammonium chloride,** $\boldsymbol{K_h = 5.6 \times 10^{-10}\ moldm^{-3}}$.
     - **(ii) percentage hydrolysis of a 0.1M ammonium chloride solution**.

(a) $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

(b) (i) $K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$

At equilibrium; $[H_3O^+] = [NH_3]$

$[NH_4^+] = [NH_4Cl] = 0.1M$

$$K_h = \frac{[H_3O^+]^2}{[NH_4^+]}$$

$$[H_3O^+] = \sqrt{K_h \times [NH_4^+]}$$

$$[H_3O^+] = \sqrt{5.6 \times 10^{-10} \times 0.1}$$

$$= 7.483 \times 10^{-6}M$$

$pH = -\log_{10}[H_3O^+]$

$= -\log_{10}(7.483 \times 10^{-6}) = \mathbf{2.13}$

(ii) From $[H_3O^+] = c\alpha$

$$\alpha = \frac{[H_3O^+]}{c} = \frac{7.483 \times 10^{-6}}{0.1}$$

$$\alpha = 7.483 \times 10^{-5}$$

$The\ percentage\ hydrolysis$

$= (7.483 \times 10^{-5} \times 100)$

$= \mathbf{7.483 \times 10^{-3}}\%$

2. Dimethylammonium chloride undergoes hydrolysis in water.

(a) Write

(i) equation for the reaction

(ii) an expression for the hydrolysis constant, K_h for dimethylammonium chloride.

(b) $25cm^3$ of 0.4M solution of dimethylammonium chloride required $7.5cm^3$ of a 0.01M sodium hydroxide solution for complete neutralisation. Calculate the:

(i) pH of the solution

(ii) the hydrolysis constant and state any assumptions made.

(a) (i) $(CH_3)_2NH_2^+(aq) + H_2O(l) \rightleftharpoons (CH_3)_2NH(aq) + H_3O^+(aq)$

(ii) $K_h = \frac{[(CH_3)_2NH][H_3O^+]}{[(CH_3)_2NH_2^+]}$

(b) (i) $Moles\ of\ NaOH\ that\ reacted = \left(\frac{7.5 \times 0.01}{1000}\right) = 7.5 \times 10^{-5}\ moles$

$$Moles\ of\ \bar{O}H\ that\ reacted\ withH_3O^+ = 7.5 \times 10^{-5}\ moles$$

$$\bar{O}H(aq) + H_3O^+(aq) \longrightarrow 2H_2O(l)$$

$$Mole\ ratio\ of\ \bar{O}H : H_3O^+ = 1:1$$

$$Moles\ of\ H_3O^+\ neutralised = 7.5 \times 10^{-5}\ moles$$

$$25\ cm^3 of\ solution\ contain\ 7.5 \times 10^{-5}\ moles$$

$$1000\ cm^3 of\ solution\ contain \left(\frac{1000 \times 7.5 \times 10^{-5}}{25}\right) moles$$

$$[H_3O^+] = 0.003M$$

$$pH = -\log_{10}[H_3O^+]$$

$$= -\log_{10}(0.003) = \mathbf{2.52}$$

(ii) At equilibrium;

$[H_3O^+] = [(CH_3)_2NH] = 0.003M$

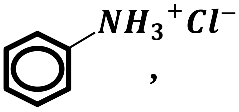
$[(CH_3)_2NH_2^+] = [(CH_3)_2NH_2^+Cl^-] = 4.0M$

$$K_h = \frac{[H_3O^+]^2}{[(CH_3)_2NH_2^+]}$$

$$K_h = \frac{(0.003)^2}{4.0}$$

$$\boldsymbol{K_h = 2.25 \times 10^{-6} moldm^{-3}}$$

3. (a)Write :



(i) an equation for the hydrolysis of phenylamine hydrochloride , when dissolved in water.

(ii) the expression for the hydrolysis constant, K_h, for phenylamine hydrochloride.

(b) A solution containing 0.4 moles of phenylamine hydrochloride per litre has a pH of 3.8. Calculate:

(i) the molar concentration of hydrogen ions in solution

(ii) the hydrolysis constant, K_h, for phenylamine hydrochloride.

(iii) State the assumptions you have made in (b)(ii) above.

(a) (i) $C_6H_5NH_3^+(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_2(aq) + H_3O^+(aq)$

(ii) $K_h = \frac{[C_6H_5NH_2][H_3O^+]}{[C_6H_5NH_3^+]}$

(b) (i) $pH = 3.8 = -\log_{10}[H_3O^+]$

$[H_3O^+] = 10^{-3.8} = \boldsymbol{1.58 \times 10^{-4} M}$

(ii) $K_h = \frac{[H_3O^+]^2}{[C_6H_5NH_3^+]}$

$$= \frac{(1.58 \times 10^{-4})^2}{0.4}$$

$$= \boldsymbol{6.28 \times 10^{-8} moldm^{-3}}$$

(iii) At equilibrium;

$[H_3O^+] = [C_6H_5NH_2] = 1.58 \times 10^{-4}M$

$[C_6H_5NH_3^+] = [C_6H_5NH_3^+Cl^-] = 0.4M$

4. $50\,cm^3$ of 0.1M aqueous ammonia solution was added to $50\,cm^3$ of 0.1M hydrochloric acid and the resultant solution had a pH less than 7.

(a) Explain why the pH of the resultant solution was less than 7

(b) Calculate the pH of the solution.

(K_h *for ammonium chloride is* $6.34 \times 10^{-8} moldm^{-3}$)

(a) ***Ammonia solution reacts hydrochloric acid*** to form a ***salt, ammonium chloride*** which ***undergoes hydrolysis*** to form ***hydrogen ions*** that make the ***solution acidic***.

$$NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$$

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

(b)

$$Moles\ of\ NH_3(aq)\ = \left(\frac{50 \times 0.1}{1000}\right) = 5 \times 10^{-3}\ moles$$

$$Moles\ of\ HCl\ = \left(\frac{50 \times 0.1}{1000}\right) = 5 \times 10^{-3}\ moles$$

$$Mole\ ratio\ of\ NH_3 : NH_4Cl = 1:1$$

$$Moles\ of\ NH_4Cl\ formed\ = 5 \times 10^{-3}\ moles$$

$$Total\ volume\ of\ solution = (50 + 50) = 100cm^3$$

$$100\ cm^3 of\ solution\ contain\ 5 \times 10^{-3}\ moles\ of\ NH_4Cl$$

$$1000\ cm^3 of\ solution\ contain \left(\frac{1000 \times 5 \times 10^{-3}}{100}\right) moles$$

$$[NH_4Cl] = \ 0.05M$$

$$K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

At equilibrium; $[H_3O^+] = [NH_3]$

$$[NH_4^+] = [NH_4Cl] = 0.05\ M$$

$$K_h = \frac{[H_3O^+]^2}{[NH_4^+]}$$

$$[H_3O^+] = \sqrt{K_h \times [NH_4^+]}$$

$$= \sqrt{6.34 \times 10^{-8} \times 0.05} = 5.36 \times 10^{-5}M$$

$$pH = -\log_{10}[H_3O^+]$$

$$= -\log_{10}(5.36 \times 10^{-5}) = \mathbf{4.27}$$

5. Calculate the pH of a 0.01M solution of sodium ethanoate if the dissociation constant of ethanoic acid is $\mathbf{1.8 \times 10^{-5}\ moldm^{-3}}$. ($\boldsymbol{K_w = 1.0 \times 10^{-14} mol^2 dm^{-6}}$)

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + \bar{O}H(aq)$$

$$K_h = \frac{[CH_3COOH][\bar{O}H]}{[CH_3COO^-]}$$

At equilibrium;

$$[\bar{O}H] = [CH_3COOH]$$

$$[CH_3COO^-] = [CH_3COONa] = 0.01M$$

$$K_h = \frac{[\bar{O}H]^2}{[CH_3COO^-]} = \frac{[\bar{O}H]^2}{0.01}$$

$$From\ K_h = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$K_h = 5.556 \times 10^{-10} moldm^{-3}$$

$$K_h = \frac{[\bar{O}H]^2}{0.01}$$

$$[\bar{O}H] = \sqrt{5.556 \times 10^{-10} \times 0.01}$$

$$= 2.357 \times 10^{-6}M$$

$$pOH = -\log_{10}[\bar{O}H]$$

$$= -\log_{10}(2.357 \times 10^{-6})$$

$$= 5.63$$

$$pH = 14 - pOH = 14 - 5.63$$

$$\boldsymbol{pH = 8.37}$$

6. **Determine the pH of an aqueous solution of sodium benzoate made by dissolving 7.2g of sodium benzoate in $500\ cm^3$ of water.**

$$(K_h\ for\ sodium\ \ benzoate\ is\ 1.6\times10^{-10}\ moldm^{-3})$$

$$Molar\ mass\ of\ C_6H_5COONa = (7\times12)+(5\times1)+(2\times16)+(1\times23) = 144g$$

$$Moles\ of\ C_6H_5COONa\ in\ 500\ cm^3 of\ solution = \frac{7.2}{144} = 0.05$$

$$500\ cm^3 of\ solution\ contain\ 0.05\ moles\ of\ C_6H_5COONa$$

$$1000\ cm^3 of\ solution\ contain\ \left(\frac{1000\times0.05}{500}\right)\ moles\ of\ C_6H_5COONa$$

$$[C_6H_5COONa] = \ 0.1M$$

$$C_6H_5COO^-(aq) + H_2O(l) \rightleftharpoons C_6H_5COOH(aq) + \bar{O}H(aq)$$

$$K_h = \frac{[C_6H_5COOH][\bar{O}H]}{[C_6H_5COO^-]}$$

At equilibrium; $[\bar{O}H] = [C_6H_5COOH]$

$$[C_6H_5COO^-] = [C_6H_5COONa] = 0.1\ M$$

$$K_h = \frac{[\bar{O}H]^2}{[C_6H_5COO^-]}$$

$$[\bar{O}H] = \sqrt{K_h\times[C_6H_5COO^-]}$$

$$= \sqrt{1.6\times10^{-10}\times0.1} = 4.6\times10^{-6}M$$

$$From\ K_w = \ [H_3O^+][\bar{O}H]$$

$$[H_3O^+] = \frac{K_w}{[\bar{O}H]} = \frac{1.0\times10^{-14}}{4.6\times10^{-6}}$$

$$= 2.174\times10^{-9}M$$

$$pH = -\log_{10}[H_3O^+]$$

$$= -\log_{10}(2.174\times10^{-9}) = \mathbf{8.66}$$

7. **The percentage of hydrolysis of a 0.1M aqueous solution of sodium propanoate is $\mathbf{7.94\times10^{-3}}$.**
   - **(i)** **Write equation for the dissolution of sodium propanoate in water**
   - **(ii)** **Calculate the pH of the resultant solution. ($K_w = \ 1.0\times10^{-14}mol^2dm^{-6}$)**

(i) $$CH_3CH_2COO^-(aq) + H_2O(l) \rightleftharpoons CH_3CH_2COOH(aq) + \bar{O}H(aq)$$

$$\alpha = \frac{7.94\times10^{-3}}{100} = 7.94\times10^{-5}$$

$$[\bar{O}H] = c\alpha = 0.1\times7.94\times10^{-5}$$

$$= 7.94\times10^{-6}M$$

$$From\ K_w = \ [H_3O^+][\bar{O}H]$$

$$[H_3O^+] = \frac{K_w}{[\bar{O}H]} = \frac{1.0\times10^{-14}}{7.94\times10^{-6}}$$

$$= 1.259\times10^{-9}M$$

$$pH = -\log_{10}[H_3O^+]$$

$$= -\log_{10}(1.259\times10^{-9}) = \mathbf{8.9}$$

8. **$25\ cm^3$ of 0.5M methanoic acid solution was reacted with $20\ cm^3$ of 0.625M sodium hydroxide solution.**
   - **(i)** **Write the equation for the reaction that took place**
   - **(ii)** **Calculate the pH of the resultant solution.**

($K_a\ for\ methanoic\ acid\ is\ 1.77\times10^{-4}moldm^{-3}, K_w\ =\ 1.0\times10^{-14}\ mol^2l^{-2}$)

   - **(iii)** **Explain why the pH of the resultant solution is not equal to seven.**

(i) $$HCOOH(aq) + NaOH(aq) \longrightarrow HCOONa(aq) + H_2O(l)$$

(ii) $$Moles\ of\ HCOOH\ = \left(\frac{25\times0.5}{1000}\right) = 0.0125\ moles$$

$$Moles\ of\ NaOH\ = \left(\frac{20\times0.625}{1000}\right) = 0.0125\ moles$$

$$Mole\ ratio\ of\ HCOOH : HCOONa = 1:1$$

$$Moles\ of\ HCOONa\ formed\ = 0.0125\ moles$$

$$Total\ volume\ of\ solution = (25+20) = 45\ cm^3$$

$$45\ cm^3 of\ solution\ contain\ 0.0125\ moles\ of\ HCOONa$$

$$1000\ cm^3 of\ solution\ contain\left(\frac{1000\times0.0125}{45}\right)\ moles$$

$$[HCOONa] = \ 0.2778M$$

$$HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + \bar{O}H(aq)$$

$$K_h = \frac{[HCOOH][\bar{O}H]}{[HCOO^-]}$$

At equilibrium; $[\bar{O}H] = [HCOOH]$

$$[HCOO^-] = [HCOONa] = 0.2778\ M$$

$$K_h = \frac{[\bar{O}H]^2}{[HCOO^-]}$$

$$[\bar{O}H] = \sqrt{K_h \times [HCOO^-]}$$

$$But\ K_h = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{1.77\times10^{-4}}$$

$$= 5.65\times10^{-11} moldm^{-3}$$

$$[\bar{O}H] = \sqrt{5.65\times10^{-11}\times0.2778}$$

$$= 3.962\times10^{-6}M$$

$$pOH = -\log_{10}[\bar{O}H]$$

$$= -\log_{10}(3.962\times10^{-6}) = 5.4$$

$$pH = 14 - pOH = 14 - 5.4$$

$$\boldsymbol{pH = 8.6}$$

(iii) ***The sodium methanoate salt formed is a salt of sodium hydroxide, a strong base*** and ***methanoic acid, a weak acid.*** Sodium methanoate therefore ***undergoes hydrolysis*** to form ***hydroxide ions*** that make the ***solution alkaline***.

9. Determine the mass of sodium ethanoate that must be added to $\boldsymbol{500\ cm^3}$ of water to give a solution of $\boldsymbol{pH}$ of 8.52.

$$\boldsymbol{(K_a\ for\ ethanoic\ acid\ is\ 1.75\times10^{-5} moldm^{-3})}$$

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + \bar{O}H(aq)$$

$$pH = -\log_{10}[H_3O^+] = 8.52$$

$$[H_3O^+] = 10^{-8.52} = 3.02\times10^{-9}M$$

$$From\ K_w = \ [H_3O^+][\bar{O}H]$$

$$[\bar{O}H] = \frac{K_w}{[H_3O^+]} = \frac{1.0\times10^{-14}}{3.02\times10^{-9}}$$

$$= 3.31\times10^{-6}M$$

$$K_h = \frac{[CH_3COOH][\bar{O}H]}{[CH_3COO^-]}$$

At equilibrium;

$$[\bar{O}H] = [CH_3COOH] = 3.31\times10^{-6}M$$

$$[CH_3COO^-] = [CH_3COONa]$$

$$K_h = \frac{[\bar{O}H]^2}{[CH_3COONa]}$$

$$K_h = \frac{(3.31\times10^{-6})^2}{[CH_3COONa]}$$

$$But\ K_h = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{1.75\times10^{-5}}$$

$$= 5.714\times10^{-10} moldm^{-3}$$

$$[CH_3COONa] = \frac{(3.31\times10^{-6})^2}{K_h}$$

$$= \frac{(3.31\times10^{-6})^2}{5.714\times10^{-10}}$$

$$= 0.0192M$$

$$1000\ cm^3 of\ solution\ contain\ 0.0192\ moles\ of\ CH_3COONa$$

$$500\ cm^3 of\ solution\ contain\ \left(\frac{0.0192 \times 500}{1000}\right)\ moles\ of\ CH_3COONa$$

$$= 0.0096\ moles\ of\ CH_3COONa$$

$$Molar\ mass\ of\ CH_3COONa\ = 24 + 3 + 32 + 23 = 82g$$

$$\boldsymbol{Mass\ of\ CH_3COONa\ \ in\ 500\ cm^3 of\ solution} = (\mathbf{82 \times 0.0096}) = \mathbf{0.79g}$$

10. (a) Explain what is meant by the term "salt hydrolysis"

(b) Sodium sulphide undergoes hydrolysis. Write the

(i) equation for hydrolysis of sodium sulphide

(ii) expression for hydrolysis constant (K_h), for sodium sulphide.

(c) Calculate the pH of solution containing $5.46gdm^{-3}$ of sodium sulphide (Hydrolysis constant of sodium sulphide at 25℃ $= 1.25 \times 10^{-10} moldm^{-3}$)

(b) (i) $S^{2-}(aq) + 2H_2O(l) \rightleftharpoons H_2S(aq) + 2\bar{O}H(aq)$

(ii) $K_h = \frac{[H_2S][\bar{O}H]^2}{[S^{2-}]}$

(c) $Molar\ mass\ of\ Na_2S$

$= 46 + 32 = 78g$

$[Na_2S] = \frac{5.46}{78} = 0.07M$

At equilibrium; $[\bar{O}H] = [H_2S]$

$[S^{2-}] = [Na_2S] = 0.07M$

$K_h = \frac{[\bar{O}H]^3}{0.07}$

$[\bar{O}H] = (1.25 \times 10^{-10} \times 0.07)^{\frac{1}{3}}$

$[\bar{O}H] = 2.06 \times 10^{-4}M$

$pOH = -\log_{10}[\bar{O}H]$

$= -\log_{10}(2.06 \times 10^{-4}) = 3.685$

$pH = 14 - pOH = 14 - 3.685$

$\boldsymbol{pH = 10.32}$

Questions

1. Calculate the percentage degree of hydrolysis in a 0.1M solution of ammonium chloride. (The ionisation constant of ammonia is $1.8 \times 10^{-5}\ moldm^{-3}$)
2. Determine the pH of a solution containing $8.6gdm^{-3}$ of ammonium chloride if the hydrolysis constant of ammonium chloride is $5.84 \times 10^{-10}\ moldm^{-3}$.
3. Dimethylammonium chloride ($(CH_3)_2NH_2Cl$) undergoes hydrolysis when dissolved in water.

   (a) Write:

      (i) the equation of hydrolysis

      (ii) the expression for the hydrolysis constant, K_h for dimethylammonium chloride

   (b) If the pH of a 4.0M aqueous solution of dimethylammonium chloride is 2.5.

(i) Calculate the hydrolysis constant, K_h. ($K_w = 1.0 \times 10^{-14}\ mol^2 dm^{-3}\ at\ 25°C$)

(ii) State the assumptions you have made in (b)(i) above.

4. (a) Phenylamine hydrochloride undergoes hydrolysis when dissolved in water. Write equation for the reaction.

(b) A 0.2M solution of phenylamine hydrochloride has a pH of 3.5. Calculate:

(i) the molar concentration of hydrogen ions in solution

(ii) the hydrolysis constant, K_h, for phenylamine hydrochloride.

5. Calculate the pH of a solution made by dissolving 6g of sodium ethanoate in water to form one litre of solution.($K_a\ for\ ethanoic\ acid\ is\ 1.8 \times 10^{-5}\ moldm^{-3}$)

6. Sodium benzoate is 0.02% hydrolysed.

(i) Write the equation for the hydrolysis of sodium benzoate.

(ii) Write the expression for the hydrolysis constant, K_h of sodium benzoate.

(iii) Calculate the K_h of a 0.1M sodium benzoate solution

(iv) Determine the pH of a 0.1M sodium benzoate solution

7. Sodium benzoate undergoes hydrolysis when dissolved in water.

(a) Write an equation for the hydrolysis of sodium benzoate in water.

(b) Write an expression for the hydrolysis constant, K_h, for sodium benzoate

(c) The hydrolysis constant of sodium benzoate is $1.6 \times 10^{-10}\ moldm^{-3}$.

(i) Calculate the concentration of hydroxide ions in a 0.1M solution of sodium benzoate ($K_w = 1.0 \times 10^{-14}\ mol^2 dm^{-6}$)

(ii) State the assumptions made in the calculation in (c) (i) above.

(iii) Using your result in c (i), calculate the pH of the solution.

8. Benzoic acid is a weak acid.

(a) Write equation for the ionisation of benzoic acid in water

(b) The pH of an aqueous solution of 0.2M benzoic acid is 5.25. Determine the acid dissociation constant, K_a for benzoic acid.

(c) Using your results from (b) above, calculate the hydrolysis constant, K_h for sodium benzoate. ($Ionic\ product\ , K_w\ for\ water\ is\ 1.0 \times 10^{-14}\ mol^2 dm^{-6}$)

9. (a) Write an equation for the hydrolysis of sodium ethanoate in water.

(b) Write an expression for the hydrolysis constant K_h of sodium ethanoate.

(c) Calculate:

(i) the value of K_h for sodium ethanoate and indicate its units ($K_a\ for\ CH_3COOH\ is\ 1.8 \times 10^{-5}, K_w = 1.0 \times 10^{-14}\ mol^2 l^{-2}$)

(ii) pH of a 0.1M sodium ethanoate solution

(d) State what would be the effect on pH of the solution in (c) (ii) if 1.0cm^3 of 0.1M ethanoic acid was added to it.

10. Methanoic acid is a stronger acid than ethanoic acid.
    (a) (i) Explain why methanoic acid is stronger than ethanoic acid
        (ii) Write an equation for ionisation of methanoic acid
        (iii) Write an expression for the ionisation constant, K_a for methanoic acid
    (b) $25cm^3$ of 0.1M methanoic acid solution was reacted with $50\,cm^3$ of 0.05M sodium hydroxide solution.
        (i) Write the equation for the reaction that took place
        (ii) Calculate the pH of the resultant solution. (K_a $for\ methanoic\ acid\ is$ $1.77 \times 10^{-4} moldm^{-3}$)
        (iii) Explain why the pH of the resultant solution is not equal to seven.
    (c) Name a reagent that can be used to distinguish between methanoic acid and ethanoic acid and state what is observed in each case when each of the acids is treated with the named reagent.
11. Calculate the pH at the end point of a titration of a $0.125\,moldm^{-3}$ nitrous acid and $0.125\,moldm^{-3}$ sodium hydroxide solution. The $p^{K_b}$of nitrous acid is 10.66.
12. Write an equation for dissolution of each of the following salt in water. State whether the resulting solution would be neutral, basic or acidic
    (a) chromium(III) chloride
    (b) Magnesium chloride
    (c) ammonium methanoate
    (d) phosphorus(V) chloride
    (e) ethylammonium chloride

BUFFER SOLUTIONS

Water and other simple aqueous solutions do not retain a constant hydrogen ion concentration, hence their pH values since they dissolve such as carbon dioxide from the air or silicates from the walls of glass containers.

To obtain solutions that maintain their pH fairly constant, buffer solutions are used.

A buffer solution is a solution which resists changes in pH when a small amount of acid or alkali is added to it.

Types of buffers

There are broadly two types of buffer solutions namely;

- ***Acidic buffer solution***
- ***Basic buffer solution***

1. *Acidic buffer solution*

***An acidic buffer solution is a solution made by mixing a weak acid and a salt of the weak acid with a strong base*.**

Some examples include:

Methanoic acid and sodium methanoate	$\boldsymbol{HCOOH}$ and $\boldsymbol{HCOONa}$
Ethanoic acid and sodium ethanoate	CH_3COOH and CH_3COONa
Propanoic acid and sodium propanoate	CH_3CH_2COOH and CH_3CH_2COONa
Phosphoric(V) acid and sodium phosphate	H_3PO_4 and Na_3PO_4
Carbonic acid and sodium hydrogencarbonate	H_2CO_3 and $NaHCO_3$
Hydrocyanic acid and sodium cyanide	HCN and $NaCN$

2. *Basic buffer solution*

***A basic buffer solution is a solution made by mixing a weak base and a salt of the weak base with a strong acid*.**

Some examples include:

Ammonia solution and ammonium chloride	$\boldsymbol{NH_3(aq)}$ and $\boldsymbol{NH_4Cl}$
Ammonia solution and ammonium nitrate	$NH_3(aq)$ and NH_4NO_3
Phenylamine and phenylammonium chloride	$C_6H_5NH_2$ and $C_6H_5NH_3^+Cl^-$
Methylamine and methylammonium chloride	CH_3NH_2 and $CH_3NH_3^+Cl^-$

The action of a buffer

Action of an acidic buffer

Describe how a solution of ethanoic acid and sodium ethanoate acts as a buffer.

Sodium ethanonate is a ***strong electrolyte*** hence fully ionises to form ethanoate ions and sodium ions.

Ethanoic acid is a ***weak base*** hence only slightly ionises and ***its ionisation is suppressed by the high concentration of ethanoate ions from the salt***.

$$CH_3COONa(aq) \longrightarrow \boldsymbol{CH_3COO^-(aq)} + Na^+(aq)$$

$$\boldsymbol{CH_3COOH(aq)} + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

The solution therefore contains ***a high concentration of ethanoate ions*** and ***a high concentration of unionised ethanoic acid molecules***.

When ***a small amount of acid is added***, ***the hydrogen ions react with ethanoate ions*** to ***form ethanoic acid resisting a decrease in pH***.

$$CH_3COO^-(aq) + H^+(aq) \longrightarrow CH_3COOH(aq)$$

When a ***small amount of base is added***, the ***hydroxide ions react with ethanoic acid*** to ***form ethanoate ions and water***, ***resisting an increase in pH***

$$CH_3COOH(aq) + \bar{O}H(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l)$$

or

The hydroxide ions react with hydrogen ions to form water and the ethanoic acid ionises to restore the hydrogen ions removed.

$$\bar{O}H(aq) + H_3O^+(aq) \longrightarrow 2H_2O(l)$$

Qn. Describe how a solution of propanoic acid and sodium propanoate acts as a buffer.

Action of a basic buffer

Describe how a solution of ammonia and ammonium chloride acts as a buffer.

Ammonium chloride is a ***strong electrolyte*** hence fully ionises to form ammonium ions and chloride ions.

Ammonia is a ***weak base*** hence only slightly ionises and ***its ionisation is suppressed by the high concentration of ammonium ions from the salt***.

$$NH_4Cl(aq) \longrightarrow \boldsymbol{NH_4^+(aq)} + Cl^-(aq)$$

$$\boldsymbol{NH_3(aq)} + H_2O(l) \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$$

The solution therefore contains ***a high concentration of ammonium ions*** and ***a high concentration of unionised ammonia molecules***.

When ***a small amount of acid is added***, ***the hydrogen ions react with ammonia molecules to form ammonium ions***, ***resisting a decrease in pH***.

$$NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$$

or

The hydrogen ions react with hydroxide ions to form water and ammonia ionises to restore the hydroxide ions removed.

$$H^+(aq) + \bar{O}H(aq) \longrightarrow H_2O(l)$$

When a ***small amount of base is added***, the ***hydroxide ions react with ammonium ions to form ammonia molecules and water***, ***resisting an increase in pH***

$$NH_4^+(aq) + \bar{O}H(aq) \longrightarrow NH_3(aq) + H_2O(l)$$

Qn. Describe how a solution of phenylamine and phenylammonium chloride acts as a buffer.

The Henderson-Hasselbalch equation

This equation is used to calculate pH of a buffer solution.

Derivation of the Henderson-Hasselbalch equation for an acidic buffer solution

Consider an acidic buffer solution of methanoic acid and sodium methanoate.
Sodium methanoate completely ionises whereas methanoic acid partially ionises.

$$HCOONa(aq) \longrightarrow HCOO^-(aq) + Na^+(aq)$$

$$HCOOH(aq) + H_2O(l) \rightleftharpoons HCOO^-(aq) + H_3O^+(aq)$$

The acid dissociation constant, K_a is given by the expression;

$$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$$

Assumptions;

(i) All methanoate ions come from fully ionised sodium methanoate.
Therefore*;* $[HCOO^-] = [HCOONa]$
(ii) $[HCOOH]$ ***remains constant since it is a weak acid***

Therefore;

$$K_a = \frac{[HCOONa][H_3O^+]}{[HCOOH]}$$

$$[H_3O^+] = K_a \frac{[HCOOH]}{[HCOONa]}$$

Introducing $-log_{10}$ both sides yields;

$$-\log_{10}[H_3O^+] = -\log_{10}\left(K_a \frac{[HCOOH]}{[HCOONa]}\right)$$

$$-\log_{10}[H_3O^+] = -\log_{10}K_a + -\log_{10}\left(\frac{[HCOOH]}{[HCOONa]}\right)$$

$$-\log_{10}[H_3O^+] = -\log_{10}K_a + \log_{10}\left(\frac{[HCOONa]}{[HCOOH]}\right)$$

$$\boldsymbol{pH = pK_a + log\frac{[Salt]}{[Acid]}}$$

Derivation of the Henderson-Hasselbalch equation for an acidic buffer solution

Consider a basic buffer solution of methylamine and methylammonium chloride.
Methylammonium chloride completely ionises whereas methylamine partially ionises.

$$CH_3NH_3^+Cl^-(aq) \longrightarrow CH_3NH_3^+(aq) + Cl^-(aq)$$

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + \bar{O}H(aq)$$

The base dissociation constant, K_b is given by the expression;

$$K_b = \frac{[CH_3NH_3^+][\bar{O}H]}{[CH_3NH_2]}$$

Assumptions;

(i) ***All methylammonium ions come from fully ionised methylammonium chloride.***
Therefore; $[CH_3NH_3^+] = [CH_3NH_3^+Cl^-]$

(ii) $[CH_3NH_2]$ ***remains constant since it is a weak base***

Therefore;

$$K_b = \frac{[CH_3NH_3^+Cl^-][\bar{O}H]}{[CH_3NH_2]}$$

$$[\bar{O}H] = K_b\frac{[CH_3NH_2]}{[CH_3NH_3^+Cl^-]}$$

Introducing $-log_{10}$ both sides yields;

$$-\log_{10}[\bar{O}H] = -\log_{10}\left(K_b\frac{[CH_3NH_2]}{[CH_3NH_3^+Cl^-]}\right)$$

$$-\log_{10}[\bar{O}H] = -\log_{10}K_b + -\log_{10}\left(\frac{[CH_3NH_2]}{[CH_3NH_3^+Cl^-]}\right)$$

$$-\log_{10}[\bar{O}H] = -\log_{10}K_b + \log_{10}\left(\frac{[CH_3NH_3^+Cl^-]}{[CH_3NH_2]}\right)$$

$$\boldsymbol{pOH = pK_b + log\frac{[Salt]}{[Base]}}$$

pH is the got from the expression;

$$\boldsymbol{pH = 14 - pOH}$$

N.B pH of a buffer solution is not affected by adding water (on dilution) since the $\frac{[\boldsymbol{Salt}]}{[\boldsymbol{Acid}]}$ ***or*** $\frac{[\boldsymbol{Salt}]}{[\boldsymbol{Base}]}$ ***ratio remains constant on adding water***

Calculations involving pH for buffer solutions

Examples

(a) Acidic buffers

1. **$3.28g$ of sodium ethanoate were dissolved in 1 litre of 0.01M ethanoic acid solution. Calculate the pH of the resulting solution. ($pK_a = 4.735$)**

$$Molar\ mass\ of\ CH_3COONa = (2 \times 12) + (3 \times 1) + (2 \times 16) + (1 \times 23) = 82g$$

$$Moles\ of\ CH_3COONa\ in\ 1\ litre\ of\ solution = \frac{3.28}{82} = 0.04$$

$$[CH_3COONa] = 0.04M$$

$$[CH_3COOH] = 0.01M$$

$$pH = pK_a + log\frac{[CH_3COONa]}{[CH_3COOH]}$$

$$pH = 4.735 + log\left(\frac{0.04}{0.01}\right)$$

$$pH = 4.735 + 0.602$$

$$\boldsymbol{pH = 5.34}$$

2. **Calculate the pH of a solution formed by adding of $15.0\ cm^3$ of 0.1M sodium hydroxide to $30.0\ cm^3$ of 0.1M propanoic acid. State any assumptions made. ($K_a = 1.35 \times 10^{-5}\ moldm^{-3}$)**

$$Moles\ of\ NaOH = \left(\frac{15 \times 0.1}{1000}\right) = 1.5 \times 10^{-3}\ moles$$

$$Moles\ of\ CH_3CH_2COOH = \left(\frac{32 \times 0.1}{1000}\right) = 3.2 \times 10^{-3}\ moles$$

$$CH_3CH_2COOH\ (aq) + NaOH(aq) \longrightarrow CH_3CH_2COONa(aq) + H_2O(l)$$

$$Mole\ ratio\ of\ CH_3CH_2COOH : NaOH : CH_3CH_2COONa = 1:1:1$$

$$Moles\ of\ CH_3CH_2COOH\ that\ reacted = Moles\ of\ NaOH\ that\ reacted$$

$$= Moles\ of\ CH_3CH_2COONa\ formed = 1.5 \times 10^{-3} moles$$

$$\boldsymbol{Excess\ moles\ of\ CH_3CH_2COOH = (3.2 - 1.5) \times 10^{-3} = 1.7 \times 10^{-3}\ moles}$$

The excess(unreacted) CH_3CH_2COOH and the CH_3CH_2COONa formed constitute a buffer solution.

$$Total\ volume\ of\ solution = (15 + 30) = 45\ cm^3$$

$$45\ cm^3\ of\ solution\ contain\ 1.7 \times 10^{-3}\ moles\ of\ CH_3CH_2COOH$$

$$1000cm^3\ of\ solution\ contain\ \left(\frac{1000 \times 1.7 \times 10^{-3}}{45}\right)\ moles\ of\ CH_3CH_2COOH$$

$$\boldsymbol{[CH_3CH_2COOH] = 0.0378\ M}$$

$$45\ cm^3\ of\ solution\ contain\ 1.5 \times 10^{-3}\ moles\ of\ CH_3CH_2COONa$$

$$1000cm^3\ of\ solution\ contain\ \left(\frac{1000 \times 1.5 \times 10^{-3}}{45}\right)\ moles\ of\ \ CH_3CH_2COONa$$

$$\boldsymbol{[CH_3CH_2COONa] = \ 0.0333M}$$

$$pH = pK_a + log\frac{[CH_3CH_2COONa]}{[CH_3CH_2COOH\ ]}$$

$$pH = -\log(1.35 \times 10^{-5}) + log\left(\frac{0.0333}{0.0378}\right)$$

$$pH = 4.87 - 0.055$$

$$\boldsymbol{pH = 4.82}$$

3. **A 0.1M solution of sodium hydroxide was added to 50cm^3 of 0.1M ethanoic acid until when the acid is half way neutralized. Determine the pH of the resultant solution formed. ($\boldsymbol{K_a\ for\ ethanoic\ acid =\ 1.8 \times 10^{-5}moldm^{-3}}$)**

$$Moles\ of\ CH_3COOH = \left(\frac{50 \times 0.1}{1000}\right) = 0.005\ moles$$

$$Moles\ of\ CH_3COOH\ neutralised = \left(\frac{1}{2} \times 0.005\right) = 0.0025\ moles$$

$$CH_3COOH\ (aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)$$

$$Mole\ ratio\ of\ CH_3COOH : NaOH : CH_3COONa = 1:1:1$$

$$Moles\ of\ CH_3COOH\ \ that\ reacted = Moles\ of\ NaOH\ that\ reacted$$

$$= Moles\ of\ CH_3COONa\ formed = \ 0.0025\ moles$$

$$\boldsymbol{Unreacted\ moles\ of\ CH_3COOH\ = (0.005 - 0.0025) = 0.0025\ moles}$$

The excess(unreacted) CH_3COOH and the CH_3COONa formed constitute a buffer solution.

$$Total\ volume\ of\ solution = (50 \times 2) = 100\ cm^3$$

$$100\ cm^3\ of\ solution\ contain\ 0.0025\ moles\ of\ \ CH_3COOH$$

$$1000cm^3\ of\ solution\ contain\ \left(\frac{1000 \times 0.0025}{100}\right)\ moles\ of\ \ CH_3COOH$$

$$\boldsymbol{[CH_3COOH] = \ 0.025\ M}$$

$$100\ cm^3\ of\ solution\ contain\ 0.0025\ moles\ of\ \ CH_3COONa$$

$$1000cm^3\ of\ solution\ contain\ \left(\frac{1000 \times 0.0025}{100}\right)\ moles\ of\ \ CH_3COONa$$

$$\boldsymbol{[CH_3COONa] = \ 0.025M}$$

$$pH = pK_a + log\frac{[CH_3COONa]}{[CH_3COOH\ ]}$$

$$pH = -\log(1.8 \times 10^{-5}) + log\left(\frac{0.025}{0.025}\right)$$

$$pH = 4.745 + 0$$

$$\boldsymbol{pH = 4.745}$$

4. **Calculate the mass of sodium ethanoate that must be dissolved in one litre of ethanoic acid of concentration $\boldsymbol{0.085\ moldm^{-3}}$ to form a solution with a $\boldsymbol{pH}$ of $\boldsymbol{5.45}$. ($\boldsymbol{K_a\ for\ ethanoic\ acid\ is\ 1.8 \times 10^{-5}\ moldm^{-3}}$)**

$$CH_3COONa(aq)\ and\ CH_3COOH\ \ constitute\ a\ buffer\ solution\ whose\ pH\ is\ given\ by:$$

$$pH = pK_a + log\frac{[CH_3COONa]}{[CH_3COOH\,]}$$

$$5.45 = -\log(1.8\times 10^{-5}) + log\left(\frac{[CH_3COONa]}{0.1}\right)$$

$$5.45 = 4.745 + log\left(\frac{[CH_3COONa]}{0.1}\right)$$

$$log\left(\frac{[CH_3COONa]}{0.1}\right) = 0.705$$

$$log[CH_3COONa] - log\;0.1 = 0.705$$

$$log[CH_3COONa] + 1 = 0.705$$

$$log[CH_3COONa] = -0.295$$

$$[CH_3COONa] = 10^{-0.295} = 0.507M$$

$$Molar\ mass\ of\ CH_3COONa$$

$$= 24 + 3 + 32 + 23$$

$$= 82g$$

$$mass\ of\ CH_3COONa\ required$$

$$= (82\times 0.507)$$

$$= \mathbf{41.57g}$$

5. **To $\mathbf{1.0\,dm^3}$ of 0.035M ethanoic acid was added to 4.1g of sodium ethanoate to make a solution. ($\boldsymbol{K_a\ for\ ethanoic\ acid\ is\ 1.75\times 10^{-5}moldm^{-3}}$)**

   (a) Calculate the pH of the resultant solution

   (b) Calculate the change in pH of the resultant solution if:

   (i) $\mathbf{1.2\,cm^3}$ of 1M hydrochloric acid was added to the resultant solution in (a) above.

   (ii) $\mathbf{1.2\,cm^3}$ of 1M sodium hydroxide solution was added to the resultant solution in (a) above.

(a)

$$\mathbf{[CH_3COOH] = 0.035\,M}$$

$$Molar\ mass\ of\ CH_3COONa = 24 + 3 + 32 + 23 = 82g$$

$$Moles\ of\ CH_3COONa = \frac{4.1}{82} = 0.05\ moles$$

$$\mathbf{[CH_3COONa] = 0.05M}$$

$$pH = pK_a + log\frac{[CH_3COONa]}{[CH_3COOH\,]}$$

$$pH = -\log(1.75\times 10^{-5}) + log\left(\frac{0.05}{0.035}\right)$$

$$pH = 4.757 + 0.155$$

$$\mathbf{pH = 4.91}$$

(b) (i)

$$Moles\ of\ HCl\ added = \left(\frac{1.2\times 1}{1000}\right) = 1.2\times 10^{-3}\ moles$$

$$Moles\ of\ H^+\ added = \left(\frac{1.2\times 1}{1000}\right) = 1.2\times 10^{-3}\ moles$$

The hydrogen ions from the acid added react with ethanoate ions from the salt to form ethanoic acid.

$$H^+(aq) + CH_3COO^-(aq) \longrightarrow CH_3COOH(aq)$$

$$since\ mole\ ratio\ of\,H^+ : CH_3COO^- : CH_3COOH = 1:1:1$$

$$[CH_3COO^-]\ reduces\ whereas\ [CH_3COOH]\ \ increases\ by 1.2\times 10^{-3}M$$

$$[CH_3COO^-] = [CH_3COONa]$$

$$[CH_3COONa]_{new} = (0.05 - \ 1.2\times 10^{-3}) = 0.0488M$$

$$[CH_3COOH]_{new} = (0.035 + \ 1.2\times 10^{-3}) = 0.0362M$$

$$pH = pK_a + log\frac{[CH_3COONa]_{new}}{[CH_3COOH]_{new}}$$

$$pH = -\log(1.75 \times 10^{-5}) + log\left(\frac{0.0488}{0.0362}\right)$$
$$pH = 4.757 + 0.1297$$
$$\boldsymbol{pH = 4.89}$$
$$\boldsymbol{pH\ change = 4.91 - 4.89 = 0.02}$$

(ii) $$Moles\ of\ NaOH\ added = \left(\frac{1.2 \times 1}{1000}\right) = 1.2 \times 10^{-3}\ moles$$
$$Moles\ of\ \bar{O}H\ added = \left(\frac{1.2 \times 1}{1000}\right) = 1.2 \times 10^{-3}\ moles$$

The hydroxide ions from the base added react with ethanoic acid to form ethanoate ions and water.

$$\bar{O}H\ (aq) + CH_3COOH(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l)$$
$$since\ mole\ ratio\ of\ \bar{O}H{:}\ CH_3COOH{:}\ CH_3COO^- = 1{:}\,1{:}\,1$$
$$[CH_3COOH]\ \ reduces\ whereas\ [CH_3COO^-]\ increases\ by\ 1.2 \times 10^{-3}M$$
$$[CH_3COO^-] = [CH_3COONa]$$
$$[CH_3COONa]_{new} = (0.05 +\ 1.2 \times 10^{-3}) = 0.0512M$$
$$[CH_3COOH]_{new} = (0.035 -\ 1.2 \times 10^{-3}) = 0.0338M$$
$$pH = pK_a + log\frac{[CH_3COONa]_{new}}{[CH_3COOH]_{new}}$$
$$pH = -\log(1.75 \times 10^{-5}) + log\left(\frac{0.0512}{0.0338}\right)$$
$$pH = 4.757 + 0.18$$
$$\boldsymbol{pH = 4.94}$$
$$\boldsymbol{pH\ change = 4.94 - 4.91 = 0.03}$$

(b) Basic buffers

1. **Determine the pH of a solution made by adding 25cm^3 of 0.2M nitric acid to 80cm^3 of 0.2M ammonia solution. ($pK_b\ for\ ammonia\ is\ 4.74$)**

$$Moles\ of\ HNO_3 = \left(\frac{25 \times 0.2}{1000}\right) = 0.005\ moles$$
$$Moles\ of\ NH_3(aq) = \left(\frac{80 \times 0.2}{1000}\right) = 0.016\ moles$$
$$NH_3\ (aq) + HNO_3(aq) \longrightarrow NH_4NO_3(aq)$$
$$Mole\ ratio\ of\ NH_3\ (aq) : HNO_3{:}\ NH_4NO_3 = 1{:}\,1{:}\,1$$
$$Moles\ of\ NH_3\ (aq)\ \ that\ reacted = Moles\ of\ HNO_3\ that\ reacted$$
$$= Moles\ of\ NH_4NO_3\ formed =\ 0.005\ moles$$
$$\boldsymbol{Excess\ moles\ of\ NH_3\ (aq)\ = (0.016 - 0.005) = 0.011\ moles}$$

The excess(unreacted) $NH_3(aq)$ and the NH_4NO_3 formed constitute a basic buffer solution.

$$Total\ volume\ of\ solution = (25 + 80) = 105\ cm^3$$
$$105\ cm^3\ of\ solution\ contain\ 0.011\ moles\ of\ \ NH_3\ (aq)$$

$$1000cm^3\ of\ solution\ contain\ \left(\frac{1000\times 0.011}{105}\right)\ moles\ of\ \ NH_3\ (aq)$$

$$\boldsymbol{[NH_3\ (aq)] =\ 0.1048\ M}$$

$$105\ cm^3\ of\ solution\ contain\ 0.005\ moles\ of\ NH_4NO_3$$

$$1000cm^3\ of\ solution\ contain\ \left(\frac{1000\times 0.005}{105}\right)\ moles\ of\ NH_4NO_3$$

$$\boldsymbol{[NH_4NO_3] =\ 0.0476M}$$

$$pOH = pK_b + log\,\frac{[NH_4NO_3]}{[NH_3\ (aq)]}$$

$$pOH = 4.74 + log\left(\frac{0.0476}{0.1048}\right)$$

$$pOH = 4.74 - 0.343 = 4.397$$

$$pH = 14 - pOH = 14 - 4.397$$

$$\boldsymbol{pH = 9.6}$$

---

2. **0.02 moles of ammonium chloride were dissolved in $1.0\ dm^3$ of 0.1M ammonia solution. Calculate the:**
   - **(a) pH before addition of the salt**
   - **(b) pH change after addition of the salt.**

($K_b\ for\ ammonia\ is\ 1.8\times 10^{-5}\ moldm^{-3}$)

$$\boldsymbol{[NH_3\ (aq)] =\ 0.1M}$$

$$\boldsymbol{[NH_4Cl] =\ 0.02M}$$

(a) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$

$$K_b = \frac{[NH_4^+][\bar{O}H]}{[NH_3]}$$

At equilibrium; $[\bar{O}H] = [NH_4^+]$

$$[NH_3] = 0.001M$$

$$K_b = \frac{[\bar{O}H]^2}{[NH_3]}$$

$$[\bar{O}H]^2 = K_b \times [NH_3]$$

$$[\bar{O}H] = \sqrt{1.8\times 10^{-5}\times 0.01} = 4.24\times 10^{-4}M$$

$$pOH = -\log_{10}(4.24\times 10^{-4}) = \mathbf{3.37}$$

$$pH = 14 - pOH$$

$$pH = 14 - 3.37 = \mathbf{10.63}$$

(b) $pOH = pK_b + log\,\frac{[NH_4Cl]}{[NH_3\ (aq)]}$

$$pOH = -\log_{10}(1.8\times 10^{-5}) + log\left(\frac{0.02}{0.1}\right)$$

$$pOH = 4.745 - 0.699$$

$$= 4.046$$

$$pH = 14 - pOH$$

$$= 14 - 4.046$$

$$\boldsymbol{pH = 9.95}$$

$$\boldsymbol{pH\ change = 10.63 - 9.95}$$

$$\boldsymbol{= 0.68}$$

---

3. **(a) Write the expression for the ionisation constant, K_b of methylamine in water.**
   - **(b) 0.25 moles of methylammonium chloride was added to one litre of 0.4M methylamine**
     - **(i) Calculate the pH of the resultant solution ($The\ ionisation\ constant\ of\ \ methylamine\ is\ 4.4\times 10^{-4}moll^{-1}$, $K_w\ =\ 1.0\times 10^{-14}\ mol^2l^{-2}$)**
     - **(ii) State the assumption(s) you have made in b(i)**

$$\boldsymbol{[CH_3NH_3\ ] =\ 0.4M}$$

$$\boldsymbol{[CH_3NH_3^+Cl^-] =\ 0.25M}$$

(b) (i)

$$pOH = pK_b + log\frac{[CH_3NH_3^+Cl^-]}{[CH_3NH_3\ ]}$$

$$pOH = -\log_{10}(4.4 \times 10^{-4}) + log\left(\frac{0.25}{0.4}\right)$$

$$pOH = 3.357 - 0.204 = 3.153$$

$$pH = pK_w - pOH = 14 - pOH = 14 - 3.153$$

$$\boldsymbol{pH = 10.85}$$

(ii) Assumptions

$[CH_3NH_3^+] = [CH_3NH_3^+Cl^-] = 0.25$

$[CH_3NH_3\ ]$ *is constant*

Volume of solution does not change when methylammonium chloride is added to methylamine solution

---

4. (a) Determine the mass of ammonium chloride that should be added to 1 dm^3 of a 0.1M ammonia solution at 25℃ to give a solution whose pH is 8.5. (K_b *of ammonia* $= 1.8 \times 10^{-5} moldm^{-3}$, $K_w = 1.0 \times 10^{-14}\ mol^2dm^{-6}$)

(b) A few drops of sodium hydroxide were added to the solution in (b).

(i) **State what happened to the pH of the solution**

(ii) **Give a reason for your answer in c(i)**

$$[\boldsymbol{NH_3}\ ] = \boldsymbol{0.1M}$$

(a)

$$pOH = pK_w - pH$$

$$= 14 - 8.5 = 5.5$$

$$pOH = pK_b + log\frac{[NH_4Cl]}{[NH_3\ (aq)]}$$

$$5.5 = -\log_{10}(1.8 \times 10^{-5}) + log\left(\frac{[NH_4Cl]}{0.1}\right)$$

$$5.5 = 4.745 + log\left(\frac{[NH_4Cl]}{0.1}\right)$$

$$log\left(\frac{[NH_4Cl]}{0.1}\right) = 0.755$$

$$log_{10}[NH_4Cl] - log(0.1) = 0.755$$

$$log_{10}[NH_4Cl] + 1 = 0.755$$

$$log_{10}[NH_4Cl] = -0.245$$

$$[NH_4Cl] = 10^{-0.245} = 0.5689M$$

$$Molar\ mass\ of NH_4Cl = 14 + 4 + 35.5$$

$$= 53.5g$$

$Mass\ of NH_4Cl\ required$

$$= (0.5689 \times 53.5)$$

$$\boldsymbol{= 30.44g}$$

(b) (i)

The pH remained almost constant.

(ii) The sodium hydroxide added reacted with ammonium ions to form ammonia molecules and water.

$$NH_4^+(aq) + \bar{O}H(aq) \longrightarrow NH_3(aq) + H_2O(l)$$

Preparation of buffer solutions of known pH

The Henderson-Hasselbalch equation can be used to obtain the ***salt : acid ratio*** or ***salt : base ratio*** that can guide us to prepare buffer solutions of known pH by calculation

Examples

1. **Describe how you would prepare a buffer solution of pH 5 using ethanoic acid.**

$$\left(\boldsymbol{K_a\ for\ ethanoic\ acid\ is\ 1.8\times 10^{-5}\ moldm^{-3}}\right)$$

$The\ solution\ should\ be\ a\ mixture\ of\ ethanoic\ acid\ and\ sodium\ ethanoate$:

$$pH = pK_a + log\frac{[CH_3COONa]}{[CH_3COOH\ ]}$$

$$5 = -\log(1.8\times 10^{-5}) + log\frac{[CH_3COONa]}{[CH_3COOH\ ]}$$

$$5 = 4.745 + log\frac{[CH_3COONa]}{[CH_3COOH\ ]}$$

$$log\frac{[CH_3COONa]}{[CH_3COOH\ ]} = 0.255$$

$$\frac{[CH_3COONa]}{[CH_3COOH\ ]} = 10^{0.255}$$

$$\frac{[CH_3COONa]}{[CH_3COOH\ ]} = \frac{\mathbf{1.799}}{\mathbf{1}}$$

The buffer solution is prepared by adding 179.9cm^3 of sodium ethanoate **solution** to 100cm^3 an ethanoic acid **solution** of the **same concentration**.

or

1.799 moles of sodium ethanoate and 1 mole of ethanoic acid are dissolved in water **to make a litre of solution**

or

147.518g of sodium ethanoate and 60g of ethanoic acid are dissolved in water **to make a litre of solution**

2. **Describe how a basic buffer solution of pH 9.5 can be prepared using dimethylamine of pK_b value 3.29**.

$The\ solution\ can\ be\ a\ mixture\ of\ dimethylamine\ and\ dimethylammonium\ chloride$:

$$pOH = pK_w - pH$$

$$= 14 - 9.5 = 4.5$$

$$pOH = pK_b + log\frac{[(CH_3)_2NH_2^+Cl^-]}{[(CH_3)_2NH\ ]}$$

$$4.5 = 3.29 + log\frac{[(CH_3)_2NH_2^+Cl^-]}{[(CH_3)_2NH\ ]}$$

$$log\frac{[(CH_3)_2NH_2^+Cl^-]}{[(CH_3)_2NH\ ]} = 1.21$$

$$\frac{[(CH_3)_2NH_2^+Cl^-]}{[(CH_3)_2NH\ ]} = 10^{1.21}$$

$$\frac{[(CH_3)_2NH_2^+Cl^-]}{[(CH_3)_2NH\ ]} = \frac{16.22}{1}$$

The buffer solution is prepared by adding 1622cm^3 of dimethylammonium chloride **solution** to 100cm^3 an dimethylamine **solution** of the **same concentration**.

or

16.22 moles of dimethylammonium chloride and 1 mole of dimethylamine are dissolved in water **to make a litre of solution**

or

1321.93g of dimethylammonium chloride and 45g of dimethylamine are dissolved in water **to make a litre of solution**

Application of buffers

- Maintaining the pH of blood in the body
- Maintaining the pH of culture solutions
- Maintaining the pH during manufacture of medicines
- Manufacture of cosmetics
- Maintaining the pH during fermentation

Questions

1. Calculate the pH of a solution containing 0.01 moles of ethanoic acid and 0.82g of sodium ethanoate in a litre of solution. ($K_a = 1.75 \times 10^{-5} moldm^{-3}$)
2. $6.8g$ of sodium methanoate are dissolved in 1 dm^3 of 0.01M methanoic acid solution. Calculate the pH of the resulting solution. ($K_a = 1.8 \times 10^{-4}\ moldm^{-3}$)
3. (i) Calculate the pH of a solution made by dissolving 0.005 moles of methanoic acid and 0.007 moles of sodium methanoate in 1.0 dm^3 of aqueous solution. ($K_a = 1.8 \times 10^{-4}\ moldm^{-3}$)
   (i) State whether the pH value you have calculate in (a) above would increase or decrease on dilution with water and give the reason for your answer.
4. Calculate the pH of a mixture of $50cm^3$ of 1M ethanoic acid with $20cm^3$ of 1M sodium hydroxide. ($K_a\ for\ ethanoic\ acid = 1.75 \times 10^{-5} moldm^{-3}$)
5. Calculate the pH of a solution prepared by addition of $50.0\ cm^3$ of 0.2M sodium hydroxide to $50.0\ cm^3$ of 0.4M ethanoic acid.
6. (a) Calculate the pH of a 0.5M propanoic acid solution. ($K_a = 1.35 \times 10^{-5}\ moldm^{-3}$)
   (b) $35.0\ cm^3$ of a 0.5M potassium hydroxide was mixed with $45.0\ cm^3$ of the solution in (a). Calculate the change in pH of the solution.
7. (a) Define the term buffer solution.
   (b) A 0.1M ethanoic acid solution was titrated with 0.1M sodium hydroxide solution until the acid was exactly half neutralised. Calculate the pH of the resultant solution. ($K_a\ for\ ethanoic\ acid = 1.8 \times 10^{-5} moldm^{-3}$)
   (c) State one application of a buffer.
8. Calculate the mass of sodium ethanoate that must be dissolved in one litre of $0.1M$ ethanoic acid to form a solution with a pH of 4. ($K_a\ for\ ethanoic\ acid\ is\ 1.8 \times 10^{-5}\ moldm^{-3}$)
9. (a) (i) Write the equation for the ionisation of phenol in water.
   (ii) If the pH of a $1.0 \times 10^{-2}\ moldm^{-3}$ solution of phenol is 5.95. Calculate the dissociation constant of, K_a of phenol.

(b) 10 litres of an aqueous solution of trichloroethanoic acid was completely neutralised by $10\,cm^3$ of 0.01M sodium hydroxide. Calculate the pH of the solution of trichloroethanoic acid. ($K_a\ for\ trichloroethanoic\ acid\ \ is\ 0.224\ moldm^{-3} at\ 25°C$)

(c) The solution of trichloroethanoic acid in (b) was added to a 0.1M sodium trichloroethanoate. Calculate the pH of the resultant solution.

10. (a) Calculate the pH of a 0.05M ethanoic acid solution. ($K_a\ for\ ethanoic\ acid\ is\ 1.75 \times 10^{-5} moldm^{-3}$)

(b) Explain what is meant by the term acidic buffer.

(c) (i) A solution was made by dissolving 7.1g of ethanoic acid and 11.3g of sodium ethanoate in water to make 1 litre. To the solution was added $0.8\,cm^3$ of 1M hydrochloric acid. Calculate the pH of the solution. State any assumptions made.

(ii) Addition of $2\,cm^3$ of 0.1M hydrochloric acid solution to a solution of sodium ethanoate and ethanoic acid showed no change in pH of the solution. Explain.

11. (a) What is meant by the term buffer solution?

(b) Calculate the mass of sodium propanoate that should be added to $1\,dm^3$ of a 0.1M propanoic acid in order to give a solution whose pH is 4.5. State any assumptions made.

($The\ dissociation\ constant\ for\ propanoic\ acid\ \ is\ 1.40 \times 10^{-5} moldm^{-3}$)

(c) Few drops of dilute hydrochloric acid were added to the solution in (b).

(i) State what happened to the pH of the solution

(ii) Give a reason for your answer in c(i)

12. (a) Define the term “**buffer solution**”

(b) Calculate the mass of sodium ethanoate that should be added to 1 litre of a 0.2M ethanoic acid solution in order to produce a solution of $pH = 3.0$ ($K_a\ for\ ethanoic\ acid\ \ is\ 1.80 \times 10^{-5} moldm^{-3}$)

(c) State what would happen to the pH of the solution in (b), if a small amount of the following were added.

(i) sodium hydroxide solution

(ii) hydrochloric acid

(d) State one biological application of a buffer solution.

13. Explain why a mixture of ammonia and ammonium chloride in solution mantains a fairly constant pH when to it a small amount of:

(i) hydrochloric acid is added

(ii) potassium hydroxide is added

14. (a) State what is meant by the term basic buffer solution.
    (b) Determine the pH of the solution made by mixing 25cm^3 of 0.1M hydrochloric acid with 45cm^3 of 0.1M ammonia solution.

$(K_b\ for\ ammonia\ is\ 1.75 \times 10^{-5}\ moldm^{-3})$

15. (a) State what is meant by the term buffer solution
    (b) Explain how a mixture of ethylamine and ethylammonium chloride acts as a buffer.
    (c) 6.8g of ammonium chloride were added to 0.7M ammonia solution. Calculate concentration of hydroxide ions:
    (i) before addition of salt
    (ii) after addition of salt.

$(\ K_b\ for\ ammonia\ is\ 1.8 \times 10^{-5}\ moldm^{-3})$

16. One litre of buffer solution was made containing 0.2 moles of ammonia and 0.3 moles of ammonium chloride.
    (a) Write the equation to show the reaction if a little hydroxide ions were added to the solution.
    (b) Calculate the pH of the buffer solution above.

$(K_b\ of\ ammonia =\ 1.8 \times 10^{-5} moldm^{-3})$

17. (a) $35\ cm^3$ of 0.1M sodium hydroxide solution was mixed with $45\ cm^3$ of 0.1M ethanoic acid.
    (i) Calculate the pH of the solution.

$(The\ dissociation\ constant, K_a\ for\ ethanoic\ acid\ \ is\ 1.80 \times 10^{-5} moldm^{-3})$

    (ii) State what would happen to the pH of the solution in c(i) when $10\ cm^3$ of 0.1M hydrochloric acid is added. Give a reason for your answer.
    (b) State one application of buffer solutions.
18. (a) At 25℃ , a 0.1M solution of ethylamine is 7.3% ionised.
    (i) Write an equation for the ionisation of ethylamine in water
    (ii) Calculate the concentration of hydroxide ions at equilibrium
    (b) 0.01 moles of ethylamine hydrochloride was added to 1 litre of ethylamine solution in (a). Calculate the hydroxide ion concentration of the resultant solution. State any assumptions made.
19. Describe how an acidic buffer solution of pH 4.2 can be prepared using methanoic acid of pK_a value 3.74.
20. Explain how a buffer solution of pH 8 can be prepared starting from ammonia solution. $(\ K_b\ for\ ammonia\ is\ 1.8 \times 10^{-5}\ moldm^{-3})$

ACID-BASE TITRATIONS

Acid-base titration is the addition of a solution of a base to an acid solution until there is just enough of the acid to neutralize the base.

Terms used in acid-base titration

Titrant

This is a reagent of known concentration that is added to another solution to determine the concentration of the second chemical species.

Titrand (analyte)

This is a reagent whose concentration is not known and has to be determined by titration.

Equivalence point

This is the point when the number of moles titrant is equal to number of moles of analyte.

It occurs before end point.

End point

A point in a titration at which the reaction is complete, observed by the colour change of an indicator and occurs when small amount of solution of known concentration is added to a solution whose concentration is to be determined.

It occurs after equivalence point.

Acid-base indicators

An Acid-base indicator is a substance which changes colour according to the hydrogen ion concentration of the solution or liquid to which it is added.

Indicators are either weak acids or weak bases and slightly dissociated when dissolved in water.

They are used to measure hydrogen ion concentration of solutions or to detect changes in pH of solutions

The indicators change colour over different ranges of . Colour of an indicator depends on the colour of the undissociated molecules and the colour of the ions produced.

Examples of indicators

- Phenolphthalein
- Methyl orange
- Methyl red
- Thymol blue
- Litmus
- Congo red
- Bromothymol blue
- Universal indicator
- Phenol red
- Cresol red

Action of an indicator

The most commonly used indicators are weak acids of the form ,HIn.
Considering phenolphthalein indicator;

Phenolphthalein indicator is a ***weak acid hence partly ionises***

$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$$

The ***unionised HIn molecules are colourless*** whereas ***the anions, In^-, are pink***.
When an ***acid is added to the indicator solution***, the ***hydrogen ion concentration increases*** and the excess ***hydrogen ions react In^- ions to form unionised HIn molecules*** , ***shifting the equilibrium to the left***, ***mantaining the value of the ionisation constant***. The ***solution becomes colourless***.

$$H^+(aq) + In^-(aq) \longrightarrow HIn(aq)$$

When a ***base is added to the indicator solution***, the ***hydroxide ions react with hydrogen ions to form water*** .

$$H^+(aq) + \bar{O}H(aq) \longrightarrow H_2O(aq)$$

More of the indicator ionises, ***shifting the equilibrium to the right*** and a ***relatively large concentration of In^- ions is produced*** to ***maintain the value of the ionisation constant***. The ***solution becomes pink***.

Considering methyl orange indicator;
Methyl orange indicator is a ***weak acid hence partly ionises***

$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$$

The ***unionised HIn molecules are red*** whereas ***the anions, In^-, are yellow***.
When an ***acid is added to the indicator solution***, the ***hydrogen ion concentration increases*** and the excess ***hydrogen ions react In^- ions to form unionised HIn molecules*** , ***shifting the equilibrium to the left***, ***mantaining the value of the ionisation constant***. The ***solution becomes red***.

$$H^+(aq) + In^-(aq) \longrightarrow HIn(aq)$$

When a ***base is added to the indicator solution***, the ***hydroxide ions react with hydrogen ions to form water*** .

$$H^+(aq) + \bar{O}H(aq) \longrightarrow H_2O(aq)$$

More of the indicator ionises, ***shifting the equilibrium to the right*** and a ***relatively large concentration of In^- ions is produced*** to ***maintain the value of the ionisation constant***. The ***solution becomes yellow***.

pH range for indicators

Every indicator has a definite range of hydrogen ion concentration or pH over which it changes colour. Methyl orange is red at a pH of 3.1, orange at a pH of 3.7 and yellow at at a pH of 4.6.

Indicator	pH range	Colour Acid-Alkali
Thymol blue	$1.2 - 2.8$	Red-Yellow
Methyl orange	$3.1 - 4.6$	Red-Yellow
Congo red	$3.0 - 5.0$	Blue-Red
Methyl red	$4.2 - 6.3$	Red-Yellow
Litmus	$5.0 - 8.0$	Red-Blue
Phenolphthalein	$8.3 - 10.0$	Colourless-Red

Choice of indicator

In an acid-base titration, it is important to use an indicator which changes colour over a range in which there is a marked pH change during the titration.

When a strong acid is titrated with a strong base, the pH at end point is about 7.

When a strong acid is titrated with a weak base, pH at end point is below 7 because the salt usually formed undergoes hydrolysis to form an acidic solution.

When a weak acid is titrated with a strong base, pH at end point is above 7 because the salt usually formed undergoes hydrolysis to form an acidic solution.

Therefore the indicator to be selected for any of the above three titrations is one which has its half-way colour nearest to the pH of the neutralised solution.

Titration	Marked pH change	Examples	Suitable indicator	pH range of indicator
Strong acid-strong base	$4.0 - 10.0$	HCl and $NaOH$	Litmus ***But almost any indicator can be used***	$5.0 - 8.0$
Strong acid-weak base	$3.5 - 6.5$	HCl and NH_3	Methyl red	$4.2 - 6.3$
Weak acid-strong base	$7.5 - 10.5$	CH_3COOH and $NaOH$	Phenolphthalein	$8.3 - 10.0$
Weak acid-weak base	***No marked change***	CH_3COOH and NH_3	***End point cannot be detected accurately by any indicator***	

Examples

1. **The pH ranges for different indicators are shown in the table below.**

Phenolphthalein	Bromothymol blue	Methyl orange
8.30-10.0	**6.00-7.60**	**3.10-4.40**

(i) Identify the most suitable indicator for the titration dimethylamine with hydrochloric acid

(ii) Briefly explain your answer above.

(i) Methyl orange indicator

(ii) Dimethylamine reacts with hydrochloric acid to form a ***salt, dimethylammonium chloride*** *which* ***undergoes hydrolysis*** *to form* ***an acidic solution*** *and the* ***pH at end point is below 7*** *and* ***within the working range of methyl orange indicator****.*

$$(CH_3)_2NH_2^+(aq) + H_2O(l) \rightleftharpoons (CH_3)_2NH(aq) + H_3O^+(aq)$$

2. **The pH ranges of some indicators are given in the table below.**

Indicator	Methyl orange	Phenolphthalein	Cresol red
pH **range**	$\mathbf{3.2-4.4}$	$\mathbf{8.3-10.0}$	$\mathbf{7.2-8.8}$

Which of the indicators is most suitable for the titration between methanoic acid and sodium hydroxide? Give a reason for your answer

Phenolphthalein indicator

Methanoic acid reacts with sodium hydroxide to form a ***salt, sodium methanoate*** *which* ***undergoes hydrolysis*** *to form* ***an alkaline solution*** *and the* ***pH at end point is above 7*** *and* ***within the working range of phenolphthalein indicator****.*

$$HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + \bar{O}H(aq)$$

Questions

1. (a) A solution made by dissolving sodium ethanoate in a standard solution of ethanoic acid has pH of 4.7. Explain what would happen when a small amount of sodium hydroxide is added to the solution.

   (b) 1.0 cm^3 of 1M sodium hydroxide was added to 1.0 dm^3 of 0.01M ethanoic acid. Calculate the pH of the resultant solution.

   $(K_a\ of\ ethanoic\ acid\ is\ 1.7 \times 10^{-5} moldm^{-3}\ at\ 25°C)$

   (c) The pH ranges over which some indicators change colour are given below.

Indicator	pH range
Phenolphthalein	8.0-10.0
Litmus	5.0-8.0
Methyl orange	3.0-5.0

(i) Which of the indicators above would be the most suitable for the reaction below?

$$M_2CO_3(aq) + H_2SO_4(aq) \longrightarrow M_2SO_4(aq) + CO_2(g) + H_2O(l)$$

(ii) Give a reason for your answer in (c)(i)

2. (a) (i) What do you understand by the term **Bronsted base**?

(ii) Classify the following species as Bronsted acids and /or bases

$$S^{2-}, HCO_3^-, H_2O, NH_3$$

(b) The dissociation of phenolphthalein can be written as follows:

$$HX(aq) \longrightarrow H^+(aq) + \ X^-(aq) \quad where\ K_a = 7 \times 10^{-10} moldm^{-3}$$

(i) What colours, if any are associated with the three species in the equation?

(ii) What should be the pH of a solution at the end point using this indicator, assuming a strong base is added to a weak acid.

3. Explain the following observations

(a) Phenolphthalein indicator, which has a pH range 8-10 is a suitable indicator in the titration of ethanoic acid with sodium hydroxide solution but not suitable for ammonia with hydrochloric acid

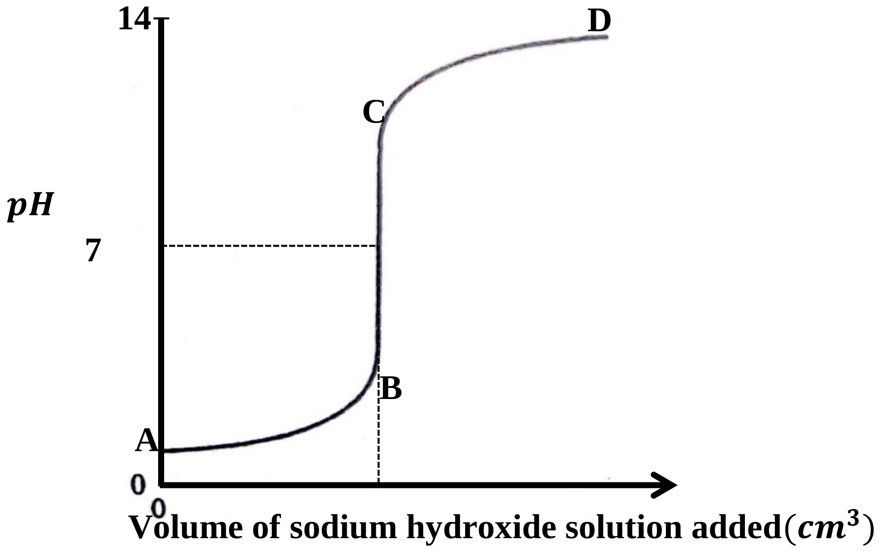
(b) The pH of pure water is 7.0 at 25℃ and 6.5 at 75℃.

(c) Methylamine is a stronger base than ammonia

pH-volume curves for acid-base titrations

1. Titration of a strong acid and a strong base

(a) Titration of sodium hydroxide solution against hydrochloric acid



Explanation of the shape of the graph

Initially, ***pH is low at A*** due to ***a high concentration of hydrogen ions*** from ***complete ionisation of strong hydrochloric acid***.

pH gradually increases along AB as sodium hydroxide solution is added due to ***excess hydrogen ions still present*** as ***some of the hydrogen ions are being neutralised***.

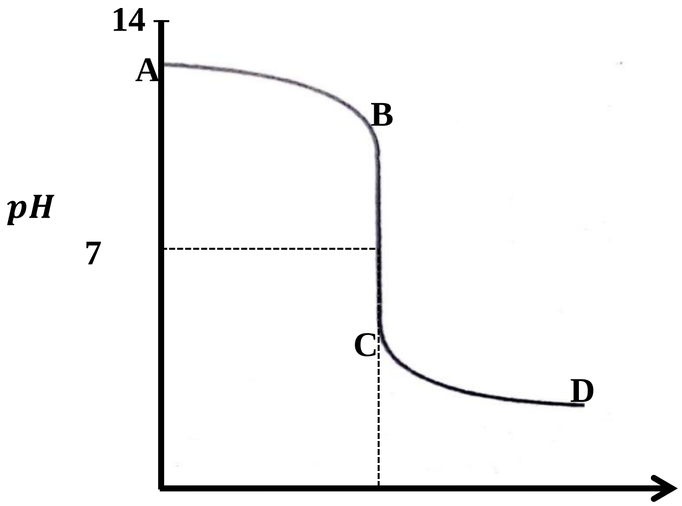
$$H^+(aq) + \bar{O}H(aq) \longrightarrow H_2O(l)$$

pH sharply increases along BC even with a little sodium hydroxide solution added because ***all the acid has been completely neutralised***. ***The end point is reached***.

pH at end point is 7 because ***sodium chloride salt formed does not undergo hydrolysis***.

Along CD, pH gradually increases due to ***excess sodium hydroxide solution added***.

(b) Titration of hydrochloric acid against sodium hydroxide solution



Volume of hydrochloric acid added(cm^3)

Explanation of the shape of the graph

Initially, ***pH is high at A*** because ***sodium hydroxide completely ionises to form very many hydroxide ions***.

pH gradually decreases along AB as sodium hydroxide solution is added due to ***excess hydroxide ions still present*** as ***some of the hydroxide ions are being neutralised***.

$$H^+(aq) + \bar{O}H(aq) \longrightarrow H_2O(l)$$

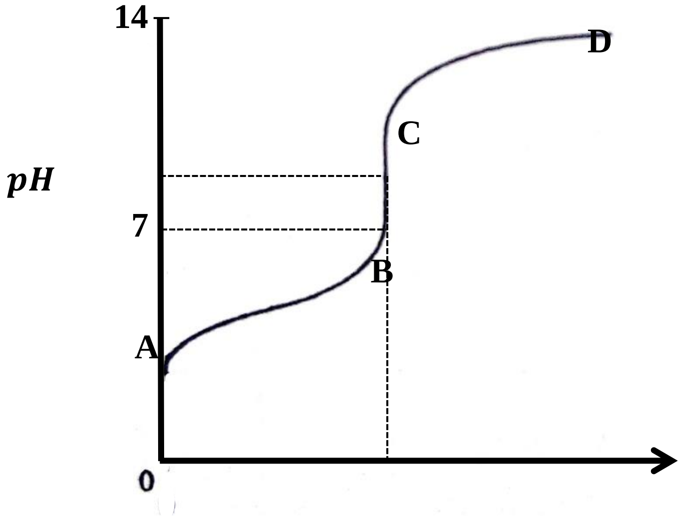
pH sharply decreases along BC even with a little hydrochloric acid added because ***all the base has been completely neutralised***. ***The end point is reached***.

pH at end point is 7 because ***sodium chloride salt formed does not undergo hydrolysis***.

Along CD, pH gradually decreases due to ***excess hydrochloric acid added***.

2. Titration of a weak acid and a strong base

(a) Titration of sodium hydroxide against ethanoic acid



Volume of sodium hydroxide solution added(cm^3)

Explanation of the shape of the graph

Initially, ***pH is relatively low at A*** due ***to a relatively high concentration of weak ethanoic acid***.

pH gradually increases along AB as sodium hydroxide solution is added because ***very few hydrogen ions are neutralised by hydroxide ions.*** Also, the ***un neutralised ethanoic acid and the sodium ethanoate salt formed constitute a buffer*** which ***resists increase in pH***.

pH sharply increases along BC even with a little sodium hydroxide solution added because ***all the acid has been completely neutralised***. ***The end point is reached***.

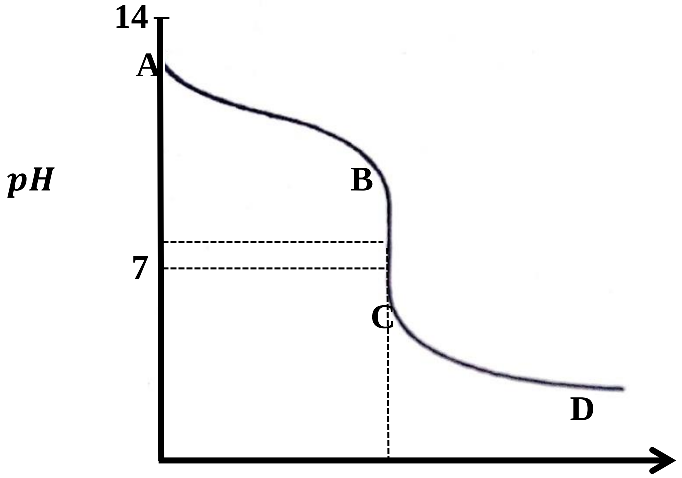
$$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)$$

pH at end point is above 7 because the ***sodium ethanoate salt formed undergoes hydrolysis to form an alkaline solution***.

$$CH_3COONa(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + \bar{O}H(aq)$$

Along CD, pH gradually increases due to ***excess sodium hydroxide solution added***.

(b) Titration of ethanoic acid against sodium hydroxide



Volume of ethanoic acid added(cm^3)

Explanation of the shape of the graph

Initially, ***pH is very high at A*** because ***sodium hydroxide is a strong base hence completely ionises to form very many hydroxide ions***.
pH gradually decreases along AB as ethanoic acid is added due to ***excess hydroxide ions still present*** as ***some of the hydroxide ions are being neutralised***.
pH sharply decreases along BC even with a little ethanoic acid added because ***all the base has been completely neutralised***. ***The end point is reached***.

$$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)$$

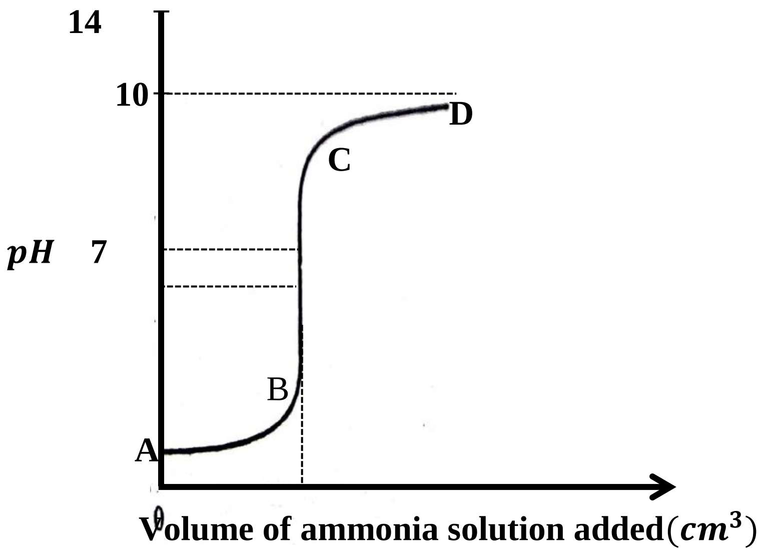
pH at end point is slightly above 7 because the ***sodium ethanoate salt formed undergoes hydrolysis to form an alkaline solution***.

$$CH_3COONa(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + \bar{O}H(aq)$$

Along CD, pH gradually decreases due to ***excess ethanoic acid added which together with the sodium ethanoate salt formed form a buffer solution***.

3. *Titration of a strong acid and weak base*

(a) Titration of ammonia solution against hydrochloric acid



Explanation of the shape of the graph

Initially, ***pH is low at A*** due to ***a high concentration of hydrogen ions*** from ***complete ionisation of strong hydrochloric acid***.

pH gradually increases along AB as ammonia solution is added because ***hydrochloric acid is being neutralised***.

$$HCl(aq) + NH_3(aq) \longrightarrow NH_4Cl(aq)$$

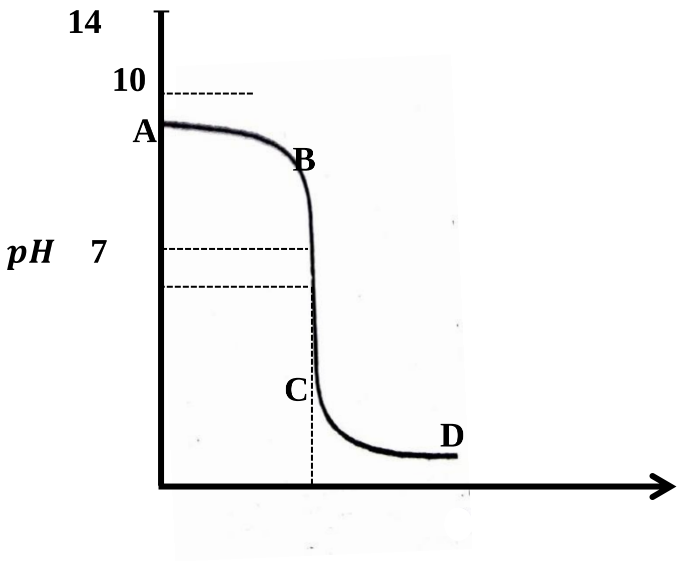
pH sharply increases along BC even with a little ammonia solution added because ***all the acid has been completely neutralised***. ***The end point is reached***.

pH at end point is below 7 because the ***ammonium chloride salt formed under goes hydrolysis to form an acidic solution***.

$$NH_4^+(aq) + H_2O(l) \longrightarrow NH_3(aq) + H_3O^+(aq)$$

Along CD, pH gradually increases due to the ***excess ammonia solution added which together the ammonium chloride salt formed form a buffer solution which resists increase in pH***.

(b) Titration of hydrochloric acid against ammonia solution



Volume of hydrochloric acid added(cm^3)

Explanation of the shape of the graph

Initially, ***pH is slightly above seven at A*** because ***ammonia is a weak base that partially ionises to form few hydroxide ions***.

pH gradually decreases along AB as hydrochloric acid is added due to ***excess ammonia solution still present which together with the ammonium chloride salt*** formed form a ***buffer solution that resists a decrease in pH***.

Also ***some of the ammonia solution is being neutralised by hydrochloric acid***.

$$NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$$

pH sharply decreases along BC even with a little hydrochloric acid added because ***the end point is reached***.

pH at end point is below 7 because the ***ammonium chloride salt formed undergoes hydrolysis to form an acidic solution***.

$$NH_4^+(aq) + H_2O(l) \longrightarrow NH_3(aq) + H_3O^+(aq)$$

Along CD, pH gradually decreases due to ***excess hydrochloric acid added.***

Questions

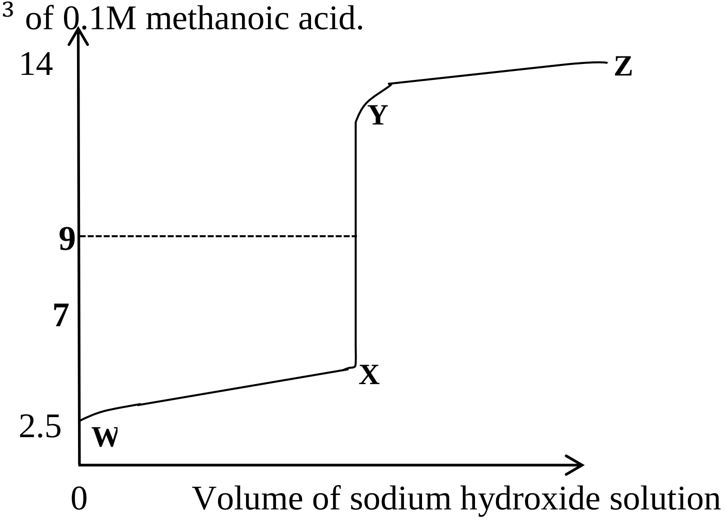
1. (a) Sketch a graph to show how pH of potassium hydroxide changes when the following are added until in excess
   - (i) Hydrochloric acid
   - (ii) Ethanoic acid

   (b) Explain the shapes of the curves

   (c) $100cm^3$ of 0.01M benzoic acid was added to an equal volume of 0.01M sodium hydroxide. Calculate the pH of the resultant solution. $(K_a\ for\ benzoic\ acid\ is\ 6.4 \times 10^{-5} moldm^{-3})$
2. (a) Sketch pH-volume curves to show the change in pH that happens when:
   - (i) 0.1M sodium hydroxide solution is added in portions to $25\ cm^3$ of 0.1M ethanoic acid.
   - (ii) 0.1M hydrochloric acid is added in portions to $20\ cm^3$ of 0.1M ammonia solution.

   (b) Explain the shapes of the graphs in both cases.
3. (a) Define the term **indicator** as used in acid-base titration

   (b) The curve below was obtained when 0.1M sodium hydroxide solution was titrated against $25\ cm^3$ of 0.1M methanoic acid.



   - (i) Explain the shape of the curve WXYZ
   - (ii) Name a suitable indicator for the above titration

   (c) Calculate the:
   - (i) dissociation constant of methanoic acid in (b) above
   - (ii) pH of the solution formed when $5\ cm^3$ of sodium hydroxide has just been added to the methanoic acid in (b) above.

4. $0.1M$ sodium hydroxide solution was added to $20\,cm^3$ of 0.1M ethanoic acid in portions.
   - (i) Sketch a graph to show the change in pH
   - (ii) Explain the shape of the graph
   - (iii) Calculate the pH of the solution formed when $20\,cm^3$ of 0.1M sodium hydroxide had been added to the ethanoic acid.
5. (a) (i) What is meant by a weak acid?
   - (ii) Calculate the pH of a $0.4M$ ethanoic acid solution. State any assumptions made ($K_a = 1.8 \times 10^{-5} moldm^{-3}$).

   (b) (i) What is meant by a buffer solution.

(ii) Calculate the pH of a buffer solution made by mixing $15cm^3$ of $0.01M$ ethanoic acid with $25cm^3$ of $0.1M$ sodium ethanoate solution.

(c) Draw a graph to show the pH changes when a strong acid is titrated with a weak base and explain its shape

6. (a) (i) Explain what is meant by an acid-base indicator.

(ii) Explain in titration experiments one or two drops of indicators are used

(b) The table below gives data obtained when $100cm^3$ of propanoic acid was titrated with 1.0M sodium hydroxide solution.

Volume of sodium hydroxide solution added (cm^3)	0.0	1.0	5.0	9.0	9.5	10.5	11.0	15.0
pH of solution	2.94	3.92	4.87	5.82	6.15	11.70	12.00	12.70

- (i) Draw a graph of pH against the volume of sodium hydroxide
- (ii) Explain the shape of the graph you have drawn in b(i).
- (iii) Determine the pH of the solutions at equivalent point.
- (iv) Which of the following indicators would be suitable for titration above? Give a reason for you answer.

Indicator	Methyl red	Bromothymol blue	Phenol red
pH range	$4.2 - 6.3$	$6.0 - 7.6$	$6.8 - 8.4$

7. The table below shows the pH changes when $10\,cm^3$ of ethanoic acid was titrated with 0.1M sodium hydroxide solution.

Volume of sodium hydroxide solution added (cm^3)	0.0	2.0	4.0	6.0	8.0	10.0	14.0
pH of solution	2.9	4.3	4.7	5.2	6.4	12.2	12.4

- (a) Plot a graph of pH against the volume of sodium hydroxide
- (b) Explain the shape of the graph you have drawn.
- (c) Use your graph to determine the :
  - (i) pH at equivalence point

(ii) volume of sodium hydroxide used to neutralize the acid

(d) Calculate the molarity of the ethanoic acid used

(e) The pH ranges of some indicators are given in the table below.

Indicator	Methyl orange	Phenolphthalein	Cresol red
pH range	$3.2-4.4$	$8.3-10.0$	$7.2-8.8$

Which of the indicators is suitable for the titration above? Give a reason for your answer

8. (a) The table below shows the pH of the solution when measured volumes of hydrochloric acid is added to $25cm^3$ of 0.1M ammonia solution.

Volume of hydrochloric acid(cm^3)	0	10.0	15.0	16.5	17.0	20.0	25.0
pH of solution	10.25	9.08	8.30	6.70	2.97	1.96	1.60

(i) Plot a graph of pH against volume of hydrochloric acid

(ii) Explain the shape of the graph

(b) Using the graph in (a) above, calculate the:

(i) molarity of hydrochloric acid

(ii) ionisation constant, K_b of ammonia.

(iii) Concentration of ammonium chloride formed

(iv) hydrolysis constant of ammonium chloride

(c) Calculate the pH of the solution formed when $5\ cm^3$ of 0.1M hydrochloric acid is added to $25cm^3$ of 0.1M ammonia solution.

$(K_b = 1.8 \times 10^{-5}\ and\ K_w = 1 \times 10^{-14}\ at\ 25℃)$

9. (a) Ethanoic acid is a weak acid.

(i) What is meant by the term weak acid?

(ii) Calculate the pH of 0.25M ethanoic acid. (pK_a of ethanoic acid is 4.76 at $25℃$)

(iii) State and explain how temperature affects the pK_a of ethanoic acid.

(b) Calculate the pH of the resultant solution when $25\ cm^3$ of 0.1M sodium ethanoate was added to $75cm^3$ of 0.25M ethanoic acid.

(c) The table below shows pH values for the titration of sodium hydroxide solution against $25.0cm^3$ of 0.1M ethanoic acid.

Volume of sodium hydroxide added(cm^3)	0	4.0	6.0	8.0	10.0	12.0	14.0	14.6	14.8	15.0	15.2	15.4	16.0
pH	2.8	3.8	4.2	4.6	5.1	5.5	6.2	6.8	7.6	9.0	9.8	10.5	11.4

(i) Plot a graph of pH against volume of sodium hydroxide added

(ii) From the graph, determine the volume of sodium hydroxide needed to neutralise the acid.

(iii) Calculate the molar concentration of sodium hydroxide solution

(iv) Determine the ratio of $[CH_3COO^-]:[CH_3COOH]$ when $5\ cm^3$ of sodium hydroxide solution has been added to $25\ cm^3$ of ethanoic acid.

10. (a) What is a **buffer solution**?

(b) Describe how a basic buffer solution works. Illustrate your answer with a solution in which phenylammonium chloride is a constituent.

(c) A solution was made by reacting 30 cm^3 of 0.1M hydrochloric acid and 50 cm^3 of 0.1M ammonia. Calculate the pH of the resulting solution.

$(K_b = 1.7\ x\ 10^{-5})$

(d) The table below shows the pH of the solution formed when 25 cm^3 of 0.1M ethanoic was titrated with sodium hydroxide solution.

Volume of sodium hydroxide solution(cm^3)	0	4	8	12	16	20	22	22.5	24	28
pH	2.8	3.5	4.0	4.5	5.1	5.8	7.0	10.5	11.4	12.3

(i) Plot a graph of pH against volume of sodium hydroxide solution

(ii) Explain the shape of your graph

(iii) Calculate the molarity of sodium hydroxide.

(iv) Calculate the ionisation constant of ethanoic acid

(e) 50 cm^3 of 0.1M sodium hydroxide was added to 50 cm^3 of 0.1M ethanoic acid. Calculate the pH of the resulting solution.

$(K_a = 1.8 \times 10^{-5})$

SOLUBILITY EQUILIBRIA

Solubility

Solubility is the <u>maximum mass of solute in grams</u> that can <u>saturate 100g of a solvent</u> at <u>a particular temperature</u> in presence of <u>excess, undissolved solute</u>.

The units for solubility are $\boldsymbol{g\ per\ 100g\ of\ solvent}\ \ or\ \ \boldsymbol{g(100g\ solvent)^{-1}}$.

Molar solubility

Molar solubility is the number of moles of a solute that can dissolve in one litre of a solution before the solution becomes saturated.

The units for molar solubility are $\boldsymbol{moles\ per\ litre}\ \ or\ \ \boldsymbol{M}$.

Experiment to determine solubility of a soluble salt

Considering potassium nitrate;

Add potassium nitrate, ***a little at a time***, ***while stirring*** to ***a known volume of water*** in a ***container immersed in a thermostat*** at ***a particular temperature*** until ***no more potassium nitrate dissolves***.
The mixture is ***allowed to settle until*** the ***excess undissolved crystals separate*** from the solution.
The excess undissolved crystals are ***filtered off using a dry filter paper and funnel*** into a ***dry container*** to obtain ***a saturated solution of potassium nitrate***.
The ***temperature of the saturated solution is measured and recorded,*** T ℃.
A clean dry dish is weighed and its mass recorded $(a\ g)$
A ***known volume of the saturated solution is added to the dish***. The ***dish and the saturated solution are also weighed again and the mass recorded*** $(b\ g)$
The dish and the saturated solution ***is placed on a steam bath until the dry potassium nitrate crystals are left***.
Allow the dish and its contents to cool and weigh the mass of the dish and the dry salt again $(c\ g)$

Treatment of results

$$Mass\ of\ \ dish = a\ g$$
$$Mass\ of\ \ dish\ and\ saturated\ solution = b\ g$$
$$Mass\ of\ \ dish\ and\ dry\ potassium\ nitrate = c\ g$$
$$Temperature\ of\ saturated\ solution = T\ ℃$$
$$Mass\ of\ saturated\ solution = (b-a)\ g$$
$$Mass\ of\ dry\ potassium\ nitrate = (c-a)\ g$$
$$Mass\ of\ water = \big((b-a)-(c-a)\big)\ g$$
$$= (b-c)g$$
$$(b-c)g\ of\ water\ dissolve\ (c-a)\ g\ of KNO_3\ at\ T\ ℃$$
$$100g\ of\ water\ \ will\ dissolve\ \left(\frac{(c-a)\times 100}{b-c}\right)\ g\ of KNO_3\ at\ T\ ℃$$
$$\boldsymbol{The\ solubility\ of\ potassium\ nitrate\ is\ \left(\frac{(c-a)\times 100}{b-c}\right)\ g\ per\ 100g\ of\ water\ at\ T}\ ℃$$

Factors that affect solubility of a soluble salt

1. ***Nature of solvent and solute.***

Polar solutes easily dissolve in polar solvents and non-polar solvents easily dissolve in non-polar solvents.

2. ***Temperature***

The solubility of most salts increases with increase in temperature. The effect of temperature is in accordance with Le Chatelier's principle.

If a solute is in equilibrium with its saturated solution, increasing temperature will favour the change which is accompanied with absorption of heat. Therefore more or less of the substance will dissolve according to which change is accompanied by absorption of heat.

3. ***Pressure***

The effect of pressure on the solubility of a solid is small because high pressures are required to affect the volumes of liquids and extremely high pressures to affect the volumes of solids.

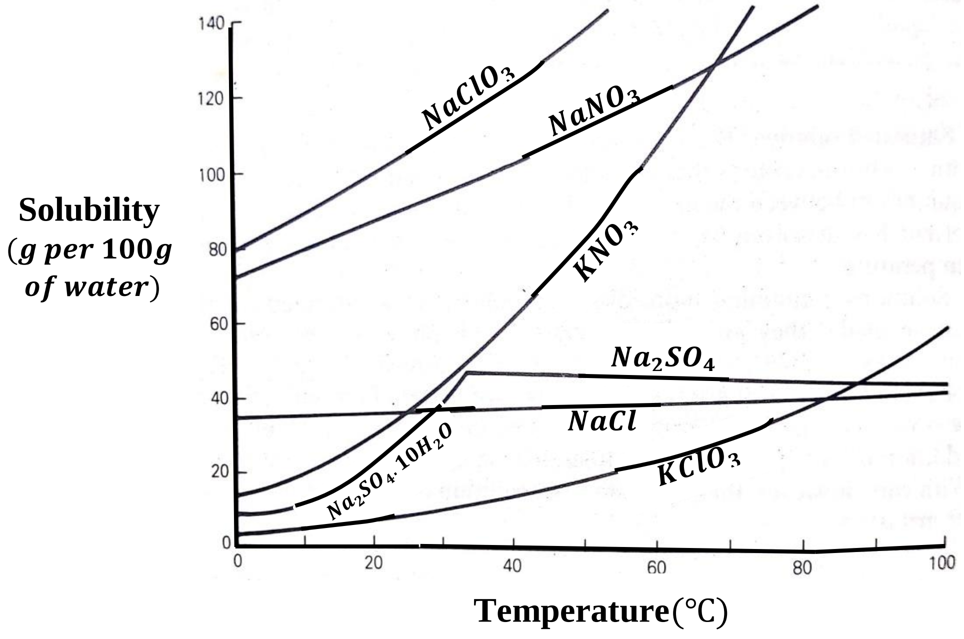
However, if pressure is sufficiently increased, an appreciable change in solubility may happen. The effect of pressure on solubility of a salt is also in accordance with Le Chatelier's principle.

Increase in pressure to 500 atm increases solubility of sodium chloride in water because the salt dissolves in water with a decrease in total volume.

Increase in pressure to 500 atm decreases solubility of ammonium chloride in water because the salt dissolves in water with an increase in total volume.

Solubility curves

The variation of solubility with temperature can be summarised by solubility curves.



For salts that form solutions endothermically, the solubility generally increases with increase in temperature.

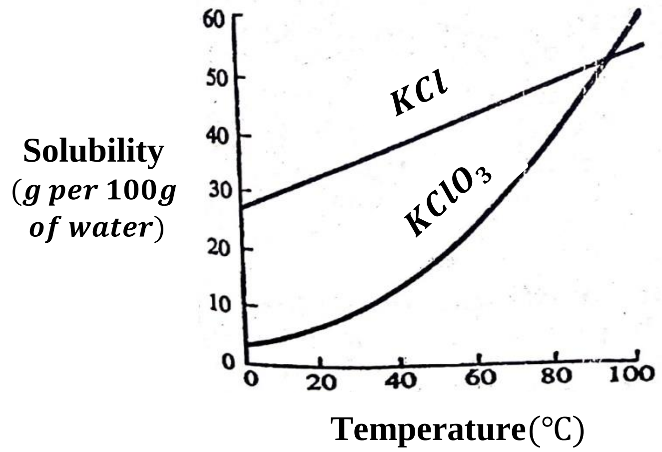
For salts whose solubility decreases with increase in temperature, such as anhydrous sodium sulphate, heat is evolved on dissolving. Other examples of such salts include calcium sulphate and calcium hydroxide.

The transition point in solubility for sodium sulphate is due to a change in hydration.

The application of solubility curves (fractional crystallisation)

Fractional crystallisation can be used to purify substances with different solubilities.

Consider a mixture of potassium chloride and potassium chlorate(V).



Potassium chloride and potassium chlorate(V) have different solubilities in water at different temperatures.

When a concentrated solution of the two salts in water is heated and then cooled, potassium chlorate(V) which is less soluble at lower temperatures crystallises first.

The first yield therefore contains potassium chlorate(V) crystals and a small amount of potassium chloride.

When the first yield of crystals is dissolved in hot water and the process of crystallisation repeated, pure crystals of potassium chlorate(V) are finally obtained from free from potassium chloride.

Calculation of solubility

Examples

(a) **(a) $350cm^3$ of water was saturated by 157.5g of potassium nitrate at 30℃. Calculate the solubility of potassium nitrate at 30℃. (Density of water is $1.0gcm^3$)**

(b) The solution in (a) was cooled to 15℃. Calculate the mass of potassium nitrate crystallised if the solubility of potassium nitrate at 15℃ is 25.0g per 100g.

(a)

$$Mass\ of\ water = (350 \times 1) = 350g$$

$$350g\ of\ H_2O\ are\ saturated\ by\ 157.5g\ of\ KNO_3\ at\ 30℃$$

$$100g\ of\ H_2O\ are\ saturated\ by\ \left(\frac{100 \times 157.5}{350}\right) g\ of\ KNO_3\ at\ 30℃$$

$$= 45g\ per\ 100g$$

$$\boldsymbol{Solubility\ of\ KNO_3\ is\ 45g\ per\ 100g\ of\ water\ at\ 30℃}$$

(b)

$$100g\ of\ H_2O\ are\ saturated\ by\ 25.0g\ of\ KNO_3\ at\ 15℃$$

$$300g\ of\ H_2O\ will\ be\ saturated\ by\ \left(\frac{300 \times 25.0}{100}\right) g\ of\ KNO_3\ at\ 15℃$$

$$= 75\ g\ of\ KNO_3\ at\ 15℃$$

$$Mass\ of\ KNO_3\ formed\ by\ cooling\ the\ solution\ from\ 30℃\ to\ 15℃ = (157.5 - 75)g$$

$$\boldsymbol{= 82.5g}$$

(b) **60g of a saturated solution of a soluble salt Q gave 17.75g of Q at 50℃. Calculate the solubility of Q at 50℃.**

$$Mass\ of\ water = (60 - 17.75) = 42.25g$$

$$42.25g\ of\ H_2O\ are\ saturated\ by\ 17.75g\ of\ Q\ at\ 50℃$$

$$100g\ of\ H_2O\ are\ saturated\ by\ \left(\frac{100 \times 17.75}{42.25}\right) g\ of\ Q\ at\ 50℃$$

$$= 42g\ per\ 100g$$

$$\boldsymbol{Solubility\ of\ Q\ is\ 42g\ per\ 100g\ of\ water\ at\ 50℃}$$

(c) **The solubility of potassium chlorate(V) is 60g per 100g of water at 100℃. Calculate the number of moles the salt that can saturate 150g of water at the same temperature.**

$$100g\ of\ H_2O\ are\ saturated\ by\ 60g\ of\ KClO_3\ at\ 100℃$$

$$150g\ of\ H_2O\ will\ be\ saturated\ by\ \left(\frac{150 \times 60}{100}\right) g\ of\ KClO_3\ at\ 100℃$$

$$= 90\ g$$

$$Molar\ mass\ of\ KClO_3 = 39 + 35.5 + 48 = 122.5g$$

$$\boldsymbol{Moles\ of\ KClO_3 = \frac{90}{122.5} = 0.735\ moles}$$

Question

21.38g of a saturated solution of a soluble salt, X, was evaporated to dryness and 4.28g of X were obtained at a certain temperature. Calculate the solubility of X at that temperature.

Solubility curves

Plotting and interpreting solubility curves for soluble salts

Questions

1. (a) Describe an experiment to determine the solubility of potassium chlorate(V) in water at room temperature.

   (b) The results below were obtained for the solubility of potassium chloride and potassium chlorate(V) in water at different temperatures.

Temperature (℃)	$KCl(g\ per\ 100g)$	$KClO_3(g\ per\ 100g)$
0	28	3
20	34	7
50	42	19
100	56	59

   - (i) Plot the solubility curves of the two salts on the same axes
   - (ii) Determine the temperature at which the two salts have equal solubilities.
   - (iii) State which of the two salts dissolves more rapidly with increase in temperature.
   - (iv) State one application of solubility curves.

2. The table below shows the solubility of potassium nitrate in water at different temperatures.

Temperature(℃)	10	15	30	40	50	57
Solubility $(g(100g\ H_2O)^{-1})$	20	25	45	63	85	106

(a) Plot a graph of solubility against temperature

(b) Use your graph to determine solubility at:
   - (ii) 36℃
   - (iii) 62℃

(c) Calculate the mass of potassium nitrate that crystallises on lowering the temperature from 50℃ to 15℃

The concept of dynamic equilibrium in a saturated salt solution

The presence of excess undissolved solute in contact with a solution ensures the solution is saturated. There exists a dynamic equilibrium between the undissolved and the dissolved solid. The dynamic equilibrium exists in the saturated solution when solute particles return to the surface of the solid at the same rate as they are dissolving. The amount of the solid dissolving balances the amount of substance that is crystallizing.

Sparingly soluble salts/ electrolytes

Many salts such as lead(II) sulphate, calcium carbonate, silver chloride and others are described as insoluble in water. There is however, in practice, no substance completely insoluble but some substances dissolve to a very small extent that their solubility cannot be determined by the ordinary method already described.

Electrolytes that dissolve only slightly in water are called sparingly soluble electrolytes.

Solubility product

Consider a ***sparingly soluble electrolyte***, A_xB_y. The ions of the electrolyte in its ***saturated solution*** will be in equilibrium with the undissolved solid at ***a given temperature***.

$$A_xB_y(s) + aq \rightleftharpoons xA^{y+}(aq) + yB^{x-}(aq)$$

From the law of mass action:

$$K = \frac{[A^{y+}]^x[B^{x-}]^y}{A_xB_y}$$

Since the concentration of a solid remains constant, then;

$$\boldsymbol{K_{sp}} = [\boldsymbol{A}^{y+}]^x[\boldsymbol{B}^{x-}]^y$$

The constant, $\boldsymbol{K_{sp}}$ is called the **solubility product** of the sparingly soluble electrolyte, A_xB_y.

Solubility product is therefore defined as the <u>product of the molar concentrations of the ions</u> of a <u>sparingly soluble electrolyte</u> in its <u>saturated solution</u> raised to <u>appropriate powers</u> at a given temperature.

Expressions for solubility product

Consider each of the sparingly soluble electrolytes below. For each the equation for solubility in water and the solubility product expression is written.

(i) ***Silver bromide***
(ii) ***Silver ethanedioate***
(iii) ***Calcium phosphate***

(i) Silver bromide

Equation : $\boldsymbol{AgBr(s) + aq \rightleftharpoons Ag^+(aq) + Br^-(aq)}$

$$\boldsymbol{K_{sp} = [Ag^+][Br^-]}$$

(ii) Silver ethanedioate

Equation : $\boldsymbol{Ag_2C_2O_4(s) + aq \rightleftharpoons 2Ag^+(aq) + C_2O_4^{2-}(aq)}$

$$\boldsymbol{K_{sp} = [Ag^+]^2[C_2O_4^{2-}]}$$

(iii) Calcium phosphate

Equation : $\boldsymbol{Ca_3(PO_4)_2(s) + aq \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)}$

$$\boldsymbol{K_{sp} = [Ca^{2+}]^3\left[PO_4^{3-}\right]^2}$$

Question

For each of the following sparingly soluble electrolytes, write the;

(i) **equation for solubility of the electrolyte in water**

(ii) **expression for the solubility product**

1. Silver chloride
2. Silver iodide
3. Silver carbonate
4. Silver sulphate
5. Silver chromate
6. Silver sulphide
7. Silver oxalate
8. Silver ethanoate
9. Silver bromate(V)
10. Silver iodate(V)
11. Silver phosphate
12. Aluminium hydroxide
13. Barium hydroxide
14. Barium sulphate
15. Barium carbonate
16. Calcium hydroxide
17. Calcium carbonate
18. Calcium sulphate
19. Copper(II) sulphide
20. Copper(II) iodate
21. Iron(III) hydroxide
22. Calcium iodate
23. Calcium ethanedioate
24. Chromium(III) hydroxide
25. Mercury sulphide
26. Mercury(I) iodide
27. Lead(II) fluoride
28. Lead(II) chloride
29. Lead(II) iodide
30. Lead(II) sulphate
31. Lead(II) sulphide
32. Magnesium hydroxide
33. Manganese(II) sulphide
34. Strontium hydroxide
35. Tin(II) sulphide
36. Zinc hydroxide
37. Zinc sulphide

Conditions under which solubility product is valid

1. ***Temperature is kept constant***
2. ***Solution must be saturated***
3. ***Electrolyte should be sparingly soluble***

Experimental determination of solubility product

Solubility product of different sparingly soluble electrolytes can be determined by any of the following methods;

- ***Direct titration***
- ***Using conductivity measurements***
- ***Using electrode potentials***

***The first two methods will be used in this topic but more about conductivity measurements and electrode potentials will be seen in the topic: Electrochemistry**.*
***However, for examination purposes, any method can be used**.*

Experiment to determine solubility product of calcium hydroxide

(a) By titration

Excess solid calcium hydroxide is added to a given volume of distilled water in a container.

The mixture is shaken for some time and ***left to settle*** at ***a given temperature*** to attain equilibrium.

The mixture is ***filtered*** to obtain a ***saturated solution of calcium hydroxide*** as filtrate.

A ***known volume of the filtrate is pipetted*** into a conical flask and ***titrated*** with a ***standard solution of hydrochloric acid*** using ***methyl orange indicator***.

$$Ca(OH)_2(aq) + 2HCl(aq) \longrightarrow CaCl_2(aq) + 2H_2O(l)$$

The ***molar concentration of calcium hydroxide solution is calculated*** using the equation above.

Taking the ***molar concentration of calcium hydroxide as $\boldsymbol{x}$ moles per litre***.

$$Ca(OH)_2(s) + aq \rightleftharpoons Ca^{2+}(aq) + 2\bar{O}H(aq)$$

$$Since\ mole\ ratio\ of Ca(OH)_2 : Ca^{2+} = 1:1$$

$$[Ca(OH)_2] = [Ca^{2+}] = x\ moldm^{-3}$$

$$Since\ mole\ ratio\ of Ca(OH)_2 : \bar{O}H = 1:2$$

$$[\bar{O}H] = 2[Ca(OH)_2] = 2x\ moldm^{-3}$$

$$K_{sp} = [Ca^{2+}][\bar{O}H]^2 = x \times (2x)^2$$

$$\boldsymbol{K_{sp} = 4x^3\ mol^3dm^{-9}}$$

***This method can be used for any sparingly soluble* metal hydroxide.**

(b) Using conductivity measurements

Excess solid calcium hydroxide is added to a given volume of distilled water in a container.

The mixture is shaken for some time and ***left to settle*** at ***a given temperature*** to attain equilibrium.

The mixture is ***filtered*** to obtain a saturated solution of calcium hydroxide as filtrate.

The electrolytic conductivity of the saturated solution, $\mathcal{K}_{solution}(ohm^{-1}cm^{-1})$ is measured using a conductivity meter.

The electrolytic conductivity of water, $\mathcal{K}_{H_2O}(ohm^{-1}cm^{-1})$ at the same temperature is obtained from books

Also the molar conductivities at infinite dilution (Λ_O) of calcium ions and hydroxide ions are read from the tables.

Treatment of results

The electrolytic conductivity of calcium hydroxide is then obtained by;

$$\mathcal{K}_{Ca(OH)_2} = \mathcal{K}_{solution} - \mathcal{K}_{H_2O}$$

The molar conductivity of calcium hydroxide at infinite dilution is obtained by the equation;

$$\Lambda_O(Ca(OH)_2) = \Lambda_O(Ca^{2+}) + 2\Lambda_O(\bar{O}H)$$

$\Lambda_O(Ca(OH)_2) = \Lambda_c(Ca(OH)_2)$, where Λ_c is molar conductivity of calcium hydroxide

$$\Lambda_c(Ca(OH)_2) = \frac{1000\,\mathcal{K}_{Ca(OH)_2}}{C}\ where\ C\ is\ solubility\ in\ moldm^{-3}$$

$$C = \frac{1000\,\mathcal{K}_{Ca(OH)_2}}{\Lambda_c(Ca(OH)_2)}$$

$$Ca(OH)_2(s) + aq \rightleftharpoons Ca^{2+}(aq) + 2\bar{O}H(aq)$$

$$[Ca(OH)_2] = C\ moldm^{-3}$$

$$Since\ mole\ ratio\ of Ca(OH)_2 : Ca^{2+} = 1:1$$

$$[Ca(OH)_2] = [Ca^{2+}] = C\ moldm^{-3}$$

$$Since\ mole\ ratio\ of Ca(OH)_2 : \bar{O}H = 1:2$$

$$[\bar{O}H] = 2[Ca(OH)_2] = 2C\ moldm^{-3}$$

$$K_{sp} = [Ca^{2+}][\bar{O}H]^2 = C \times (2C)^2$$

$$\boldsymbol{K_{sp} = 4C^3\ mol^3dm^{-9}}$$

This method can be used for any electrolyte whose solution cannot be titrated with any suitable reagent.

Experiment to determine solubility product of silver ethanedioate

(a) By titration

Excess solid silver ethanedioate is added to a given volume of distilled water in a container.

The mixture is shaken for some time and ***left to settle*** at ***given temperature*** to attain equilibrium.

The mixture is ***filtered*** to obtain a ***saturated solution of silver ethanedioate*** as filtrate.

A ***known volume of the filtrate is pipetted*** into a conical flask , **acidified** and **warmed**.

The **warm solution** is then ***titrated*** with a ***standard solution of potassium manganate(VII) solution***.

The molar concentration of the oxalate(ethanedioate) ions in the solution is calculated using the equation below.

$$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

Taking the ***molar concentration of ethanedioate ions as*** $\boldsymbol{x}$ ***moles per litre***.

$$Ag_2C_2O_4(s) + aq \rightleftharpoons 2Ag^+(aq) + C_2O_4^{2-}(aq)$$

$$[C_2O_4^{2-}] = x\,moldm^{-3}$$

$$Since\ mole\ ratio\ of\ C_2O_4^{2-} : Ag^+ = 1:2$$

$$[Ag^+] = 2[C_2O_4^{2-}] = 2x\,moldm^{-3}$$

$$K_{sp} = [Ag^+]^2[C_2O_4^{2-}] = (2x)^2 \times x$$

$$\boldsymbol{K_{sp} = 4x^3\,mol^3dm^{-9}}$$

This method can be used for any sparingly soluble metal oxalate (ethanedioate).No indicator is required because potassium permanganate acts as own indicator.

(b) Using conductivity measurements

Excess solid silver ethanedioate is added to a given volume of distilled water in a container.

The mixture is shaken for some time and ***left to settle*** at ***a given temperature*** to attain equilibrium.

The mixture is ***filtered*** to obtain ***a saturated solution of silver ethanedioate*** as filtrate.

The electrolytic conductivity of the saturated solution, $\mathcal{K}_{solution}(ohm^{-1}cm^{-1})$ is measured using a conductivity meter.

The electrolytic conductivity of water, $\mathcal{K}_{H_2O}(ohm^{-1}cm^{-1})$ at the same temperature is obtained from books

Also the molar conductivities at infinite dilution (Λ_O) of silver ions and ethanedioate ions are read from the tables.

Treatment of results

The electrolytic conductivity of silver ethanedioate is then obtained by;

$$\mathcal{K}_{Ag_2C_2O_4} = \mathcal{K}_{solution} - \mathcal{K}_{H_2O}$$

The molar conductivity of silver ethanedioate at infinite dilution is obtained by the equation;

$$\Lambda_O(Ag_2C_2O_4) = 2\Lambda_O(Ag^+) + \Lambda_O(C_2O_4^{2-})$$

$\Lambda_O(Ag_2C_2O_4) = \Lambda_c(Ag_2C_2O_4)$, where Λ_c is molar conductivity of silver ethanedioate

$$\Lambda_c(Ag_2C_2O_4) = \frac{1000\,\mathcal{K}_{Ag_2C_2O_4}}{C} \ where\ C\ is\ solubility\ in\ moldm^{-3}$$

$$Ag_2C_2O_4(s) + aq \rightleftharpoons 2Ag^+(aq) + C_2O_4^{2-}(aq)$$

$$[Ag_2C_2O_4] = C\ moldm^{-3}$$

$$Since\ mole\ ratio\ of\ Ag_2C_2O_4 : Ag^+ = 1:2$$

$$[Ag^+] = 2[Ag_2C_2O_4] = 2C\ moldm^{-3}$$

$$[C_2O_4^{2-}] = [Ag_2C_2O_4] = C\ moldm^{-3}$$

$$K_{sp} = [Ag^+]^2[C_2O_4^{2-}] = (2C)^2 \times C$$

$$\boldsymbol{K_{sp} = 4C^3\ mol^3dm^{-9}}$$

Experiment to determine solubility product of copper(II) iodate

(a) By titration

Excess solid copper(II) iodate is added to a given volume of distilled water in a container.

The mixture is shaken for some time and ***left to settle*** at ***given temperature*** to attain equilibrium.

The mixture is ***filtered*** to obtain a ***saturated solution of copper(II) iodate*** as filtrate.

A ***known volume of the filtrate is pipetted*** into a conical flask and **a known volume potassium iodide solution added** and **acidified with a known volume of sulphuric acid**.

The **resultant solution containing iodine** liberated is then ***titrated*** with a ***standard solution of sodium thiosulphate solution*** using ***starch indicator***.

$$IO_3^-(aq) + 6H^+(aq) + 5I^-(aq) \longrightarrow 3I_2(aq) + 3H_2O(l)$$

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

The molar concentration of the iodate(V) ions in the solution is calculated using the two equations above.

Taking the ***molar concentration of iodate(V) ions as $\boldsymbol{x\ moles\ per\ litre}$***.

$$Cu(IO_3)_2(s) + aq \rightleftharpoons Cu^{2+}(aq) + 2IO_3^-(aq)$$

$$[IO_3^-] = x\ moldm^{-3}$$

$$Since\ mole\ ratio\ of\ IO_3^- : Cu^{2+} = 2:1$$

$$[Cu^{2+}] = \frac{1}{2}[IO_3^-] = \frac{x}{2}\ moldm^{-3}$$

$$K_{sp} = [Cu^{2+}][IO_3^-]^2 = \frac{x}{2} \times (x)^2$$

$$\boldsymbol{K_{sp} = \frac{x^3}{2}\ mol^3dm^{-9}}$$

This method can be used for any sparingly soluble metal iodate.

(b) Using conductivity measurements

Excess solid copper(II) iodate is added to a given volume of distilled water in a container.

The mixture is shaken for some time and ***left to settle*** at ***a given temperature*** to attain equilibrium.

The mixture is ***filtered*** to obtain ***a saturated solution of copper(II) iodate*** as filtrate.

The electrolytic conductivity of the saturated solution, $\mathcal{K}_{solution}(ohm^{-1}cm^{-1})$ is measured using a conductivity meter.

The electrolytic conductivity of water, $\mathcal{K}_{H_2O}(ohm^{-1}cm^{-1})$ at the same temperature is obtained from books

Also the molar conductivities at infinite dilution (Λ_O) of copper(II) ions and iodate ions are read from the tables.

Treatment of results

The electrolytic conductivity of copper(II) iodate is then obtained by;

$$\mathcal{K}_{Cu(IO_3)_2} = \mathcal{K}_{solution} - \mathcal{K}_{H_2O}$$

The molar conductivity of copper(II) iodate at infinite dilution is obtained by the equation;

$$\Lambda_O(Cu(IO_3)_2) = 2\Lambda_O(Cu^{2+}) + \Lambda_O(IO_3^-)$$

$\Lambda_O(Cu(IO_3)_2) = \Lambda_c(Cu(IO_3)_2)$, where Λ_c is molar conductivity of copper(II) iodate

$$\Lambda_c(Cu(IO_3)_2) = \frac{1000\,\mathcal{K}_{Cu(IO_3)_2}}{C}\ where\ C\ is\ solubility\ in\ moldm^{-3}$$

$$Cu(IO_3)_2(s) + aq \rightleftharpoons Cu^{2+}(aq) + 2IO_3^-(aq)$$

$$[Cu(IO_3)_2] = C\ moldm^{-3}$$

$$Since\ mole\ ratio\ of\ Ca(IO_3)_2 : Ca^{2+} = 1:1$$

$$[Cu^{2+}] = [Cu(IO_3)_2] = C\ moldm^{-3}$$

$$Since\ mole\ ratio\ of\ Cu(IO_3)_2 : IO_3^- = 1:2$$

$$[IO_3^-] = 2[Cu(IO_3)_2] = 2C\ moldm^{-3}$$

$$K_{sp} = [Cu^{2+}][IO_3^-]^2 = C \times (2C)^2$$

$$\boldsymbol{K_{sp} = 4C^3\ mol^3dm^{-9}}$$

Factors affecting solubility of sparingly soluble electrolytes

(a) Common ion effect

Common ion effect is the <u>precipitation</u> of <u>a sparingly soluble electrolyte</u> from its <u>saturated solution</u> by addition of a <u>solution of a more soluble electrolyte</u> containing <u>one of the ions</u> of the sparingly soluble electrolyte.

When a solution contains a similar ion is added to a saturated solution of a sparingly soluble electrolyte, the ***solubility of the electrolyte decreases***.

Examples

1. **Silver chromate is sparingly in water. Explain what will happen to the solubility of silver chromate when each of the following is separately added.**
   - **(i) Silver nitrate**
   - **(ii) Potassium chromate**

$$Ag_2CrO_4(s) + aq \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$
$$AgNO_3(aq) \longrightarrow Ag^+(aq) + NO_3^-(aq)$$

(i) Addition of silver nitrate ***decreases the solubility of silver chromate*** because silver nitrate contains ***silver ions that are common*** to silver ions in silver chromate. The ***excess silver ions added combine with chromate ions*** in solution to ***precipitate silver chromate*** in order to restore the equilibrium, ***maintaining the value of the equilibrium constant***.

$$Ag_2CrO_4(s) + aq \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$
$$K_2CrO_4(aq) \longrightarrow K^+(aq) + CrO_4^{2-}(aq)$$

(ii) Addition of potassium chromate ***decreases the solubility of silver chromate*** because potassium chromate contains ***chromate ions that are common*** to chromate ions in silver chromate. The ***excess chromate ions added combine with silver ions*** in solution to ***precipitate silver chromate*** in order to restore the equilibrium, ***maintaining the value of the equilibrium constant***.

2. **Explain what would happen to the solubility of calcium phosphate in water when:**
   - **(i) Sodium phosphate is added**
   - **(ii) Calcium nitrate is added**

$$Ca_3(PO_4)_2(s) + aq \rightleftharpoons \boldsymbol{3Ca^{2+}(aq)} + 2PO_4^{3-}(aq)$$
$$Na_3PO_4(aq) \longrightarrow 3Na^+(aq) + \boldsymbol{PO_4^{3-}(aq)}$$

(i) Addition of sodium phosphate ***decreases the solubility of calcium phosphate*** because sodium phosphate contains ***phosphate ions that are common*** to phosphate ions in calcium phosphate. The ***excess phosphate ions added combine with calcium ions*** in solution to ***precipitate calcium phosphate*** in order to restore the equilibrium, ***maintaining the value of the equilibrium constant***.

$$Ca_3(PO_4)_2(s) + aq \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$
$$Ca(NO_3)_2(aq) \longrightarrow Ca^{2+}(aq) + 2NO_3^-(aq)$$

(ii) Addition of calcium nitrate ***decreases the solubility of calcium phosphate*** because calcium nitrate contains ***calcium ions that are common*** to calcium ions in calcium nitrate. The ***excess calcium ions added combine with phosphate ions*** in solution to ***precipitate calcium phosphate*** in order to restore the equilibrium, ***maintaining the value of the equilibrium constant***.

3. **State what happens to the solubility of lead(II) iodide in water when:**
    (i) **Potassium iodide is added-** ***solubility decreases***
    (ii) **Lead(II) nitrate is added-** ***solubility decreases***

The applications of common ion effect

(i) Purification of sodium chloride (common salt)

Sodium chloride commonly contains small quantities of calcium chloride and magnesium chloride that cause it to be deliquescent.

$$NaCl(s) \rightleftharpoons Na^{+}(aq) + Cl^{-}(aq)$$

The sodium chloride is purified by adding concentrated hydrochloric acid into its saturated solution which increases the concentration of chloride ions. The equilibrium is displaced to the left, decreasing the degree of dissociation of sodium chloride, hence precipitating sodium chloride since the solution is already saturated by the sodium chloride.

(ii) Salting out soap

During saponification, hot concentrated sodium chloride is added to the mixture to precipitate soap.

Soap is a sodium salt of a long chain carboxylic acid. In a saturated solution of soap exists the equilibrium;

$$RCOONa(aq) \rightleftharpoons RCOO^{-}(aq) + Na^{+}(aq)\ ; R\ is\ a\ long\ alkyl\ group\ chain$$

Adding concentrated sodium chloride to a saturated soap solution increases the concentration of sodium ions. The excess sodium ions react with the carboxylate ions hence precipitating soap.

(a) Complex ion formation

When to a saturated solution of a sparingly soluble electrolyte is added a solution of a soluble salt that forms a complex with the electrolyte, ***its solubility increases***.

Examples

1. **Silver carbonate is sparingly soluble in water. Explain what happens to the solubility of silver carbonate if ammonia solution is added to its saturated solution**.

$$Ag_2CO_3(s) + aq \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$$

Addition of ammonia solution ***increases the solubility of silver carbonate*** because ***ammonia solution reacts with silver ions*** to form a soluble ***complex of diammine silver(I) ion.***

$$Ag^+(aq) + 2NH_3(aq) \longrightarrow Ag(NH_3)_2^+(aq)$$

This ***lowers the concentration of silver ions*** and ***more silver carbonate dissolves***, to restore the equilibrium, ***maintaining the value of the equilibrium constant***.

Note: Ammonia solution has the same effect on the solubility of sparingly soluble copper(I) chloride.

2. **Copper(II) iodate is more soluble in ammonia solution than in water.**

$$Cu(IO_3)_2(s) + aq \rightleftharpoons Cu^{2+}(aq) + 2IO_3^-(aq)$$

Addition of ammonia solution ***increases the solubility of copper(II) iodate*** because ***ammonia solution reacts with copper(II) ions*** to form a soluble ***complex of tetraammine copper(II) ion.***

$$Cu^{2+}(aq) + 4NH_3(aq) \longrightarrow Cu(NH_3)_4^+(aq)$$

This ***lowers the concentration of copper(II) ions*** and ***more copper(II) iodate dissolves***, to restore the equilibrium, ***maintaining the value of the equilibrium constant***.

3. **The solubility of lead(II) chloride in cold water decreases on addition of dilute hydrochloric acid but increases on addition concentrated hydrochloric acid**.

Lead(II) chloride is sparingly soluble in cold water.

$$PbCl_2(s) + aq \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

Addition of dilute hydrochloric acid to a solution of lead(II) chloride ***decreases its solubility*** because dilute hydrochloric acid contains ***chloride ions that are common*** to chloride ions in lead(II) chloride. The ***excess chloride ions added combine with chloride ions*** in solution to ***precipitate lead(II) chloride*** in order to restore the equilibrium, ***maintaining the value of the equilibrium constant***.

Addition of concentrated hydrochloric acid ***increases the solubility of lead(II) chloride*** because ***the chloride ions present in high concentration react with lead(II) chloride*** to form a soluble ***complex of tetrachloroplumbate(II) ion.***

$$PbCl_2(s) + 2Cl^-(aq) \longrightarrow PbCl_4^{2-}(aq)$$

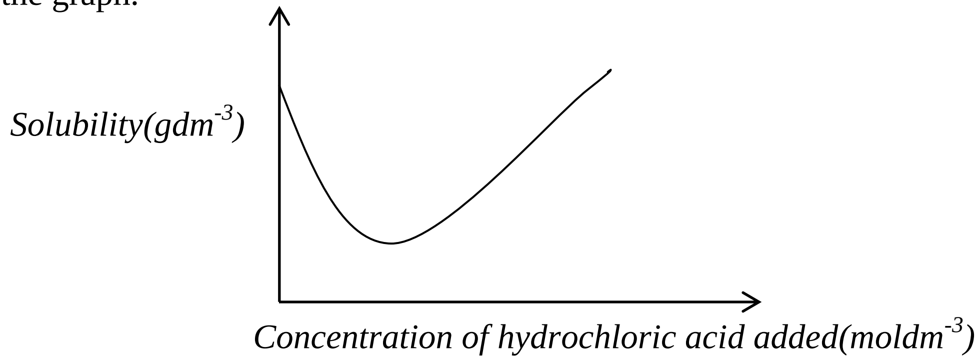
Questions

1. Silver ions , iron(III) ions and calcium ions form complexes with sodium thiosulphate solution, potassium hexacyanoferrate(II) solution and triphosphate ions respectively.

State what will happen to the solubility of:

   (i) Silver chloride if sodium thiosulphate solution is added
   (ii) Iron(III) hydroxide if potassium hexacyanoferrate(II) solution is added
   (iii) Calcium sulphate if sodium triphosphate is added

2. Both aluminium hydroxide and zinc hydroxide are do not easily dissolve in water but their solubility increases on addition of sodium hydroxide solution.
3. When hydrochloric acid is added to lead(II) nitrate solution drop wise until in excess, at varying concentrations of the acid, the curve below is obtained. Explain the shape of the graph.



(c) Addition of a soluble compound containing no similar ion as those of the sparingly soluble electrolyte

When a soluble compound with no common ions to a saturated solution of a sparingly soluble electrolyte is added, the ***solubility of the electrolyte increases***

Example

Explain why calcium ethanedioate is less soluble in calcium nitrate but more soluble in dilute hydrochloric acid

Calcium oxalate is sparingly soluble in water

$$CaC_2O_4(s) + aq \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$
$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

Addition of calcium nitrate ***decreases the solubility of calcium oxalate*** because calcium nitrate contains ***calcium ions that are common*** to calcium ions in calcium oxalate. The ***excess calcium ions added combine with oxalate ions*** in solution to ***precipitate calcium oxalate*** in order to restore the equilibrium, ***maintaining the value of the equilibrium constant***.

In the presence of dilute hydrochloric acid, the ***hydrogen ions react with oxalate ions*** to ***form oxalic acid***.

$$2H^+(aq) + C_2O_4^{2-}(aq) \longrightarrow H_2C_2O_4(aq)$$

This ***reduces the concentration of oxalate ions*** in solution hence ***more calcium oxalate dissolves*** to restore the equilibrium, ***maintaining the value of the equilibrium constant***.

The relationship between ionic product, solubility product (K_{sp}) and precipitation

For any sparingly soluble electrolyte, A_xB_y.

$$\boldsymbol{K_{sp} = [A^{y+}]^x[B^{x-}]^y}$$

$$\boldsymbol{Ionic\ product = [A^{y+}]^x[B^{x-}]^y}$$

Both the solubility product have the same expressions but the difference is that ionic product is applicable to all types of solutions at any concentration and keeps increasing with the increase in the concentration of ions

On the other hand, solubility product is applicable to only saturated solutions and is constant at a constant temperature for a given electrolyte.

- ***When the ionic product is less than the solubility product, more of the sparingly soluble salt dissolves since the solution is unsaturated***
- ***When the ionic product is equal the solubility product, no more of the sparingly soluble salt dissolves since the solution is saturated***
- ***When the ionic product exceeds the solubility product, precipitation of a sparingly soluble electrolyte occurs***.

In general:

$\boldsymbol{For\ K_{sp} > [A^{y+}]^x[B^{x-}]^y}$	Solution is not saturated, more electrolyte can dissolve
$\boldsymbol{For\ K_{sp} = [A^{y+}]^x[B^{x-}]^y}$	Solution is saturated, cannot dissolve any more electrolyte can dissolve
$\boldsymbol{For\ K_{sp} < [A^{y+}]^x[B^{x-}]^y}$	Precipitation occurs

Examples

1. **When ammonia solution is added to magnesium chloride solution, a white precipitate insoluble in excess is formed but when the same solution is added to calcium chloride solution, there is no observable change.**

Magnesium ions react with hydroxide ions *to form* ***insoluble magnesium hydroxide****. Magnesium hydroxide is basic hence cannot react with excess sodium hydroxide*

$$Mg^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Mg(OH)_2(s)$$

Ammonia is a ***weak base*** *which partially ionises to form few hydroxyl ions*

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$$

*The **concentration of the hydroxyl ions formed from the weak ammonia base is low** for the **ionic product of calcium hydroxide to exceed its solubility product**. Therefore, **no precipitation occurs**.*

2. **When ammonia solution is added to a solution of magnesium sulphate, a white precipitate is formed. However, when ammonia solution is added in presence of ammonium chloride solution, no precipitate is formed. Explain**

Ammonia is a ***weak base*** that partially ionises in water to form ***ammonium ions and hydroxyl ions***.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$$

*The **concentration of the hydroxyl ions formed from the ammonia solution is enough to react with magnesium ions** for the **ionic product of magnesium hydroxide to exceed its solubility product**. Therefore, **magnesium hydroxide is precipitated**.*

$$Mg^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Mg(OH)_2(s)$$

Ammonium chloride is a ***strong electrolyte*** that completely ionises to form ammonium ions.

$$NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

The ***ammonium ions from the salt suppress the ionisation of ammonia solution*** due to ***common ion effect***. This ***reduces the concentration of hydroxide ions*** in solution hence the ***ionic product of magnesium hydroxide does not exceed its solubility product***.

3. **When hydrogen sulphide gas is bubbled through a solution of manganese(II) nitrate, no observation occurs in the presence of dilute hydrochloric acid but in presence of ammonia solution, a pink precipitate is formed. Explain**.

$$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$$

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

Hydrogen sulphide is a ***weak electrolyte*** that partially ionises in solution to form sulphide ions and hydrogen ions.

In the presence of dilute hydrochloric acid which is a ***strong electrolyte***, the ***hydrogen ions from the completely ionised acid suppress the ionisation of hydrogen sulphide due to common ion effect***. This ***reduces the concentration of sulphide ions*** in solution hence the ***ionic product of manganese(II) sulphide does not exceed its solubility product***. ***No precipitation occurs***.

In the presence of ammonia solution which is a ***weak base***, the ***hydroxide ions from ammonia acid react with the hydrogen ions from hydrogen sulphide to form water***.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$$

$$\bar{O}H(aq) + H^+(aq) \longrightarrow H_2O(l)$$

This ***reduces the concentration of hydrogen ions in solution*** hence ***more hydrogen sulphide ionises***, forming ***a concentration of sulphide ions high enough*** for the ***ionic***

product of manganese(II) sulphide to exceed its solubility product. The ***insoluble manganese(II) sulphide*** is formed hence ***precipitation then occurs***.

$$Mn^{2+}(aq) + S^{2-}(aq) \longrightarrow MnS(s)$$

Application of solubility product, K_{sp}

- ***Salting out soap***
- ***Purification of common salt***
- ***precipitation of hydroxides***
- ***Precipitation of sulphides***
- ***Precipitation of chlorides***

Questions

Explain the following observations:

(a) Calcium phosphate is sparingly soluble in water but soluble in dilute hydrochloric acid.

(b) Zinc sulphide is more soluble in dilute hydrochloric acid than in water.

(c) Barium chromate is more soluble in dilute nitric acid than in water

(d) A concentrated solution of calcium chloride forms a white precipitate with sodium hydroxide solution but no observable change with ammonia solution.

(e) When hydrogen sulphide gas is bubbled through a solution containing lead(II) nitrate and zinc nitrate, only lead(II) sulphide is precipitated.

(f) The solubility of silver(I) ethanedioate in pure water decreases on addition of silver nitrate solution.

(g) When ammonia solution is added to a solution of manganese(II) sulphate, a dirty white precipitate is formed. However when it is added to the same solution in presence of ammonium chloride solution, no precipitate is formed.

Calculations involving solubility and solubility products

Examples

1. The solubility of calcium phosphate is 0.0011g per 100g of water at 25℃. Calculate the solubility product of calcium phosphate at 25℃.

$$Ca_3(PO_4)_2(s) + aq \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$
$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$
$$Volume\ of\ H_2O = \frac{mass}{density} = \frac{100g}{1.0gcm^{-3}} = 100cm^3$$
$$100cm^3\ contain\ 0.0011g\ of\ Ca_3(PO_4)_2$$
$$1000cm^3\ contain\ \left(\frac{0.0011 \times 1000}{100}\right) g\ of\ Ca_3(PO_4)_2$$
$$= 0.011g\ of\ Ca_3(PO_4)_2$$
$$Molar\ mass\ of\ Ca_3(PO_4)_2 = (3 \times 40) + (2 \times 31) + (4 \times 2 \times 16) = 310g$$
$$Moles\ of Ca_3(PO_4)_2\ in\ 1000cm^3 = \frac{0.011}{310} = 3.548 \times 10^{-5}\ moles$$
$$[Ca_3(PO_4)_2] = 3.548 \times 10^{-5}M$$

$Since\ mole\ ratio\ of\ Ca_3(PO_4)_2 : Ca^{2+} = 1:3$ Then:

$$\boldsymbol{[Ca^{2+}] = 3[Ca_3(PO_4)_2] = (3 \times 3.548 \times 10^{-5}) = 1.06 \times 10^{-4}M}$$

$Since\ mole\ ratio\ of\ Ca_3(PO_4)_2 : PO_4^{3-} = 1:2$. Then:

$$\boldsymbol{[PO_4^{3-}] = 2[Ca_3(PO_4)_2] = (2 \times 3.548 \times 10^{-5}) = 7.096 \times 10^{-5}M}$$
$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$
$$= (1.06 \times 10^{-4})^3 \times (7.096 \times 10^{-5})^2 \quad (moldm^{-3})^5$$
$$\boldsymbol{K_{sp} = 5.997 \times 10^{-21}\ mol^5dm^{-15}}$$

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2. (a) The solubility product, K_{sp}, of zinc hydroxide is $4.5 \times 10^{-17} mol^3dm^{-9}$ at 25°C. Write an expression for solubility product of zinc hydroxide.

(b) Determine the concentration in moles per litre of zinc ions and hydroxide ions in a saturated solution of zinc hydroxide at 25°C

(c) State how solubility of zinc hydroxide would change if its saturated solution is treated separately with:

(i) aqueous zinc sulphate

(ii) ammonia solution

(d) Briefly explain your answer in (c).

(a) $K_{sp} = [Zn^{2+}][\bar{O}H]^2$

(b) $Let\ the\ solubility\ of Zn(OH)_2\ in\ water = p\ moldm^{-3}$

$$[Zn(OH)_2] = p\ moldm^{-3}$$

$Since\ mole\ ratio\ of\ Zn(OH)_2 : Zn^{2+} = 1:1$

$Then: [Zn^{2+}] = p\ moldm^{-3}$

$Since\ mole\ ratio\ of\ Zn^{2+} : \bar{O}H = 1:2$. Then:

$$[\bar{O}H] = 2[Zn^{2+}] = 2p\ moldm^{-3}$$
$$K_{sp} = [Zn^{2+}][\bar{O}H]^2$$
$$K_{sp} = p \times (2p)^2$$
$$4.5 \times 10^{-17} = 4p^3$$
$$p^3 = \frac{4.5 \times 10^{-17}}{4} = 1.125 \times 10^{-17}$$
$$p = \sqrt[3]{1.125 \times 10^{-17}}$$
$$p = 2.24 \times 10^{-6}$$

$Solubility\ of Zn(OH)_2\ in\ water\ is\ 2.24 \times 10^{-6}\ moldm^{-3}$

$$\boldsymbol{[Zn^{2+}] = 2.24 \times 10^{-6}\ moldm^{-3}}$$

$$\boldsymbol{[\bar{O}H] = 2[Zn^{2+}] = 2 \times 2.24 \times 10^{-6} = 4.48 \times 10^{-6} moldm^{-3}}$$

(c) ***(i) Solubility would decrease.***

(ii) Solubility would increase.

(d) Addition of zinc sulphate solution ***decreases the solubility of zinc hydroxide*** because zinc sulphate contains ***zinc ions that are common*** to zinc ions in zinc hydroxide. The ***excess zinc ions added combine with hydroxide ions*** in solution to ***precipitate zinc hydroxide*** in order to restore the equilibrium, ***maintaining the value of the equilibrium constant***.

Addition of ammonia solution ***increases the solubility of zinc hydroxide*** because ***ammonia solution reacts with zinc ions*** to form a soluble ***complex of tetrammine zinc(II) ions.***

$$Zn^{2+}(aq) + 4NH_3(aq) \longrightarrow Zn(NH_3)_4^{2+}(aq)$$

This ***lowers the concentration of zinc ions*** and ***more zinc hydroxide dissolves***, to restore the equilibrium, ***maintaining the value of the equilibrium constant***.

3. (a) Magnesium hydroxide is sparingly soluble in water.

Write:

- **(i) the equation for the solubility of magnesium hydroxide in water**
- **(ii) the expression for the solubility product, K_{sp} of magnesium hydroxide**

(b) If the solubility product of magnesium hydroxide at 18℃ is $4.2 \times 10^{-12}\ mol^3dm^{-9}$. Calculate the solubility in moles per litre at 18℃ of magnesium hydroxide in:

- **(i) water**
- **(ii) a 0.01M sodium hydroxide**

(c) Comment on your answers in (b) above

(a) (i) $Mg(OH)_2(s) + aq \rightleftharpoons Mg^{2+}(aq) + 2\bar{O}H(aq)$

(ii) $K_{sp} = [Mg^{2+}][\bar{O}H]^2$

(b) (i)

$Let\ the\ solubility\ of Mg(OH)_2\ in\ water = x\ moldm^{-3}$

$[Mg(OH)_2] = x\ moldm^{-3}$

$Since\ mole\ ratio\ of\ Mg(OH)_2 : Mg^{2+} = 1:1$

$Then: [Mg^{2+}] = x\ moldm^{-3}$

$Since\ mole\ ratio\ of\ Mg^{2+} : \bar{O}H = 1:2$. Then:

$[\bar{O}H] = 2[Mg^{2+}] = 2x\ moldm^{-3}$

$K_{sp} = [Mg^{2+}][\bar{O}H]^2$

$K_{sp} = x \times (2x)^2$

$4.2 \times 10^{-12} = 4x^3$

$$x^3 = \frac{4.2 \times 10^{-12}}{4} = 1.05 \times 10^{-12}$$

$x = \sqrt[3]{1.05 \times 10^{-12}}$

$x = 1.02 \times 10^{-4}$

$\boldsymbol{Solubility\ of Mg(OH)_2\ in\ water\ is\ 1.02 \times 10^{-4}\ moldm^{-3}}$

(ii) $Let\ the\ solubility\ of Mg(OH)_2\ in$ $0.01M\ NaOH = y\ moldm^{-3}$

$$\begin{array}{ccc} NaOH(aq) & \longrightarrow & Na^+(aq) + \boldsymbol{\bar{O}H(aq)} \\ \boldsymbol{0.01M} & & \boldsymbol{0.01M} \quad \boldsymbol{0.01M} \end{array}$$

$$\begin{array}{ccc} Mg(OH)_2(s) + aq & \rightleftharpoons & Mg^{2+}(aq) + \boldsymbol{2\bar{O}H(aq)} \\ \boldsymbol{y} & & \boldsymbol{y} \quad \boldsymbol{2y} \end{array}$$

$[Mg^{2+}] = y\ moldm^{-3}$

$[\bar{O}H] = (2y + 0.01)\ moldm^{-3}$

$\boldsymbol{But\ y\ is\ very\ small\ such\ that}$

$\boldsymbol{(2y + 0.01) \approx 0.01}$

$[\bar{O}H] \approx 0.01\ moldm^{-3}$

$K_{sp} = [Mg^{2+}][\bar{O}H]^2 = y \times (0.01)^2$

$y \times (0.01)^2 = 4.2 \times 10^{-12}$

$$y = \frac{4.2 \times 10^{-12}}{(0.01)^2} = 4.2 \times 10^{-8}$$

$\boldsymbol{Therefore\ solubility\ of Mg(OH)_2\ in\ 0.01M\ NaOH\ is\ 4.2 \times 10^{-8}\ moldm^{-3}}$

(c) ***Magnesium hydroxide is more soluble in water than sodium hydroxide. The decrease in its solubility in sodium hydroxide is due to common ion effect.***

4. The solubility of lead(II) sulphate in water is $0.035\ gdm^{-3}$ at 17℃. Calculate the solubility of lead(II) sulphate in 0.02M lead(II) nitrate solution at the same temperature in grams per litre.

$$PbSO_4(s) + aq \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$$

$$K_{sp} = [Pb^{2+}][SO_4^{2-}]$$

$$Molar\ mass\ of\ PbSO_4 = 207 + 32 + 64$$
$$= 303\ g$$

$$Moles\ of PbSO_4\ in\ 1\ litre = \frac{0.035}{303}$$
$$= 1.16 \times 10^{-4}\ moles$$
$$[PbSO_4] = 1.16 \times 10^{-4}M$$

$Since\ mole\ ratio\ of\ PbSO_4: Pb^{2+}SO_4^{2-} = 1:1:1$

Then: $[\boldsymbol{Pb^{2+}}] = \mathbf{1.16 \times 10^{-4}M}$

Also: $[\boldsymbol{SO_4^{2-}}] = \mathbf{1.16 \times 10^{-4}M}$

$$K_{sp} = [Pb^{2+}][SO_4^{2-}]$$
$$= (1.16 \times 10^{-4})^2$$
$$\boldsymbol{K_{sp} = 1.33 \times 10^{-8}\,mol^2dm^{-6}}$$

$Let\ the\ solubility\ of PbSO_4\ in$
$0.01M\ Pb(NO_3)_2 = x\ moldm^{-3}$

$$\begin{array}{lll} Pb(NO_3)_2(aq) \longrightarrow & Pb^{2+}(aq) + & 2NO_3^-(aq) \\ \mathbf{0.02M} & \mathbf{0.02M} & \mathbf{0.04M} \end{array}$$

$$\begin{array}{lll} PbSO_4(s) + aq \rightleftharpoons & Pb^{2+}(aq) + & SO_4^{2-}(aq) \\ \boldsymbol{x} & \boldsymbol{x} & \boldsymbol{x} \end{array}$$

$$[Pb^{2+}] = (0.02 + x)\ \ moldm^{-3}$$

But x is very small such that
$$(\mathbf{0.02} + \boldsymbol{x}) \approx \mathbf{0.02}$$
$$[Pb^{2+}] \approx 0.02\,moldm^{-3}$$
$$[SO_4^{2-}] = x\,moldm^{-3}$$
$$K_{sp} = [Pb^{2+}][SO_4^{2-}] = 0.02 \times x$$
$$0.02x = 1.33 \times 10^{-8}$$
$$x = \frac{1.33 \times 10^{-8}}{0.02} = 6.65 \times 10^{-7}\ moldm^{-3}$$

$\boldsymbol{Solubility\ of PbSO_4\ in\ 0.02M}$
$\boldsymbol{Pb(NO_3)_2\ in\ g\ per\ litre}$
$$= (303 \times 6.65 \times 10^{-7})$$
$$= \mathbf{2.01 \times 10^{-4}}\boldsymbol{gdm^{-3}}$$

5. (a) Write:

- **(i) equation for the solubility of silver chromate in water.**
- **(ii) expression for solubility product, K_{sp}, of silver chromate.**

(b) The solubility of silver chromate at 25℃ is $3.207 \times 10^{-2}gl^{-1}$.Calculate the solubility product of silver chromate at 25℃.

(c) A solution containing silver ions was separately added to a solution containing $5.0 \times 10^{-3}M$ chromate ions and $5.0 \times 10^{-3}M$ chloride ions. State which of the salts silver chloride or silver chromate would precipitate first. Give a reason for your answer. ($\boldsymbol{K_{sp}\ for\ AgCl\ =\ 1.96 \times 10^{-10}\ mol^2dm^{-6}}$)

(a) (i) $$Ag_2CrO_4(s) + aq \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$

(ii) $$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

(b) $Molar\ mass\ of\ Ag_2CrO_4$
$= (2 \times 108) + 52 + (4 \times 16) = 332\ g$

Then: $[\boldsymbol{Ag^+}] = (\mathbf{2 \times 9.66 \times 10^{-5}})$
$= \mathbf{1.93 \times 10^{-4}M}$

$Moles\ of\ Ag_2CrO_4\ in\ 1\ litre = \frac{3.207 \times 10^{-2}}{332}$ $= 9.66 \times 10^{-5}\ moles$ $[Ag_2CrO_4] = 9.66 \times 10^{-5}M$ $Since\ mole\ ratio\ of\ Ag_2CrO_4 : Ag^{+} = 1:2$	$Since\ mole\ ratio\ of\ Ag_2CrO_4 : CrO_4^{2-} = 1:1$. Then: $\mathbf{\left[CrO_4^{2-}\right] = 9.66 \times 10^{-5}M}$ $K_{sp} = [Ag^{+}]^2[CrO_4^{2-}]$ $= (1.93 \times 10^{-4})^2 \times 9.66 \times 10^{-5}$ $\mathbf{K_{sp} = 3.60 \times 10^{-12}\ mol^3dm^{-9}}$
(c) $K_{sp} = [Ag^{+}]^2[CrO_4^{2-}]$ $3.60 \times 10^{-12} = [Ag^{+}]^2 \times 5.0 \times 10^{-3}$ $[Ag^{+}] = \sqrt{\frac{3.60 \times 10^{-12}}{5.0 \times 10^{-3}}}$ $\mathbf{[Ag^{+}] = 2.68 \times 10^{-5}M}$	$For\ AgCl, K_{sp} = [Ag^{+}][Cl^{-}]$ $1.96 \times 10^{-10} = [Ag^{+}] \times 5.0 \times 10^{-3}$ $[Ag^{+}] = \frac{1.96 \times 10^{-10}}{5.0 \times 10^{-3}}$ $\mathbf{[Ag^{+}] = 3.92 \times 10^{-8}M}$ ***Silver chloride would precipitate first because it requires a lower concentration of silver ions to be formed.***

6. Calcium hydroxide is sparingly soluble in water.

(a) Write the expression for the solubility product of calcium hydroxide

(b) If the solubility of calcium hydroxide in water at 20℃ is $2.8gl^{-1}$.Calculate the molar concentration of:

(i) calcium ions

(ii) hydroxide ions

(c) (i) Calculate the solubility product of calcium hydroxide at 20℃ and give its units. ($H = 1, O = 16, Ca = 40$)

(ii) Calculate the volume of 0.5M potassium iodate that must be added to 1 litre of a saturated solution of calcium hydroxide above to precipitate calcium iodate at the same temperature.

($K_{sp}\ of\ Calcium\ iodate\ is\ 6.47 \times 10^{-6}mol^3dm^{-9}$)

(a) $K_{sp} = [Ca^{2+}][\bar{O}H]^2$

(b) (i)

$$Molar\ mass\ of\ Ca(OH)_2 = 40 + 32 + 2 = 74g$$

$$Moles\ of Ca(OH)_2\ in\ 1000cm^3 = \frac{2.8}{74} = 0.0378$$

$$[Ca(OH)_2] = 0.0378M$$

$$Ca(OH)_2(s) + aq \rightleftharpoons Ca^{2+}(aq) + 2\bar{O}H(aq)$$

$Since\ mole\ ratio\ of\ Ca(OH)_2 : Ca^{2+} = 1:1$ Then:

$$\mathbf{[Ca^{2+}] = 0.0378M}$$

(ii) $Since\ mole\ ratio\ of\ Ca^{2+} : \bar{O}H = 1:2$. Then:

$$[\bar{O}H] = 2[Ca^{2+}] = 2 \times 0.0378$$

$$\mathbf{[\bar{O}H] = 0.0756M}$$

(c) (i)

$$K_{sp} = [Ca^{2+}][\bar{O}H]^2$$

$$= 0.0378 \times (0.0756)^2$$

$$= \mathbf{2.16 \times 10^{-4}mol^3dm^{-9}}$$

(ii) $$Ca(IO_3)_2(s) + aq \rightleftharpoons Ca^{2+}(aq) + 2IO_3^-(aq)$$

$$K_{sp} = [Ca^{2+}][IO_3^-]^2$$

$$6.47 \times 10^{-6} = 0.0378 \times [IO_3^-]^2$$

$$[IO_3^-]^2 = \frac{6.47 \times 10^{-6}}{0.0378}$$

$$[IO_3^-] = \sqrt{\frac{6.47 \times 10^{-6}}{0.0378}} = 1.31 \times 10^{-2} M$$

$$From\ KIO_3(aq) \longrightarrow K^+(aq) + IO_3^-(aq)$$

$Since\ mole\ ratio\ of\ KIO_3 : IO_3^- = 1:1$. Then:

$$[IO_3^-] = [KIO_3] = 0.5M$$

$$0.5\ moles\ of\ IO_3^-\ are\ contained\ in\ 1000cm^3$$

$$1.31 \times 10^{-2}\ moles\ are\ contained\ in\ \left(\frac{1.31 \times 10^{-2} \times 1000}{0.5}\right) cm^3$$

$$= \mathbf{26.2\ cm^3}$$

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7. (a) The solubility product of silver chromate at 25℃ is $1.3 \times 10^{-12} mol^3 dm^{-9}$. When a saturated solution of silver chromate was shaken with an aqueous solution of silver nitrate, the solubility of silver chromate reduced by 94.5% of the solubility in pure water. Calculate the concentration of silver nitrate solution in grams per litre.

(b) When silver nitrate is titrated with a solution containing both potassium chromate and potassium chloride, a white precipitate is formed rather than a red precipitate.

(a) $Ag_2CrO_4(s) + aq \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$

$Let\ the\ solubility\ of\ Ag_2CrO_4\ in\ water$
$= y\ moldm^{-3}$

$$[Ag_2CrO_4] = y\ moldm^{-3}$$

$Since\ mole\ ratio\ of\ Ag_2CrO_4 : Ag^+ = 1:2$

$Then: [Ag^+] = 2y\ moldm^{-3}$

$Since\ mole\ ratio\ of\ Ag_2CrO_4 : CrO_4^{2-} = 1:1$.

Then: $[CrO_4^{2-}] = [Ag_2CrO_4] = y\ moldm^{-3}$

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

$$K_{sp} = (2y)^2 \times y$$

$$1.3 \times 10^{-12} = 4y^3$$

$$y^3 = \frac{1.3 \times 10^{-12}}{4} = 3.25 \times 10^{-13}$$

$$y = \sqrt[3]{3.25 \times 10^{-13}}$$

$$y = 6.875 \times 10^{-5}$$

$\boldsymbol{Solubility\ of Ag_2CrO_4\ in\ water\ is}$
$\boldsymbol{6.875 \times 10^{-5}\ moldm^{-3}}$

$Let\ the\ concentration\ of\ AgNO_3\ used\ be\ x\ M$

$$AgNO_3(aq) \longrightarrow Ag^+(aq) + NO_3^-(aq)$$

$\boldsymbol{x\ M} \qquad \boldsymbol{x\ M} \qquad \boldsymbol{x\ M}$

$$Ag_2CrO_4(s) + aq \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$

$$[Ag^+] = (\mathbf{2 \times 3.78 \times 10^{-6}} + \boldsymbol{x})\ moldm^{-3}$$

$\boldsymbol{But\ 2.08 \times 10^{-9}\ is\ very\ small\ such\ that}$

$$(\mathbf{7.56 \times 10^{-6}} + \boldsymbol{x}) \approx \boldsymbol{x}$$

$$[Ag^+] \approx \boldsymbol{x}\ moldm^{-3}$$

$$[CrO_4^{2-}] = \mathbf{3.78 \times 10^{-6}}\boldsymbol{M}$$

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = x^2 \times 3.78 \times 10^{-6}$$

$$3.78 \times 10^{-6} x^2 = 1.3 \times 10^{-12}$$

$$x = \sqrt{\frac{1.3 \times 10^{-12}}{3.78 \times 10^{-6}}} = 5.86 \times 10^{-4}\ moldm^{-3}$$

$Concentration\ of\ AgNO_3\ used\ is$
$5.86 \times 10^{-4}\ M$

$Molar\ mass\ of AgNO_3 = 108 + 14 + 48$
$= 170g$

The new solubility of Ag_2CrO_4 *in* $x\ M\ AgNO_3$

$= \left(\frac{100-94.5}{100}\right) \times 6.875 \times 10^{-5}$

$= \mathbf{3.78 \times 10^{-6}\ M}$

Concentration of $\mathbf{AgNO_3}$ **in g per litre**

$= (170 \times 5.86 \times 10^{-4})$

$= \mathbf{0.099 gdm^{-3}}$

(b) *Silver chloride has* ***a lower solubility than that of silver chromate****. In the solution,* ***the ionic product of silver chloride exceeds its solubility product before the ionic product of silver chromate exceeds the solubility product of silver chromate****. Therefore silver chromate can only be precipitated when* ***sufficient silver nitrate has been added to the solution to precipitate all the silver chloride.***

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$
$$2Ag^+(aq) + CrO_4^{2-}(aq) \longrightarrow Ag_2CrO_4(s)$$

8. Mercury(I) iodide was dissolved in 0.3M sodium iodide solution. Calculate the concentration of the mercury(I) iodide in the solution in $\mathbf{gdm^{-3}}$**. The solubility of mercury(I) iodide in water is** $\mathbf{3.0 \times 10^{-7} gdm^{-3}}$ **at** $\mathbf{25}$**℃ and mercury(I) iodide dissolves in water according to the following equation:**

$$\mathbf{Hg_2I_2(s) + (aq) \rightleftharpoons Hg_2^{2+}(aq) + 2I^-(aq)}$$
$$\mathbf{(Hg = 201, I = 127)}$$

$$Hg_2I_2(s) + aq \rightleftharpoons Hg_2^{2+}(aq) + 2I^-(aq)$$

Molar mass of Hg_2I_2

$= (2 \times 201) + 127 = 529g$

Moles of Hg_2I_2 *in* 1 *litre* $= \frac{3.0 \times 10^{-7}}{529}$

$= 5.67 \times 10^{-10}$ *moles*

$[Hg_2I_2] = 5.67 \times 10^{-10}M$

Since mole ratio of $Hg_2I_2 : Hg_2^{2+} = 1:1$

Then: $\mathbf{[Hg_2^{2+}] = 5.67 \times 10^{-10}M}$

Since mole ratio of $Hg_2I_2 : I^- = 1:2$. Then:

$\mathbf{[I^-] = 2[Hg_2I_2] = (2 \times 5.67 \times 10^{-10})}$

$\mathbf{= 1.134 \times 10^{-9}M}$

$K_{sp} = [Hg_2^{2+}][I^-]^2$

$= 5.67 \times 10^{-10} \times (1.134 \times 10^{-9})^2$

$\mathbf{K_{sp} = 7.29 \times 10^{-28}\ mol^3dm^{-9}}$

Let the solubility of Hg_2I_2 *in* $0.3M\ KI =\ x\ moldm^{-3}$

$$KI(aq) \longrightarrow K^+(aq) + \mathbf{I^-(aq)}$$
$$\mathbf{0.3M} \qquad \mathbf{0.3M} \qquad \mathbf{0.3M}$$

$$Hg_2I_2(s) + aq \rightleftharpoons Hg_2^{2+}(aq) + \mathbf{2I^-(aq)}$$
$$\mathbf{x} \qquad \mathbf{x} \qquad \mathbf{2x}$$

$[I^-] = (0.3 + x)\ moldm^{-3}$

But x is very small such that

$\mathbf{(0.3 + x) \approx 0.3}$

$[I^-] \approx 0.3\ moldm^{-3}$

$[Hg_2^{2+}] = x$

$K_{sp} = [Hg_2^{2+}][I^-]^2 = x \times (0.3)^2$

$x \times (0.3)^2 = 7.29 \times 10^{-28}$

$x = \frac{7.29 \times 10^{-28}}{(0.3)^2} = 8.1 \times 10^{-27}$

Solubility of Hg_2I_2 *in* $0.3M$ *KI is* $8.1 \times 10^{-27}\ moldm^{-3}$

Concentration of $\mathbf{Hg_2I_2}$ **in g per litre**

$= (529 \times 8.1 \times 10^{-27})$

$\mathbf{= 4.285 \times 10^{-24} gdm^{-3}}$

9. (a) The solubility of lead(II) iodide in 0.2M potassium iodide at 25℃ is $\mathbf{8.544 \times 10^{-4} gdm^{-3}}$.Write an equation for the solubility equilibrium reaction of lead(II) iodide.

(b) Calculate the:

(i) solubility product, K_{sp} of lead(II) iodide

(ii) solubility of lead(II) iodide in water

(c) Explain the difference between your answer in b(ii) above and the solubility of lead(II) iodide in 0.2M potassium iodide.

(a) $PbI_2(s) + aq \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$

(b) (i) $The\ solubility\ of PbI_2\ in\ 0.2M\ KI$

$$= 8.544 \times 10^{-4} gdm^{-3}$$

$$Molar\ mass\ of\ PbI_2 = 207 + (2 \times 127)$$

$$= 461\ g$$

$Moles\ of PbI_2\ in\ 1\ litre\ of\ 0.2M\ KI$

$$= \frac{8.544 \times 10^{-4}}{461} = 1.85 \times 10^{-6}$$

$$[PbI_2]\ in\ 0.2M\ KI = 1.85 \times 10^{-6} M$$

$$\underset{\mathbf{0.2M}}{KI(aq)} \longrightarrow \underset{\mathbf{0.2M}}{K^+(aq)} + \underset{\mathbf{0.2M}}{I^-(aq)}$$

$$PbI_2(s) + aq \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

$$[\boldsymbol{Pb^{2+}}] = \mathbf{1.85 \times 10^{-6} M}$$

$$[\boldsymbol{I^-}] = (\mathbf{2 \times 1.85 \times 10^{-6} + 0.2})\boldsymbol{M}$$

$$\boldsymbol{But\ 1.85 \times 10^{-6}\ is\ very\ small\ such\ that}$$

$$(\mathbf{2 \times 1.85 \times 10^{-6} + 0.2}) \approx \mathbf{0.2}$$

$$[\boldsymbol{I^-}] \approx \mathbf{0.2}\ \boldsymbol{M}$$

$$K_{sp} = [Pb^{2+}][I^-]^2 = 1.85 \times 10^{-6} \times (0.2)^2$$

$$\boldsymbol{K_{sp} = 7.4 \times 10^{-8} mol^3 dm^{-9}}$$

(ii) $Let\ the\ solubility\ of PbI_2\ in\ water$

$$= x\ moldm^{-3}$$

$$Since\ mole\ ratio\ of\ PbI_2 : Pb^{2+} = 1:1$$

Then: $[Pb^{2+}] = x\ moldm^{-3}$

$$Since\ mole\ ratio\ of\ PbI_2 : I^- = 1:2$$

Then: $[I^-] = 2x\ moldm^{-3}$

$$K_{sp} = [Pb^{2+}][I^-]^2$$

$$7.4 \times 10^{-8} = x \times (2x)^2$$

$$7.4 \times 10^{-8} = 4x^3$$

$$x^3 = \frac{7.4 \times 10^{-8}}{4} = 1.85 \times 10^{-8}$$

$$x = \sqrt[3]{1.85 \times 10^{-8}}$$

$$x = 2.645 \times 10^{-3}$$

$$Solubility\ of PbI_2\ in\ water\ is$$

$$2.645 \times 10^{-3}\ moldm^{-3}$$

$\boldsymbol{Solubility\ of PbI_2\ in\ water\ \ in\ g\ per\ litre\ is}\ (\mathbf{461 \times 2.645 \times 10^{-3}}) = \mathbf{1.219} \boldsymbol{gdm^{-3}}$

(c) The solubility of lead(II) iodide in 0.2M potassium iodide ***is lower than its solubility in water****. Addition of potassium iodide* ***decreases the solubility of lead(II) iodide*** *because potassium iodide contains* ***iodide ions that are common*** *to iodide ions in lead(II) iodide. The* ***excess iodide ions added combine with lead(II) ions*** *in solution to* ***precipitate lead(II) iodide*** *in order to restore the equilibrium,* ***maintaining the value of the equilibrium constant****.*

10. (a) The solubility product of copper(II) iodate at 25℃ is $\mathbf{1.4 \times 10^{-7}} \boldsymbol{mol^3 dm^{-9}}$.Calculate the concentration of iodate ions in a saturated solution of copper(II) iodate at 25℃:

(b) (i) 0.25 moles of copper(II) chloride was added to 500 $\boldsymbol{cm^3}$ of a saturated solution of copper(II) iodate and the mixture stirred. Calculate the mass of copper(II) iodate that was precipitated.

(ii) State any assumptions made in b(i) above.

(a) $Cu(IO_3)_2(s) + aq \rightleftharpoons Cu^{2+}(aq) + 2IO_3^-(aq)$

$Let\ the\ solubility\ of\ Cu(IO_3)_2\ in\ water$

$= x\ moldm^{-3}$

$Since\ mole\ ratio\ of\ Cu(IO_3)_2 : Cu^{2+} = 1:1$

$[Cu^{2+}] = x\ moldm^{-3}$

$Since\ mole\ ratio\ of\ Cu(IO_3)_2 : IO_3^- = 1:2$

$[IO_3^-] = 2x\ moldm^{-3}$

$K_{sp} = [Cu^{2+}][IO_3^-]^2$

$1.4 \times 10^{-7} = x \times (2x)^2$

$1.4 \times 10^{-7} = 4x^3$

$$x^3 = \frac{1.4 \times 10^{-7}}{4} = 3.5 \times 10^{-8}$$

$x = \sqrt[3]{3.5 \times 10^{-8}}$

$x = 3.27 \times 10^{-3}$

$\boldsymbol{[IO_3^-] = 2x} = (\mathbf{2 \times 3.27 \times 10^{-3}})$

$= \mathbf{6.54 \times 10^{-3} moldm^{-3}}$

(b) (i)

$500cm^3\ of\ solution\ contain\ 0.25\ moles$

$$1000cm^3\ of\ solution\ contain\ \left(\frac{1000 \times 0.25}{500}\right)$$

$= 0.5\ M$

$[CuCl_2] = 0.5M$

$Let\ the\ solubility\ of\ Cu(IO_3)_2\ in\ 0.5M\ CuCl_2$

$= y\ moldm^{-3}$

$$\begin{array}{lll} CuCl_2(aq) \longrightarrow & Cu^{2+}(aq) + & 2Cl^-(aq) \\ \mathbf{0.5M} & \mathbf{0.5M} & \mathbf{0.1M} \end{array}$$

$$\begin{array}{lll} Cu(IO_3)_2(s) + aq \rightleftharpoons & Cu^{2+}(aq) + & 2IO_3^-(aq) \\ \boldsymbol{y} & \boldsymbol{y} & \boldsymbol{2y} \end{array}$$

$[Cu^{2+}] = (0.5 + y)\ moldm^{-3}$

$\boldsymbol{But\ y\ is\ very\ small\ such\ that}$

$(\mathbf{0.5} + \boldsymbol{y}) \approx \mathbf{0.5}$

$[Cu^{2+}] \approx 0.5\ moldm^{-3}$

$[IO_3^-] = 2y\ moldm^{-3}$

$K_{sp} = [Cu^{2+}][IO_3^-]^2 = 0.5 \times (2y)^2$

$2y^2 = 1.4 \times 10^{-7}$

$$y = \sqrt{\frac{1.4 \times 10^{-7}}{2}} = 2.65 \times 10^{-4}\ moldm^{-3}$$

$\boldsymbol{[Cu(IO_3)_2] = y = 2.65 \times 10^{-4}\ M}$

$Moles\ of\ Cu(IO_3)_2\ precipitated = x - y$

$= (3.27 \times 10^{-3})$

$- (2.65 \times 10^{-4})$

$= 2.935 \times 10^{-3}$

$Molar\ mass\ of\ Cu(IO_3)_2$

$= 63.5 + (127 \times 2) + (3 \times 2 \times 16) = 413.5g$

$\boldsymbol{Mass\ of\ Cu(IO_3)_2\ precipitated}$

$\mathbf{= 413.5 \times 2.935 \times 10^{-3} = 1.214}\boldsymbol{g}$

b(ii) Assumptions in b(i)

- ***No change in temperature occurs***
- $\boldsymbol{[Cu^{2+}]}$ ***from copper(II) iodate is negligible in comparison to that from copper(II) chloride. (***$\boldsymbol{[Cu^{2+}] \approx 0.5\ moldm^{-3}}$***)***
- ***There is no change in total volume of the solution***

11. **Barium sulphate is sparingly soluble in water. If the solubility product of barium sulphate is $\mathbf{1.08 \times 10^{-10}}\ \boldsymbol{mol^2dm^{-6}}$ at $\mathbf{25}$℃. Calculate the mass of barium nitrate that should be added to the saturated solution of barium sulphate in order to reduce the concentration of sulphate ions to one third of its original value**.

$BaSO_4(s) + aq \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

$Let\ the\ solubility\ of\ BaSO_4\ in\ water$

$= x\ moldm^{-3}$

$Since\ mole\ ratio\ of\ BaSO_4 : Ba^{2+} : SO_4^{2-}$

$= 1:1:1$

$[Ba^{2+}] = [SO_4^{2-}] = x\ moldm^{-3}$

$K_{sp} = [Ba^{2+}][SO_4^{2-}] = x^2$

$1.08 \times 10^{-10} = x^2$

$[Ba^{2+}] = (3.463 \times 10^{-6} + y)\ moldm^{-3}$

$\boldsymbol{But\ 3.463 \times 10^{-6}\ is\ very\ small\ such\ that}$

$(\mathbf{3.463 \times 10^{-6}} + \boldsymbol{y}) \approx \boldsymbol{y}$

$[Ba^{2+}] \approx y\ moldm^{-3}$

$[SO_4^{2-}] = 3.463 \times 10^{-6}\ moldm^{-3}$

$K_{sp} = [Ba^{2+}][SO_4^{2-}] = y \times 3.463 \times 10^{-6}$

$$x = \sqrt{1.08 \times 10^{-10}} = 1.039 \times 10^{-5}$$

$$\boldsymbol{[SO_4^{2-}] = x = 1.039 \times 10^{-5} moldm^{-3}}$$

$$\boldsymbol{[SO_4^{2-}]_{new} = \left(\frac{1}{3} \times 1.039 \times 10^{-5}\right)}$$

$$\boldsymbol{= 3.463 \times 10^{-6}\ moldm^{-3}}$$

Let the concentration of $Ba(NO_3)_2$ *added* $= y\ moldm^{-3}$

$$Ba(NO_3)_2(aq) \longrightarrow Ba^{2+}(aq) + 2NO_3^-(aq)$$

$$\boldsymbol{y\ M} \qquad \boldsymbol{y\ M} \qquad \boldsymbol{2y\ M}$$

$$BaSO_4(s) + aq \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

$$\boldsymbol{3.463 \times 10^{-6} M} \quad \boldsymbol{3.463 \times 10^{-6} M}$$

$$3.463 \times 10^{-6} y = 1.08 \times 10^{-10}$$

$$y = 3.119 \times 10^{-5}$$

Concentration of $Ba(NO_3)_2$ *added* $= 3.119 \times 10^{-5}\ moldm^{-3}$

Molar mass of $Ba(NO_3)_2$

$$= 137 + 28 + (6 \times 16) = 261g$$

Mass of $\boldsymbol{Ba(NO_3)_2}$ ***added***

$$\boldsymbol{= (261 \times 3.119 \times 10^{-5})}$$

$$\boldsymbol{= 0.008g}$$

12. (a) Silver sulphate is sparingly soluble in water. Write the;

(i) equation for solubility of silver sulphate in water.

(ii) expression for solubility constant.

(b) 50 cm^3 of 0.13M silver nitrate was mixed with 150cm^3 of 0.02M sodium sulphate at 25°C . Calculate the concentrations in the resultant soltion of;

(i)silver ions

(ii) sulphate ions

(c) (i) Calculate the ionic product of silver sulphate at 25°C.

(ii) State whether silver sulphate will be precipitated or not in the solution in (b). Give a reason for your answer. (The solubility product of silver sulphate at 25℃ is $\boldsymbol{1.6 \times 10^{-5} mol^3 dm^{-9}}$)

(a)(i) $Ag_2SO_4(s) + aq \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$

(ii) $K_{sp} = [Ag^+]^2[SO_4^{2-}]$

(b)(i)

$$Moles\ of\ AgNO_3 = \left(\frac{50 \times 0.13}{1000}\right) = 0.0065$$

$$Total\ volume\ of\ solution = (50 + 150) = 200\ cm^3$$

$$AgNO_3(aq) \longrightarrow Ag^+(aq) + NO_3^-(aq)$$

$200\ cm^3$ *of solution contain* 0.0065 *moles of* Ag^+

$1000\ cm^3$ *of solution contain* $\left(\frac{1000 \times 0.0065}{200}\right)$ *moles of* Ag^+

$$\boldsymbol{= 0.0325 moldm^{-3}}$$

(ii)

$$Moles\ of\ Na_2SO_4 = \left(\frac{150 \times 0.02}{1000}\right) = 0.003$$

$$Na_2SO_4(aq) \longrightarrow 2Na^+(aq) + SO_4^{2-}(aq)$$

$200\ cm^3$ *of solution contain* 0.003 *moles of*

$1000\ cm^3$ *of solution contain* $\left(\frac{1000 \times 0.003}{200}\right)$ *mo*

$$\boldsymbol{= 0.015 moldm^{-3}}$$

(c)(i)

Ionic product of Ag_2SO_4

$$= [Ag^+]^2[SO_4^{2-}]$$

$$= (0.0325)^2 \times 0.015$$

$$\boldsymbol{= 1.58 \times 10^{-5} mol^3 dm^{-9}}$$

(ii) Silver sulphate ***will not be precipitated****. This is because* ***the ionic product of silver sulphate does not exceed its solubility product.***

Questions

1. (a) The solubility product of a sparingly soluble base $M(OH)_2$ is $6.0 \times 10^{-14}\, mol^3 dm^{-9}$.

Define the term solubility product.

(b) Calculate its solubility in:

(i) Water

(ii) 0.1M sodium hydroxide solution.

(iii) 0.5M ammonia solution

(c) Explain the differences in your answers in c(i) and (ii) above

2. (a) State the two methods by which the solubility of a sparingly soluble salt may be determined.

(b) Copper(II) iodate is sparingly soluble in water.

Write:

(i) an equation for the solubility of copper(II) iodate

(ii) an expression for the solubility product, K_{sp} of copper(II) iodate.

(c) The solubility product of copper(II) iodate at $25℃$ is $1.4 \times 10^{-7} mol^3 dm^{-9}$.

Calculate the solubility in grams per litre at $25℃$ of copper(II) iodate in:

(i) water

(ii) a 0.1M potassium iodate

(d) Comment on your answer in (c) above.

3. (a) Define :

(i) Solubility

(ii) Solubility product

(b) Describe an experiment that can be carried out to determine the solubility product of silver chromate in the laboratory.

(c) The solubility of silver chromate at $25℃$ is $3.21 \times 10^{-2} gdm^{-3}$.Calculate the;

(i) solubility product at this temperature.

(ii) Solubility of silver chromate in 0.2M potassium chromate solution.

(iii) Solubility of silver chromate in 0.05M silver nitrate solution

(d) Explain the effect of adding the following solutions on the solubility of silver chromate.

(i) Ammonia solution

(ii) Silver nitrate solution

(e) A solution of silver nitrate wad added to a solution containing 0.05M potassium chloride and 0.05M potassium chromate. Calculate the concentration of silver ions required to precipitate :

(i) Silver chloride

(ii) Silver chromate

(f) State which of the compounds in (d) will be precipitate first. Give a reason for your answer.(Solubility product of silver chloride $= 1.0 \times 10^{-10} mol^2 dm^{-6}$ at 25℃)

$$(Ag = 108, Cr = 52, O = 16)$$

(g) State two applications of solubility product.

4. The solubility of silver chloride in water is $1.3 \times 10^{-11} moldm^{-3}$.Calculate the solubility of silver chloride in 0.1M potassium chloride solution.

5. (a) Silver carbonate is sparingly soluble in water. Write:
   (i) the equation for solubility of silver carbonate in water.
   (ii) the expression for K_{sp} for silver carbonate

   (b) The solubility of silver carbonate at 15℃ is $0.03 gdm^{-3}$ Calculate the solubility product of silver carbonate at 15℃.

   (c) State what would happen to the solubility of silver carbonate when a 0.1M solution of silver nitrate is added to the saturated solution. Explain your answer.

6. (a) (i) Write an equation for the solubility of silver sulphate in water
   (ii) Determine the molar concentrations of silver ions and sulphate ions in a saturated solution of silver sulphate at 25℃. (The K_{sp}, of silver sulphate is $1.7 \times 10^{-5}\ moldm^{-3}$ at 25℃)

   (b) State how the solubility of silver sulphate would be affected if the following substances were added.
   (i) Sodium sulphate solution
   (ii) Ammonia solution

   (c) Explain your answer in (b)

7. Powdered magnesium hydroxide was shaken with water at 25°C to form a saturated solution. The mixture was filtered and $100 cm^3$ of the filtrate required $6.4 cm^3$ of a 1M hydrochloric acid for complete reaction.
   (a) Write an expression for the solubility product of magnesium hydroxide and give its units.
   (b) Calculate the solubility product of magnesium hydroxide at 25°C.
   (c) Explain the effect, if any, on the solubility of magnesium hydroxide if the following substances were added separately ;
   (i) sodium hydroxide solution
   (ii) a compound which forms a stable complex with magenesium ions
   (iii) aluminium nitrate solution℃. (The K_{sp}, of $Al(OH)_3$ is $1.0 \times 10^{-32}\ mol^4 dm^{-12}$ at 25℃)

8. (a) Explain what is meant by the terms:
    - (i) **common ion effect**.
    - (ii) **solubility of a salt**.

(b) Silver chromate is sparingly soluble in water .Write:
- (i) equation for the solubility of silver chromate in water
- (ii) the expression for the solubility product, K_{sp}, for silver chromate.

(c) A saturated solution of silver chromate contains $2.4 \times 10^{-2} g$ per litre at $20°C$. Calculate the value for the solubility product, K_{sp}, for silver chromate at $20°C$.

(d) Chloride ions in solution can be detected by titration with silver nitrate solution in the presence of chromate ions. The end point is indicated by a red precipitate of silver chromate.
- (i) Explain why silver chromate does not precipitate until the end point is reached
- (ii) 25cm^3 of a solution containing 0.1moles of potassium chloride and 0.001 moles of chromate ion is required on titration with 50cm^3 of 0.1M silver nitrate solution to reach the end point. Calculate the concentration of chloride ions at the end point. [Solubility product for silver chloride is $1.6 \times 10^{-10} mol^2 l^{-2}$]

9. (a)Explain what is meant by the terms:
    - **(i)** salt hydrolysis
    - (ii) common ion effect
    - (iii) solubility product constant

(b) When sodium hydroxide solution is added to aqueous calcium hydroxide solution, a white precipitate is formed but when ammonia solution is used instead of sodium hydroxide solution, no precipitate is formed. Explain the observation.

(c) Describe an experiment to determine the solubility product of silver phosphate in the laboratory.

(d) Write:

(i) the equation for the solubility of silver phosphate in water

(ii) an expression for the solubility product, K_{sp} of silver phosphate

(e) If the solubility of silver phosphate at $25°C$ is $3.25 \times 10^{-3} gdm^{-3}$. Calculate the value of the K_{sp} at $25°C$.

(f) State how solubility of silver phosphate would be affected if the following substances were added.

(i) ammonia solution

(ii) silver nitrate solution

(g) Explain your answer in (c) above.

10. (a) Silver chromate is sparingly soluble in water. Write:

(i) an equation for the solubility of silver chromate in water

(ii) an expression for the solubility product constant, K_{sp} for silver chromate.

(b) The solubility of silver chromate is $6.64 \times 10^{-4} g$ per 100g of water at a certain temperature. Calculate the solubility product of silver chromate.

(c) Calculate the solubility of silver chromate in $1.0\ dm^3$ of 0.1M silver nitrate solution.

11. Lead(II) chloride is sparingly soluble in cold water.

(a)(i) Write the equation for the solubility of lead(II) chloride in water.

(ii)Write the expression for the solubility product, K_{sp} of lead(II) chloride

(b) At $25°C$, a saturated solution contains 1.1g of lead(II) chloride per litre. Calculate the solubility product at this temperature.

(c) Solid lead(II) chloride can be prepared in the laboratory by heating lead(II) oxide with dilute hydrochloric acid and the mixture cooled. However, solid lead(II) chloride cannot be formed when lead(II) oxide is reacted with concentrated hydrochloric acid. Give reasons for this observation and illustrate your answer with an equation.

12. (a) The solubility of lead(II) iodide is 0.122g in 100 cm^3 of water at $40°C$.

(i) Write equation for the solubility of lead(II) iodide in water

(ii) Calculate the solubility constant, K_{sp} for lead(II) iodide at $40°C$.

(b) Sodium chromate solution was added to a saturated solution of lead(II) iodide until in excess.

(i) State what is observed and give a reason for your answer.

(ii) Write equation for the reaction that took place

(c) 50 cm^3 of 0.001M lead(II) nitrate solution was mixed with 50 cm^3 of 0.001M potassium iodide. Deduce whether lead(II) iodide will be precipitate or not. Show your working clearly and give a reason for your answer.

(d) The saturated solution of lead (II) iodide of concentration 0.122g per 100 cm^3 of solution was heated to $60°C$ in a closed system.

(i) State whether the solution remains saturated at $60°C$

(ii) Give a reason for your answer.

13. (a) $5.9852 \times 10^{-4} g$ of solid silver(I) chromate solution dissolve in 1 litre of 0.1M potassium chromate to form a saturated solution at $25°C$.

(i) Define the term saturated solution

(ii) Calculate the solubility of silver(I) chromate in pure water at $25°C$.

(b) Ammonia solution is added to a saturated solution of silver(I) chromate in water at $25°C$.

(i) State the effects of adding ammonia on the solubility of silver(I) chromate.

(ii) Explain your answer in b(i) above

(c) State any two practical applications of solubility product.

14. Aluminium hydroxide is sparingly soluble in water.
    (a) Write equation for solubility of aluminium hydroxide in water.
    (b) The solubility of aluminium hydroxide is $1.92 \times 10^{-8} g$ per $100 cm^3$ at 18℃. Calculate the solubility product of aluminium hydroxide at 18℃.
15. Calculate the solubility product, K_{sp}, of aluminium sulphide if its solubility in water at 25℃ is $0.0072\ gdm^{-3}$.
16. Lead(II) sulphide is sparingly soluble in water.
    (a) Write an expression for the solubility product of lead(II) sulphide.
    (b) 3.80g of lead(II) sulphide was shaken with one litre of water at 15℃. Calculate the percentage of lead(II) sulphide that dissolved in water.

($The\ solubility\ product\ of\ lead(II)\ sulphide\ is\ 3.4 \times 10^{-28}\ mol^2 dm^{-6}\ at$ 15℃)

    (c) If 0.05 molar solution of lead(II) nitrate was used instead of water in (b), Calculate the percentage of lead(II) sulphide that dissolved and state any assumption made.

17. The solubility product of iron(III) hydroxide at 18℃ is $1 \times 10^{-38}\ mol^4 dm^{-12}$. Calculate the mass of iron(III) hydroxide that can be dissolved in one litre of 0.01M sodium hydroxide solution at 18℃.

CHAPTER EIGHT

CHEMICAL KINETICS

Introduction

Chemical kinetics is the study of rates of chemical reactions and how the reactions depend on the factors affecting them.

It deals with experimental determination of rates of reaction and interpretation of kinetic data. Reaction rates cannot be predicted theoretically and so they are determined experimentally. It as well investigates the mechanism by which a reaction occurs.

Some reactions occur very slowly and may take months for completion like rusting of iron. Others are very fast and may take seconds like precipitation of silver chloride using sodium chloride and silver nitrate

Rate of a chemical reaction

***Rate of a chemical reaction is the decrease in concentration of reactants or the increase in concentration of products formed per unit time*.**

Consider the reaction: $\boldsymbol{W} + \boldsymbol{X} \longrightarrow \boldsymbol{Y} + \boldsymbol{Z}$

$$Rate\ of\ reaction = \frac{change\ in\ concentraton\ of\ reactant}{Time\ interval}$$

$$or$$

$$Rate\ of\ reaction = \frac{change\ in\ concentraton\ of\ product}{Time\ interval}$$

In terms of reactants;

$$Rate\ of\ reaction = \frac{-d[W]}{dt}\ or \frac{-d[X]}{dt}$$

The negative sign inserted indicates that the concentrations of reactants decrease with time.

In terms of products;

$$Rate\ of\ reaction = \frac{d[Y]}{dt}\ or \frac{d[Z]}{dt}$$

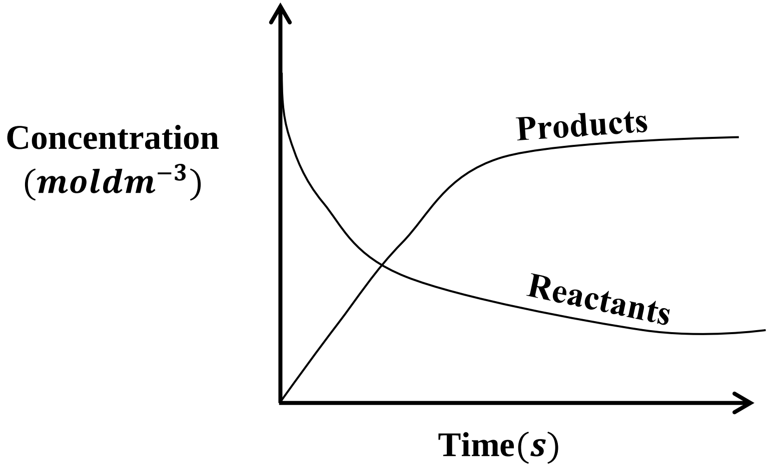
***The rate of the reaction is not the same when expressed in terms of W or X as it is in terms of Y or Z. It is usually necessary to specify which species is used when expressing rate of a chemical reaction*.**

Units of rate of reaction

Different units can be used but if concentration is given in $moldm^{-3}$ and time in seconds, then ;

$$Unit\ of\ rate\ of\ reaction = \frac{Unit\ of\ concentration}{Unit\ of\ time} = \frac{moldm^{-3}}{s} = \boldsymbol{moldm^{-3}s^{-1}}$$

Rate of reaction can be represented graphically in terms of concentration of reactant or product plotted against time.



The slope of any of the graphs gives the rate of the reaction in $moldm^{-3}s^{-1}$at a given time.

The rate law

The rate law is an experimentally determined expression that gives the relationship between rate of reaction and concentration of reactants.

The rate law states that ***the rate of a reaction is directly proportional to the molar concentrations of reactants raised to their appropriate powers which are experimentally determined at a given temperature***.

Consider the reaction:

$$xA + yB + zC \longrightarrow Products$$

$$Rate\ of\ reaction \propto [A]^l[B]^m[C]^n$$

$$\boldsymbol{Rate\ of\ reaction = k[A]^l[B]^m[C]^n}$$

k is the rate constant. l , m and n are experimentally determined values

The equation above is known as the ***rate law*** or ***rate equation***.

The rate equation is an expression that relates the rate of reaction and the product of the molar concentrations of reactants raised to their appropriate powers.

Note that the rate law for any reaction cannot be from the balanced chemical equation using the stoichiometric coefficients but it is determined experimentally.

The rate constant, *K*

Rate constant of a reaction is the proportionality constant in an experimentally determined rate equation.

or

Rate constant of a reaction is the ratio of rate of reaction to the product of the molar concentrations of reactants raised to appropriate powers which are experimentally determined at a given temperature.

The rate constant for a particular reaction has a constant value hence does not change with changes in concentration of the reactant.

Order of a reaction

For the reaction discussed above with the rate equation;

$$Rate\ of\ reaction = k[A]^l[B]^m[C]^n$$

l is the order of reaction with respect to A

m is the order of reaction with respect to B

n is the order of reaction with respect to C

The overall order is $(l + m + n)$

Order of a reaction is the sum of the powers to which the molar concentrations of the reactants are raised in the experimental rate equation.

Order of a reaction helps us classify reactions ***zero order, first order*** or ***third order*** reactions.

Order of a reaction ***can be a whole number (positive or negative) or a fraction***.

Note that the order of a reaction with respect to a given reactant cannot be deduced using stoichiometric coefficients in the equation. For example using the equation below:

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

The experimentally determined rate equation is:

$$Rate = k[BrO_3^-][Br^-][H^+]^2$$

The order of reaction with respect to BrO_3^- is 1

The order of reaction with respect to Br^- is 1

The order of reaction with respect to H^+ is 2

The overall order is $(1 + 1 + 2) = 4$

Molecularity

Molecularity of a reaction is the total number of molecules, atoms or ions involved in the rate determining step of a reaction.

For a reaction that takes place in more than one step, the rate determining step is the slowest step in the reaction mechanism.

Molecularity is always a whole number and never greater than three.

Therefor Molecularity can be one, two or three. Molecularity is a theoretical postulate and not experimentally measured. It must be a whole number.

Differences between order of reaction and molecularity

Order of reaction	Molecularity
Sum of the powers to which the molar concentrations of the reactants are raised in the experimental rate equation	The number of molecules, atoms or ions involved in the rate determining step of a reaction
Order is experimentally determined	Molecularity is a theoretical concept
Order can be a zero or any whole number	Molecularity is never more than three and never zero
Order can be a fraction	Molecularity is always a whole number
Order does not tell anything about mechanism of a reaction	Molecularity explains mechanism of a reaction

Mechanism of a reaction

Many reactions proceed through a number of stages or steps. These steps or stages are called a mechanism. Such reactions involve formation of intermediates before the final product(s) is/ are formed. The rates of such reactions are determined by the ***slowest step*** which is called the ***rate determining step***.

A rate determining step is the slowest step in the reaction mechanism of a chemical reaction that proceeds through more than one step.

A reaction can be ***unimolecular***, ***bimolecular*** and rarely ***termolecular*** depending on the number of molecules, atoms or ions involved in the rate determining step.

1. Unimolecular reaction

A unimolecular reaction involves only one reactant molecule in the rate determining step. For example

(a) ***the decomposition of hydrogen peroxide***;

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

The reaction occurs in the following steps:

$$\boldsymbol{H_2O_2 \xrightarrow{slow} H_2O + O}$$

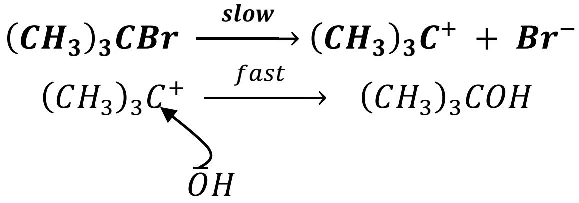
$$O + O \xrightarrow{Fast} O_2$$

The first step is the rate determining step and involves only ***one molecule of hydrogen peroxide*** forming water and an oxygen atom. The rate of reaction depends on this step hence the rate equation if given as $Rate = k[H_2O_2]$

Therefore the reaction is first order and has molecularity one.

(b) the reaction of 2-bromo-2-methyl propane (tertiary alkylhalides) with potassium hydroxide;

The reaction occurs by the following mechanism;



$$(CH_3)_3CBr \xrightarrow{slow} (CH_3)_3C^+ + Br^-$$

$$(CH_3)_3C^+ \xrightarrow{fast} (CH_3)_3COH$$

$$\bar{O}H$$

The first step is the rate determining step and involves only ***one molecule of 2-bromo-2-methyl propane*** forming a carbocation and a bromide ion. The rate of reaction depends on this step hence the rate equation if given as $Rate = k[(CH_3)_3CBr\ ]$

Therefore the reaction between tertiary alkylhalides and potassium hydroxide to form alcohols is first order and has molecularity 1. From the rate equation, the rate of reaction only depends on the concentration of the alkylhalide but independent on the concentration of hydroxyl ions.

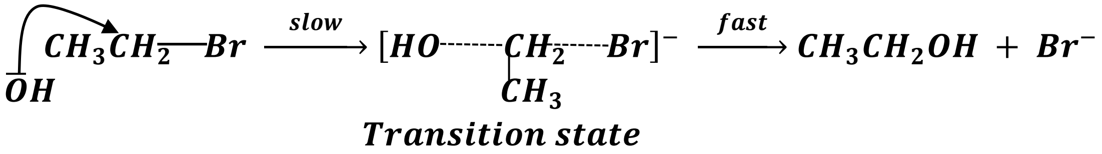
The type of reaction is nucleophilic substitution unimolecular.

2. Bimolecular reaction

A bimolecular reaction involves two reactant molecules in the rate determining step. For example

(a) ***the reaction of bromoethane (primary alkylhalides) with potassium hydroxide;***

The reaction occurs by the following mechanism;



$$\bar{O}H \quad CH_3CH_2{-}Br \xrightarrow{slow} [HO\cdots\underset{CH_3}{CH_2}\cdots Br]^- \xrightarrow{fast} CH_3CH_2OH + Br^-$$

$$Transition\ state$$

The first step is the rate determining step and involves only ***one molecule of 2-bromo-2-methyl propane*** forming a carbocation and a bromide ion. The rate of reaction depends on this step hence the rate equation if given as $Rate = k[CH_3CH_2Br\ ][\bar{O}H]$

Therefore the reaction between primary alkylhalides and potassium hydroxide to form alcohols is second order and has molecularity 2. From the rate equation, the rate of reaction depends on both the concentration of the alkylhalide and the concentration of hydroxyl ions.

The type of reaction is nucleophilic substitution bimolecular.

MATHEMATICAL DERIVATION OF ZERO, FIRST AND SECOND ORDER RATE EQUATIONS AND HALF LIFE

Half-life of a reaction is the time taken for the concentration of a reactant to reduce to half its original value.

1. Zero order reactions

A zero order reaction is a reaction in which the rate of reaction is independent of the concentration of the reactant.

Consider a reaction: $A \xrightarrow{\hspace{2em}} Products$

$$\boldsymbol{Rate = k[A]^0}$$

$$\boldsymbol{Rate = k}$$

For a zero order reaction, the units for rate constant are $moldm^{-3}s^{-1}$

Integrated form of rate equation for a zero order reaction

$Rate = k[A]^0$ $Rate = -\frac{d[A]}{dt}$ $-\frac{d[A]}{dt} = k[A]^0$ $-\frac{d[A]}{dt} = k \text{ since } [A]^0 = 1$ $-\frac{d[A]}{dt} = k$ $-d[A] = k\,dt$	*If* $[A]_0$ *is the initial concentration of* A *at* $t = 0$ *, and* $[A]_t$ *is the concentration of* A *after time* t *Integrating using the above limits yields;* $-\int_{[A]_0}^{[A]_t} d[A] = k\int_0^t dt$ $-[A]_{[A]_0}^{[A]_t} = k[t]_0^t$ $-([A]_t - [A]_0) = k(t-0)$ $[A]_0 - [A]_t = kt$ $\boldsymbol{[A]_t = [A]_0 - kt}$

Expression for half-life of a zero order reaction

$Rate = k[A]^0$ $Rate = -\frac{d[A]}{dt}$ $-\frac{d[A]}{dt} = k[A]^0$ $-\frac{d[A]}{dt} = k \text{ since } [A]^0 = 1$ $-\frac{d[A]}{dt} = k$ $-d[A] = k\,dt$ *If* $[A]_0$ *is the initial concentration of* A *at* $t = 0$ *,* *then at halflife,* $t_{1/2}$ *, the concentration is* $\frac{1}{2}[A]_0$ *Integrating using the above limits yields;*	$-\int_{[A]_0}^{\frac{1}{2}[A]_0} d[A] = k\int_0^{t_{1/2}} dt$ $-[A]_{[A]_0}^{\frac{1}{2}[A]_0} = k[t]_0^{t_{1/2}}$ $-\left(\frac{1}{2}[A]_0 - [A]_0\right) = k\left(t_{1/2} - 0\right)$ $[A]_0 - \frac{1}{2}[A]_0 = kt_{1/2}$ $\frac{[A]_0}{2} = kt_{1/2}$ $\boldsymbol{t_{1/2} = \frac{[A]_0}{2k}}$

Examples of zero order reactions include:

(i) *Iodination of propanone*

$$CH_3COCH_3(aq) + I_2(aq) \longrightarrow CH_3COCH_2I(aq) + HI(aq)$$

This reaction is zero order with respect to iodine. The rate of reaction does not change if the concentration of iodine is changed.

(ii) *The decomposition of hydrogen iodide on a gold surface.*

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

(iii) *Decomposition of ammonia to nitrogen and hydrogen by a hot tungsten wire catalyst.*

2. First order reactions

A first order reaction is a reaction in which the rate of reaction is proportional to the concentration of the reactant raised to power one.

Consider a reaction: $A \longrightarrow Products$

$$\boldsymbol{Rate = k[A\,]}$$

For a first order reaction, the units for rate constant can be derived.

$$From\ Rate = k[A\,]$$

$$k = \frac{Rate}{[A\,]} = \frac{moldm^{-3}s^{-1}}{moldm^{-3}} = \boldsymbol{s^{-1}}$$

Integrated form of rate equation for a first order reaction

$$Rate = -\frac{d[A\,]}{dt} = k[A\,]$$

$$Rate = -\frac{d[A\,]}{dt}$$

$$-\frac{d[A\,]}{dt} = k[A\,]$$

$$Separating\ variables\ yields:$$

$$-\frac{d[A\,]}{[A\,]} = kdt$$

$$If\ [A\,]_0\ is\ the\ initial\ concentration\ of\ A\ at\ t = 0\ ,$$
$$and\ \ [A\,]_t\ is\ the\ concentration\ of\ A\ after\ time\ t$$
$$Integrating\ using\ the\ above\ limits\ yields;$$

$$-\int_{[A\,]_0}^{[A\,]_t} \frac{d[A\,]}{[A\,]} = k\int_0^t dt$$

$$-\big[ln\ [A]\big]_{[A\,]_0}^{[A\,]_t} = k[t]_0^t$$

$$-(ln[A\,]_t - ln[A\,]_0) = k(t-0)$$

$$ln[A\,]_0 - ln[A\,]_t = kt$$

$$\boldsymbol{ln\left(\frac{[A\,]_0}{[A\,]_t}\right) = kt}$$

$$The\ equation\ can\ also\ be\ written\ as$$

$$\boldsymbol{2.303log\left(\frac{[A\,]_0}{[A\,]_t}\right) = kt}$$

Expression for half-life of a first order reaction

$$Rate = k[A\,]$$

$$Rate = -\frac{d[A\,]}{dt}$$

$$-\frac{d[A\,]}{dt} = k[A\,]$$

$$Separating\ variables\ yields:$$

$$-\frac{d[A\,]}{[A\,]} = kdt$$

$$ln\left(\frac{[A\,]_0}{\frac{[A\,]_0}{2}}\right) = kt_{1/2}$$

$$ln\,2 = kt_{1/2}$$

$$t_{1/2} = \frac{ln2}{k}$$

$$\boldsymbol{t_{1/2} = \frac{0.693}{k}}$$

If $[A]_0$ *is the initial concentration of* A *at* $t = 0$, *and* $[A]_t$ *is the concentration of* A *after time* t *Integrating using the above limits yields;* $-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = k\int_0^t dt$ $-\left[ln\,[A]\right]_{[A]_0}^{[A]_t} = k[t]_0^t$ $-(ln[A]_t - ln[A]_0) = k(t-0)$ $ln[A]_0 - ln[A]_t = kt$ $\boldsymbol{ln\left(\frac{[A]_0}{[A]_t}\right) = kt}$ $\boldsymbol{For\ half\ life, t = t_{1/2}\ and\ [A]_t = \frac{[A]_0}{2}}$	*Also from:* $\boldsymbol{2.303log\left(\frac{[A]_0}{[A]_t}\right) = kt}$ $\boldsymbol{For\ half\ life, t = t_{1/2}\ and\ [A]_t = \frac{[A]_0}{2}}$ $2.303log\left(\frac{[A]_0}{\frac{[A]_0}{2}}\right) = kt_{1/2}$ $2.303log\,2 = kt_{1/2}$ $t_{1/2} = \frac{2.303log\,2}{k}$ $\boldsymbol{t_{1/2} = \frac{0.693}{k}}$

Examples of first order reactions include:

(i) *All radioactive decays*

(ii) *Decomposition of hydrogen peroxide to form water and oxygen*

$$2H_2O_2(aq) \longrightarrow H_2O(l) + O_2(g)$$

(iii) *Reaction of 2-chloro-2-methylpropane with sodium hydroxide*

$$(CH_3)_3CCl \longrightarrow (CH_3)_3COH + Cl^-$$

(iv) *Decomposition of dinitrogen pentoxide to nitrogen dioxide and oxygen*

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

3. Second order reactions

A second order reaction is a reaction in which the rate of reaction is proportional to the concentration of the reactant raised to the second power.

Or a reaction in which the rate of reaction is proportional to the product of the concentration of two reactants each raised to power one.

Consider a reaction: $2A \longrightarrow Products$

$$\boldsymbol{Rate = k[A]^2}$$

or

Consider a reaction: $A + B \longrightarrow Products$

$$\boldsymbol{Rate = k[A][B]}$$

For a second order reaction, the units for rate constant can be derived:

$$From\ Rate = k[A]^2$$

$$k = \frac{Rate}{[A]^2} = \frac{moldm^{-3}s^{-1}}{(moldm^{-3})^2} = \boldsymbol{mol^{-1}dm^3s^{-1}}$$

Integrated form of rate equation for a second order reaction

$$Rate = k[A]^2$$

$$Rate = -\frac{d[A]}{dt}$$

$$-\frac{d[A]}{dt} = k[A]^2$$

$$Separating\ variables\ yields:$$

$$-\frac{d[A]}{[A]^2} = kdt$$

$$If\ [A]_0\ is\ the\ initial\ concentration\ of\ A\ at\ t = 0,$$

$$and\ [A]_t\ is\ the\ concentration\ of\ A\ after\ time\ t$$

$$Integrating\ using\ the\ above\ limits\ yields;$$

$$-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = k\int_0^t dt$$

$$-\int_{[A]_0}^{[A]_t} [A]^{-2}\, d[A] = k\int_0^t dt$$

$$-\left[\frac{[A]^{-1}}{-1}\right]_{[A]_0}^{[A]_t} = k[t]_0^t$$

$$-[-[A]^{-1}]_{[A]_0}^{[A]_t} = k[t]_0^t$$

$$-\left[-\frac{1}{[A]}\right]_{[A]_0}^{[A]_t} = k[t]_0^t$$

$$\left[\frac{1}{[A]}\right]_{[A]_0}^{[A]_t} = k[t]_0^t$$

$$\left(\frac{1}{[A]_t} - \frac{1}{[A]_0}\right) = k(t-0)$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$\boldsymbol{\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt}$$

Expression for half-life for a second order reaction

$$Rate = k[A]^2$$

$$Rate = -\frac{d[A]}{dt}$$

$$-\frac{d[A]}{dt} = k[A]^2$$

$$Separating\ variables\ yields:$$

$$-\frac{d[A]}{[A]^2} = kdt$$

$$If\ [A]_0\ is\ the\ initial\ concentration\ of\ A\ at\ t = 0,$$

$$and\ [A]_t\ is\ the\ concentration\ of\ A\ after\ time\ t$$

$$Integrating\ using\ the\ above\ limits\ yields;$$

$$-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = k\int_0^t dt$$

$$-\int_{[A]_0}^{[A]_t} [A]^{-2}\, d[A] = k\int_0^t dt$$

$$-\left[\frac{[A]^{-1}}{-1}\right]_{[A]_0}^{[A]_t} = k[t]_0^t$$

$$-[-[A]^{-1}]_{[A]_0}^{[A]_t} = k[t]_0^t$$

$$-\left[-\frac{1}{[A]}\right]_{[A]_0}^{[A]_t} = k[t]_0^t$$

$$\left[\frac{1}{[A]}\right]_{[A]_0}^{[A]_t} = k[t]_0^t$$

$$\left(\frac{1}{[A]_t} - \frac{1}{[A]_0}\right) = k(t-0)$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$\boldsymbol{\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt}$$

$$\boldsymbol{For\ half\ life, t = t_{1/2} and\ [A]_t = \frac{[A]_0}{2}}$$

$$\frac{1}{\frac{[A]_0}{2}} = \frac{1}{[A]_0} + kt_{1/2}$$

$$\frac{2}{[A]_0} = \frac{1}{[A]_0} + kt_{1/2}$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{2-1}{[A]_0} = kt_{1/2}$$

$$\frac{1}{[A]_0} = kt_{1/2}$$

$$\boldsymbol{t_{1/2} = \frac{1}{k[A]_0}}$$

Examples of second order reactions include:

(i) *Reaction between hydrogen and iodine to form hydrogen iodide*

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

(ii) *Oxidation of iodide ions to iodine by peroxodisulphate ions*

$$S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

(iii) *Reaction of bromoethane with sodium hydroxide*

$$CH_3CH_2Br \longrightarrow CH_3CH_2OH + Br^-$$

In summary:

Order of reaction	Differential rate equation	Integrated rate equation	Units for rate constant	Expression for half-life
Zero	$-\frac{d[A]}{dt} = k$	$[A]_t = [A]_0 - kt$	$moldm^{-3}s^{-1}$	$t_{1/2} = \frac{[A]_0}{2k}$
First	$-\frac{d[A]}{dt} = k[A]$	$ln\left(\frac{[A]_0}{[A]_t}\right) = kt$ *or* $2.303log\left(\frac{[A]_0}{[A]_t}\right) = kt$	s^{-1}	$t_{1/2} = \frac{0.693}{k}$
Second	$-\frac{d[A]}{dt} = k[A]^2$	$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$	$mol^{-1}dm^3s^{-1}$	$t_{1/2} = \frac{1}{k[A]_0}$

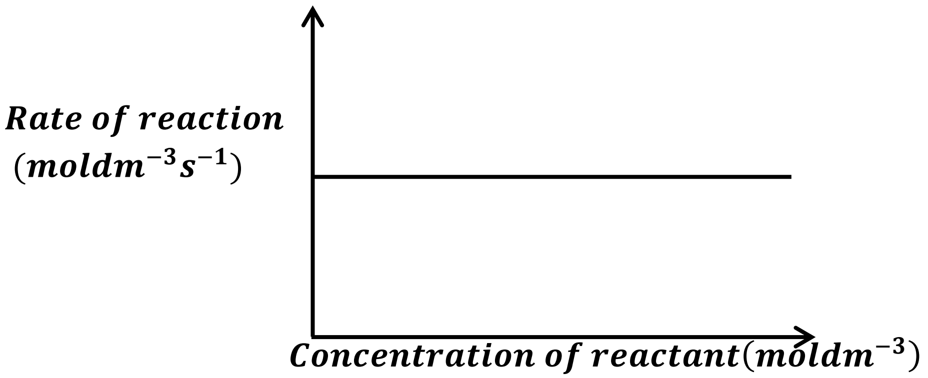
Sketching plotting and interpreting the graphs obtained using rates of reaction data and rate equations

1. Graphs for zero order reactions

From the rate equation: $Rate = k[A]^0$

$$Rate = k$$

A graph of rate of reaction against concentration of reactant is a straight line with zero gradient.



Also the integrated form of the rate equation for a zero order reaction is given as:

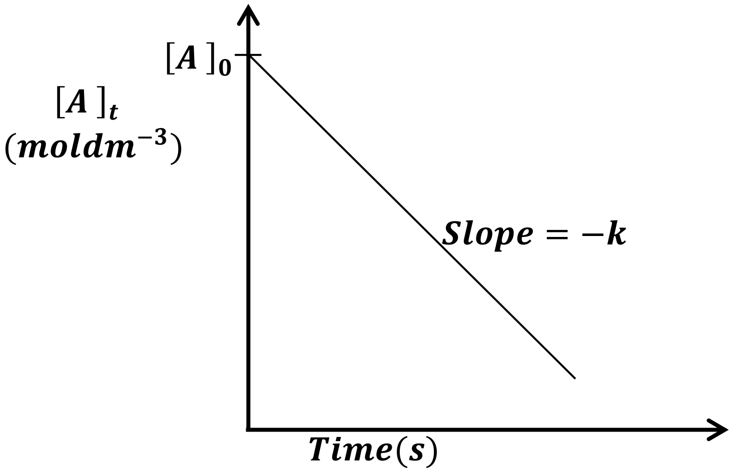
$$[A]_t = [A]_0 - kt$$

The equation when expressed in the form $y = mx + c$ is:

$$[A]_t = -kt + [A]_0$$

$$y = mx + c$$

A graph of molar **concentration of reactant,** $[A]_t$ against **time** can be plotted;



The graph of ***concentration of reactant*** *against* ***time*** *is a* ***straight line*** *with* ***a negative gradient*** *with an* ***intercept on the concentration axis****. The intercept on the concentration axis gives the* ***initial concentration,*** $[A]_0$. *The slope of the graph* , $Slope = -k$ *from which the* ***rate constant can be obtained*** *with units* $moldm^{-3}s^{-1}$

Half-life is then obtained from

$$t_{1/2} = \frac{[A]_0}{2k}$$

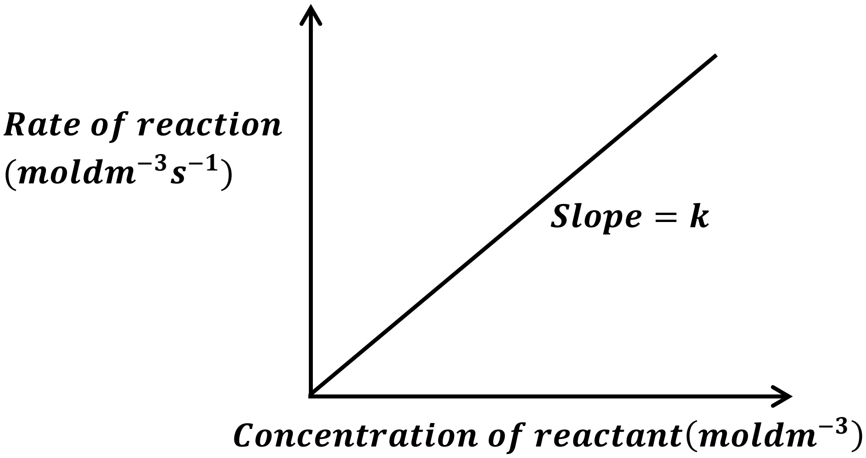
2. Graphs for first order reactions

A number of six graphs can be drawn to represent first order reactions.

From the rate equation $Rate = k[A]$

Comparing with: $y = mx + 0$

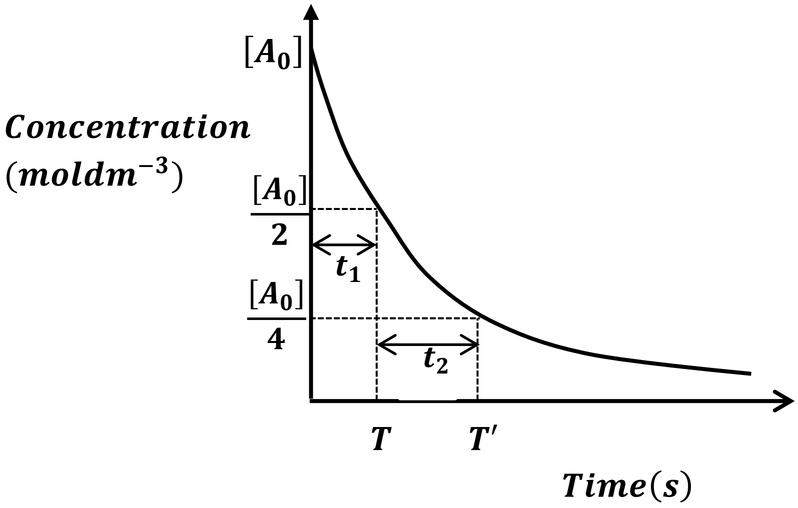
A graph of rate of reaction against concentration of reactant, $[A]$ **can be plotted**



The graph of ***rate of reaction*** *against* ***concentration of reactant*** *is a* ***straight line through the origin.*** *The slope of the graph* , $Slope = k$ *from which the* ***rate constant can be obtained*** *with units* s^{-1}

Half-life is then obtained *from* $t_{1/2} = \frac{0.693}{k}$

A graph of concentration of reactant against time



*The graph of **concentration** against **time** is a **curve with a negative gradient.** The slope of the graph **at a given point is the rate of reaction at that time.***

***From this graph half-life can be got directly from the graph and can be used to find the rate constant k using the expression** $t_{1/2} = \frac{0.693}{k}$.*

***Half-life is got by getting the time that corresponds to** $\frac{[A_0]}{2}$ **and then** $\frac{[A_0]}{4}$**. The half-life can then be got by the expression** $t_{1/2} = \frac{t_1+t_2}{2}$ **. The values** t_1 **and** t_2 **are got from the graph by** $t_1 = T - 0$ **and** $t_2 = T' - T$*

$$2.303\log\left(\frac{[A]_0}{[A]_t}\right) = kt$$

$$\log\left(\frac{[A]_0}{[A]_t}\right) = \frac{k}{2.303}t$$

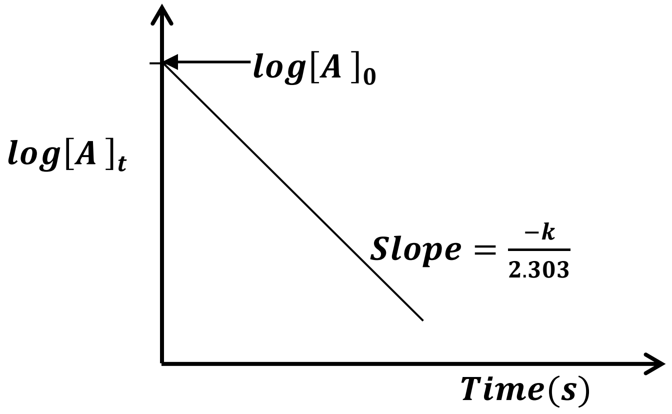
$$\log[A]_0 - \log[A]_t = \frac{k}{2.303}t$$

$$-\log[A]_t = \frac{k}{2.303}t - \log[A]_0$$

$$\log[A]_t = -\frac{k}{2.303}t + \log[A]_0$$

$$\text{compare with } y \quad = \quad mx \quad + \ c$$

A graph of $\log[A]_t$ against time(t) can be plotted;



*The graph of $\log[A]_t$ against **time** is a **straight line** with **a negative gradient** with an **intercept on the $\log[A]_t$ axis**. The intercept on the concentration axis gives the value of $\log[A]_0$*

$$if \ \log[A]_0 = x$$

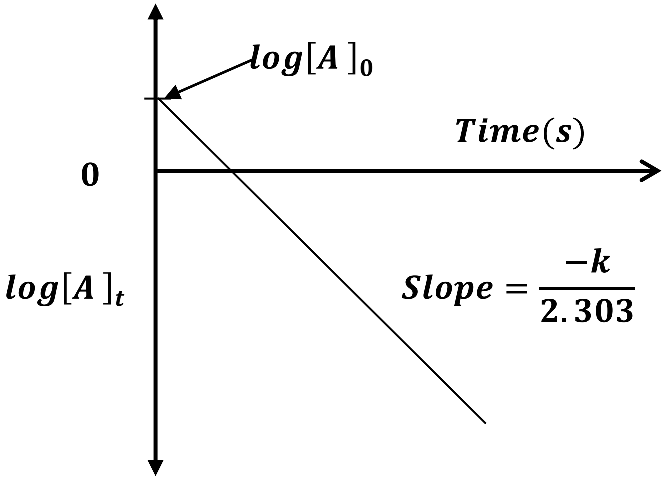
$$then \ [A]_0 = 10^x.$$

*The slope of the graph , $Slope = \frac{-k}{2.303}$ from which th**e rate constant can be obtained** with units s^{-1}*

***Half-life is then obtained** from*

$$t_{1/2} = \frac{0.693}{k}$$

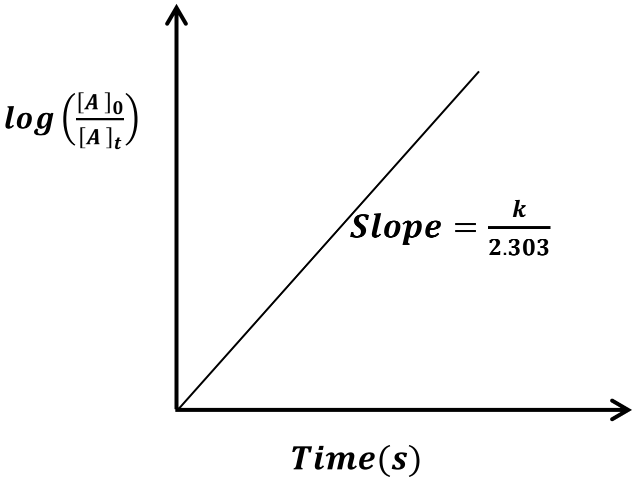
N.B; The graph above has a slightly different look when some or all the values of $[A]_t$ are less than one.



Also:

$$2.303\log\left(\frac{[A]_0}{[A]_t}\right) = kt$$
$$\log\left(\frac{[A]_0}{[A]_t}\right) = \frac{k}{2.303}t$$
$$compare\ with\ y \quad = \quad mx \quad + \ 0$$

A graph of $\log\left(\frac{[A]_0}{[A]_t}\right)$ against time (t) can be plotted;



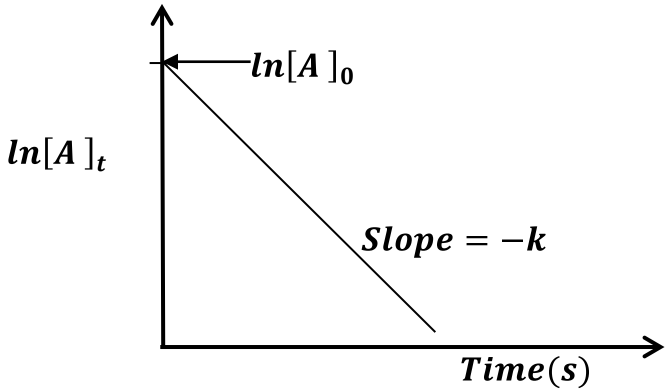
The graph of $\log\left(\frac{[A]_0}{[A]_t}\right)$ *against* ***time*** *is a* ***straight line*** *with* ***a positive gradient*** *through* ***the origin****.*
The slope of the graph **,** $Slope = \frac{k}{2.303}$ *from which th****e rate constant can be obtained*** *with units* s^{-1}
Half-life is then obtained *from*
$$t_{1/2} = \frac{0.693}{k}$$

The integrated form of the rate equation for a first order reaction can also be given as:

$$\boldsymbol{ln\left(\frac{[A\,]_0}{[A\,]_t}\right) = kt}$$
$$\boldsymbol{ln[A\,]_0 - ln[A\,]_t = kt}$$

$$\boldsymbol{-ln[A\,]_t = kt - ln[A\,]_0}$$
$$\boldsymbol{ln[A\,]_t = -kt + log[A\,]_0}$$
$$\boldsymbol{compare\ with\ \ y \ = \ \ mx \ + \ c}$$

A graph of $ln[A\,]_t$ against time(t) can be plotted;



The graph of $\boldsymbol{ln[A\,]_t}$ *against* ***time*** *is a* ***straight line*** *with* ***a negative gradient*** *with an* ***intercept on the*** $\boldsymbol{ln[A\,]_t}$ ***axis****. The intercept on the concentration axis gives the value of* $\boldsymbol{ln[A\,]_0}$

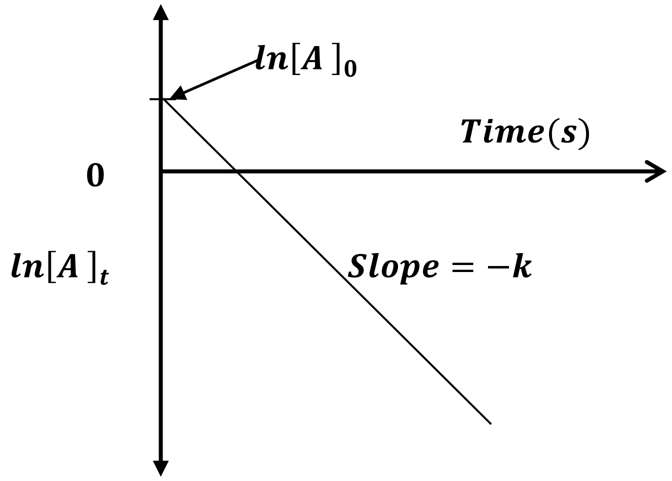
$$\boldsymbol{if\ ln[A\,]_0 = x}$$
$$\boldsymbol{then\ [A\,]_0 = 10^x.}$$

The slope of the graph **,** $\boldsymbol{Slope = -k}$ *from which th****e rate constant can be obtained*** *with units* $\boldsymbol{s^{-1}}$

Half-life is then obtained *from*

$$\boldsymbol{t_{1/2} = \frac{0.693}{k}}$$

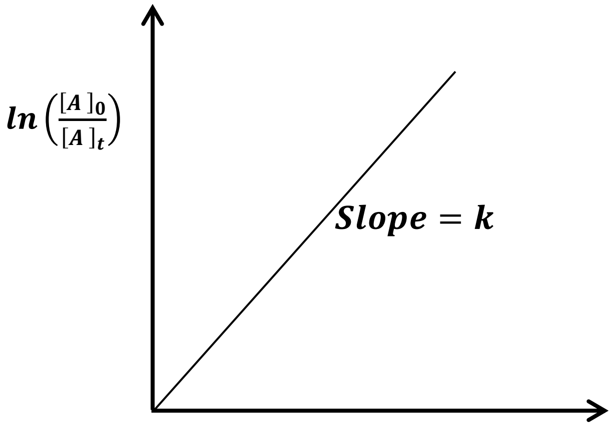
N.B; The graph above has a slightly different look $[A\,]_t$ are less than one.



Also:

$$\boldsymbol{ln\left(\frac{[A\,]_0}{[A\,]_t}\right) = kt}$$
$$\boldsymbol{ln\left(\frac{[A\,]_0}{[A\,]_t}\right) = kt}$$
$$\boldsymbol{compare\ with \quad y \quad = mx \quad + \ 0}$$

A graph of $ln\left(\frac{[A]_0}{[A]_t}\right)$ against time (t) can be plotted;



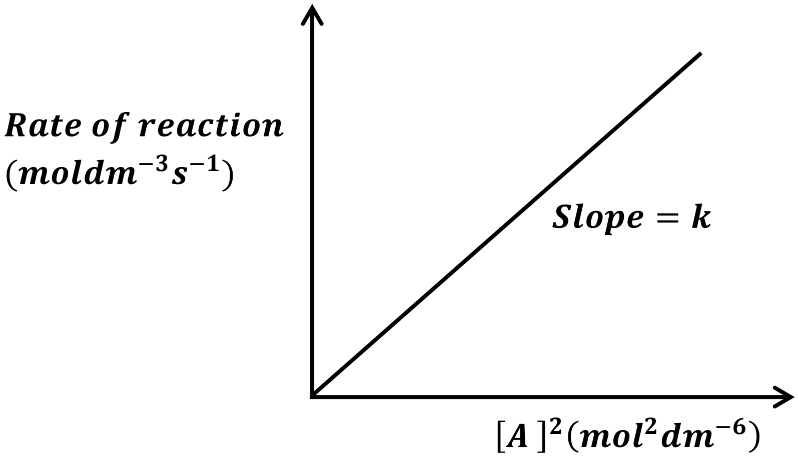
The graph of $ln\left(\frac{[A]_0}{[A]_t}\right)$ *against* ***time*** *is a* ***straight line*** *with* ***a positive gradient*** *through* ***the origin****.*
The slope of the graph **,** $Slope = k$ *from which th****e rate constant can be obtained*** *with units* s^{-1}
Half-life is then obtained *from*
$t_{1/2} = \frac{0.693}{k}$

3. Graphs for second order reactions

From the rate equation $Rate = k[A]^2$

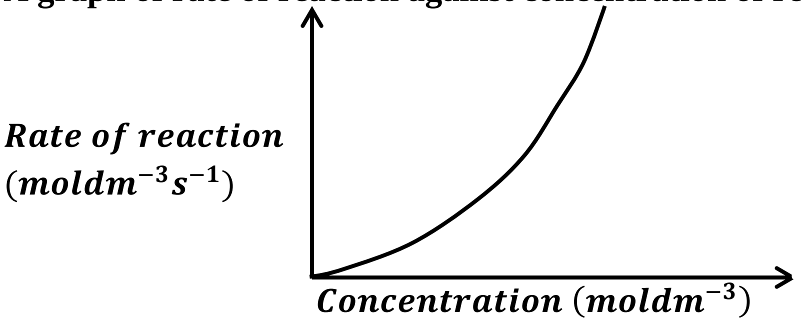
Comparing with: $y = ax^2$

A graph of rate of reaction against square of concentration of reactant, $[A]^2$ can be plotted



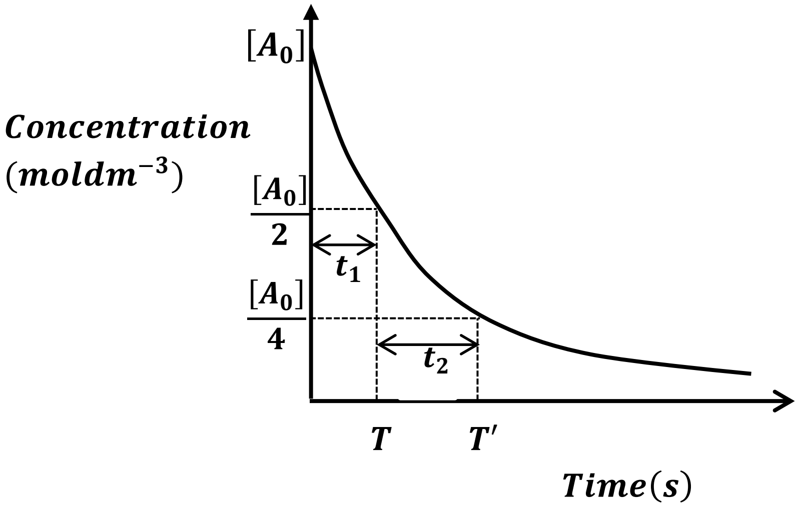
The graph of ***rate of reaction*** *against* ***square of concentration of reactant*** *is a* ***straight line through the origin.*** *The slope of the graph* **,** $Slope = k$ *from which th****e rate constant can be obtained*** *with units* s^{-1}
Half-life is then obtained *from*
$t_{1/2} = \frac{1}{k[A]_0}$

A graph of rate of reaction against concentration of reactant, $[A]$can be plotted



The graph of ***rate of reaction*** *against* ***concentration of reactant*** *is a* ***curve through the origin with a positive gradient.***

A graph of concentration of reactant against time



The graph of ***concentration*** *against* ***time*** *is a* ***curve with a negative gradient.*** *The slope of the graph* ***at a given point is the rate of reaction at that time.***

From this graph half-life is inversely proportional to concentration. Therefore the half-life gets greater as the reaction proceeds. Therefore $t_2 = 2t_1$

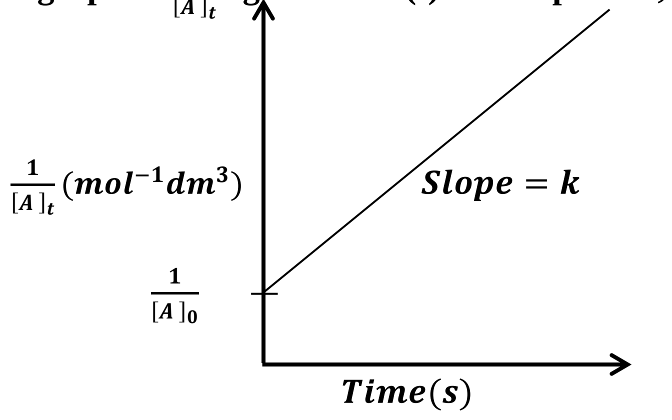
The integrated form of the rate equation for a second order reaction is given as:

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$compare\ with\ y = mx + c$$

A graph of $\frac{1}{[A]_t}$ against time(t) can be plotted;



The graph of $\frac{1}{[A]_t}$ *against* ***time*** *is a* ***straight line*** *with* ***a positive gradient*** *and* ***an intercept on the*** $\frac{1}{[A]_t}$ ***axis****. The intercept is equal to* $\frac{1}{[A]_0}$ ***from which the initial concentration*** $[A]_0$ *can be obtained.*

The slope of the graph **,** $Slope = k$ *from which th****e rate constant can be obtained*** *with units* $mol^{-1}dm^{3}s^{-1}$

Half-life is then obtained *from*

$$t_{1/2} = \frac{1}{k[A]_0}$$

N.B: For the graphs where concentration of reactant is used, volume of reactant can as well be used.

USING KINETICS DATA TO OBTAIN ORDER OF REACTION, RATE OF REACTION, RATE CONSTANTS AND HALF-LIFE

Order of reaction can be determined by the following methods:

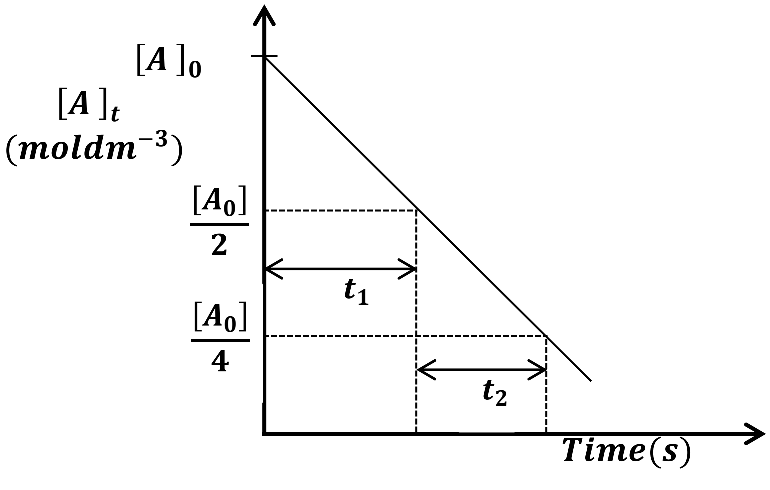
(a) Half-life method
(b) Graphical method
(c) Initial rate method

(a) ***Using the half-life method***.

The half-life can be used to deduce order of reaction by relating it to the initial concentration of the reactant. This can be interpreted using a graph of concentration against time.

For a zero order reaction, half-life is directly proportional to the initial concentration of the reactant.

A graph of concentration of reactant against time for a zero order reaction

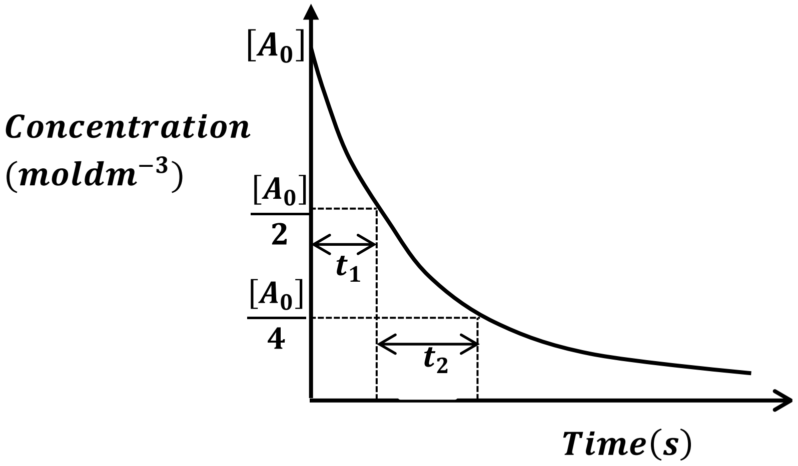


$$t_{1/2} = \frac{[A]_0}{2k}$$

If it is found that $t_1 > t_2$, then the reaction is zero order with respect to the reactant. The half life decreases as the initial concentration is reduced

For a first order reaction, half-life is independent of the initial concentration of the reactant

A graph of concentration of reactant against time for a first order reaction

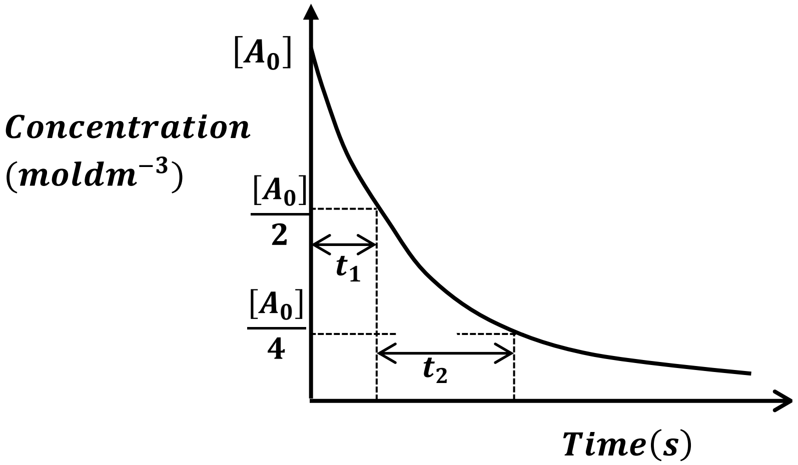


$$t_{1/2} = \frac{0.693}{k}$$

If it is found that $t_1 \approx t_2$, then the reaction is first order. The half life remains constant as the initial concentration is reduced

For a second order reaction, half-life is inversely proportional to the initial concentration of the reactant

A graph of concentration of reactant against time for a second order reaction



$$t_{1/2} = \frac{1}{k[A]_0}$$

If it is found that $t_2 > t_1$, then the reaction is second order. The half life increases as the initial concentration is reduced

Questions

1. The kinetics data for the reaction between P and sodium hydroxide is shown in the table below.

Concentration of P$(moll^{-1})$	1.05	0.88	0.74	0.51	0.37	0.26	0.16	0.10
Time (minutes)	0.0	3.5	7.0	14.5	20.0	27.0	35.5	45.0

(b) Plot a graph of concentration of P against time

(c) From the graph determine:

(i) the half-life of P

(ii) order of the reaction

(iii) the rate constant for the reaction.

2. Hydrogen peroxide decomposes in presence of iron(III) chloride catalyst. The order of the reaction can be found by withdrawing aliquots of the solution, adding dilute sulphuric acid and titrating with potassium manganate(VII) solution. The volume of manganate(VII) solution is a measure of concentration of hydrogen peroxide remaining after a certain time. The table below shows the volume of potassium manganate(VII) required at various time intervals.

Time (minutes)	0	5	10	15	20	25	30
Volume of potassium manganate(VII)(cm^3)	30	23.4	18.3	14.7	14.2	8.7	6.8

(a) Plot a graph of volume of potassium manganate(VII) solution against time.

(b) From the graph determine the:

(i) half-life of the reaction

(ii) order of the reaction. Give a reason for your answer.

(c) Write down the rate equation for the decomposition of hydrogen peroxide

(d) Calculate the rate constant for the reaction.

3. (a) State what is meant by the term:

(i) Order of reaction

(ii) Half-life of reaction

(b) The table below shows the kinetic data obtained for hydrolysis of methylethanoate in acidic media.

$[CH_3COOCH_3](moldm^{-3})$	0.241	0.161	0.109	0.073	0.046	0.034
Time (minutes)	0	60	120	180	240	320

Plot a graph of concentration of methyl ethanoate against time

(c) Using the graph in (b), determine the:

(i) half-life of the reaction

(ii) order of the reaction with respect to CH_3COOCH_3. Give a reason for your answer

(d) Calculate the rate constant and indicate its units.

4. (a) Dinitrogen pentoxide decomposes according to the equation;

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

The mechanism for the reaction is as shown below:

$$Step\ 1 : \quad N_2O_5 \longrightarrow NO_2 + NO_3$$
$$Step\ 2 : \quad N_2O_5 + NO_3 \longrightarrow 3NO_2 + O_2$$

(i) Define the term molecularity

(ii) Given that the above reaction is unimolecular. Identify the rate determining step of the reaction. Give a reason for your answer.

(b) 0.2M benzene diazonium chloride decomposes in the presence of water according to the equation:

$$C_6H_5N_2^+Cl^-(aq) + H_2O(l) \longrightarrow C_6H_5OH(aq) + N_2(g)$$

The volume of nitrogen gas evolved was recorded at different time intervals shown below.

Time (seconds)	0	10	20	30	40	50	60	70	80
Volume of $N_2(dm^3)$	0.0	0.42	0.70	0.90	1.08	1.22	1.28	1.30	1.30

(i) Plot a graph of volume of nitrogen gas against time. Use your graph to determine the initial rate

(ii) The experiment was repeated with 0.05M benzene diazonium chloride at 40℃ and the initial rate was found to be $0.0205dm^3s^{-1}$. Calculate the order of reaction with respect to benzene diazonium chloride.

(c) Write the rate equation if the concentration of water remains constant during the reaction

(d) State the effect of increasing temperature on the value of the rate constant.

5. The data below was obtained for the reaction between benzoyl chloride with phenylamine, starting with equal concentrations of the reactants.

Time (minutes)	0	5	10	20	30
Concentration of phenylamine$(moldm^{-3})$	0.0200	0.0133	0.0100	0.0069	0.0051

(i) Plot a graph of concentration of phenylamine against time

(ii) Use your graph to determine the deduce the order of reaction. Explain your answer.

(b) Using the graphical method

The order of a given reaction can be obtained by finding out a suitable graph that forms a straight line against. The graph should have a given variable of experimental data plotted against time as summarised below. The same graphs can be used to find the **rate constants** hence **the half-life.**

Order of reaction	**Zero order**	**First order**	**Second order**
Integrated rate equation	$[A]_t = -kt + [A]_0$	$ln[A]_t = -kt + ln[A]_0$ or $log[A]_t = -\frac{kt}{2.303} + log[A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
Suitable straight line graph to verify the order of reaction	**A graph of concentration of reactant against time is a straight line graph with a negative gradient**	**A graph of $ln[A]_t$ against time is a straight line graph with a negative gradient** **or** **A graph of $log[A]_t$ against time is a straight line graph with a negative gradient**	**A graph of $\frac{1}{[A]_t}$ against time is a straight line graph with a positive gradient**

Expression to obtain the rate constant	$slope = -k$	$For\ ln\ graph, slope = -k$ $For\ log\ graph, slope = \frac{-k}{2.303}$	$slope = k$
Expression for half-life	$t_{1/2} = \frac{[A\,]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A\,]_0}$

Questions

1. The data in the table below was obtained for the reaction

$$2B \longrightarrow C\ +\ D$$

Time (minutes)	0	1.3	2.0	4.0	5.3
$\boldsymbol{[B](moldm^{-3})}$	0.851	0.575	0.468	0.269	0.182

(a) Plot a graph of $log_{10}[B]$ against time.

(b) From the graph, determine the order of the reaction. Give a reason for your answer.

(c) Calculate:

(i) the rate constant for the reaction

(ii) the half-life of the reaction

2. The table below shows the kinetics data for oxidation of methanoic acid using bromine water.

$$Br_2(aq) + HCOOH(aq) \longrightarrow 2HBr(aq) + CO_2(g)$$

Time ($\boldsymbol{s}$)	10	20	30	40	50	60
$\boldsymbol{ln[Br_2]}$	0.22	0.04	-0.16	-0.33	-0.51	-0.71

(i) Plot a graph of $ln[Br_2]$ against time

(ii) Use the graph to find the order of reaction. Give a reason for your answer.

(iii) Find the original concentration of bromine solution

(iv) Calculate the rate constant.

3. The table below shows the kinetics data for the reaction:

$$A + H_2O \xrightarrow{H^+\ catalyst} 2B$$

Time ($\boldsymbol{minutes}$)	0	10	20	30	40	50	60
$\boldsymbol{log_{10}[A]}$	0.398	0.199	0.041	-0.200	-0.377	-0.602	-0.796

(a) Plot a graph of $log_{10}[A]$ against time

(b) From the graph to deduce the order of reaction. State a reason for your answer.

(c) Calculate the ;

(i) rate constant for the reaction

(ii) half life for the reaction

4. Buta-1,3-diene (C_4H_6) reacts to form products above room temperature. The table below shows the concentration of buta-1,3-diene at 326℃ after different intervals of time.

Time, t ($\boldsymbol{s}$)	900	1800	3600	6000
$[\boldsymbol{C_4H_6}](\boldsymbol{moldm^{-3}})$	0.0143	0.0123	0.00952	0.00730

(a) Plot a graph of $^1/_t$ against concentration of buta-1,3-diene.

(b) Plot a graph of $\frac{1}{[\boldsymbol{C_4H_6}]}$ against time.

(c) Using your graph to:
  (i) state the order of the reaction and give a reason for your answer.
  (ii) Calculate the initial concentration of buta-1,3-diene.
  (iii) Calculate the rate constant for the reaction and state its units.
  (iv) Determine the half life of the reaction.
  (v) Write the rate equation for the reaction

5. The decomposition of nitrogen dioxide was investigated at 300℃.

$$2NO_2(g) \xrightarrow{\qquad} 2NO(g) + O_2(g)$$

The following data was obtained.

Time, t ($\boldsymbol{s}$)	0	100	200	300
$[\boldsymbol{NO_2}](\boldsymbol{moldm^{-3}})$	0.01	0.0065	0.0045	0.0038

(a) Plot a graph of $\frac{1}{[NO_2]}$ against time.

(b) Using your graph to state the order of the reaction and give a reason for your answer.

(c) Calculate the :
  (i) rate constant for the reaction and state its units.
  (ii) Determine the half life of the reaction.
  (iii) Write the rate equation for the reaction

(c) ***Using the initial rate method***

The initial rate method can be used to find the order of reaction with respect to each reactant hence the overall order. The rate equation / rate law can therefore be deduced hence the rate constant calculated.

A number of experiments are done by varying the concentration of one of the reactants and the concentrations of all the other reactants are kept constant. The initial rates of the reaction at each concentration are got as the slope form concentration-time graph.

The experiments are repeated by varying the concentration of the second reactant and keeping the concentrations of all the other reactants constant.

The orders with respect to all the reactants are then determined either by **deduction** or **calculation**.

Order of reaction with respect to a given reactant	Effect on concentration of reactant	Effect on initial rate of reaction
Zero order	***Halved***	**Rate remains constant**
	multiplied by a quarter	
	Doubled	
	Trebled	
	quadrupled	
First order	***Halved***	***also halved***
	multiplied by a quarter	***also multiplied by a quarter***
	Doubled	***also doubled***
	Trebled	***also trebled(multiplied by 3)***
	Quadrupled	***also quadrupled***
Second order	***Halved***	***divided by four (multiplied by $\frac{1}{4}$)***
	multiplied by a quarter	***multiplied by $\frac{1}{8}$***
	Doubled	***Quadrupled(multiplied by 4)***
	Trebled	***multiplied by six***
	Quadrupled	***multiplied by eight***

Both methods will be used in the examples below but choose the simpler alternative of your choice.

Examples

1. For the reaction $A(g) + B(g) \xrightarrow{\quad\quad} Products$

The following data was obtained.

Experiment	**Concentration of A($moldm^{-3}$)**	**Concentration of B($moldm^{-3}$)**	**Initial rate ($moldm^{-3}s^{-1}$)**
1	2.50×10^{-1}	4.00×10^{-1}	1.50×10^{-3}
2	2.50×10^{-1}	8.00×10^{-1}	3.00×10^{-3}
3	5.00×10^{-1}	4.00×10^{-1}	6.00×10^{-3}

(a) Determine the order of reaction with respect to:

(i) A

(ii) B

(b) Write the rate equation

(c) Calculate the rate constant and state its units.

(a)

(i) ***In experiments 1 and 3, when the concentration of B is kept constant and that of A doubled, the rate of reaction quadruples. Therefore the order of reaction with respect to A is 2.***

or

Let the order of reaction with respect to A be x and order of reaction with respect to B be y.

Considering experiments 1 and 3 where $[B]$ is constant;

$$Rate = k[A]^x[B]^y$$

$$1.50 \times 10^{-3} = k(2.50 \times 10^{-1})^x(4.00 \times 10^{-1})^y \ldots\ldots.(i)$$

$$6.00 \times 10^{-3} = k(5.00 \times 10^{-1})^x(4.00 \times 10^{-1})^y \ldots\ldots(ii)$$

$$Equation\ (ii) \div Equation(i)$$

$$\frac{6.00 \times 10^{-3}}{1.50 \times 10^{-3}} = \frac{k(5.00 \times 10^{-1})^x}{k(2.50 \times 10^{-1})^x}\frac{(4.00 \times 10^{-1})^y}{(4.00 \times 10^{-1})^y}$$

$$4 = 2^x$$

$$2^2 = 2^x$$

$$\boldsymbol{x} = \mathbf{2}$$

(i) ***In experiments 1 and 2, when the concentration of A is kept constant and that of B doubled, the rate of reaction also doubles. Therefore the order of reaction with respect to B is 1.***

or

Considering experiments 1 and 2 where $[A]$ is constant;

$$Rate = k[A]^x[B]^y$$

$$1.50 \times 10^{-3} = k(2.50 \times 10^{-1})^x(4.00 \times 10^{-1})^y \ldots\ldots.(i)$$

$$3.00 \times 10^{-3} = k(2.50 \times 10^{-1})^x(8.00 \times 10^{-1})^y \ldots\ldots(ii)$$

$$Equation\ (ii) \div Equation(i)$$

$$\frac{3.00 \times 10^{-3}}{1.50 \times 10^{-3}} = \frac{k(2.50 \times 10^{-1})^x}{k(2.50 \times 10^{-1})^x}\frac{(8.00 \times 10^{-1})^y}{(4.00 \times 10^{-1})^y}$$

$$2 = 2^y$$

$$2^1 = 2^y$$

$$\boldsymbol{y} = \mathbf{1}$$

(b) $\boldsymbol{Rate = k[A]^2[B]}$

(c) Considering experiment one;

$$Rate = k[A]^2[B]$$

$$k = \frac{Rate}{[A]^2[B]} = \frac{1.50 \times 10^{-3}}{(2.50 \times 10^{-1})^2(4.00 \times 10^{-1})}\frac{moldm^{-3}s^{-1}}{mol^3dm^{-9}} = \mathbf{0.06}\boldsymbol{mol^{-2}dm^6s^{-1}}$$

2. (a) Explain what is meant by the term order of a reaction

(b) The following kinetics data was obtained for the reaction between an alkylhalide, Q and sodium hydroxide solution

Experiment	$[Q](moldm^{-3})$	$[\bar{O}H](moldm^{-3})$	**Initial rate** $(moldm^{-3}s^{-1})$
1	**0.100**	**0.500**	2.0×10^{-3}
2	**0.050**	**0.250**	1.0×10^{-3}
3	**0.100**	**0.250**	2.0×10^{-3}
4	**0.075**	**0.250**	1.5×10^{-3}

Determine the order of the reaction with respect to Q and sodium hydroxide and give a reason for your answer.

(i) order with respect to Q and reason

(ii) order with respect to sodium hydroxide and reason

(c) (i) Write the rate equation for the reaction

(ii) Calculate the rate constant and give its units

(iii) Write the general structure of Q and give a reason for your answer.

(b)

(i) ***The order of reaction with respect to Q is 1.***

Reason: When the concentration of $\bar{O}H$ is kept constant and that of Q doubled, the rate of reaction doubles.

or

The order of reaction with respect to Q is 1.

Reason: Considering experiments 2 and 3 where $[\bar{O}H\ ]$ is constant;

$$Rate = k[Q]^x[\bar{O}H\ ]^y$$

$$1.0 \times 10^{-3} = k(0.05)^x(0.25)^y \ldots\ldots\ldots\ldots(i)$$

$$2.0 \times 10^{-3} = k(0.1)^x(0.25)^y \ldots\ldots\ldots\ldots\ldots\ldots(ii)$$

$$Equation\ (ii) \div Equation(i)$$

$$\frac{2.0 \times 10^{-3}}{1.0 \times 10^{-3}} = \frac{k(0.1)^x}{k(0.05)^x}\frac{(0.25)^y}{(0.25)^y}$$

$$2 = 2^x$$

$$2^1 = 2^x$$

$$\boldsymbol{x} = \mathbf{1}$$

(ii) ***The order of reaction with respect to sodium hydroxide is zero.***

Reason: When the concentration of Q is kept constant and that of $\bar{O}H$ halved, the rate of reaction remains constant.

or

The order of reaction with respect to sodium hydroxide is 0.

Reason: Considering experiments 1 and 3 where $[Q\ ]$ is constant;

$$Rate = k[Q]^x[\bar{O}H\ ]^y$$

$$2.0 \times 10^{-3} = k(0.1)^x(0.5)^y \ldots\ldots\ldots\ldots(i)$$

$$2.0\times10^{-3}=k(0.1)^{x}(0.25)^{y}\ \dots\dots\dots\dots\dots\dots\dots(ii)$$

$$Equation\ (ii)\div Equation(i)$$

$$\frac{2.0\times10^{-3}}{2.0\times10^{-3}}=\frac{k(0.1)^{x}}{k(0.1)^{x}}\frac{(0.25)^{y}}{(0.5)^{y}}$$

$$1\quad=\quad0.5^{y}$$

$$0.5^{0}\quad=\quad0.5^{y}$$

$$\boldsymbol{y}\quad=\quad\mathbf{0}$$

(c) (i) $\boldsymbol{Rate=k[Q]}$

(ii) Considering experiment one;

$$Rate=k[Q]$$

$$k=\frac{Rate}{[Q]}=\frac{2.0\times10^{-3}}{0.1}\frac{moldm^{-3}s^{-1}}{moldm^{-3}}=\mathbf{0.02\ s^{-1}}$$

(iii) $\boldsymbol{R_3CX\ where\ R\ is\ an\ alkyl\ group\ and\ X\ is\ a\ halogen\ atom}$

Reason: Q is a tertiary alkylhalide because the ***rate of reaction depends*** on the ***concentration of alkylhalide*** but ***independent of the hydroxyl ion***.

3. (a) What is meant by the term rate constant

(b) The following results were obtained for two compounds A and B reacting to give product C.

$$\boldsymbol{A+B\longrightarrow C}$$

Experiment	Initial $[A](moldm^{-3})$	Initial $[B](moldm^{-3})$	Initial rate $(moldm^{-3}s^{-1})$
1	0.2	0.24	2.0×10^{-4}
2	0.4	0.24	8.0×10^{-4}
3	0.6	0.48	2.88×10^{-2}

(i) Deduce the rate equation

(ii) Calculate the rate constant and give its units

(b)

(i) Let order of reaction with respect to A be m and order of reaction with respect to B be n.

Considering experiments 1 and 2 where $[B\ ]$ is constant;

$$Rate=k[A]^{m}[B\ ]^{n}$$

$$2.0\times10^{-4}=k(0.2)^{m}(0.24)^{n}\ \dots\dots\dots\dots..(i)$$

$$8.0\times10^{-4}=k(0.4)^{m}(0.24)^{n}\ \dots\dots\dots\dots\dots\dots\dots(ii)$$

$$Equation\ (ii)\div Equation(i)$$

$$\frac{8.0\times10^{-4}}{2.0\times10^{-4}}=\frac{k(0.4)^{m}}{k(0.2)^{m}}\frac{(0.24)^{n}}{(0.24)^{n}}$$

$$4\quad=\quad2^{m}$$

$$2^{2}\quad=\quad2^{m}$$

$$\boldsymbol{m}\quad=\quad\mathbf{2}$$

Also considering experiments 2 and 3;

$$Rate=k[A]^{m}[B\ ]^{n}$$

$$m = 2$$
$$8.0 \times 10^{-4} = k(0.4)^2(0.24)^n \ldots\ldots\ldots(i)$$
$$2.88 \times 10^{-2} = k(0.6)^2(0.48)^n \ldots\ldots\ldots\ldots..(ii)$$
$$Equation\ (ii) \div Equation(i)$$
$$\frac{2.88 \times 10^{-2}}{8.0 \times 10^{-4}} = \frac{k(0.6)^2}{k(0.4)^2}\frac{(0.48)^n}{(0.24)^n}$$
$$36 \quad = \quad 1.5^2 \times 2^n$$
$$36 \quad = 2.25 \times\ 2^n$$
$$\mathbf{16} \quad = \quad \mathbf{2^n}$$
$$\mathbf{2^4} \quad = \quad \mathbf{2^n}$$
$$\boldsymbol{n} \quad = \quad \mathbf{4}$$
$$\boldsymbol{Therefore\ Rate = k[A]^2[B]^4}$$

(ii) Considering experiment one;

$$Rate = k[A]^2[B]^4$$
$$k = \frac{Rate}{[A]^2[B]^4} = \frac{2.0 \times 10^{-4}}{(0.2)^2(0.24)^4}\frac{moldm^{-3}s^{-1}}{(moldm^{-3})^6} = \mathbf{1.507\ mol^{-5}dm^{15}\ s^{-1}}$$

4. (a)(i) Explain what is meant by the order of chemical reaction.

(ii) Name two methods used to determine orders of reactions.

(b) The results obtained for the kinetics of the decomposition of nitrogen(V) oxide are given in the table below.

$[\boldsymbol{N_2O_5}](\boldsymbol{moldm^{-3}})$	**Initial rate** $(\boldsymbol{moldm^{-3}s^{-1}})$
$\mathbf{1.6 \times 10^{-3}}$	$\mathbf{0.12}$
$\mathbf{2.4 \times 10^{-3}}$	$\mathbf{0.18}$
$\mathbf{3.2 \times 10^{-3}}$	$\boldsymbol{x}$

Calculate the:

(i) **order of reaction**

(ii) **value of $\boldsymbol{x}$**

(b) (i) ***When the concentration of nitrogen(V) oxide is multiplied by 1.5, the rate of reaction also increases by 1.5 times. Therefore the order of reaction is one.***

or

Let the order of reaction be f.

Considering experiments 1 and 2;

$$Rate = k[N_2O_5]^f$$
$$1.6 \times 10^{-3} = k(0.12)^f \ldots\ldots\ldots\ldots..(i)$$
$$2.4 \times 10^{-3} = k(0.18)^f \ldots\ldots\ldots\ldots..(ii)$$
$$Equation\ (ii) \div Equation(i)$$
$$\frac{2.4 \times 10^{-3}}{1.6 \times 10^{-3}} = \frac{k(0.18)^f}{k(0.12)^f}$$
$$1.5^1 \quad = \quad 1.5^f$$
$$\boldsymbol{f} \quad = \quad \mathbf{1}$$

(ii) Consider experiments 2 and 3

$$2.4 \times 10^{-3} = k(0.18)^f$$
$$2.4 \times 10^{-3} = 0.18k \ldots\ldots\ldots(i)$$
$$3.2 \times 10^{-3} = x\ k \ldots\ldots\ldots..(ii)$$
$$Equation\ (ii) \div Equation(i)$$
$$\frac{3.2 \times 10^{-3}}{2.4 \times 10^{-3}} = \frac{x\ k}{0.18\ k}$$
$$x = \frac{0.18 \times 3.2 \times 10^{-3}}{2.4 \times 10^{-3}}$$
$$\boldsymbol{x = 0.24}$$

5. (a) Differentiate between order of reaction and molecularity

(b) The rate equation for the reaction between substances A, B and C is given by;

$\boldsymbol{Rate = k[A]^x[B]^y[C]^z}$**, where** $\boldsymbol{x + y + z = 4}$**.**

The kinetics of the reaction is given below.

Experiment	$[A](moldm^{-3})$	$[B](moldm^{-3})$	$[C](moldm^{-3})$	Initial rate $(moldm^{-3}s^{-1})$
1	0.20	0.10	0.20	8.0×10^{-5}
2	0.05	0.10	0.20	2.0×10^{-5}
3	0.10	0.05	0.20	2.0×10^{-5}
4	0.10	0.10	0.10	n

(i) Deduce the order of reaction with respect to A, B and C respectively.

(ii) Determine the value of n

(iii) Calculate the value of the rate constant, $\boldsymbol{k}$ **and state its units.**

(iv) Find the initial rate of reaction when $\boldsymbol{[A] = 0.15\ moldm^{-3}}$ **,** $\boldsymbol{[B] = 0.25\ moldm^{-3}}$**and** $\boldsymbol{[C] = 0.30\ moldm^{-3}}$.

(b)(i) ***In experiments 1 and 2, when both the concentrations of B and C are kept constant and the concentration of A reduced four times, the rate of reaction also reduces four times. Therefore the order of reaction with respect to A is 1.***

or

Considering experiments 1 and 2 where $[B]$ and $[C]$ are constant;

From $= k[A]^x[B]^y[C]^z$.

$$8.0 \times 10^{-5} = k(0.2)^x(0.1)^y(0.2)^z \ldots\ldots(i)$$

$$2.0 \times 10^{-5} = k(0.05)^x(0.1)^y(0.2)^z \ldots\ldots(ii)$$

$$Equation\ (ii) \div Equation(i)$$

$$\frac{2.0 \times 10^{-5}}{8.0 \times 10^{-5}} = \frac{k(0.2)^x}{k(0.05)^x}\frac{(0.1)^y}{(0.1)^y}\frac{(0.2)^z}{(0.2)^z}$$

$$0.25^1 = 0.25^x$$

$$\boldsymbol{x = 1}$$

In experiments 1 and 3, when the concentration of C is kept constant and both the concentrations of A and B halved, the rate of reaction is multiplied by a quarter (reduces four times). Therefore the reaction is first order with respect to A and also first order with respect to B

Or

Considering experiments 1 and 3 where $[C]$ is constant;

From $Rate = k[A]^x[B]^y[C]^z$

$$x = 1$$

$$8.0 \times 10^{-5} = k(0.2)^1(0.1)^y(0.2)^z \ldots\ldots(i)$$

$$2.0 \times 10^{-5} = k(0.1)^1(0.05)^y(0.2)^z \ldots\ldots(ii)$$

$$Equation\ (ii) \div Equation(i)$$

$$\frac{2.0 \times 10^{-5}}{8.0 \times 10^{-5}} = \frac{k(0.1)^1}{k(0.2)^1}\frac{(0.05)^y}{(0.1)^y}\frac{(0.2)^z}{(0.2)^z}$$

$$0.25 = 0.5 \times 0.5^y$$

$$0.5 = 0.5^y$$

$$\boldsymbol{y} = \mathbf{1}$$

$$x + y + z = 4$$

$$1 + 1 + z = 4$$

$$z = 4 - 2$$

$$\boldsymbol{z = 2}$$

Therefore the order of reaction with respect to C is 2.

(ii) Consider experiments 1 and 4

$$Rate = k[A][B][C]^2$$

$$8.0 \times 10^{-5} = k \times 0.2 \times 0.1 \times (0.2)^2$$

$$8.0 \times 10^{-5} = 0.0008k \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(i)$$

$$n = k \times 0.1 \times 0.1 \times (0.1)^2$$

$$n = 0.0001k \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(ii)$$

$$Equation\ (ii) \div Equation(i)$$

$$\frac{n}{8.0 \times 10^{-5}} = \frac{0.0001k}{0.0008k}$$

$$n = \frac{8.0 \times 10^{-5} \times 0.0001}{0.0008} = \mathbf{1.0 \times 10^{-5}}$$

(iii) Considering experiment one;

$$Rate = k[A][B][C]^2$$

$$k = \frac{Rate}{[A][B][C]^2} = \frac{8.0 \times 10^{-5}}{0.2 \times 0.1 \times (0.2)^2}\frac{moldm^{-3}s^{-1}}{(moldm^{-3})^4} = \mathbf{0.1\ mol^{-3}dm^9s^{-1}}$$

(iv) $Rate = k[A][B][C]^2 = 0.1 \times 0.15 \times 0.25 \times 0.3^2 = \mathbf{3.38 \times 10^{-4} moldm^{-3}s^{-1}}$

6. The kinetics data for the reaction between nitrogen monoxide and oxygen are shown in the table below.

Experiment	$[NO](moldm^{-3})$	$[O_2](moldm^{-3})$	Initial rate $(moldm^{-3}s^{-1})$
1	$\mathbf{0.03}$	$\mathbf{0.03}$	$\mathbf{2.7 \times 10^{-5}}$
2	$\mathbf{0.03}$	$\mathbf{0.06}$	$\mathbf{5.4 \times 10^{-5}}$
3	$\mathbf{0.06}$	$\mathbf{0.03}$	$\mathbf{10.8 \times 10^{-5}}$

(a) Determine the order of reaction with respect to:

(i) nitrogen monoxide

(ii) oxygen

(b) Write the rate equation for the reaction

(c) Calculate the rate constant for the reaction and indicate its units.

(d) The rate of the reaction under certain conditions and a given temperature is x. Express the rate of reaction in terms of x when the following changes are made.

- **(i)** **The concentration of oxygen is halved while the concentration of nitrogen monoxide remains unchanged.**
- **(ii)** **The rate constant is doubled, by increasing temperature, but keeping the concentrations of oxygen and nitrogen monoxide unchanged.**
- **(iii)** **If 90% of oxygen is removed, without affecting the concentration of nitrogen monoxide**.

(a)

(i) ***In experiments 1 and 3, when the concentration of oxygen is kept constant and that of nitrogen monoxide is doubled, the rate of reaction quadruples. Therefore the order of reaction with respect to nitrogen monoxide is 2.***

or

Let the order of reaction with respect to nitrogen monoxide be x and order of reaction with respect to oxygen be y. Considering experiments 1 and 3 where $[O_2]$ is constant;

$$Rate = k[NO]^x[O_2]^y$$
$$2.7 \times 10^{-5} = k(0.03)^x(0.03)^y \ldots\ldots.(i)$$
$$10.8 \times 10^{-5} = k(0.06)^x(0.03)^y \ldots\ldots(ii)$$
$$Equation\ (ii) \div Equation(i)$$
$$\frac{10.8 \times 10^{-5}}{2.7 \times 10^{-5}} = \frac{k(0.06)^x}{k(0.03)^x}\frac{(0.03)^y}{(0.03)^y}$$
$$4 = 2^x$$
$$2^2 = 2^x$$
$$\boldsymbol{x} = \mathbf{2}$$

(ii) ***In experiments 1 and 2, when the concentration of nitrogen monoxide is kept constant and that of oxygen doubled, the rate of reaction also doubles. Therefore the order of reaction with respect to oxygen is 1.***

or

Considering experiments 1 and 2 where $[NO]$ is constant;

$$Rate = k[NO]^x[O_2]^y$$
$$2.7 \times 10^{-5} = k(0.03)^x(0.03)^y \ldots\ldots.(i)$$
$$5.4 \times 10^{-5} = k(0.03)^x(0.06)^y \ldots\ldots(ii)$$
$$Equation\ (ii) \div Equation(i)$$
$$\frac{5.4 \times 10^{-5}}{2.7 \times 10^{-5}} = \frac{k(0.03)^x}{k(0.03)^x}\frac{(0.06)^y}{(0.03)^y}$$
$$2 = 2^y$$
$$2^1 = 2^y$$
$$\boldsymbol{y} = \mathbf{1}$$

(b) $\boldsymbol{Rate = k[NO]^2[O_2]}$

(c) Considering experiment one;

$$Rate = k[NO]^2[O_2]$$
$$k = \frac{Rate}{[NO]^2[O_2]} = \frac{2.7 \times 10^{-5}}{(0.03)^2(0.03)}\frac{moldm^{-3}s^{-1}}{mol^3dm^{-9}} = \mathbf{1.0\ mol^{-2}dm^{6}s^{-1}}$$

(d) (i) $Rate = \frac{1}{2}x$

(ii) $Rate = 2x$

(iii) $Rate = \frac{10}{100}x = 0.1x$

Questions

1. The results below were obtained in an experiment to investigate the rate of hydrolysis of methylmethanoate at 298K.

Experiment	$[HCO_2CH_3](moldm^{-3})$	$[H^+](moldm^{-3})$	**Initial rate** $\times 10^3$ $(moldm^{-3}s^{-1})$
1	0.50	1.00	0.56
2	2.00	1.00	2.24
3	2.00	0.50	1.13

(a) Deduce the order of reaction with respect to:

(i) methlymethanoate

(ii) hydrogen ions

(b) (i) Calculate the overall order of reaction

(ii) Write the rate equation

(iii) Calculate the rate constant, k ate 298K . State its units

2. The initial rate of the reaction between the gases NO and H_2 was measured in a series of experiments at a constant temperature and the following rate equation was determined.

Experiment	**Initial** $[NO](moldm^{-3})$	**Initial** $[H_2](moldm^{-3})$	**Initial rate** $(moldm^{-3}s^{-1})$
1	3.0×10^{-3}	1.0×10^{-3}	7.2×10^{-5}
2	3.0×10^{-3}	0.5×10^{-3}	1.8×10^{-5}
3	1.5×10^{-3}	1.0×10^{-3}	3.6×10^{-5}

Using the data from experiment one, calculate the value for the rate constant, k, and state its units.

3. Various concentrations of X and Y were reacted at a constant temperature. The table below shows the initial concentrations of X and Y and their initial rates for the reaction.

Experiment	$[X](moldm^{-3})$	$[Y](moldm^{-3})$	**Initial rate** $(moldm^{-3}s^{-1})$
1	0.2	0.2	3.5×10^{-4}
2	0.4	0.4	1.4×10^{-3}
3	0.8	0.4	5.6×10^{-3}

(a) State the order of reaction with respect to:

(i) X

(ii) Y

(b) Give reasons for your answers in (a)

(c) Determine the overall order of the reaction

(d) Calculate the value for the rate constant for the reaction.

4. (a) Complete the following reaction and write the accepted mechanism.

$$CH_3CO_2C_2H_5(l) + \bar{O}H(aq) \xrightarrow{H_2O/\ heat}$$

(b) The results obtained for the kinetics of the reaction in (a) above are shown in the table below.

Experiment	$[CH_3CO_2C_2H_5](moldm^{-3})$	$[\bar{O}H](moldm^{-3})$	**Initial rate** $(moldm^{-3}s^{-1})$
1	0.076	0.076	1.13×10^{-3}
2	0.038	0.152	1.13×10^{-3}
3	0.019	0.152	5.65×10^{-4}

Deduce the order of reaction with respect to:

(i) $\bar{O}H$

(ii) $CH_3CO_2C_2H_5$

(b) Write the rate equation for the reaction

(c) Calculate the rate constant, k, for the reaction and state its units.

5. The following results were obtained for the reaction between two substances A and B at different conditions.

Experiment	**Initial** $[A](moldm^{-3})$	**Initial** $[B](moldm^{-3})$	**Initial rate** $(moldm^{-3}s^{-1})$
1	0.50	0.50	2.0×10^{-2}
2	1.00	0.50	8.0×10^{-2}
3	1.00	1.00	16.0×10^{-2}

(a) Determine the :

(i) orders of reaction with respect to A and B respectively.

(ii) overall order of reaction

(b) Write an expression for the rate of reaction.
(c) Calculate the rate constant and state its units
(d) Determine the initial rate of reaction when $[A] = 0.60\, moldm^{-3}$ and $[B] = 0.30\, moldm^{-3}$.

6. The results of the experiments on the reaction of persulphate(peroxodisulphate) ions and iodide ions are shown below:

$$S_2O_8^{2-}(aq) + 2I^-(aq) \xrightarrow{\qquad} 2SO_4^{2-}(aq) + I_2(aq)$$

Experiment	**Concentration** $(moldm^{-3})$		**Initial rate** $(moldm^{-3}s^{-1})$
	$S_2O_8^{2-}$	I^-	
1	0.040	0.040	9.60×10^{-6}
2	0.080	0.040	1.92×10^{-5}
3	0.080	0.020	9.60×10^{-6}

(i) Write the rate equation for the reaction
(ii) Calculate the rate constant.
(iii) Find the initial rate of reaction when $[S_2O_8^{2-}] = 0.12\, moldm^{-3}$ and $[I^-] = 0.015\, moldm^{-3}$.

7. The data below was obtained for the reaction

$$A + B \xrightarrow{\qquad} Products$$

Experiment	**Initial concentrations** $(moldm^{-3})$		**Initial rate** $(moldm^{-3}s^{-1})$
	A	B	
1	2.0	2.0	3.2×10^{-5}
2	2.0	4.0	6.4×10^{-5}
3	4.0	2.0	x
4	4.0	4.0	2.56×10^{-4}

(a) Write the rate equation

(b) Calculate ;
  (i) the value of x
  (ii) the rate constant for the reaction and state its units

8. (a) An acidified solution of potassium bromide was added to aqueous potassium bromate(V) solution.
(i) State what was observed
(ii) Write equation for the reaction that took place
(d) The results of kinetics of the reaction in (a)(ii) are given in the table below.

Experiment	$[Br^-](moldm^{-3})$	$[BrO_3^-](moldm^{-3})$	$[H^+](moldm^{-3}$	**Initial rate** $(moldm^{-3}s^{-1})$
1	0.1	0.1	0.1	8.0×10^{-4}
2	0.1	0.2	0.1	1.6×10^{-3}
3	0.2	0.2	0.1	3.2×10^{-3}
4	0.1	0.1	0.2	4.8×10^{-3}

(i) Deduce the order(s) with respect to each of the reactants
(ii) State the overall order for the reaction
(iii) Write the rate equation

9. Bromine is formed by the reaction between bromide ions and bromate(V) ions and an acid.

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

The results of some experiments on the reaction in are given in the table below.

Experiment	**Concentration**$(moldm^{-3})$			**Initial rate** $(moldm^{-3}s^{-1})$
	$[BrO_3^-]$	$[Br^-]$	$[H^+]$	
1	0.10	0.10	0.10	1.2×10^{-3}
2	0.10	0.30	0.10	3.6×10^{-3}
3	0.20	0.10	0.10	2.4×10^{-3}
4	0.20	0.10	0.20	9.6×10^{-3}

(i) Deduce the rate law for the reaction.
(ii) State the overall order for the reaction
(iii) Find the value of the rate constant

10. The following data was obtained for the reaction between hydrogen peroxide and iodine ions and hydrogen ions

Experiment	**Concentration** $(moldm^{-3})$			**Initial rate** $(moldm^{-3}s^{-1})$
	$[I^-]$	$[H_2O_2]$	$[H^+]$	
1	0.01	0.01	0.01	1.76×10^{-6}
2	0.01	0.03	0.01	5.25×10^{-6}
3	0.02	0.03	0.01	1.05×10^{-5}
4	0.02	0.03	0.02	1.05×10^{-5}

(i) State the order of reaction with respect to:
H_2O_2
I^-
H^+
(ii) Write the rate equation for the reaction.
(iii) Calculate the rate constant, k for the reaction and indicate its units.

EXPERIMENTAL PROCEDURE FOR DETERMINING RATES OF REACTION AND ORDERS OF A REACTION

(a) Experiment to show that iodination of propanone is a zero order reaction with respect to iodine

A ***solution of propanone***, a ***solution of iodine in potassium iodide*** and ***a solution of sulphuric acid***, ***all of known concentration are prepared*** and put into a ***thermostat bath*** at the ***required temperature***.

A known volume of the propanone solution is pipetted and ***put into a conical flask followed by a known volume of the sulphuric acid to catalyse the reaction.***

A known volume of iodine in potassium iodide solution is added to the mixture and a ***stop watch is started simultaneously***.

The mixture is ***shaken*** and allowed to settle ***at a constant temperature***

After a few minutes, a ***fixed volume of the reacting mixture is pipetted*** and put into a container containing ***sodium hydrogencarbonate solution*** to ***stop the reaction*** by ***neutralizing the acid***.

The time at which the reaction stops is recorded.

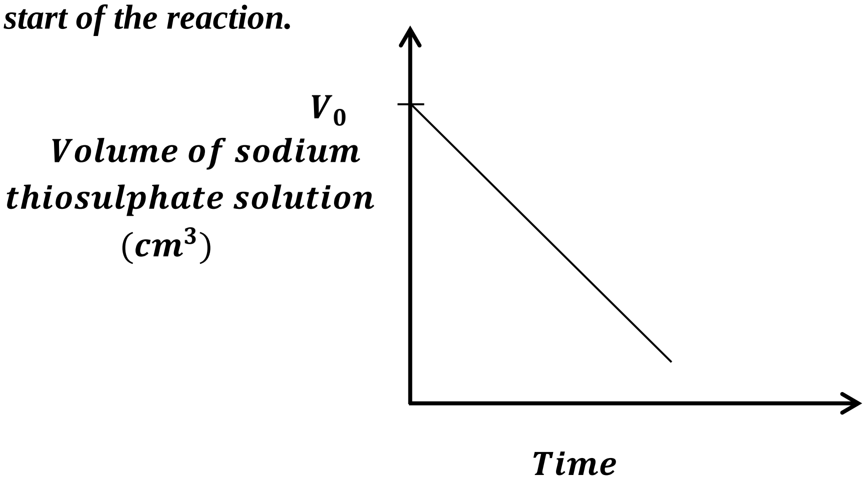
The ***resultant solution is titrated against a standard solution of sodium thiosulphate*** using ***starch indicator*** to ***determine the amount of iodine remaining***.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}$$

The analysis of the reacting mixture is repeated several times by changing the time taken for the reaction to take place before adding the reacting mixture to sodium hydrogen carbonate.

The original iodine in potassium iodide solution is also pipetted with a standard solution of sodium thiosulphate to obtain volume of sodium thiosulphate that reacts with it.

The ***volume of sodium thiosulphate required is plotted against the time elapsed since the start of the reaction.***



The graph obtained is a straight line with a negative gradient. This shows that the reaction is zero order with respect to iodine.

$$CH_3COCH_3(aq) + I_2(aq) \longrightarrow CH_3COCH_2I(aq) + HI(aq)$$

(b) Experiment to find the rate of reaction for the iodination of propanone

The procedure is the same as above but to find the rate of reaction, the gradient/slope of the graph at a given time is calculated. The value of the slope gives the rate of reaction.

(a) Experiment to show that the reaction between sodium thiosulphate and hydrochloric acid is first order reaction with respect to sodium thiosulphate

A known volume of sodium thiosulphate solution of known concentration is measured into a clean conical flask using a measuring cylinder.

The conical flask is placed on a white piece of paper marked with a cross.

A known volume of hydrochloric acid of a slightly higher concentration than sodium thiosulphate solution is added using and a stop clock started simultaneously.

The mixture is ***shaken*** and allowed to settle ***at a constant temperature***

Through the mixture, the cross on the white piece of paper is viewed and the stop clock stopped when the cross just becomes invisible.

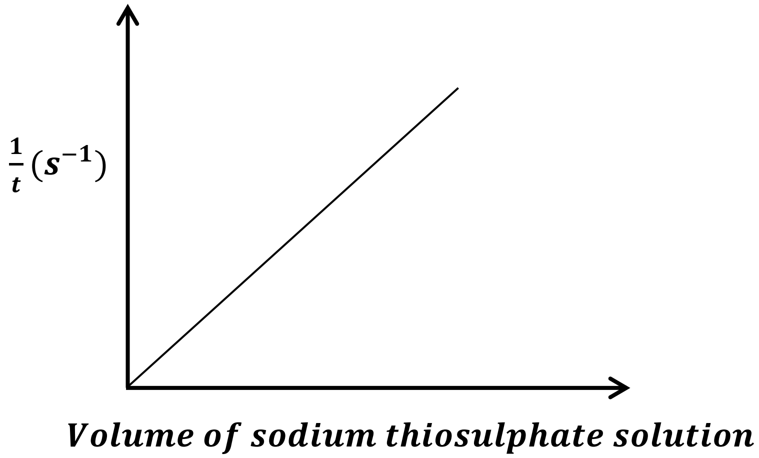
The time taken for the cross to become invisible is recorded.

$$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(s) + SO_2(g) + H_2O(l)$$

The procedure is repeated several times using different volumes of sodium thiosulphate solution and making up with distilled water such that the total volume of solution used in each experiment is equal but maintaining the volume and concentration of hydrochloric acid .

Values of $\frac{1}{t}$ (reciprocals of time) for each experiment are computed.

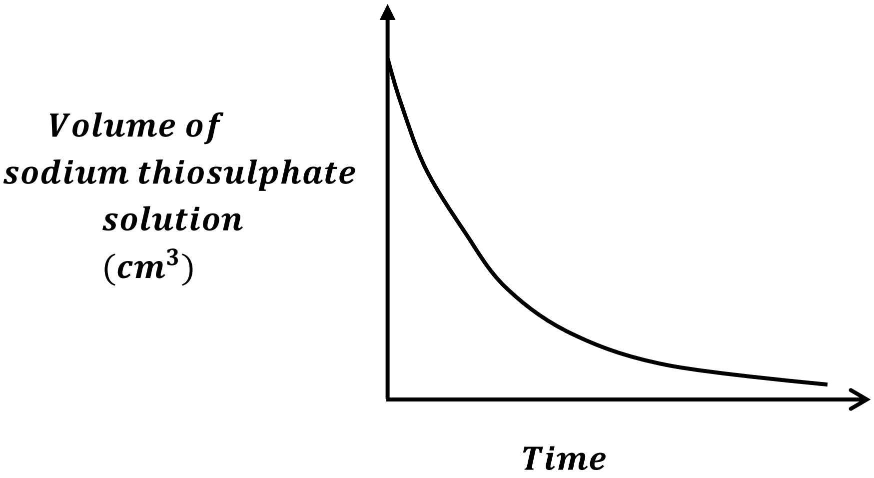
A graph of $\frac{1}{t}$ ***against volume of sodium thiosulphate is plotted.***



The graph obtained is a straight line with through the origin. This shows that the reaction is first order with respect to sodium thiosulphate.

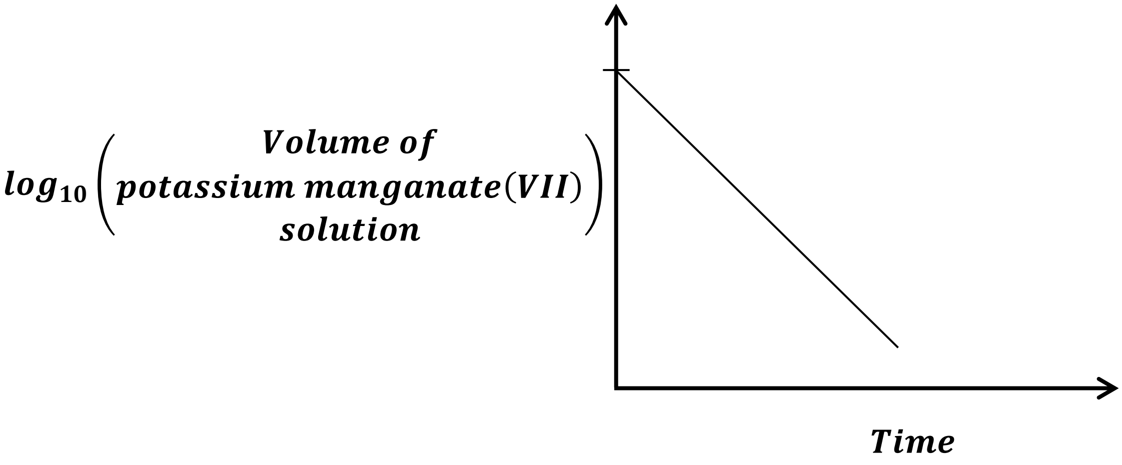
(b) Experiment to show find the rate of reaction for the reaction between sodium thiosulphate and hydrochloric acid

The procedure is the same as above but instead a graph of volume of sodium thiosulphate against time is plotted. The rate of reaction at a specific time is determined by drawing a tangent to the curve at given time and calculating the gradient at that point.



(a) Experiment to show that the catalytic decomposition of hydrogen peroxide is first order reaction.

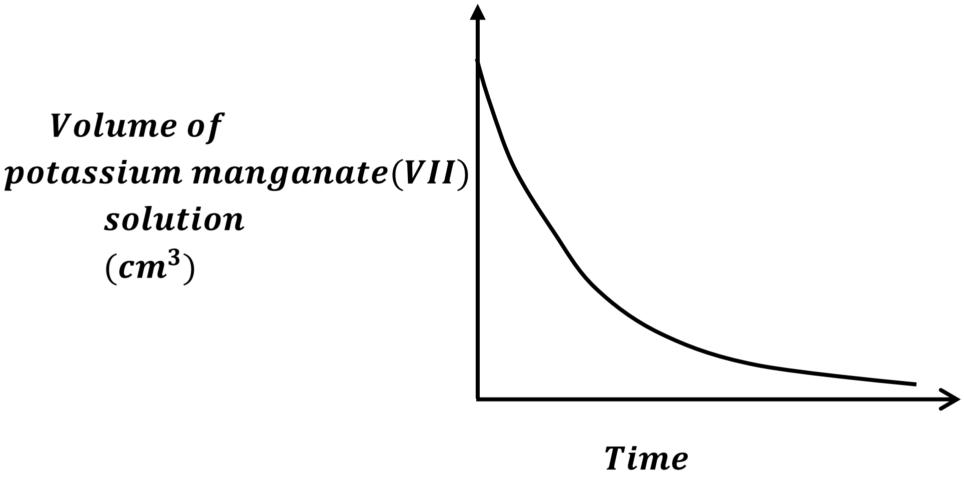
A known volume of standard hydrogen peroxide is transferred into a clean conical flask.
A small amount of iron(III) chloride solution as a catalyst followed by a small amount of sodium hydroxide solution are added and a stop clock is started simultaneously.
The mixture is shaken and allowed to stand at a constant temperature.
After a specific time interval, dilute sulphuric acid is added to stop the reaction.
The reaction mixture is titrated against a standard solution of potassium manganate(VII) and the volume of potassium manganate(VII) required is noted.
The experiment is repeated several times by changing the time taken for the reaction to take place before adding dilute sulphuric acid.
A graph of log_{10} $(volume\ of\ potassium\ manganate(VII)$***against time is plotted.***



The graph obtained is a straight line with a negative gradient. This shows that the reaction is first order.

(b) Experiment to find the rate of reaction for catalytic decomposition of hydrogen peroxide.

The procedure is the same as above but instead a graph of volume of potassium manganate(VII) against time is plotted. The rate of reaction at a specific time is determined by drawing a tangent to the curve at given time and calculating the gradient at that point.



MORE CALCULATIONS INVOLVING RATES OF REACTION DATA

All the questions below involve first order kinetics. Try them out using the first order rate expression.

1. (a) Derive the expression for the half-life for the first order reaction whose integrated rate equation is $2.303 log\frac{N_O}{N} = kt$, where N_O is the initial concentration of the reactant and N is the concentration after time t.
   (b) The half-life for a first order reaction is 200 seconds.
      (i) Calculate the rate constant
      (ii) Determine the time taken for the reaction to be two-thirds complete.
2. (a) State the rate law
   (b) Explain why reactions of high molecularity are rare.
   (c) A solution of hydrogen peroxide when titrated against acidified potassium manganate(VII) solution at different time intervals gave the following results.

Time (minutes)	5	10	20	30
Volume of acidified potassium manganate(VII) used(cm^3)	37.1	29.8	19.6	12.3

      (i) Show that the decomposition of hydrogen peroxide is first order.
      (ii) Calculate the half-life of the decomposition of hydrogen peroxide.
3. A certain amount of methylethanoate was hydrolysed in the presence of excess of 0.05M hydrochloric acid solution at 25°C. When $25cm^3$ portions of the reaction mixture were removed and titrated with sodium hydroxide solution after some time intervals, the volumes of the alkali required for neutralisation were as follows:

Time (minutes)	0	20	79
Volume of sodium hydroxide solution used(cm^3)	24.2	25.8	29.3

Show mathematically, that the reaction is a first order reaction.

4. In a first order reaction, the initial concentration of the reactant was $0.05\ moldm^{-3}$ and the rate constant is $1.5 \times 10^{-3} s^{-1}$. Calculate the initial rate of the reaction.
5. The rate constant of a reaction with respect to a reactant A is $6\ min^{-1}$. If the original concentration of A is $0.8\ mol\ dm^{-3}$. Calculate the time when the concentration of A reaches $0.08\ mol\ dm^{-3}$.
6. The rate of inversion of cane sugar is of first order. If 25% of a sample of cane sugar is hydrolysed in 60 seconds. How long will it take for 50% to be hydrolysed?
7. (a) Explain the following terms:
   (i) Order of reaction
   (ii) Rate equation
   (iii) Molecularity of a reaction
   (b) In the presence of iron(III) chloride catalyst, hydrogen peroxide decomposes according to the equation:

$$2H_2O_2(aq) \xrightarrow{FeCl_3\ catalyst} 2H_2O(l) + O_2(g)$$

The rate equation is given by: $Rate = k[H_2O_2]$

Describe an experiment to determine the order of reaction with respect to hydrogen peroxide.

(c) The following data was obtained for the decay of a radioactive isotope.

Time (minutes)	10	20	30	40	50
$-\boldsymbol{log_{10}(Activity)(counts\ per\ minute)}$	-14	2.0	19	36	52

(i) Plot a graph of $-log_{10}(Activity)$ against time.

(ii) Use the graph to determine the initial activity of the radioactive isotope

(d) Determine the decay constant.

(e) Calculate the half-life of the radioactive isotope.

8. Hydrogen gas reacts with nitrogen(II) oxide according to the equation below at 500K.

$$2H_2(g) + 2NO(g) \longrightarrow N_2(g) + 2H_2O(g)$$

The rate law is given by: $Rate = k[NO]^2[H_2]$ and the mechanism as shown below:

(i) $2NO \rightleftharpoons N_2O_2$

(ii) $N_2O_2 + H_2 \xrightarrow{slow} N_2O + H_2O$

(iii) $N_2O + H_2 \longrightarrow N_2 + H_2O$

(a) Define the term;

(i) order of reaction

(ii) molecularity

(b) State the order and molecularity of the reaction. Give a reason for your answer.

(c) State the effect on the rate of reaction and in each case explain your answer.

(i) doubling the molar concentration of nitrogen(II) oxide while the partial pressure of hydrogen is reduced to a quarter its original value

(ii) increasing temperature above 500K while the concentration of both reactants remain constant

(d) Sketch a graph to show the variation in reciprocal of time$\left(\frac{1}{t}\right)$ with concentration of hydrogen gas in an experiment where nitrogen(II) oxide is used.

9. (a) Hydrogen peroxide oxidises bromide ions in an acidic solution.

(i) State what is observed

(ii) Write an equation for the reaction that takes place.

(b) The rate expression for the reaction that takes place in (a) above is;

$$Rate = k[H_2O_2][H^+][Br^-]$$

(i) Determine the overall order of the reaction

(ii) State the units for the rate constant

(c) (i) If the concentration of bromide ions was doubled, what would be the effect on the rate of reaction.

(ii) Explain how raising the pH of the reaction mixture affects the rate of reaction.

FACTORS AFFECTING RATES OF REACTIONS

The way factors affect rates of chemical reactions is explained basing on the theories of chemical reactions.

Theories of chemical reactions (collision theory and transition state theory)

1. The collision theory

Also known as the Arrhenius theory and proposed by Swedish scientist,
Svante Arrhenius.

In a reaction between two gaseous substances, a molecule of one gas must collide with a molecule of the other gas for a reaction to occur.

The basic idea of the collision theory is that ***if every collision results into reaction, then rates of reaction are equal to the frequency of collision between activated molecules***.

The total number of collisions (Z) between molecules in a gas per unit volume per unit time can be calculated.

$$\begin{pmatrix} Frequency\ of\ collision \\ between\ activated\ molecules \end{pmatrix} = \begin{pmatrix} rate\ of\ reaction\ in \\ molecules\ s^{-1}cm^{-3} \end{pmatrix} = Ze^{-E/RT}$$

On this basis, reaction rates ***would be expected*** to depend on:

Z –total number of collisions
E-Activation energy
T-Temperature

The collision frequency is therefore proportional to the product of the molar concentrations of gaseous reactants.

However, the rate of reaction for most reactions is lower than rate of collision because only a small fraction of collisions results into reaction.

The collision theory was developed for bimolecular reactions in the gas phase, it also applies to reactions in solution.

The theory therefore states that in order for molecules to react, they must collide in a favourable orientation and with enough energy to react.

2. The transition state theory

The transition state theory considers the nature of molecular collisions in a more detailed way than the collision theory. It is also known as the activated complex theory.

For example in a reaction: $AB + X \longrightarrow A + BX$

When AB and X are far away from each other, they have some energy. When X approaches AB with sufficient energy, its electrons begin to overlap with those of AB so that some bonding between B and X begins to form. At the same time the AB bond becomes longer and weaker. As the BX bond becomes stronger and the AB bond becomes weaker, an ***activated complex*** or ***transition state;*** $[A\text{-----}B\text{-----}X]$ is formed. The activated complex then decomposes into A and BX.

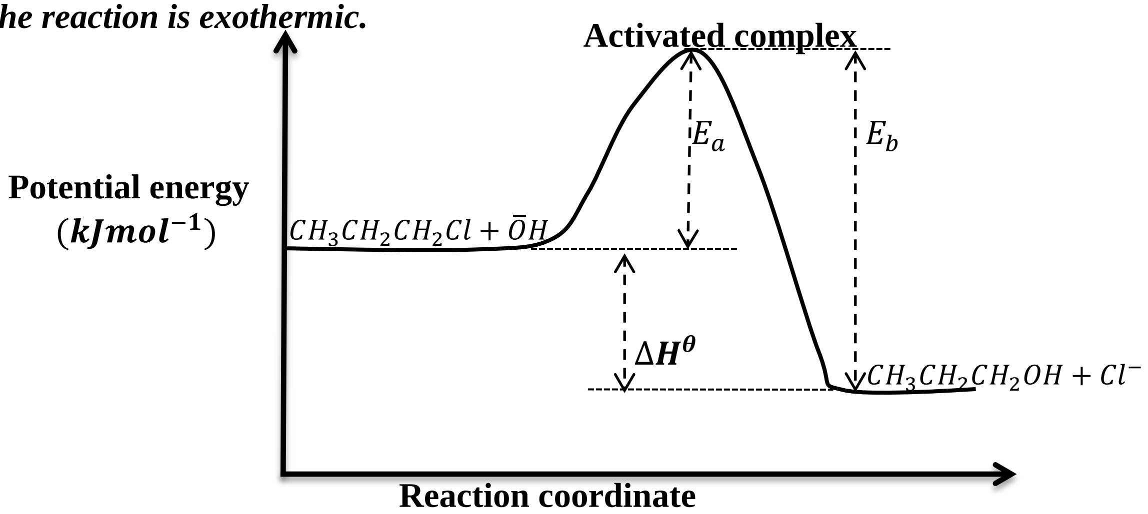
In general; $AB + X \longrightarrow [A\text{-----}B\text{-----}X] \longrightarrow A + BX$

The changes in energy can be represented on an ***energy profile/ enthalpy profile/ reaction profile or potential energy diagram***.

This is usually a sketch of ***potential energy*** against ***reaction coordinate/ reaction pathway.***

(a) Reaction profile for a nucleophilic substitution bimolecular reaction

Consider a reaction between 1-chloropropane and aqueous sodium hydroxide.
The reaction is exothermic.



E_a is the ***activation energy for the reaction(can also be called the energy barrier)***.

E_b is ***activation energy for backward reaction***

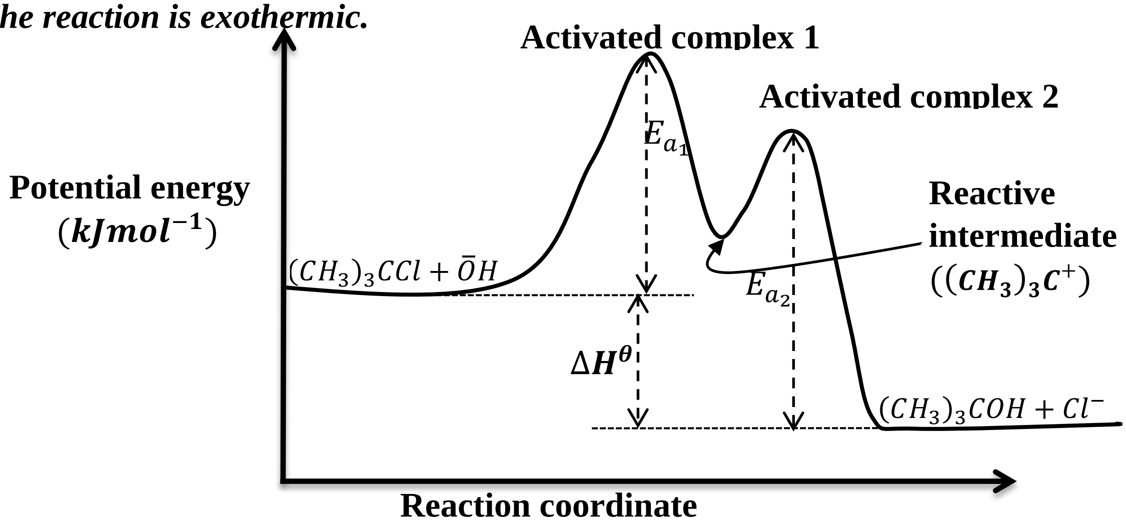
ΔH^{θ} ***is the enthalpy of reaction***

(b) Reaction profile for a nucleophilic substitution unimolecular reaction

Consider a reaction between 2-chloro-2-methylpropane and aqueous sodium hydroxide.

This reaction takes place via a reactive intermediate. The reactive intermediate is preceded and also followed by a transition state.

The reaction is exothermic.



E_{a_1} is the ***activation energy for the first step***.

E_{a_2} is ***activation energy for second step***

Activation energy is the minimum energy which is required to be possessed by reactants in order to react and form products.

Activated complex is the intermediate unstable compound formed immediately once the reactants have absorbed the activation energy available.

This unstable compound undergoes bond re-organization by releasing some of the energy to form the final stable product. The activated complex can also be called a **transition state.**

Questions

1. Ethylbromide reacts with aqueous sodium hydroxide as in the equation;

$$CH_3CH_2Br + NaOH \longrightarrow CH_3CH_2OH + NaBr$$

   (a) Name the reaction
   (b) (i) Write the rate equation for the reaction between the hydroxide and ethylbromide
   (ii) Outline a mechanism for the reaction involved
   (iii) Sketch a labelled diagram to show the energy profile for the reaction.
   (c) Write equation to show how CH_3CH_2Br can be converted to $HOCH_2CH_2Br$.
2. 2-Bromo-2-methyl propane reacts with aqueous sodium hydroxide.
   (a) (i) Write an equation for the reaction.
      (i) Write the rate equation for the reaction.
      (ii) State the molecularity of the reaction
   (b) Draw the energy diagram for the reaction

3. (a) Define the terms:
   (i) Order of reaction
   (ii) Molecularity of a reaction
   (iii) Rate constant
   (iv) Rate equation

(b) Propanone reacts with iodine according to the equation:

$$CH_3COCH_3 + I_2 \longrightarrow CH_2ICOCH_3 + HI$$

The reaction is first order with respect to propanone and zero order with respect to iodine. Describe an experiment to determine the rate of the reaction.

(c) The table below shows the concentration of bromine at various intervals of time for the reaction;

$$Br_2(aq) + HCOOH(aq) \longrightarrow 2HBr(aq) + CO_2(g)$$

Time (s)	0	30	60	90	120	180	240	360	480	600
$[Br_2] \times 10^{-3}(moldm^{-3})$	10	9	8.1	7.3	6.6	5.3	4.4	2.8	2.0	1.3

(i) Plot a graph of concentration of bromine against time
(ii) Use the graph to find the order of reaction. Explain your answer.
(iii) Calculate the rate constant.

(d) The table below shows the results for the hydrolysis of a bromoalkane, C_4H_9Br with sodium hydroxide solution. The enthalpy for the reaction is $-160kJmol^{-1}$.

Experiment	$[C_4H_9Br](moldm^{-3})$	$[\bar{O}H](moldm^{-3})$	**Initial rate** $(moldm^{-3}s^{-1})$
1	0.05	0.10	1.0×10^{-5}
2	0.20	0.10	4.0×10^{-5}
3	0.20	0.05	4.0×10^{-5}

(i) Determine the order of the reaction with reasons to explain your answer.
(ii) Write the structural formula and name of the alkylhalide
(iii) Draw a well labelled energy diagram for the reaction.

4. (a) What is meant by the terms:
   (i) order of reaction
   (ii) half-life of a reaction

   (b) The equation for the reaction between sodium thiosulphate and hydrochloric acid is:

$$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow SO_2(g) + S(s) + H_2O(l)$$

The rate equation for the reaction is $Rate = k[S_2O_3^{2-}][H^+]^2$

(i) State how the rate will affected if the concentrations of the reactants are both doubled.
(ii) Describe an experiment to determine the order of reaction with respect to sodium thiosulphate in the laboratory.

(c) The table below shows the kinetics data for the reaction between an alkylbromide, C_4H_9Br and aquoeus potassium hydroxide. The reaction is exothermic.

Experiment	$[C_4H_9Br](moldm^{-3})$	$[\bar{O}H](moldm^{-3})$	**Initial rate** $(moldm^{-3}s^{-1})$
1	1.0×10^{-3}	1.0×10^{-3}	5.0×10^{-8}
2	2.0×10^{-3}	1.0×10^{-3}	1.0×10^{-7}
3	2.0×10^{-3}	2.0×10^{-3}	2.0×10^{-7}

(i) Determine the overall order of the reaction.
(ii) Determine the rate constant for the reaction and state its units.
(iii) Identify the alkylbromide

(d) Write the mechanism for the reaction in (c) above

(e) Draw a well labelled energy level diagram for the reaction mechanism illustrated in (d) above.

Using the theories of reaction to explain factors affecting rates of reaction

The following factors affect the rate of a chemical reaction:

(i) ***Concentration of the reactants in solution***
(ii) ***Temperature***
(iii) ***Pressure for gaseous reactants***
(iv) ***Particle size/ surface area for solid reactants***
(v) ***Catalyst***

(i) The effect of concentration of the reactants in solution on rate of reaction

Increase in concentration of the reactants increases the rate of reaction. This is because ***as concentration increases***, the reacting ***molecules/ ions become closer to each other*** thus ***colliding more frequently***. The ***greater the number of collisions, the greater the rate of reaction***

Question

The rate equation for the reaction between substances X, Y and Z is given by

$$Rate = k[X]^2[Y][Z]$$

State how the rate of reaction would change if:

(i) **concentration of X is doubled while concentrations of Y and Z are kept constant**
(ii) **concentrations of all the reactants are halved**
(iii) **concentration of X is kept constant while both concentrations of Y and Z are trebled**

(iv) **concentration of X is halved, that of Y doubled and that of Z kept constant**
(v) **the temperature is increased to double the rate constant.**

(i) $Rate = k[X]^2[Y][Z]$

$$New\ rate = k(2[X])^2[Y][Z] = 4k[X]^2[Y][Z]$$

The rate of reaction quadruples (rate of reaction increases four times)

(ii) $Rate = k[X]^2[Y][Z]$

$$New\ rate = k\left(\frac{1}{2}[X]\right)^2\left(\frac{1}{2}[Y]\right)\left(\frac{1}{2}[Z]\right)$$
$$= \frac{1}{4}\times\frac{1}{2}\times\frac{1}{2}k[X]^2[Y][Z]$$
$$= \frac{1}{16}k[X]^2[Y][Z]$$

The rate of reaction decreases by 16 times

(iii) $Rate = k[X]^2[Y][Z]$

$$New\ rate = k[X]^2(3[Y])(3[Z]) = 9k[X]^2[Y][Z]$$

The rate of reaction increases by nine times

(iv) $Rate = k[X]^2[Y][Z]$

$$New\ rate = k\left(\frac{1}{2}[X]\right)^2(2[Y])[Z]$$
$$= \frac{1}{4}\times 2k[X]^2[Y][Z]$$
$$= \frac{1}{2}k[X]^2[Y][Z]$$

The rate of reaction is halved(decreases by 2 times)

(v) $New\ rate = 2k[X]^2[Y][Z]$

The rate of reaction doubles

(ii) The effect of temperature on rate of reaction

The ***higher the temperature***, the ***higher the kinetic energy of the ions or molecules*** of reactants. The ions or molecules hence ***move at a higher speed*** and ***collide more frequently*** and ***with more energy***. The ***higher the collision frequency***, the ***higher the rate of reaction***.

The rate constant is also only constant at a fixed temperature. Therefore increase in temperature increases the value of the rate constant.

The rate of reaction doubles for every $10℃\ or\ 10K$ increase in temperature.

The Arrhenius theory suggests that a molecule would only react if it had higher than the average energy (if it is activated, has gained the activation energy)

Arrhenius found the experimental relationship between the rate constant and temperature. The Arrhenius equation is therefore given as;

$$\boldsymbol{k = Ae^{-E_a/RT}\ where}:$$
$$A\ is\ the\ pre-exponential\ constant\ or\ Arrhenius\ factor\ or\ frequency\ factor$$
$$E\ is\ Activation\ energy\ for\ the\ reaction(Jmol^{-1})$$

$$R \text{ is the molar gas constant}$$
$$T \text{ is Absolute tempeature}(Kelvin)$$

From the Arrhenius equation above, more equations can be formed as follows:

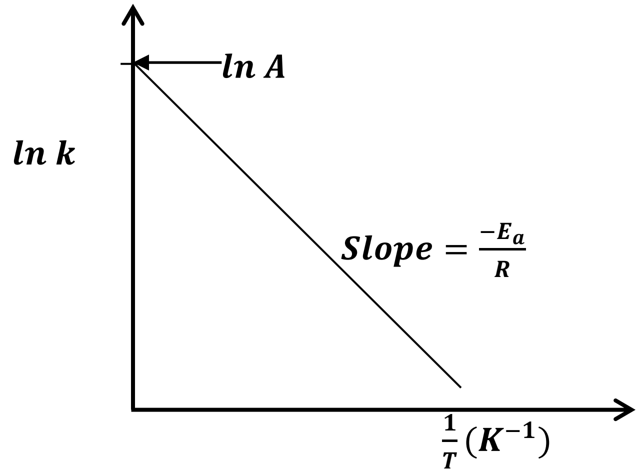
Introducing ln both sides

$$lnk = ln\left(Ae^{-E_a/RT}\right)$$
$$lnk = lnA + ln\left(e^{-E_a/RT}\right)$$
$$\boldsymbol{lnk = lnA - \frac{E_a}{R}\frac{1}{T}} \ldots\ldots\ldots.(\boldsymbol{i})$$

The equation can also be written in terms of log_{10}:

$$2.303log_{10}k = 2.303log_{10}A - \frac{E_a}{R}\frac{1}{T}$$
$$\boldsymbol{log_{10}k = log_{10}A - \frac{E_a}{2.303R}\frac{1}{T}} \ldots\ldots.(\boldsymbol{ii})$$

From equation (i), a graph of lnk against $\frac{1}{T}$ can be plotted.



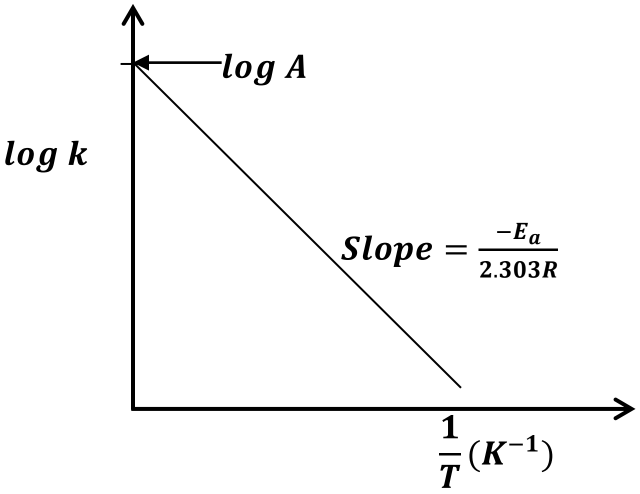
The graph of $\boldsymbol{ln\ k}$ *against* $\frac{1}{T}$ *is a* ***straight line*** *with* ***a negative gradient*** *with an* ***intercept on the*** $\boldsymbol{ln\ k}$ ***axis***. *The intercept gives the value of* $\boldsymbol{ln\ A}$

$$\boldsymbol{if\ ln\ A = x}$$
$$\boldsymbol{Then\ A = e^x.}$$

The slope of the graph **,** $\boldsymbol{Slope = \frac{-E_a}{R}}$ *from which th**e activation energy can be obtained*** *with units* $\boldsymbol{Jmol^{-1}}$

$$\boldsymbol{R = 8.314Jmol^{-1}K^{-1}}$$

From equation (ii), a graph of $log\ k$ against $\frac{1}{T}$ can be plotted.



The graph of $\boldsymbol{log\ k}$ *against* $\frac{1}{T}$ *is a* ***straight line*** *with* ***a negative gradient*** *with an* ***intercept on the*** $\boldsymbol{log\ k}$ ***axis***. *The intercept gives the value of* $\boldsymbol{log\ A}$

$$\boldsymbol{if\ log\ A = x}$$
$$\boldsymbol{Then\ A = 10^x.}$$

The slope of the graph **,** $\boldsymbol{Slope = \frac{-E_a}{2.303R}}$ *from which th**e activation energy can be obtained*** *with units* $\boldsymbol{Jmol^{-1}}$

$$\boldsymbol{R = 8.314Jmol^{-1}K^{-1}}$$

The following conclusions can be made from the Arrhenius equation:

1. ***The rate constant of a reaction increases with increase in the temperature of the reaction.***
2. ***The rate of reaction increases with increase in temperature***
3. ***At the same temperature, the higher the activation energy, the slower the reaction***
4. ***The higher the activation energy, the lower the rate constant hence the lower the rate of reaction.***

Questions

1. (a) (i) Distinguish between activation energy and rate constant.
   (ii) Briefly explain how activation energy and rate constant affect the rate of reaction
   (b) Hydrogen reacts with iodine according to the following equations;

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad \Delta H = +25.9kJmol^{-1}$$

The table below shows the rate constant for the reaction varying with temperature.

Temperature, $T(K)$	556	629	700	781
Rate constant, $k(mol^{-1}dm^3s^{-1})$	7.04×10^{-7}	6.04×10^{-5}	2.32×10^{-3}	7.90×10^{-2}

   (i) Plot a graph of $log_{10}\, k$ against $\frac{1}{T}$
   (ii) Use the graph to determine the activation energy of the reaction from the Arrhenius equation, $k = Ae^{-E_a/RT}$ $(R = 8.314JK^{-1}mol^{-1})$
   (iii) Draw an energy level diagram for the reaction in (b) above and use it to determine the activation energy for the backward reaction.
   (iv) Briefly explain how temperature affects the activation energy of a reaction.

2. (a) Explain the following terms:
   (i) Rate of reaction
   (ii) Rate law
   (iii) Activation energy
   (b) Describe an experiment to show that iodination of propanone is zero order with respect to iodine.
   (c) The reaction between manganate(VII) ions and ethanedioate ions in acidic medium is described by the equation:

$$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$$

The reaction was carried out at different temperatures and the following values for the rate constant, k were obtained.

Temperature, $T(K)$	293	308	318	338
Rate constant, $k(s^{-1})$	1.76×10^{-5}	1.34×10^{-4}	4.98×10^{-4}	4.87×10^{-3}

   (i) Plot a graph of $log_{10}\, k$ against $\frac{1}{T}$
   (ii) Use your graph to determine the activation energy for the reaction
   (iii) Determine the value of the pre-exponential constant, A.
   (iv) Explain the effect of temperature on the rate of chemical reaction.

3. The table below shows the rate constants for the decomposition of hydrogen iodide at various temperatures.

Temperature, $T(K)$	**Rate constant, $k(mol^{-1}dm^{3}s^{-1})$**
500	3.75×10^{-9}
600	6.65×10^{-6}
700	1.15×10^{-3}
800	7.75×10^{-2}

   (a) Plot a graph of $\ln k$ against $\frac{1}{T}$
   (b) Use the graph to determine the activation energy of the reaction from the Arrhenius equation, $k = Ae^{-E_a/RT}$ $(R = 8.314JK^{-1}mol^{-1})$
   (c) Determine the value of A.

4. The decomposition of dinitrogen pentoxide is a first order reaction. The rate constant depends on the rate constant as shown in the table below.

Temperature, T(℃)	0	20	40	60	80
Rate constant, k	7.87×10^{-7}	1.70×10^{-5}	2.57×10^{-4}	1.78×10^{-3}	2.14×10^{-2}
$T(K)$					
$\frac{1}{T}(K^{-1})$					
$\log k$					

   (a) Complete the table above.
   (b) Plot a graph of $\log k$ against $\frac{1}{T}$
   (c) Use the graph to determine the activation energy of the reaction from the Arrhenius equation, $k = Ae^{-E_a/RT}$ $(R = 8.314JK^{-1}mol^{-1})$

(iii) The effect of pressure for gaseous reactants on rate of reaction

Increase in pressure of gaseous reactants increases the rate of chemical reaction because the ***gas molecules are pushed closer together***, hence ***collide more frequently*** and ***react more rapidly***.

(iv) The effect of particle size/ surface area of solid reactants

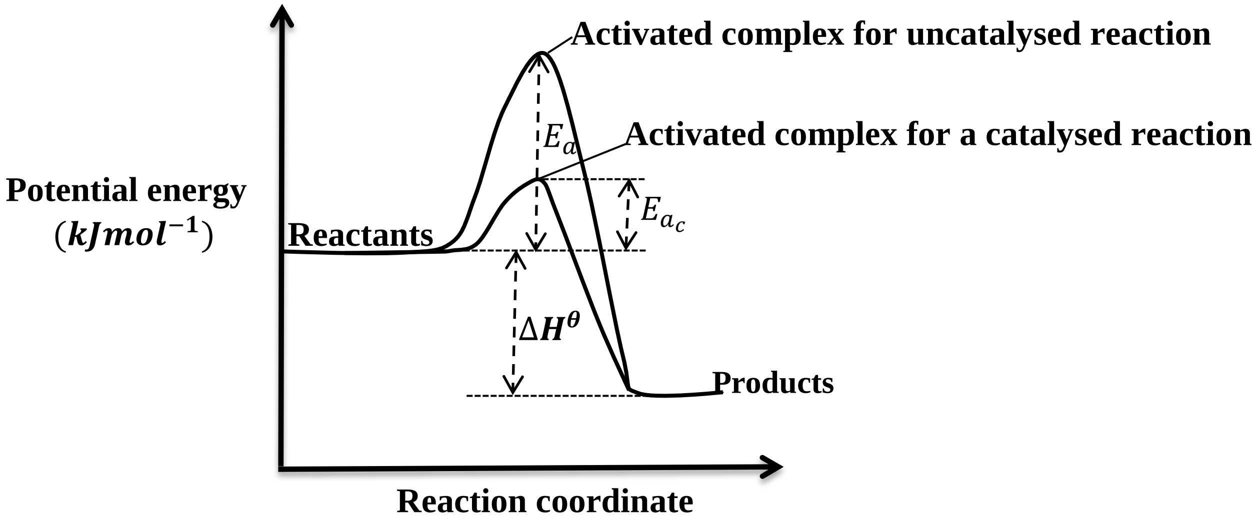
The larger the surface area(the smaller the particle size), the higher the rate of reaction because smaller reactant particles have a higher chance of colliding with each other.

(v) The effect of a catalyst

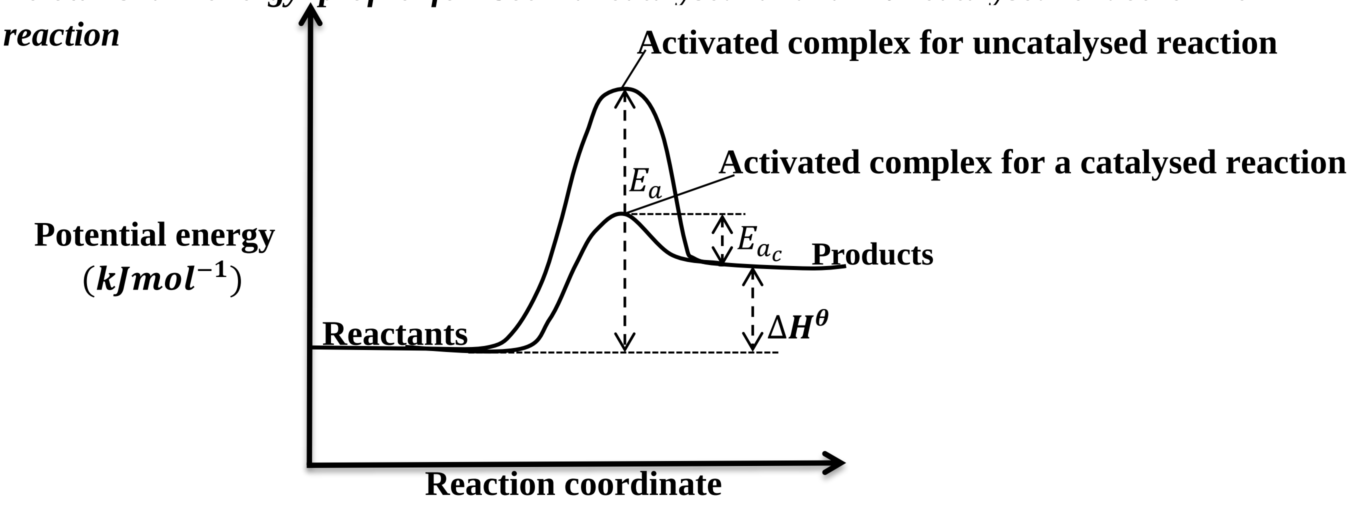
A catalyst is a substance which alters the rate of a chemical reaction but remains unchanged in quantity at the end of the reaction or at equilibrium.

The presence of a ***catalyst increases the rate of a chemical reaction***. This is because a catalyst provides ***an alternative pathway/ mechanism*** with ***lower activation energy***.

Below is an energy profile for both a catalysed and an uncatalysed exothermic reaction



Below is an energy profile for both a catalysed and an uncatalysed endothermic reaction



In both cases above;

E_a is the ***activation energy for the uncatalysed reaction***

E_{a_c} is ***activation energy for the catalysed reaction***

ΔH^θ is the enthalpy of reaction

The activation energy for the catalysed reaction is lower than activation energy for the uncatalysed reaction

Types of catalysts

A catalyst can be ***homogeneous*** or ***heterogeneous***.

A homogeneous catalyst is one which is in the same phase as the reactants.

A heterogeneous catalyst is one whose phase is different from that of the reactants.

How catalysts work

A ***homogeneous catalyst*** works by ***lowering the activation energy*** of the ***rate determining step*** by ***forming an intermediate***. It is generally used for reactions in aqueous solution.
The catalyst reacts with one of the reactants to form an intermediate which the reacts with the other product to form the ***final product***, ***regenerating the catalyst***.
Consider a reaction between A and B in presence of catalyst C to form product X.

$$A + B \longrightarrow X$$

The reaction takes place in via quicker steps as shown below:

$$A + C \longrightarrow AC$$
$$AC + B \longrightarrow X + C$$

For example:

1. ***Dilute sulphuric acid as a catalyst in iodination of propanone or in the reaction between hydrogen peroxide and iodide ions.***
2. ***Oxidation of vanadium(III) ions to vanadium(IV) ions by iron(III) ions using copper(II) ions as catalyst***.
3. ***Esterification of ethanol by ethanoic acid in the presence of sulphuric acid***

The heterogeneous catalysts used are commonly transition metals in processes like hydrogenation (nickel), cracking and polymerisation. It's the surface of the catalysts that helps in catalysis.
They work by ***using their empty d-orbitals to form weak temporary bonds with the reactant molecules***. This ***weakens the internal bonding of the reactant molecules*** and also ***increases the concentration of the reactant molecules at the surface of the catalyst*** thereby ***reducing the activation energy*** hence ***increasing the rate of reaction***.
For example:

1. ***Finely divided iron in the Haber process.***
2. ***Nickel in hydrogenation of alkenes***.
3. ***Combination of hydrogen and iodine vapour using platinum catalyst***

Light as factor that speeds up a chemical reaction

Some reactions take place slowly or not at all in the absence of light. Reactions accelerated by light include:

- ***Photosynthesis***
- ***Decomposition of hydrogen peroxide***
- ***Combination of hydrogen and chlorine***

- ***The substitution of hydrogen in methane by chlorine***
- ***Formation of silver from silver salts***

Experimental investigation of factors affecting rates of reactions

1. Experiment to show the effect of concentration on the rate of reaction between sodium thiosulphate and hydrochloric acid

A known volume of sodium thiosulphate solution of known concentration is measured into a clean conical flask using a measuring cylinder.

The conical flask is placed on a white piece of paper marked with a cross.

A known volume of hydrochloric acid of a slightly higher concentration than sodium thiosulphate solution is added using and a stop clock started simultaneously.

The mixture is ***shaken*** and allowed to settle ***at a constant temperature***

Through the mixture, the cross on the white piece of paper is viewed and the stop clock stopped when the cross just becomes invisible.

The time taken for the cross to become invisible is recorded.

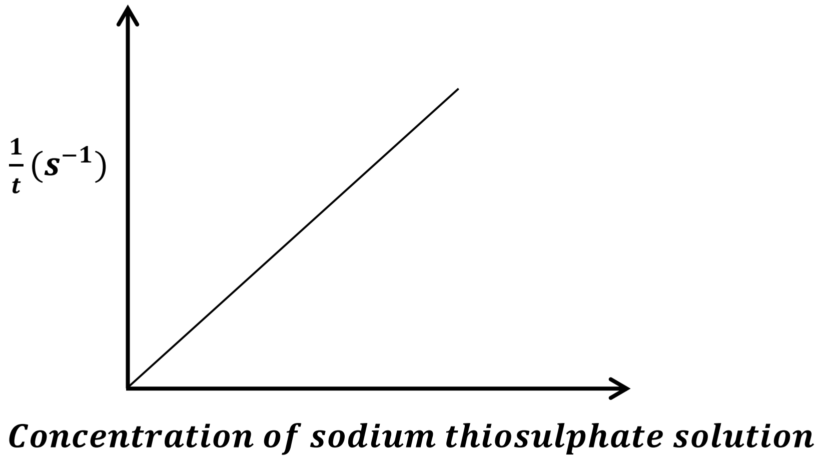
$$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(s) + SO_2(g) + H_2O(l)$$

The procedure is repeated several times using different volumes of sodium thiosulphate solution and making up with distilled water such that the total volume of solution used in each experiment is equal but maintaining the volume and concentration of hydrochloric acid.

The concentration of sodium thiosulphate in each of the solutions is computed.

Values of $\frac{1}{t}$ (reciprocals of time) for each experiment are computed.

A graph of $\frac{1}{t}$ ***against volume of sodium thiosulphate is plotted.***



The graph obtained is a straight line with through the origin with a positive gradient. This shows that the rate of reaction$\left(\frac{1}{t}\right)$ increases with increase in concentration of sodium thiosulphate.

Note: The same experiment can be done by maintaining the concentration of sodium thiosulphate but varying the concentration of hydrochloric acid.

2. **Experiment to show the effect of temperature on the rate of reaction between sodium thiosulphate and hydrochloric acid**

A known volume of sodium thiosulphate solution of known concentration is measured into a clean conical flask using a measuring cylinder.

The initial temperature of the solution $(T_1°C)$ ***is measured and recorded from a thermometer.***

The conical flask is placed on a white piece of paper marked with a cross.

A known volume of hydrochloric acid of a slightly higher concentration than sodium thiosulphate solution is added using and a stop clock started simultaneously.

The mixture is ***shaken*** and allowed to settle.

Through the mixture, the cross on the white piece of paper is viewed and the stop clock stopped when the cross just becomes invisible.

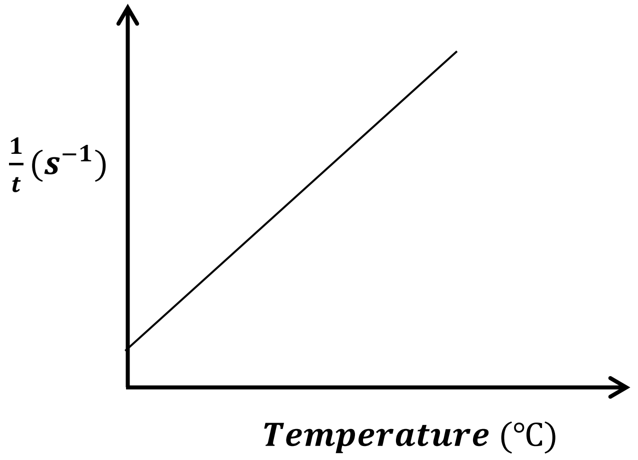
The time taken for the cross to become invisible is recorded.

$$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(s) + SO_2(g) + H_2O(l)$$

The mixture is poured away, the flask is rinsed and procedure is repeated several times using the same volume of sodium thiosulphate solution and the same volume and of hydrochloric acid of the same concentrations but in each experiment warming the sodium thiosulphate solution to a higher recorded temperature than the previous one before adding hydrochloric acid.

Values of $\frac{1}{t}$ ***(reciprocals of time) for each experiment are computed.***

A graph of $\frac{1}{t}$ ***against temperature is plotted.***



The graph obtained is a straight line with a positive gradient and an intercept on the $\frac{1}{t}$ ***axis.*** This shows that the rate of reaction$\left(\frac{1}{t}\right)$ increases with increase in temperature.

3. Experiment to show the effect of particle size(surface area) on the rate of reaction between calcium carbonate and hydrochloric acid

A known volume of excess dilute hydrochloric acid of known concentration is measured into a test tube tied with a thread.

The test tube and its contents is stoppered in a clean reaction flask containing a known mass of calcium carbonate <u>lumps</u> and connected to a gas syringe.

The stopper is gently opened to relax the thread so that the acid pours onto the calcium carbonate lumps and a stop clock started simultaneously.

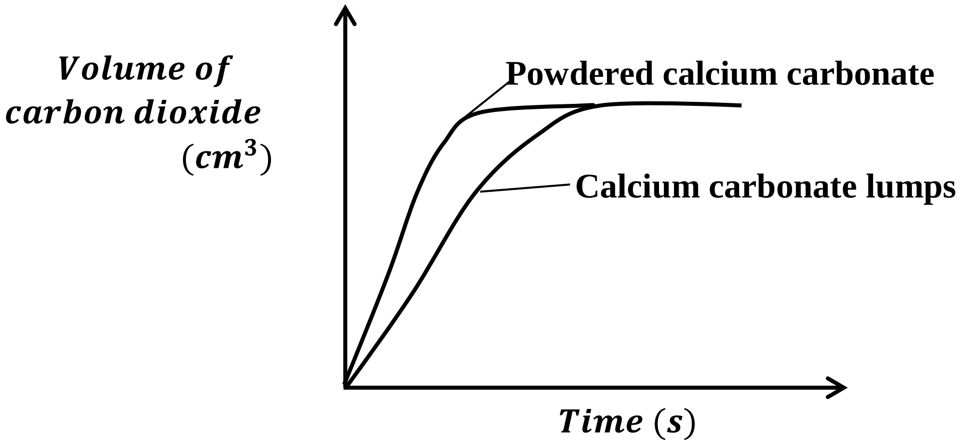
The mixture is ***shaken*** and allowed to settle at a constant temperature.

The volume of carbon dioxide evolved is recorded at fixed specific intervals of time until no more bubbles are formed.

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

The procedure is repeated using the same mass of <u>powdered</u> calcium carbonate and the same volume of hydrochloric acid of the same concentration.

On the same axes, graphs of ***volume of carbon dioxide against time are plotted.***



The rates of reaction at a specific time are determined by drawing tangents on each curve at that point and calculating the gradient.

The values obtained are compared and those obtained from the graph when powdered calcium carbonate is used are higher.

This shows that the rate of reaction increases when that particle size is reduced (surface area is increased)

More questions

1. (a) State and explain how the following factors affect the rate of a chemical reaction.
    (i) Temperature
    (ii) Catalyst
    (b) The graph below shows the kinetics data obtained for the decomposition of nitrogen(V) oxide dissolved in carbon tetrachloride at 45℃.

Time (seconds)	250	750	1500	2000	2500
Concentration of N_2O_5 ($moldm^{-3}$)	1.95	1.42	0.95	0.70	0.50

Plot a graph of log_{10}Concentration of N_2O_5 against time.

    (c) Use the graph in (b) to:
        (i) determine the original concentration of N_2O_5
        (ii) deduce the order of the reaction. Give a reason for your answer.
    (d) Calculate the:
        (iii) rate constant for the reaction and indicate its units
        (ii) half-life of the reaction
2. (a) Define the term catalyst
    (b) Differentiate between a positive catalyst and a negative catalyst
    (c) State four general properties of a positive catalyst
    (d) Give one example of a catalyst used in industry and in nature. Name the process involved.
    (e) State the difference between a homogeneous and a heterogeneous catalyst.
3. (a) Explain why transition metals commonly act as catalysts
    (b) In each case, write equation for the reaction catalyzed by the following substances.
        (i) Finely divided iron
        (ii) vanadium(V) oxide
        (iii) manganese(II) ions
    (c) Explain the action of a positive catalyst.
4. (a) Apart from temperature and concentration, state any two other factors that affect the rate of a chemical reaction.
    (b) Describe an experiment to determine the rate for the reaction between sodium thiosulphate and hydrochloric acid.
    (c) The table below shows variation in the concentration of sodium thiosulphate with time when a fixed volume of hydrochloric acid was added to sodium thiosulphate at various concentrations.

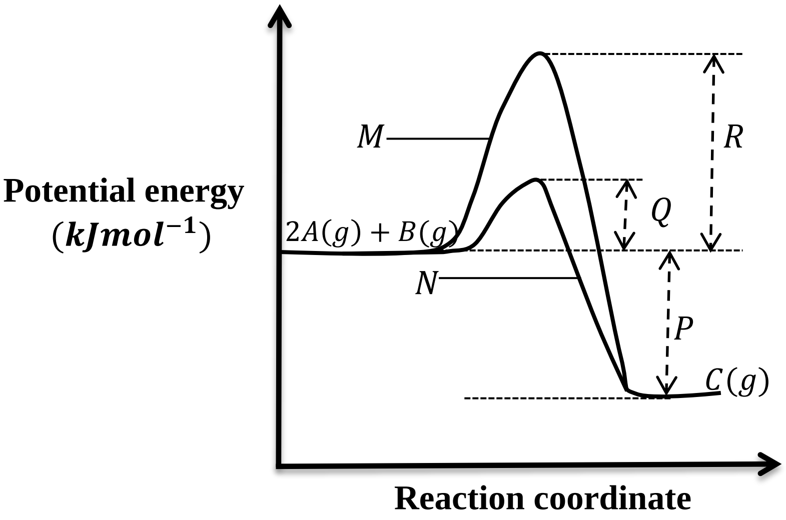
Time, t (s)	24	29	39	60	138
Concentration of sodium thiosulphate ($moldm^{-3}$)	0.2	0.16	0.12	0.08	0.04

(i) Plot a graph of $^1/_t$ against concentration of sodium thiosulphate

(ii) State the order of the reaction. Give a reason for your answer.
(iii) Calculate the rate constant for the reaction and indicate its units
(iv) Determine the time taken for the concentration of sodium thiosulphate to decrease from 0.2 $moldm^{-3}$ to 0.15 $moldm^{-3}$.

5. The figure below shows the variation of energy with reaction coordinate for a catalysed and an uncatalysed reaction

$$2A(g) + B(g) \rightleftharpoons C(g)$$



(a) Identify
- (i) the curve for catalyzed reaction
- (ii) the curve for uncatalysed reaction
- (iii) ***P***
- (iv) ***Q***
- (v) ***R***

(b) From the figure, state how a catalyst increases the rate of reaction.

(c) The kinetic data for the reaction above are shown below.

Experiment	$[A](moldm^{-3})$	$[B](moldm^{-3})$	**Initial rate** $(moldm^{-3}s^{-1})$
1	0.50	1.00	2.00
2	0.50	2.00	8.00
3	1.00	3.00	36.00
4	2.00	3.00	72.00

(i) Deduce the rate equation.
(ii) Calculate the rate constant for the reaction and state its units.

CHAPTER NINE

ELECTROCHEMISTRY

Electrochemistry is the branch of chemistry that deals with chemical changes that are produced by passing electric current into a chemical system or the generation of electricity by spontaneous chemical reactions.

MODES OF CONDUCTION OF SUBSTANCES

The substances that allow electric current to flow through them are called conductors. Those that do not allow electric current to flow through them are called non-conductors or insulators. The conductors are classified into two type i.e. ***metallic conductors*** and ***electrolytic conductors***.

1. **Metallic conductors**

Metals or alloys allow electric current to flow through them without undergoing any chemical change. The metals conduct electric current by use of ***free mobile electrons (delocalised electrons)***. These include copper, silver, aluminium and others. This mode of conduction is called ***electronic conduction***.

2. **Electrolytic conductors**

These include ***aqueous solutions of electrolytes*** or molten electrolytes. They are compounds and chemical changes occur when they conduct electricity. The electrolytes conduct electric current by use of ***free mobile ions***. Examples include dilute hydrochloric acid, aqueous sodium chloride, molten lead(II) bromide and others. This mode of conduction is called ***electrolytic conduction***.

ELECTROLYSIS

Electrolysis is the decomposition of a compound in its molten state or in solution by passage of an electric current through it.

or

The overall chemical change that occurs at the electrodes when an electric current passes through a fused electrolyte or its aqueous solution

The electrolyte, solvent or electrode may all be involved in the electrolytic reaction

The common terms used in electrolysis

1. **Electrolytes**

These are compounds which conduct electric current in solution or in molten state and are decomposed by it.

A non-electrolyte is a substance which does not conduct electric current in molten state or aqueous solution and cannot be decomposed by electric current. For example sucrose

Electrolytes can be salts, acids or bases.

Electrolytes can be classified as ***strong*** or ***weak***.

(i) Strong electrolytes

These are electrolytes which almost completely ionise in solution. Their solutions do not contain unionized molecules.

They include most salts, strong acids and strong alkalis.

(ii) Weak electrolytes

These are electrolytes which partly ionise in solution. Their solutions contain ions in equilibrium with unionized molecules.

They include most organic acids and bases and ammonia.

Examples of strong and weak electrolytes

Strong electrolytes	Weak electrolytes
Sodium chloride	Ethanoic acid
Calcium chloride	Ammonia solution
Sodium hydroxide	Ethylamine
Hydrochloric acid	Carbonic acid

Electrolytes can as well be ***ionic*** or ***covalent***.

(i) Ionic electrolytes

These electrolytes are made up of ions in the solid state but the ions are not free to move. For example sodium chloride, Na^+Cl^-.

When ionic electrolytes are heated, sufficient energy is absorbed to break the crystal lattice so that the ions are free to move within the molten electrolyte.

When ionic electrolytes are dissolved in water (or any other ionizing solvent), the crystal lattice is broken, the ions become free to move. The ions are hydrated (solvated, completely surrounded by water molecules)

(ii) Covalent electrolytes

These electrolytes do not contain ions so they conduct electricity in the liquid state as ionic electrolytes do. The covalent electrolytes usually contain polar bonds such as $O - H$ or $H - halogen$ bonds. They react with water or any other ionizing solvent to form hydrated ions. These include all mineral acids.

2. Electrodes

These are conductors which carry electricity into and out of the cell. The electrodes include the ***anode*** and the ***cathode***.

(i) Anode

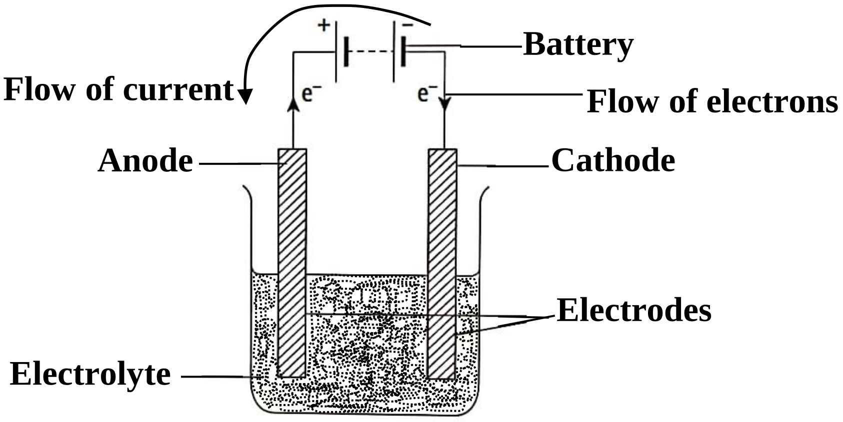
This is the electrode at which oxidation takes place

(ii) Cathode

This is the electrode at which reduction takes place

Explaining the changes that take place during electrolysis

Electrolysis is generally carried out in an ***electrolytic cell*** as shown below.



The electrolytic cell is set up as shown above. The electrolyte contains both cations and anions. During electrolysis, the anions migrate to the anode and lose electrons (are oxidised) to form neutral elements or new molecules.

$$A^{n-}(aq) \longrightarrow A + ne$$

The cations migrate to the cathode and combine with the electrons there (are reduced) to form neutral elements or new molecules.

$$C^{n+}(aq) + ne \longrightarrow C$$

Principles of electrolysis (selective discharge of ions)

Under similar conditions, when two or more ions with a similar charge are present in a solution, i.e. H^+ and Na^+ or Cl^- and $\bar{O}H$, one ion is preferentially selected for discharge at each electrode and the selection of the ion depends on the following factors:

- ***(i)*** ***Position of the ion in the electrochemical series***
- ***(ii)*** ***Concentration of the ions in solution***
- ***(iii)*** ***Nature of the electrode.***

(i) Position of the ion in the electrochemical series

Cations (move to cathode)	**Anions (move to anode)**
K^+	F^-
Ca^{2+}	SO_4^{2-}
Na^+	NO_3^-
Mg^{2+}	Cl^-
Al^{3+}	Br^-
Zn^{2+}	I^-
Fe^{2+}	$\bar{O}H$
Sn^{2+}	
Pb^{2+}	
H^+	
Cu^{2+}	
Ag^+	
$\downarrow$ **Increasing ease of discharge at cathode**	$\downarrow$ **Increasing ease of discharge at anode**

If all the other factors (stated above) are constant, any ion is discharged from solution in preference to the ions above it in the electrochemical series.

For example in electrolysis of sodium hydroxide solution, the solution contains the cations; H^+ from water and Na^+. The hydrogen ion discharges in preference to the sodium ion at the cathode. Hydrogen gas is formed at the cathode.

$$2H^+(aq) + 2e \longrightarrow H_2(g)$$

During electrolysis of silver nitrate solution, the solution contains the anions; $\bar{O}H$ from water and NO_3^- . The hydroxide ion is discharged in preference to the nitrate ion at the anode. Oxygen gas is formed at the anode.

$$4\bar{O}H(aq) \longrightarrow O_2(g) + 2H_2O(l) + 4e$$

Note: The order of preferential discharge given in the table above only applies for discharge from aqueous solutions containing ions at comparable concentrations approximately 1M. Sometimes exceptions arise as a result of large differences in concentration.

(ii) Concentration of the ions in solution

An ion present at a lower concentration is more difficult to discharge than an ion present at a higher concentration.

The electrolysis of sodium chloride solution liberates chlorine at the anode during manufacture of chlorine. This is because although the solution contains the anions; $\bar{O}H$ and Cl^- . The chloride ion is discharged because it is present in a higher concentration than the hydroxide ion.

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e$$

The electrolysis of concentrated hydrochloric acid liberates chlorine at the anode for the same reason as in the case above.

(iii) Nature of the electrode.

Inert electrodes like platinum may not affect the products of electrolysis. Some electrodes may affect the products of electrolysis. For example:

(a) Electrolysis of concentrated sodium chloride solution (saturated brine) using platinum cathode and mercury cathode.

When a platinum cathode is used, hydrogen ions are discharged in preference to sodium ions because hydrogen is lower than sodium in the electrochemical series. Hydrogen gas is therefore formed at the platinum cathode.

$$2H^{+}(aq) + 2e \longrightarrow H_2(g)$$

When a mercury cathode is used, sodium ions are discharged in preference to hydrogen ions because the discharge of sodium ion requires less energy than the discharge of hydrogen ions. Sodium amalgam is therefore formed at the mercury cathode by the reaction between sodium and the mercury cathode.

$$Na^{+}(aq) + e \longrightarrow Na(l)$$

$$Na(l) + Hg(l) \longrightarrow NaHg(l)$$

(b) Electrolysis of copper(II) sulphate solution using platinum anode and copper anode.

When a platinum anode is used, hydroxide ions are discharged in preference to sulphate ions because the hydroxide ion is lower than the sulphate ion in the electrochemical series. Oxygen gas is therefore formed at the platinum anode. The solution at the anode also becomes acidic due to the reaction between hydrogen ions and sulphate ions to form sulphuric acid.

$$4\bar{O}H(aq) \longrightarrow O_2(g) + 2H_2O(l) + 4e$$

$$2H^{+}(aq) + SO_4^{2-}(aq) \longrightarrow H_2SO_4(aq)$$

When a copper anode is used, neither the hydroxide ions nor the sulphate ions are discharged but instead the copper anode dissolves in the solution to form copper(II) ions. The electrolysis is merely a transfer of copper from the anode to the cathode.

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e$$

Laws of electrolysis

Micheal Faraday studied the quantitative relationships between the electricity passed through an electrolyte and the amount of material liberated or deposited at the electrodes.

1. Faraday's first law of electrolysis states that ***the mass of the substance liberated at an electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte***.

$$m \propto Q \;\; but \; Q = It$$
$$Therefore \;\; m \propto It$$
$$m = EIt$$

Where; m is the mass of substance consumed or produced at an electrode
Q is the quantity of charge passed in Coulombs
I is the current in amperes
t is the time in **seconds** for which the current was passed.
E is a proportionality constant called the electro-chemical equivalent.

2. Faraday's second law of electrolysis states that ***the quantity of electricity required to liberate one mole of any element is proportional to the charge number of its ion***.

The charge number of an ion, represented by z is the number of positive or negative charges which the ion possesses. It can be positive or negative. For example for $H^+; z = 1$, for $Al^{3+}; z = 3$, for $Cl^-; z = -1$ and for $O^{2-}; z = -2$.

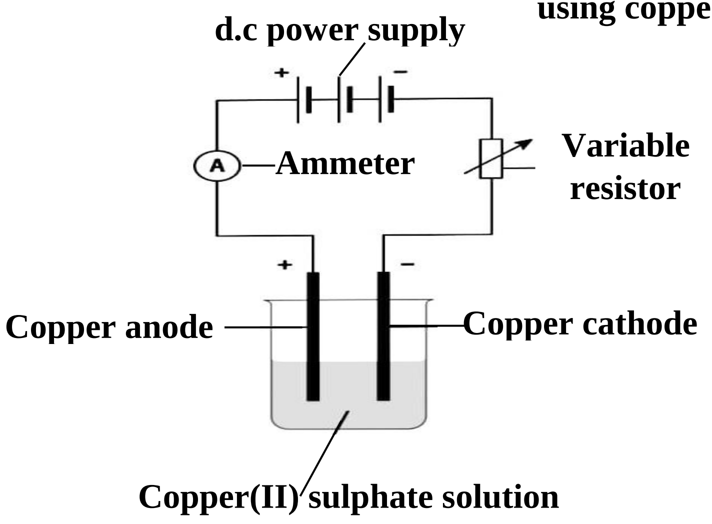
The magnitude of the charge number(z) is usually equal to the number of moles electrons required for the ion to be discharged.

$$Al^{3+}(aq) + 3e \longrightarrow Al(s)$$
$$3 \; moles \; of \; electrons \; are \; required \; for \; discharge \; of \; 1 \; mole \; of \; Al^{3+}$$
$$3 \; Faraday \; are \; transferred \; for \; discharge \; of \; 1 \; mole \; of \; Al^{3+}$$
$$(3 \times 96500) \; Coulombs \; are \; transferred \; for \; discharge \; of \; 27g \; of \; Al^{3+}$$
$$(3 \times 96500 \times 6.02 \times 10^{23}) \; electrons \; are \; transferred \; for \; discharge \; of \; 27g \; of \; Al^{3+}$$

Note that $1 \; mole \; of \; electrons \; has \; a \; charge \; of \; 96500 \; Coulombs$

$$1 \; Faraday = 96500 \; Coulombs$$
$$Therefore \; 1 \; Faraday = 1 \; mole \; of \; electrons$$
$$Since \; 1 \; mole \; of \; electrons = 6.02 \times 10^{23} \; electrons$$
$$Then \; 1 \; Faraday = 6.02 \times 10^{23} \; electrons$$

Experiment to determine the Faraday constant by electrolysis of copper(II) sulphate using copper electrodes.



Arrange the apparatus as shown
The variable resistor is used to keep the current constant
Weigh the mass of the pure copper anode($x_1 \; g$) and pure copper cathode($y_1 \; g$) separately
Pass a constant electric current($I \; Amperes$) for a measured time interval($t \; seconds$)
Remove the cathode and anode and wash them with distilled water and then propanone and dry them.

The washed and dried cathode and anode are weighed again and their new masses($x_2\ g$) and ($y_2\ g$) recorded respectively.

Treatment of results

$$\text{Mass of copper removed from the anode} = (x_1 - x_2)g$$
$$\text{Quantity of charge passed, } Q = (It)\ Coulombs$$
$$(x_1 - x_2)g\ of\ Cu\ are\ deposited\ by\ (It)C\ of\ charge$$
$$63.5g\ \ of\ Cu\ are\ deposited\ by\ \left(\frac{63.5 \times I \times t}{(x_1 - x_2)}\right)\ C\ of\ charge$$
$$Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$$
$$1\ mole\ of\ Cu\ \ is\ deposited\ by\ 2\ moles\ of\ electrons$$
$$63.5g\ \ of\ Cu\ are\ deposited\ by\ 2\ moles\ of\ electrons$$
$$Therefore\ 2\ moles\ of\ electrons\ have\ a\ charge\ of\ \left(\frac{63.5 \times I \times t}{(x_1 - x_2)}\right)\ C$$
$$1\ mole\ of\ electrons\ has\ a\ charge\ of\ \left(\frac{63.5 \times I \times t}{(x_1 - x_2) \times 2}\right)\ C$$
$$\boldsymbol{The\ value\ of\ \left(\frac{63.5 \times I \times t}{(x_1 - x_2) \times 2}\right)\ \ is\ found\ to\ be}$$
$$\boldsymbol{\approx 96500C\ which\ is\ the\ Faraday's\ constant}$$

Trial question;

A student passed a constant electric current of 0.15A through a solution of silver nitrate using pure silver electrodes for exactly 45 minutes. The mass of the anode decreased by 0.45g. Use this data to calculate the charge on a mole of electrons. ($Ag = 108$)

Calculations of electrolysis

Examples

1. **Calculate the quantity of charge required to deposit 40.5g of aluminium during electrolysis of a solution of aluminium ions.** $(\mathbf{1F = 96500C; Al = 27})$

$$Q = ? \qquad m = 40.5g$$
$$Al^{3+}(aq) + 3e \longrightarrow Al(s)$$
$$1\ mole\ of\ Al\ is\ deposited\ by\ 3\ moles\ of\ electrons$$
$$(1 \times 27)g\ \ are\ deposited\ by\ (3 \times 96500)\ C\ of\ charge$$
$$40.5\ g\ \ are\ deposited\ by\ \left(\frac{3 \times 96500 \times 40.5}{27}\right) C\ of\ charge$$
$$= 434250\ Coulombs$$
$$Q = 434250\ C$$

---

2. **When current was passed through a solution of silver nitrate for 10 minutes, 0.54g of silver was deposited at the cathode. Calculate the current.**

$$(\mathbf{1F = 96500C; Ag = 108})$$

$$I = ? \quad t = 10\ minutes \quad m = 0.54g$$

$$Ag^+(aq) + e \longrightarrow Ag(s)$$

$$1\ mole\ of\ Ag\ is\ deposited\ by\ 1\ mole\ of\ electrons$$

$$(1 \times 108)g\ \ are\ deposited\ by\ (1 \times 96500)\ C\ of\ charge$$

$$0.54\ g\ \ are\ deposited\ by\ \left(\frac{96500 \times 0.54}{108}\right) C\ of\ charge$$

$$= 482.5\ Coulombs$$

$$Q = 482.5C$$

$$Q = It$$

$$482.5 = I \times 10 \times 60$$

$$\boldsymbol{I = \frac{482.5}{600} = 0.804\ A}$$

3. **Determine the time taken to deposit 1.0g of chromium when a current of 0.120A flows through a solution of chromium(III) sulphate.**

$$(\boldsymbol{Faraday's\ constant = 96500C; Cr = 52})$$

$$I = 0.120A \quad t = ? \quad m = 1.0g$$

$$Cr^{3+}(aq) + 3e \longrightarrow Cr(s)$$

$$1\ mole\ of\ Cr\ is\ deposited\ by\ 3\ moles\ of\ electrons$$

$$(1 \times 52)g\ \ are\ deposited\ by\ (3 \times 96500)\ C\ of\ charge$$

$$1.0\ g\ of\ Cr\ are\ deposited\ by\ \left(\frac{3 \times 96500 \times 1.0}{52}\right) C\ of\ charge$$

$$= 5567.308\ Coulombs$$

$$Q = 5567.308\ C$$

$$Q = It$$

$$5567.308 = 0.120 \times t$$

$$\boldsymbol{t = \frac{5567.308}{0.120}}$$

$$\boldsymbol{t = 46394\ seconds}$$

4. **Calculate the mass of lead deposited at the cathode during electrolysis when a current of 1.50A flows through molten lead(II) bromide for 20 minutes.**

$$(\boldsymbol{Pb = 207})$$

$$I = 1.50A \quad t = 20\ minutes \quad m = ?$$

$$Q = It = 1.50 \times 20 \times 60$$

$$Q = 1800C$$

$$Pb^{2+}(aq) + 2e \longrightarrow Pb(s)$$

$$2\ moles\ of\ electrons\ deposit\ 1\ mole\ of\ Pb$$

$$(2 \times 96500)\ C\ of\ charge\ deposit (1 \times 207)g\ \ of\ Pb$$

$$1800\ C\ \ deposit\ \ \left(\frac{1800 \times 207}{2 \times 96500}\right) g\ of\ Pb$$

$$= \boldsymbol{1.931 g\ of\ Pb}$$

5. **An electric current was passed through a solution of copper(II) sulphate electrolyzed using platinum electrodes for 1 hour.**
   (a) Calculate the strength of the current used to deposit 0.106g of copper.
   (b) If the electrolytic cell above was in series with a silver nitrate cell. Calculate the mass of silver deposited on the cathode of the second cell.

(a)

$$I = ? \quad t = 1\ hour \quad m = 0.106g$$

$$Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$$

$$1\ mole\ of\ Cu\ is\ deposited\ by\ 2\ moles\ of\ electrons$$

$$(1 \times 63.4)g\ \ are\ deposited\ by\ (2 \times 96500)\ C\ of\ charge$$

$$0.106\ g\ \ are\ deposited\ by\ \left(\frac{2 \times 96500 \times 0.106}{63.4}\right) C\ of\ charge$$

$$= 322.68\ Coulombs$$

$$Q = 322.68\ C$$

$$Q = It$$

$$322.68 = I \times 1 \times 60 \times 60$$

$$\boldsymbol{I = \frac{322.68}{3600} = 0.0896\ A}$$

(b) $I = 0.0896A \quad t = 1\,hour \quad m = ?$

$For\ cells\ in\ series, the\ quantity\ of\ charge\ is\ the\ same; Q = 322.68C$

$$Ag^+(aq) + e \longrightarrow Ag(s)$$
$$1\,mole\ of\ electrons\ deposit\ 1\,mole\ of\ Ag$$
$$(1 \times 96500)\ C\ of\ charge\ deposit (1 \times 108)g\ \ of\ Ag$$
$$322.68\,C\ \ deposit\ \ \left(\frac{322.68 \times 108}{96500}\right) g\ of\ Ag$$
$$= \mathbf{0.361} \boldsymbol{g\ of\ Ag}$$

6. **A current of 89.6mA was passed through an electrolytic cell containing dilute sulphuric acid electrolyzed between platinum electrodes for 1 hour. Calculate the total volume of gas measured at 15℃ and 100kPa liberated**.

$$I = 89.6 \times 10^{-3}A \ \ t = 1\,hour$$
$$Q = It = 0.0896 \times 1 \times 60 \times 60$$
$$Q = 322.56C$$
$$At\ cathode\ ; 2H^+(aq) + 2e \longrightarrow H_2(g)$$
$$2\,moles\ of\ electrons\ liberate\ 1\,mole\ of\ H_2$$
$$(2 \times 96500)\ C\ of\ charge\ liberate\ 1\,mole\ of\ H_2$$
$$322.56\,C\ \ liberate\ \ \left(\frac{1 \times 322.56}{2 \times 96500}\right) moles\ of\ H_2$$
$$= \mathbf{0.001671}\ \boldsymbol{moles\ of\ H_2}$$

$$At\ anode\ ; 4\bar{O}H(aq) \longrightarrow 2H_2O(l) + O_2(g) + 4e$$
$$4\,moles\ of\ electrons\ are\ released\ for\ 1\,mole\ of\ O_2$$
$$(4 \times 96500)\ C\ of\ charge\ liberate\ 1\,mole\ of\ O_2$$
$$322.56\,C\ \ liberate\ \ \left(\frac{1 \times 322.56}{4 \times 96500}\right) moles\ of\ O_2$$
$$= \mathbf{0.000836}\ \boldsymbol{moles\ of\ O_2}$$
$$Total\ moles\ of\ gas\ produced$$
$$= (0.001671 + 0.000836\ ) = 0.002507\ moles$$
$$\boldsymbol{pV = nRT}$$
$$V = \frac{nRT}{p} = \frac{0.002507 \times 8.31 \times (15 + 273)}{100 \times 1000}$$
$$= \mathbf{5.999 \times 10^{-5}} \boldsymbol{m^3}$$

7. **Calculate the volume of oxygen liberated at anode at s.t.p in the electrolysis of copper(II) sulphate solution when a current of 1500 milliamperes is passed for 10 minutes**.

$$I = 1500\,mA \quad t = 10\,minutes$$
$$Q = It = 1500 \times 10^{-3} \times 10 \times 60$$
$$Q = 900C$$
$$At\ anode\ ; 4\bar{O}H(aq) \longrightarrow 2H_2O(l) + O_2(g) + 4e$$
$$4\,moles\ of\ electrons\ are\ released\ for\ 1\,mole\ of\ O_2$$
$$(4 \times 96500)\ C\ of\ charge\ liberate\ 1\,mole\ of\ O_2$$
$$900\,C\ \ liberate\ \ \left(\frac{1 \times 900}{4 \times 96500}\right) moles\ of\ O_2$$
$$= \mathbf{0.002332}\ \boldsymbol{moles\ of\ O_2}$$
$$1\,mole\ of\ O_2\ occupies\ 22.4\ dm^3\ at\ s.t.p$$
$$0.002332\ moles\ of\ O_2\ occupy\ (0.002332 \times 22.4) dm^3$$
$$= \mathbf{0.0522} \boldsymbol{dm^3}$$

8. **(a) A current of 32.2A was passed through molten lead(II) bromide for 5 hours and the bromine liberated reacted with 94g of hydroxybenzene. Calculate the number of moles of ;**
   (i) bromine liberated
   (ii) hydroxybenzene that reacted

(b) State what is observed and write equation for the reaction that took place between bromine and hydroxybenzene in (a) above.

(a) (i)

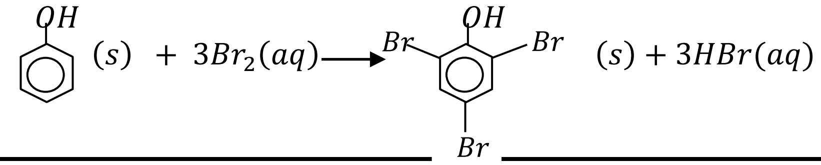
$$I = 32.2A \quad t = 4\ hours$$
$$Q = It = 32.2 \times 5 \times 60 \times 60$$
$$Q = 579600\ C$$
$$At\ anode\ ;\ 2Br^-(l) \longrightarrow Br_2(l) + 2e$$
$$2\ moles\ of\ electrons\ are\ released\ for\ 1\ mole\ of\ Br_2$$
$$(2 \times 96500)\ C\ of\ charge\ liberate\ 1\ mole\ of\ Br_2$$
$$579600\ C\ \ liberate\ \left(\frac{1 \times 579600}{2 \times 96500}\right) moles\ of\ Br_2$$
$$\boldsymbol{= 3\ moles\ of\ Br_2}$$

(ii)

$$Molar\ mass\ of\ C_6H_5OH = 72 + 6 + 16 = 94g$$
$$Moles\ of\ C_6H_5OH = \frac{94.0}{94} = \mathbf{1\ mole}$$

(b) Observation: ***White precipitate***

Equation:



9. $20cm^3$ of 0.05M aqueous phenylamine was mixed with $50cm^3$ of 1M sodium bromide and electrolyzed at current of 0.2A. The first permanent bromine colour was observed after 48.25 minutes and then electrolysis was stopped. ($\boldsymbol{Faraday's\ constant =\ \ 96500Cmol^{-1}}$).

(i) Calculate the moles of bromine that reacted with 1 mole of phenylamine

(ii) Hence write equation of the reaction between bromine and phenylamine. Name the product

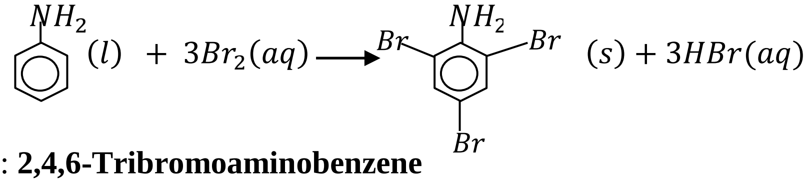
(i)

$$I = 0.2A \quad t = 48.25\ minutes$$
$$Q = It = 0.2 \times 48.25 \times 60$$
$$Q = 579\ C$$
$$At\ anode\ ;\ 2Br^-(l) \longrightarrow Br_2(l) + 2e$$
$$2\ moles\ of\ electrons\ are\ released\ for\ 1\ mole\ of\ Br_2$$
$$(2 \times 96500)\ C\ of\ charge\ liberate\ 1\ mole\ of\ Br_2$$
$$579\ C\ \ liberate\ \left(\frac{1 \times 579}{2 \times 96500}\right) moles\ of\ Br_2$$
$$\boldsymbol{= 0.003\ moles\ of\ Br_2}$$
$$Moles\ of\ C_6H_5NH_2 = \left(\frac{20 \times 0.05}{1000}\right) = \mathbf{0.001\ moles}$$
$$0.001\ moles\ of\ C_6H_5NH_2\ react\ with\ 0.003\ moles\ of\ Br_2$$
$$1\ mole\ of\ C_6H_5NH_2\ reacts\ with\ \left(\frac{1 \times 0.003}{0.001}\right)\ moles\ of\ Br_2$$
$$=\ 3\ moles\ of\ Br_2$$

Hint: Electrolysis of sodium bromide yields bromine at the anode. The sodium bromide was such an excess such that enough bromine is liberated to react with all the phenylamine. The first bromine colour only appears if just enough bromine has been formed to react with all the phenylamine present.

(ii) Observation: ***White precipitate***

Equation:



Name of product: **2,4,6-Tribromoaminobenzene**

10. A direct current of 0.45A was passed through a dilute solution of copper(II) sulphate using graphite electrodes for 5.96 hours.

(a) Write equation for the reaction at the:

(i) cathode

(ii) anode

(b) If 3.1767g of copper was deposited and $560cm^3$ of oxygen at stp were evolved, calculate the quantity of electricity required to produce 1 mole of each substance at their respective electrodes.

(a) (i) At cathode: $Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$

(iii) At anode: $4\bar{O}H(aq) \longrightarrow 2H_2O(l) + O_2(g) + 4e$

(b)

$$I = 0.45A \quad t = 5.96\ hours$$

$$Q = It = 0.45 \times 5.96 \times 60 \times 60 = 9655.2\ C$$

$$Moles\ of\ Cu\ deposited\ at\ cathode = \frac{3.1767}{63.5} = 0.05\ moles$$

$$0.05\ moles\ of\ Cu\ are\ deposited\ by\ 9655.2\ coulombs$$

$$1\ mole\ of\ Cu\ is\ deposited\ by\ \left(\frac{1 \times 9655.2}{0.05}\right) coulombs$$

$$= \mathbf{193,104\ C}$$

$$560\ cm^3\ of\ O_2\ are\ evolved\ by\ 9655.2\ coulombs$$

$$22400\ cm^3\ of\ O_2\ are\ evolved\ by\ \left(\frac{22400 \times 9655.2}{560}\right)\ coulombs$$

$$= \mathbf{386,208\ C}$$

$$\frac{193{,}104C}{193{,}104C} \quad : \quad \frac{386{,}208C}{193{,}104C}$$

$$\mathbf{1} \quad : \quad \mathbf{2}$$

Questions

1. 3 Faraday are needed to electroplate a given amount of metal using a current of 5.0A. How long will it take to electroplate the metal?
2. Calculate the mass of copper deposited at the cathode when a current of 1.0A was passed through copper(II) sulphate solution for 10 minutes.
3. Calculate the mass of silver deposited at the cathode during electrolysis when a current of 1.80A flows through an aqueous solution of silver nitrate for 45.0 minutes.

4. The same current was passed through molten sodium chloride and through molten cryolite containing aluminium oxide. If 4.60g of sodium were liberated in one cell. Calculate the mass of aluminium liberated in the other cell.
5. During the extraction of aluminium, a current of 0.2 ampere was passed for one hour through aluminium sulphate solution.
   (a) Write an equation for the reaction that took place at each electrode
   (b) Calculate the mass of aluminium produced
6. Calculate the mass of chlorine that can be produced by the electrolysis of molten sodium chloride with a current of 5.5 amperes for 25 minutes.
7. Calculate the mass of lead deposited when 0.2 moles of electrons are passed through lead(II) nitrate solution during electrolysis.
8. Calculate the volume of oxygen liberated at anode at s.t.p in the electrolysis of copper(II) sulphate solution when a current of 1500 milliamperes is passed for 10 minutes.
9. Calculate the volume of chlorine liberated at standard temperature and pressure by passing 0.2 moles of electrons during electrolysis sodium chloride solution.
10. Determine the mass of hydrogen liberated by passing 0.5 moles of electrons during electrolysis sodium chloride solution.
11. If a current is passed through a cell for 2 hours deposits 0.4818g of silver. Calculate the volume of oxygen that would be liberated in the same circuit where dilute sulphuric acid is electrolysed.
    $(1F = 96500C; 1\ mole\ of\ gas\ occupies\ 22.4dm^3\ at\ stp)$
12. Calculate the volume of oxygen produced at room temperature when a concentrated aqueous solution of sulphuric acid is electrolyzed for 30 minutes using a current of 0.50A. $(1F = 96500C; 1\ mole\ of\ gas\ occupies\ 24.0dm^3\ at\ room\ temperature)$
13. During the electrolysis of a 1M copper(II) sulphate solution at $20℃$, a current of 0.1A was passed for one hour through the electrolyte. The mass of the copper cathode increased by 0.118g. State how the change in mass would be affected if the experiment was repeated:
    (a) at a current of 0.2A
    (b) at $30℃$
    (c) with a 2M copper(II) sulphate solution
    (d) for a time of 2 hours
14. (a) An aqueous solution of copper(II) sulphate was electrolyzed between copper electrodes.
    Write equation for the reaction at the;
    (i) Cathode

(ii) Anode

(b) (i)Identify the species which carry the current through the solution and state their direction of flow.

(ii) Explain the changes in the mass of each electrode and in the concentration of copper(II) sulphate near the anode.

(iii) Calculate the change in mass of the anode if a current of 1.0A is maintained for one hour.

(c) During the electrolysis of aqueous hydrogen chloride between silver electrodes, the anode mass increases and a white coating form on it. Explain this observation.

The applications of electrolysis in industry

The elements potassium, calcium, sodium, magnesium and aluminium being very reactive, are never found as free elements. They are extracted by electrolysis.

Potassium is extracted from fused potassium hydroxide. Sodium from molten sodium chloride, calcium from fused calcium chloride and aluminium from Bauxite.

1. **Extraction of sodium by electrolysis of molten sodium chloride in the Down's process. (The same process is used for manufacture of chlorine)**

Sodium is extracted by ***electrolysis of molten sodium chloride*** in the ***Down's cell***.

A ***carbon anode*** is used and an ***iron cathode*** and are separated from each other by an ***iron gauze diaphragm***.

Calcium chloride is added to the electrolyte ***to lower its melting point of sodium chloride from about 800***℃ ***to about 600***℃.

Sodium chloride is decomposed by electric current to form sodium ions and chloride ions.

$$NaCl(l) \longrightarrow Na^+(l) + Cl^-(l)$$

Sodium ions are preferentially discharged at the cathode at the temperature used ***forming sodium***.

$$Na^+(l) + e \longrightarrow Na(l)$$

Chloride ions migrate to the anode and form chlorine gas which escapes from the cell.

$$2Cl^-(l) \longrightarrow Cl_2(g) + 2e$$

2. **Anodisation of aluminium**

Aluminium is normally covered by a thin coating of aluminium oxide to protect it from corrosion and to make it resistant from chemical attack. The thickness of the oxide layer is increased by electrolyzing dilute sulphuric acid or chromic(VI) acid with the aluminium made the anode. The oxygen liberated at the anode reacts with the aluminium to form the protective layer of aluminium oxide.

$$4\bar{O}H(aq) \longrightarrow 2H_2O(l) + O_2(g) + 4e$$
$$4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s)$$

3. **Electroplating**

This is the electrical coating of one metal with another metal to make it resistant to corrosion and improve its appearance. The metal to be electroplated is made the cathode and the electroplating metal made the anode. The electrolyte must contain a solution of ions of the electroplating metal.

4. **Manufacture of sodium chlorate(I) and sodium chlorate(V) by electrolysis of concentrated sodium chloride solution.**

A ***cold concentrated solution of sodium chloride*** is electrolyzed using ***platinum electrodes placed close together***. The chlorine liberated at the anode combines with the hydroxyl ions left at the cathode to form sodium chlorate(I).

$$Cl_2(g) + 2\bar{O}H(aq) \longrightarrow ClO^-(aq) + Cl^-(aq) + H_2O(l)$$

If the electrolysis is done using ***a hot concentrated solution of sodium chloride at*** $\mathbf{80}$℃ The chlorine liberated at the anode combines with the hydroxyl ions left at the cathode to form sodium chlorate(V).

$$3Cl_2(g) + 6\bar{O}H(aq) \longrightarrow ClO_3^-(aq) + 5Cl^-(aq) + 3H_2O(l)$$

5. **Extraction of aluminium by electrolysis of molten aluminium oxide**
6. **Manufacture of sodium hydroxide by electrolysis of concentrated sodium chloride solution (saturated brine) using a mercury cell (Castner-Kellner cell) or a diaphragm cell.**
   (The same process can as well be used for manufacture of chlorine)
7. **Refining of copper**
   (Check for the details of 5, 6 and 7 in Demystifying Inorganic Chemistry by the same author)

CONDUCTIVITY OF SOLUTIONS OF ELECTROLYTES

When electric current flows through an electrolyte, there is resistance to the flow of current. The current that flows through a given solution under given conditions is inversely proportional to the reciprocal of resistance.

$$Current\ flowing\ through\ an\ electrolytic\ solution \propto \frac{1}{Resistance\ of\ the\ solution}$$

The common terms used

1. **Conductance**

Conductance is the reciprocal of resistance of an electrolytic solution.

$$Conductance = \frac{1}{R}\ where\ R\ is\ Resistance$$

The SI unit of conductance is the siemens (S) although it used to be measured in reciprocal ohms(Ω^{-1}) . Therefore $1S = 1\Omega^{-1}$.

High resistance means low conductance and low resistance means high conductance.

2. Resistivity (ρ)

To compare resistances of different electrolytic solutions, the idea of resistivity is used.

Resistivity is the resistance of a solution placed between two parallel electrodes of cross-sectional area $1\ m^2$ and separated by a distance of $1\ m$ apart.

Resistance(R) of an electrolytic solution is directly proportional to the length (l) between the electrodes;

$$R \propto l \ldots\ldots..(i)$$

The resistance(R) of an electrolytic solution is also inversely proportional to the cross sectional area (A) of the electrodes;

$$R \propto \frac{1}{A} \ldots\ldots..(ii)$$

Combining (i) and (ii);

$$R \propto \frac{l}{A}$$

$$\boldsymbol{R = \rho \frac{l}{A}} \ldots\ldots.(iii)$$

Where R is resistance
ρ is resistivity
l is length between the electrodes
A is the cross sectional area of the electrodes

From (iii) $R = \rho \frac{l}{A}$, then Resistivity, $\boldsymbol{\rho = \frac{RA}{l}}$

Since R is measured in ohms (Ω) , is Area is measured in m^2 and length in metres(m) , then the SI unit of resistivity is ohm metre(Ωm) . But Ωcm can also be used.

3. Electrolytic conductivity ($\mathcal{K}$)

It is also called ***specific conductivity*** or ***specific conductance***.

To compare conductance of different electrolytes, electrolytic conductivity$(\mathcal{K})$ is used.

Electrolytic conductivity is defined as the conductivity of a solution of an electrolyte placed between two parallel electrodes of cross-sectional area $1\ m^2$ and separated by a distance of $1\ m$ apart.

or

It is the reciprocal of resistivity.

$$\mathcal{K} = \frac{1}{\rho} = \frac{1}{RA/l} = \frac{l}{RA} = \frac{1}{R} \times \frac{l}{A}$$

The SI unit of electrolytic conductivity is siemen per metre(Sm^{-1}) . But Scm^{-1} can also be used.

$$1Sm^{-1} = 1\Omega^{-1}m^{-1}$$
$$1Scm^{-1} = 1\Omega^{-1}cm^{-1}$$

4. Cell constant

From $R = \rho \frac{l}{A}$, the cell constant is the value of $\frac{l}{A}$. Its units are m^{-1} or can be cm^{-1}.
l and A for any cell are constant.

Cell constant is therefore the distance between two parallel electrodes of a cell divided by the cross sectional area of one electrode.

$$\text{Therefore, } R = \rho \frac{l}{A} = resistivity \times Cell\ constant$$

$$\text{Also } \mathcal{K} = \frac{1}{R} \times \frac{l}{A} = conductance \times cell\ constant$$

$$\text{or } \mathcal{K} = \frac{l}{A}/R = \frac{cell\ constant}{Resistance}$$

5. Molar conductivity($\boldsymbol{\Lambda_c}$)

It is also called ***molar conductance***.

Molar conductivity is the conductivity of a solution of containing 1 mole of an electrolyte placed between two parallel electrodes of cross-sectional area $\mathbf{1\ m^2}$ and separated by a distance of $\mathbf{1\ m}$ apart.

or

It is the electrolytic conductivity divided by concentration.

$$\Lambda_c = \frac{\mathcal{K}}{c}$$

$$\text{since } \frac{1}{c} = Dilution(V), \text{ then } \Lambda_c = \mathcal{K} \times \frac{1}{c} = \mathcal{K} \times V$$

The two above formulae show the relationship between electrolytic conductivity and molar conductivity.

The SI unit of molar conductivity is m^2mol^{-1} . But Scm^2mol^{-1} can also be used.

$$1Sm^2mol^{-1} = 1\Omega^{-1}m^2mol^{-1}$$

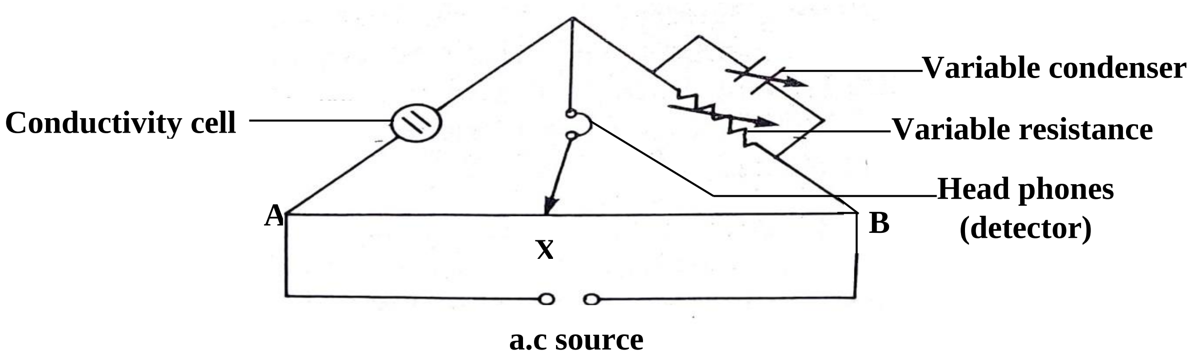
$$1Scm^2mol^{-1} = 1\Omega^{-1}cm^2mol^{-1}$$

The formula of molar conductivity used in calculations depends on the units of $\mathcal{K}$ and c given.The formula used is intended to make units consistent.

If unit of $\mathcal{K}$ is $S\boldsymbol{cm^2}mol^{-1}(\Omega^{-1}\boldsymbol{cm^2}mol^{-1})$ and that of c is $mol\boldsymbol{dm^{-3}}$ then; $\boldsymbol{\Lambda_c = \frac{1000\mathcal{K}}{c}}$	If unit of $\mathcal{K}$ is $S\boldsymbol{m^2}mol^{-1}(\Omega^{-1}\boldsymbol{m^2}mol^{-1})$ and that of c is $mol\boldsymbol{dm^{-3}}$ then; $\boldsymbol{\Lambda_c = \frac{\mathcal{K}}{1000c}}$	The expression $\Lambda_c = \frac{\mathcal{K}}{c}$ is only and only used if the units are consistent.

Note: When the definitions are stated in terms of formulae, each term in the formula should be well defined.

Measurement of conductivity of solutions



A solution of the electrolyte of known concentration is prepared using conductivity water (demineralized water or water purified by ion exchange)

A known volume of the standard solution of the electrolyte is then pipetted and placed in a conductivity cell.

The conductivity cell and its solution is connected in a Wheatstone bridge circuit where it's made the unknown resistance.

A rapidly alternating current is applied from a small induction coil or a vacuum tube oscillator.

The variable resistance and the position X along wire AB are changed until no current passes through the head phones

At this balance point the buzzing sound in the head phones (used as detector) is a minimum.

The distances AX and XB at balance point are measured.

The area of the electrodes(A) in the conductivity cell and their distance of separation(l) is also measured.

Treatment of results

At the balance point ;

$$\frac{Resistance\ of\ conductivity\ cell(solution)}{Resistance\ of\ variable\ resistance} = \frac{AX}{XB}$$

The resistance of the solution is then calculated and used to find conductance from;

$$Conductance = \frac{1}{R}\ where\ R\ is\ Resistance\ of\ solution$$

$$\boldsymbol{The\ electrolytic\ conductivity, \mathcal{K} = \frac{1}{R} \times \frac{l}{A}}$$

Calculations involving electrolytic conductance

Examples

1. (a) State what is meant by the term cell constant.

(b) The resistivity of 0.02M potassium chloride solution is 361 Ωcm and a conductivity cell having such a solution was found to have a resistance of 550 Ω.

(i) Calculate the cell constant

(ii) if the same cell was filled with 0.1M zinc sulphate solution had a resistance of 72 Ω. Calculate the conductivity of 0.1M zinc sulphate solution.

(b) (i) $\rho = 361\Omega cm \; R = 550\Omega$

$$From\ R = \rho\frac{l}{A}$$

$$R = \rho \times Cell\ constant$$

$$Cell\ constant = \frac{R}{\rho} = \frac{550\Omega}{361\Omega cm}$$

$$= \mathbf{1.5235 cm^{-1}}$$

(ii) $R = 72\Omega$

$$\mathcal{K} = \frac{1}{R}\times\frac{l}{A} = \frac{1}{R}\times Cell\ constant$$

$$\mathcal{K} = \frac{1}{R}\times Cell\ constant$$

$$= \frac{1}{72\Omega}\times 1.5235cm^{-1}$$

$$\boldsymbol{\mathcal{K} = 0.02116\ Scm^{-1}}$$

2. (a) A conductivity cell with electrodes $2cm^2$ in area and $1cm$ apart has a resistance of 7.25 Ω when filled with 5 percent potassium chloride solution. Calculate the:

(i) cell constant

(ii) the conductivity of the potassium chloride solution.

(b) If the same cell was filled with 0.02M potassium chloride with a resistivity of 361 Ωcm. Calculate the resistance.

(a) (i) $A = 2cm^2 \; l = 1cm \;\; R = 7.25\Omega$

$$Cell\ constant = \frac{l}{A} = \frac{1}{2} = \mathbf{0.5 cm^{-1}}$$

(ii) $\mathcal{K} = \frac{1}{R}\times\frac{l}{A} = \frac{1}{R}\times Cell\ constant$

$$\mathcal{K} = \frac{1}{R}\times Cell\ constant$$

$$= \frac{1}{7.25\Omega}\times 0.5cm^{-1}$$

$$\boldsymbol{\mathcal{K} = 0.06897\ Scm^{-1}}$$

(b) $\rho = 361\Omega cm$

$$R = \rho\frac{l}{A}$$

$$R = \rho \times Cell\ constant$$

$$\boldsymbol{R = 361 \times 0.5}$$

$$\boldsymbol{R = 180.5\Omega}$$

3. The resistance of a 0.01M sodium chloride solution in a conductivity cell was found to be 210 Ω. The specific conductance of the solution is $\mathbf{4.5 \times 10^{-3}\ Scm^{-1}}$. Determine the cell constant.

$R = 210\Omega \qquad \mathcal{K} = 4.5 \times 10^{-3}\ Scm^{-1}$

$$\mathcal{K} = \frac{1}{R} \times \frac{l}{A} = \frac{1}{R} \times Cell\ constant$$

$$\mathcal{K} = \frac{Cell\ constant}{R}$$

$$Cell\ constant = \mathcal{K} \times R$$

$$= 4.5 \times 10^{-3} \times 210$$

$$\boldsymbol{Cell\ constant = 0.945cm^{-1}}$$

---

4. A conductivity cell has electrodes of cross sectional area $4cm^2$ and $2cm$ apart. The cell is filled with pure water of conductivity $8 \times 10^{-7}Scm^{-1}$ and a potential difference of 10V applied. Calculate the current that would flow through the cell.

$A = 4cm^2\ l = 2cm\ \mathcal{K} = 8 \times 10^{-7}\ Scm^{-1}$

$V = 10V$

$$\mathcal{K} = \frac{1}{R} \times \frac{l}{A}$$

$$8 \times 10^{-7} = \frac{1}{R} \times \frac{2}{4}$$

$$R = \frac{2}{4 \times 8 \times 10^{-7}} = 625000\Omega$$

$$V = IR$$

$$I = \frac{V}{R} = \frac{10}{625000} = \boldsymbol{1.6 \times 10^{-5}A}$$

---

5. A 0.1M solution of ethanoic acid when placed between two electrodes , each $2.5\ cm^2$ in area and separated by $0.8\ cm$ has a resistance of 6956 ohms. Calculate the:

(i) specific conductivity,

(ii) molar conductivity of the solution.

$c = 0.1moldm^{-3}\ A = 2.5cm^2$

$l = 0.8cm\ R = 6956\Omega$

(i) $\mathcal{K} = \frac{1}{R} \times \frac{l}{A} = \frac{1}{6956} \times \frac{0.8}{2.5}$

$$\boldsymbol{\mathcal{K} = 4.6 \times 10^{-5}\Omega^{-1}cm^{-1}}$$

(ii) $\Lambda_c = \frac{1000\mathcal{K}}{c} = \frac{1000 \times 4.6 \times 10^{-5}}{0.1}$

$$\boldsymbol{\Lambda_c = 0.46\Omega^{-1}cm^2mol^{-1}}$$

---

6. The molar conductivity of 0.1M ethanoic acid solution is $4.6\ Scm^2mol^{-1}$. Calculate the:

(i) electrolytic conductivity

(ii) resistivity.

(i) $\Lambda_c = 4.6Scm^2mol^{-1}c = 0.1moldm^{-3}$

$\mathcal{K} = ?$

$$\Lambda_c = \frac{1000\mathcal{K}}{c} \qquad \mathcal{K} = \frac{\Lambda_c \times c}{1000}$$

$$\mathcal{K} = \frac{4.6 \times 0.1}{1000} = \boldsymbol{4.6 \times 10^{-4}Scm^{-1}}$$

(ii) $\mathcal{K} = \frac{1}{\rho}$

$$\rho = \frac{1}{\mathcal{K}} = \frac{1}{4.6 \times 10^{-4}Scm^{-1}}$$

$$\boldsymbol{\rho = 2173.91\Omega cm}$$

---

7. The resistance of a conductivity cell of a conductivity cell when filled with 0.05M solution of an electrolyte M_2N is 100 Ω at 40°C. The same conductivity cell when filled with 0.01M XY solution has a resistance of 50 Ω. If the electrolytic conductivity of 0.05M M_2N is $0.0001\ Scm^{-1}$. Calculate the:

(i) electrolytic conductivity of 0.01M XY solution

(ii) molar conductivity of 0.01M XY solution

(i) For $\boldsymbol{M_2N}$;

$c = 0.05moldm^{-3} R = 100\Omega$

$\mathcal{K} = 0.0001Scm^{-1}$

$\mathcal{K} = \frac{1}{R} \times cell\ constant$

$0.0001 = \frac{1}{100} \times cell\ constant$

$Cell\ constant = 0.0001 \times 100$

$\boldsymbol{Cell\ constant = 0.01cm^{-1}}$

For XY;

$c = 0.01moldm^{-3} R = 50\Omega$

$Cell\ constant = 0.01cm^{-1}$

$\mathcal{K} = \frac{1}{R} \times cell\ constant$

$\mathcal{K} = \frac{1}{50} \times 0.01 = \boldsymbol{0.0002\Omega^{-1}cm^{-1}}$

(ii) $\Lambda_c = \frac{1000\mathcal{K}}{c}$

$\Lambda_c = \frac{1000 \times 0.0002}{0.01}$

$\boldsymbol{\Lambda_c = 20\ \Omega^{-1}cm^{2}mol^{-1}}$

8. Calculate the mass of ethanoic acid that must be dissolved in a litre of water to make a solution of molar conductivity $\boldsymbol{75.08\,\Omega^{-1}cm^{2}mol^{-1}}$ and electrolytic conductivity $\boldsymbol{0.027\,\Omega^{-1}cm^{-1}}$.

$\Lambda_c = 75.08\Omega^{-1}cm^{2}mol^{-1}$

$\mathcal{K} = 0.027\Omega^{-1}cm^{-1}$

$\Lambda_c = \frac{1000\mathcal{K}}{c} \qquad c = \frac{1000\mathcal{K}}{\Lambda_c}$

$c = \frac{1000 \times 0.027}{75.08} = \boldsymbol{0.3596\,moldm^{-3}}$

$Molar\ mass\ of\ CH_3COOH$

$= 24 + 4 + 32$

$= 60g$

$\boldsymbol{Mass\ of\ CH_3COOH\ in\ one\ litre}$

$\boldsymbol{= 60 \times 0.3596}$

$\boldsymbol{= 21.576g}$

Questions

1. A conductivity cell with electrodes 4 cm^2 in area and 1.5 cm apart has a resistance of 35.6 Ω when filled with 2.085 percent barium chloride solution. Calculate the:
   (i) cell constant
   (ii) the electrolytic conductivity of the barium chloride solution.
2. A conductivity cell has electrodes of cross-sectional area of $5cm^2$ in area and $2cm$ apart. Calculate the cell constant of the conductivity cell.
3. A conductivity cell has electrodes of cross-sectional area of $10\ cm^2$ in area and $2cm$ apart. Calculate the cell constant of the conductivity cell.
4. The electrolytic conductivity of 2M potassium chloride solution of $0.3704\,Scm^{-1}$. The resistance of 2M potassium chloride solution in a conductivity cell is 1.5 Ω. Calculate the cell constant of the conductivity cell.
5. The conductivity of an aqueous solution of sodium chloride in a cell is $92\,ohm^{-1}cm^{-1}$.The resistance offered by the cell is 247.8 ohm. Calculate the cell constant.
6. The molar conductance of 2M potassium chloride solution is $185.2\,\Omega^{-1}cm^{2}$. Calculate the specific conductance of the solution.

7. A 0.05M sodium hydroxide solution offered a resistance of 31.6 Ω in a conductivity cell at 298K. If the cell constant of the cell is $0.367cm^{-1}$.Calculate the molar conductivity of the sodium hydroxide solution.
8. (a) Define the terms;
    (i) conductivity
    (ii) conductance

    (b) Using the same conductivity cell, the resistance of potassium chloride solution and 0.1M chloroethanoic acid solution were found to be 24.9 and 66.5 ohms respectively at 25℃. The conductivity of potassium chloride at 25℃ is $0.01164\Omega^{-1}cm^{-1}$.
    (i) Calculate the cell constant
    (ii) Calculate the conductivity of 0.1M chloroethanoic acid.

Factors affecting electrolytic conductivity of electrolytes

The factors affecting electrolytic conductivity include:

(i) Concentration
(ii) Temperature

(i) Concentration

For a strong electrolyte, ***as concentration increases, conductivity increases up to a maximum and then decreases***.

Explanation;

As ***concentration increases***, ***the total number of conducting ions per unit volume solution increases***. This increases the conductivity. As ***concentration increases further***, the total number ions in solution increases further since the electrolyte is completely ionized at all concentrations, ***inter-ionic distance decreases***, ***ionic interference increases*** and ***ionic mobility decreases***. This decreases the electrolytic conductivity.

For a weak electrolyte, ***as concentration increases, conductivity increases up to a maximum and then decreases***.

Explanation;

As ***concentration increases***, ***the total number of conducting ions per unit volume solution increases***. This increases the conductivity. As ***concentration increases further***, the total number unionized molecules of the electrolyte increases, ***degree of dissociation decreases*** and ***the number of conducting ions per unit volume of solution decreases***. This decreases the electrolytic conductivity.

(ii) Temperature

For a strong electrolyte, ***conductivity increases with increase in temperature***.

Explanation;

As ***temperature increases***, ***the average kinetic energy of the conducting ions increases***. The ***viscosity of the water decreases*** and the ***ionic mobility increases***.

For weak electrolytes, ***the effect of temperature depends on the enthalpy change which accompanies ionization.***

For a weak electrolyte that ***ionizes exothermically, increase in temperature decreases the degree of dissociation*** according to Le Chatelier's principle. Hence ***the number of conducting ions per unit volume of solution decreases***. This ***decreases the electrolytic conductivity***.

For a weak electrolyte that ***ionizes endothermically, increase in temperature increases the degree of dissociation*** according to Le Chatelier's principle. Hence ***the number of conducting ions per unit volume of solution increases***. This ***increases the electrolytic conductivity***.

Factors affecting molar conductivity of electrolytes

The factors affecting molar conductivity include:

(i) ***Temperature of the solution***
(ii) ***Magnitude of the charge on the ions***
(iii) ***Ionic radius***
(iv) ***Viscosity of the solvent***
(v) ***Concentration of the solution***

(i) Temperature of the solution

For a strong electrolyte, ***molar conductivity increases with increase in temperature***.

Explanation;

As ***temperature increases***, ***the average kinetic energy of the conducting ions increases***. The ***viscosity of the water decreases*** and the ***ionic mobility increases***.

For weak electrolytes, ***the effect of temperature depends on the enthalpy change which accompanies ionization.***

For a weak electrolyte that ***ionizes exothermically, increase in temperature decreases the degree of dissociation*** according to Le Chatelier's principle. Hence ***the number of conducting ions per unit volume of solution decreases***. This ***decreases the molar conductivity***.

For a weak electrolyte that ***ionizes endothermically, increase in temperature increases the degree of dissociation*** according to Le Chatelier's principle. Hence ***the number of conducting ions per unit volume of solution increases***. This ***increases the molar conductivity***.

Question

(a) Distinguish between electrolytic conductivity and molar conductivity

(b) The molar conductivity of ethanoic acid containing $0.03 mol dm^{-3}$ is 8.50 units at 18℃ and 14.7 units at 100℃. Explain the difference in molar conductivities at the two temperatures.

(ii) Magnitude of the charge on the ions

Molar conductivity increases with increase in the magnitude of ionic charge. Ions with high charges are ***more strongly attracted by the oppositely charged electrode*** and ***move faster***.

(iii) Ionic radius

Molar conductivity increases with increase in ionic radius. The ***higher the ionic radius, the lower the charge density*** and ***the less hydrated the ion***. The less hydrated ions ***move faster than heavily hydrated ions*** hence ions with smaller ionic radius are more conducting than ions with higher ionic radius.

Question; Explain why the:

(a) magnesium ion has a higher molar conductivity than the sodium ion

(b) sulphate ion has a higher molar conductivity than the chloride ion.

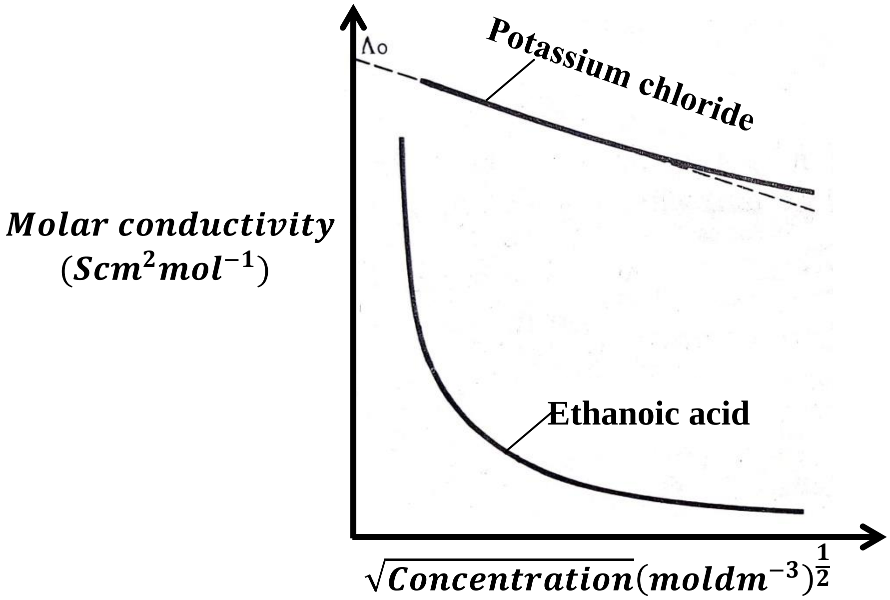
(c) the molar conductivity of the lithium ion is smaller than that of the sodium ion

(iv) Viscosity of the solvent

The ***higher the viscosity of the solvent***, the ***lower the ionic mobility*** hence ***the lower the molar conductivity***.

(v) Concentration of the solution

The sketches below show the variation of *molar conductivity* with the *square root of concentration* for both *a strong electrolyte* and a *weak electrolyte*.



Explanation of the shapes of the graphs

For potassium chloride, ***as concentration increases***, ***molar conductivity decreases***.

Potassium chloride is a ***strong electrolyte***. As ***concentration increases***, ***the total number of conducting ions per unit volume increases***, ***inter ionic distance decreases***, ***ionic interference increases*** and ***ionic mobility decreases***.

At ***zero concentration (infinite dilution)***, ***molar conductivity reaches a maximum value*** called molar conductivity at infinite dilution because ***ionic interference is negligible***.

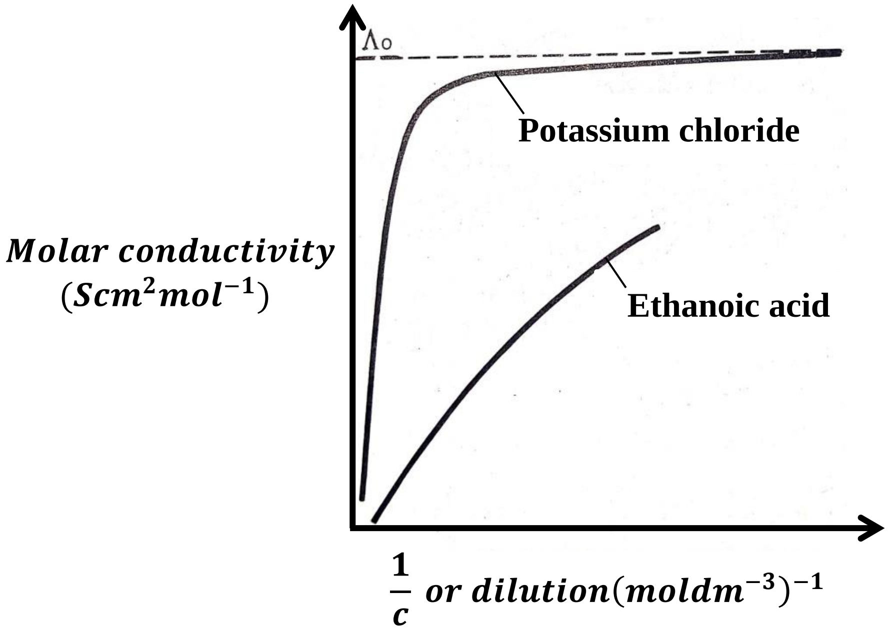
N.B Molar conductivity at infinite dilution is obtained from the graph by extrapolation.

For Ethanoic acid, ***as concentration increases***, ***molar conductivity decreases***.

Ethanoic acid is a ***weak electrolyte***. As ***concentration increases***, ***the degree of dissociation decreases*** and ***the number of conducting ions per unit volume of solution decreases***.

Instead of concentration, reciprocal of concentration$\left(\frac{1}{c}\right)$, also called dilution can be used.

The sketches below show the variation of *molar conductivity* with the *dilution* for both a *strong electrolyte* and a *weak electrolyte*.



Note that neither the graphs against concentration nor those against dilution begin from the origin.
The graphs do not coincide anywhere too

Explanation of the shapes of the graphs

For potassium chloride, *as dilution increases, molar conductivity increases to a maximum value at which it remains constant at infinite dilution.*

Potassium chloride is a ***strong electrolyte***. As ***dilution increases***, ***inter-ionic distance increases, ionic interference decreases*** and ***ionic mobility increases***.

At ***zero concentration (infinite dilution), the ionic interference is negligible***.

N.B Molar conductivity at infinite dilution is obtained from the graph by extrapolation.

For Ethanoic acid, ***as dilution increases, molar conductivity increases***.

Ethanoic acid is ***a weak electrolyte***. As ***dilution increases***, ***degree of dissociation increases*** and the ***number of conducting ions per unit volume of solution increases***.

Questions

1. The table below shows values of molar conductivity of ethanoic and potassium chloride at different concentrations.

Concentration$(moldm^{-3})$	0.0001	0.001	0.01	0.1	1	2	3
$\Lambda_c, CH_3COOH(\Omega^{-1}cm^2mol^{-1})$	107.0	41.0	14.3	4.6	1.32	0.80	0.54
$\Lambda_c, KCl(\Omega^{-1}cm^2mol^{-1})$	129.1	127.3	122.4	112.0	98.3	92.6	88.3
$(Concentration)^{\frac{1}{2}}(moldm^{-3})^{\frac{1}{2}}$							

   (a) Complete the table above.
   (b) On the same axes, plot graphs for molar conductivity against the square root of concentration.
   (c) State and explain the shapes of the graphs in (b) above.

2. The table below shows values of molar conductivity of hydrochloric acid and ammonia solution at different concentrations at 18℃.

Concentration$(moldm^{-3})$	0.001	0.01	0.1	1	3
$\Lambda_c, HCl(Scm^2mol^{-1})$	377	370	351	301	215
$\Lambda_c, NH_3(aq)(Scm^2mol^{-1})$	28	9.6	3.3	0.89	0.36
$Dilution(moldm^{-3})^{-1}$					

   (a) Complete the table above.
   (b) On the same axes, plot graphs for molar conductivity against dilution.
   (c) State and explain the shapes of the graphs in (b) above.

3. The table below shows values of molar conductivity of sodium chloride solution at different concentrations at 25℃.

Concentration$(moldm^{-3})$	0.2	0. 1	0.05	0.02	0.01	0.005	0.001
Molar conductivity of sodium chloride(Sm^2mol^{-1})	0.01015	0.0107	0.0111	0.0116	0.0118	0.0122	0.0124
$Dilution(moldm^{-3})^{-1}$							
$\sqrt{Concentration}(moldm^{-3})^{\frac{1}{2}}$							

   (a) Complete the table above.
   (b) On different axes, plot a graph for:
      (i) molar conductivity against dilution.
      (ii) molar conductivity against $\sqrt{Concentration}$
   (c) From each of the graphs determine the molar conductivity at infinite dilution of sodium chloride.
   (d) Explain the shape of each of the graphs in (b) above.

4. The table below shows values of molar conductivity of ethanoic acid solution at different concentrations at 18℃.

Concentration, $C(moldm^{-3})$	0.001	0.01	0.1	1.0	3.0
$\Lambda_c, CH_3COOH(\Omega^{-1}cm^2mol^{-1})$	41.00	14.30	4.60	1.32	0.54
$C^{\frac{1}{2}}\left(mol^{\frac{1}{2}}dm^{-\frac{3}{2}}\right)$					
$\frac{1}{C}(moldm^{-3})^{-1}$					

   (a) Complete the table above.
   (b) On different axes, plot a graph for:
      (i) molar conductivity against the square root of concentration.
      (ii) molar conductivity against dilution
   (c) Explain the shape of each of the graphs in (b) above.

5. (a)Define the term molar conductivity
   - (b) On the same sketch, draw a graph to show variation of molar conductivity of aluminium sulphate and ethanoic acid.
   - (c) Compare and explain the shape of your graph for:
     - (i) ethanoic acid
     - (ii) aluminium sulphate

Kohlrausch's law of independent migration of ions and its application

Kohlrausch Friedrich investigated the molar conductivity at infinite dilution of a large number of electrolytes and found that it was a sum of two quantities.

Kohlrausch's law states that the molar conductivity at infinite dilution of an electrolyte is equal to the sum of the molar conductivities at infinite dilution of the ions produced by the electrolyte.

$$\Lambda_0(NaCl) = \Lambda_0(Na^+) + \Lambda_0(Cl^-)$$
$$\Lambda_0(CH_3COOH) = \Lambda_0(CH_3COO^-) + \Lambda_0(H^+)$$
$$\Lambda_0(MgCl_2) = \Lambda_0(Mg^{2+}) + 2\Lambda_0(Cl^-)$$
$$\Lambda_0(Na_2SO_4) = 2\Lambda_0(Na^+) + \Lambda_0(SO_4^{2-})$$
$$\Lambda_0(Al_2(SO_4)_3) = 2\Lambda_0(Al^{3+}) + 3\Lambda_0(SO_4^{2-})$$

Applications of Kohlrausch's law

- ***(i) Indirect determination of molar conductivity at infinite dilution for weak electrolytes.***
- ***(ii) To determine solubility of sparingly soluble electrolytes***
- ***(iii) To determine solubility product of sparingly soluble electrolytes***
- ***(iv) To determine degree of dissociation and equilibrium constant of a weak electrolyte***

(i) Indirect determination of molar conductivity at infinite dilution for weak electrolytes.

The molar conductivity at infinite dilution of a weak electrolyte can be obtained if the molar conductivities of selected strong electrolytes are known.

For ethanoic acid, the molar conductivity at infinite dilution can be obtained from the molar conductivities at infinite dilution of hydrochloric acid, potassium ethanoate and potassium chloride.

$$\Lambda_0(HCl) = \Lambda_0(H^+) + \Lambda_0(Cl^-) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(i)$$
$$\Lambda_0(CH_3COOK) = \Lambda_0(CH_3COO^-) + \Lambda_0(K^+) \ldots\ldots\ldots..(ii)$$
$$\Lambda_0(KCl) = \Lambda_0(K^+) + \Lambda_0(Cl^-) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots...(iii)$$
$$\Lambda_0(CH_3COOH) = \Lambda_0(CH_3COO^-) + \Lambda_0(H^+) \ldots\ldots\ldots\ldots.(iv)$$

Since equation (iv) can be obtained by adding (i) and (ii) and subtracting equation (iii);
Therefore;

$$\Lambda_0(CH_3COOH) = [\Lambda_0(CH_3COO^-) + \Lambda_0(K^+)] + [\Lambda_0(H^+) + \Lambda_0(Cl^-)] - [\Lambda_0(K^+) + \Lambda_0(Cl^-)]$$

$$\boldsymbol{\Lambda_0(CH_3COOH) = \Lambda_0(CH_3COOK) + \Lambda_0(HCl) - \Lambda_0(KCl)}$$

Examples

1. **Given that the molar conductivities at infinite dilution of some electrolytes are as shown below;**

Compound	$\boldsymbol{\Lambda_o(Scm^2mol^{-1})}$
Sodium chloride	**113**
Ammonium chloride	**134.1**
Sodium hydroxide	**225.2**
Sodium methanoate	**101.2**
Hydrochloric acid	**397.8**

(a) Calculate the molar conductivity at infinite dilution of:

- **(i) methanoic acid**
- **(ii) ammonia solution**
- **(iii) ammonium methanoate**

(b) Explain the differences in your answers in a(i) and (iii) above

(i)
$$\Lambda_0(HCOOH) = \Lambda_0(HCOONa) + \Lambda_0(HCl) - \Lambda_0(NaCl)$$
$$\Lambda_0(\boldsymbol{HCOOH}) = (101.2 + 397.8 - 113) = \boldsymbol{386\ Scm^2mol^{-1}}$$

(ii)
$$\Lambda_0(NH_3(aq)) = \Lambda_0(NH_4Cl) + \Lambda_0(NaOH) - \Lambda_0(NaCl)$$
$$\Lambda_0(NH_3(aq)) = (134.1 + 225.2 - 113) = \boldsymbol{246.3\ Scm^2mol^{-1}}$$

(iii)
$$\Lambda_0(HCOONH_4) = \Lambda_0(HCOONa) + \Lambda_0(NH_4Cl) - \Lambda_0(NaCl)$$
$$\Lambda_0(\boldsymbol{HCOONH_4}) = (101.2 + 134.1 - 113) = \boldsymbol{122.3\ Scm^2mol^{-1}}$$

(b) ***The molar conductivity at infinite dilution of methanoic acid is higher than that of ammonium methanoate because the hydrogen ion in methanoic acid has a higher molar conductivity than the ammonium ion in ammonium methanoate.***

2. **The molar conductivity at infinite dilution of the sulphate ion is 160 $\Omega^{-1}\boldsymbol{cm^2mol^{-1}}$. If the molar conductivity at infinite dilution of aluminium sulphate is 858 $\Omega^{-1}\boldsymbol{cm^2mol^{-1}}$, calculate the molar conductivity at infinite dilution of the aluminium ion**.

$$\Lambda_0(Al_2(SO_4)_3) = 2\Lambda_0(Al^{3+}) + 3\Lambda_0(SO_4^{2-})$$
$$858 = 2\Lambda_0(Al^{3+}) + 3(160)$$
$$2\Lambda_0(Al^{3+}) = 858 - 480$$
$$\Lambda_0(Al^{3+}) = \frac{378}{2} = \boldsymbol{189}\Omega^{-1}\boldsymbol{cm^2mol^{-1}}$$

(i) Determining solubility and solubility product of sparingly soluble electrolytes

The solubility of a sparingly soluble salt can be determined from the molar conductivity of its saturated solution using the steps below:

The electrolytic conductivity of the saturated solution($\mathcal{K}_{solution}$) is measured using a conductivity meter.

Using a known value of $\mathcal{K}_{H_2O}$, the electrolytic conductivity of the electrolyte is then obtained from the expression;

$$\mathcal{K}_{electrolyte} = \mathcal{K}_{solution} - \mathcal{K}_{water}$$

The molar conductivity at infinite dilution of the electrolyte (Λ_O) is obtained from the known values molar conductivity at infinite dilution of its constituent ions or from the known values molar conductivity at infinite dilution of selected electrolytes using Kohlrausch's law. Since the solution is very dilute then; $\Lambda_O = \Lambda_c$.

The expression; $\Lambda_c = \frac{1000\,\mathcal{K}_{electrolyte}}{C}$ or $\Lambda_c = \frac{\mathcal{K}_{electrolyte}}{1000\,C}$ is then used to calculate the solubility, $C\ \ in\ moldm^{-3}$ depending on the units of $\mathcal{K}$.

The stoichiometry of reaction is then used to determine the solubility product, K_{sp}.

Experiment to determine solubility and solubility product of silver chloride

Excess solid silver chloride is added to a given volume of distilled water in a container.

The mixture is shaken for some time and ***left to settle*** at ***a given temperature*** to attain equilibrium.

The mixture is ***filtered*** to obtain ***a saturated solution of silver chloride*** as filtrate.

The electrolytic conductivity of the saturated solution, $\mathcal{K}_{solution}(ohm^{-1}cm^{-1})$ is measured using a conductivity meter.

The electrolytic conductivity of water, $\mathcal{K}_{H_2O}(ohm^{-1}cm^{-1})$ at the same temperature is obtained from books

Also the molar conductivities at infinite dilution (Λ_O) of silver ions and chloride ions are read from the tables.

Treatment of results

The electrolytic conductivity of silver chloride is then obtained by;

$$\mathcal{K}_{AgCl} = \mathcal{K}_{solution} - \mathcal{K}_{H_2O}$$

The molar conductivity of silver chloride at infinite dilution is obtained by the equation;

$$\Lambda_O(AgCl) = \Lambda_O(Ag^+) + \Lambda_O(Cl^-)$$

$\Lambda_O(AgCl) = \Lambda_c(AgCl)$, where Λ_c is molar conductivity of silver chloride

$$\Lambda_c(AgCl) = \frac{1000\,\mathcal{K}_{AgCl}}{C}\ where\ C\ is\ solubility\ in\ moldm^{-3}$$

$$AgCl(s) + aq \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$[AgCl] = C\ moldm^{-3}$$

$$Since\ mole\ ratio\ of AgCl{:}\ Ag^+ = 1{:}\,1$$

$$[AgCl] = [Ag^+] = [Cl^-] = C\ moldm^{-3}$$
$$K_{sp} = [Ag^+][Cl^-] = C^2$$
$$\boldsymbol{K_{sp} = C^2\ mol^2dm^{-6}}$$

(Revisit the experiments on solubility product in the topic IONIC EQUILIBRIA for more experiments on solubility product)

Examples

1. **The electrolytic conductivity of a saturated solution of silver chloride at 25℃ is $3.1 \times 10^{-4}\Omega^{-1}m^{-1}$. The molar conductivities at infinite dilution of silver and chloride ions are $6.2 \times 10^{-3}\Omega^{-1}m^2mol^{-1}$ and $7.7 \times 10^{-3}\Omega^{-1}m^2mol^{-1}$ respectively.**
   The electrolytic conductivity of pure water at 25℃ is $1.6 \times 10^{-4}\Omega^{-1}m^{-1}$
   Calculate the:
   (a) solubility of silver chloride at 25℃ in grams per litre
   (b) solubility product of silver chloride
   $(Ag = 108, Cl = 35.5)$

(a) $\mathcal{K}_{AgCl} = \mathcal{K}_{solution} - \mathcal{K}_{water}$
$$\mathcal{K}_{AgCl} = (3.1 \times 10^{-4}) - (1.6 \times 10^{-4})$$
$$= \boldsymbol{1.5 \times 10^{-4}\Omega^{-1}m^{-1}}$$
$$\Lambda_0(AgCl) = \Lambda_0(Ag^+) + \Lambda_0(Cl^-)$$
$$= (6.2 \times 10^{-3}) + (7.7 \times 10^{-3})$$
$$\boldsymbol{\Lambda_0(AgCl) = 0.0139\Omega^{-1}m^2mol^{-1}}$$
$$\Lambda_0(AgCl) = \Lambda_c(AgCl)$$
$$\boldsymbol{\Lambda_c(AgCl) = \frac{\mathcal{K}_{AgCl}}{1000\ C}}$$
$$C = \frac{\mathcal{K}_{AgCl}}{1000\Lambda_c(AgCl)} = \frac{1.5 \times 10^{-4}}{1000 \times 0.0139}$$
$$= 1.079 \times 10^{-5}moldm^{-3}$$
$$Molar\ mass\ of\ AgCl = 108 + 35.5 = 143.5g$$
Solubility in $gdm^{-3} = (143.5 \times 1.079 \times 10^{-5})$
$$= \boldsymbol{1.548 \times 10^{-5}gdm^{-3}}$$
(b) $AgCl(s) + aq \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
$$K_{sp} = [Ag^+][Cl^-] = (1.079 \times 10^{-5})^2$$
$$= \boldsymbol{1.164 \times 10^{-10}mol^2dm^{-6}}$$

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2. **The electrolytic conductivity of a saturated solution of silver bromide at 25℃ is $8.486 \times 10^{-7}\Omega^{-1}cm^{-1}$. The electrolytic conductivity of pure water at 25℃ is $7.5 \times 10^{-7}\Omega^{-1}cm^{-1}$. Calculate the solubility product of silver bromide.**
   (*The molar conductivities at infinite dilution of potassium bromide, silver nitrate and potassium nitrate at infinite dilution are 137.4, 133 and 131*$\Omega^{-1}cm^2mol^{-1}$ *respectively* at 25℃)

$$\mathcal{K}_{AgBr} = \mathcal{K}_{solution} - \mathcal{K}_{water}$$
$$\mathcal{K}_{AgBr} = (8.486 \times 10^{-7}) - (7.5 \times 10^{-7})$$
$$= \boldsymbol{9.86 \times 10^{-8}\ \Omega^{-1}cm^{-1}}$$
$$\Lambda_0(AgBr) = \Lambda_0(AgNO_3) + \Lambda_0(KBr) - \Lambda_0(KNO_3)$$
$$= (133 + 137.4 - 131)\Omega^{-1}cm^2mol^{-1}$$
$$\boldsymbol{\Lambda_0(AgBr) = 139.4\Omega^{-1}cm^2mol^{-1}}$$
$$\Lambda_0(AgBr) = \Lambda_c(AgBr)$$
$$\boldsymbol{\Lambda_c(AgBr) = \frac{1000\mathcal{K}_{AgBr}}{C}}$$
$$C = \frac{1000\mathcal{K}_{AgBr}}{\Lambda_c(AgBr)} = \frac{1000 \times 9.86 \times 10^{-8}}{139.4}$$
$$= \boldsymbol{7.073 \times 10^{-7}moldm^{-3}}$$
$$AgBr(s) + aq \rightleftharpoons Ag^+(aq) + Br^-(aq)$$
$$K_{sp} = [Ag^+][Br^-] = (7.073 \times 10^{-7})^2$$
$$= \boldsymbol{5 \times 10^{-13}mol^2dm^{-6}}$$

3. (a) Calcium phosphate is sparingly soluble in water.
Write:

- **(i) equation for the solubility of calcium phosphate in water**
- **(ii) the expression for the solubility product of calcium phosphate**

(b) The molar conductivities of calcium chloride, sodium phosphate and sodium chloride at infinite dilution at $25℃$ are 271.8, 390.3 and 126.5$\Omega^{-1}\boldsymbol{cm^2mol^{-1}}$ respectively. Calculate the:

- **(i) molar conductivity of calcium phosphate at infinite dilution at $25℃$.**
- **(ii) solubility product of calcium phosphate at $25℃$.**
  (Electrolytic conductivity of calcium phosphate is $\mathbf{1.31\times10^{-2}}\Omega^{-1}\boldsymbol{cm^{-1}}$)

(a) (i) $Ca_3(PO_4)_2(s) + aq \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$

(iii) $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$

$$3CaCl_2(aq) + 2Na_3PO_4(aq) \longrightarrow Ca_3(PO_4)_2(s) + 6NaCl(aq)$$

(b) (i)

$$\Lambda_0(Ca_3(PO_4)_2) = 3\Lambda_0(Ca^{2+}) + 2\Lambda_0(PO_4^{3-})$$
$$\Lambda_0(Ca_3(PO_4)_2) = 3\Lambda_0(CaCl_2) + 2\Lambda_0(Na_3PO_4) - 6\Lambda_0(NaCl)$$
$$\Lambda_0(Ca_3(PO_4)_2) = [3(271.8) + 2(390.3) - 6(126.5)]\Omega^{-1}cm^2mol^{-1}$$
$$\boldsymbol{\Lambda_0(Ca_3(PO_4)_2) = 837\Omega^{-1}cm^2mol^{-1}}$$

(ii)

$$\Lambda_0(Ca_3(PO_4)_2) = \Lambda_c(Ca_3(PO_4)_2)$$
$$\mathcal{K}_{Ca_3(PO_4)_2} = 1.31\times10^{-2}\ \Omega^{-1}cm^{-1}$$
$$\boldsymbol{\Lambda_c(Ca_3(PO_4)_2) = \frac{1000\mathcal{K}_{Ca_3(PO_4)_2}}{C}}$$
$$C = \frac{1000\mathcal{K}_{Ca_3(PO_4)_2}}{\Lambda_c(Ca_3(PO_4)_2)} = \frac{1000\times1.31\times10^{-2}}{837} = \mathbf{0.01565}\ \boldsymbol{moldm^{-3}}$$
$$\boldsymbol{[Ca^{2+}] = 3[Ca_3(PO_4)_2] = (3\times0.01565) = 0.04695M}$$
$$\boldsymbol{\left[PO_4^{3-}\right] = 2[Ca_3(PO_4)_2] = (2\times0.01565) = 0.0313M}$$
$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (0.04695)^3\times(0.0313)^2\ (moldm^{-3})^5$$
$$\boldsymbol{K_{sp} = 1.014\times10^{-7}\ mol^5dm^{-15}}$$

(ii) Determining degree of dissociation and equilibrium constant of a weak electrolyte

The degree of dissociation(α) of a weak electrolyte can be obtained if the molar conductivity at a given concentration (Λ_c) and the molar conductivity at infinite dilution(Λ_o) are known.

$$\boldsymbol{\alpha = \frac{\Lambda_c}{\Lambda_o}}$$

The acid dissociation constant, $\boldsymbol{K_a}$ of a weak acid can then be obtained from the expression;

$$\boldsymbol{K_a = \frac{c\alpha^2}{(1-\alpha)}}$$

However, if $\boldsymbol{\alpha}$ is small compared to 1, then $(\boldsymbol{1-\alpha})$ is approximately equal to one, so that; $\boldsymbol{K_a = c\alpha^2}$

The concentration of hydrogen ions is obtained from the expression $[\boldsymbol{H^+}] = \boldsymbol{c\alpha}$ and the pH can be calculated.

The base dissociation constant and hydrolysis constant for salts.

Examples

1. **The electrolytic conductivity of a 0.16M ethanoic acid solution at 18℃ is $0.0195\ \Omega^{-1}m^{-1}$. The molar conductivity at infinite dilution of hydrogen ion and ethanoate ion are $3.15 \times 10^{-2}\Omega^{-1}m^2mol^{-1}$ and $0.35 \times 10^{-2}\Omega^{-1}m^2mol^{-1}$ respectively. Calculate the:**
   (i) degree of dissociation , α of ethanoic acid.
   (ii) acid dissociation constant, K_a, at 25℃.

(i) $c = 0.16M \qquad \mathcal{K} = 0.0195\Omega^{-1}m^{-1}$

$$\Lambda_0(CH_3COOH) = \Lambda_0(CH_3COO^-) + \Lambda_0(H^+)$$

$$\Lambda_0(CH_3COOH) = (0.35 \times 10^{-2}) + (3.15 \times 10^{-2})$$

$$= \boldsymbol{3.5 \times 10^{-2}\Omega^{-1}m^2mol^{-1}}$$

$$\Lambda_c = \frac{\mathcal{K}}{1000c} = \frac{0.0195}{1000 \times 0.16} = \boldsymbol{1.22 \times 10^{-4}\Omega^{-1}m^2mol^{-1}}$$

$$\alpha = \frac{\Lambda_c}{\Lambda_o} = \frac{1.22 \times 10^{-4}}{3.5 \times 10^{-2}} = \boldsymbol{3.486 \times 10^{-3}}$$

(ii) Since α is very small compared to one, (0.3486%)

$$K_a = c\alpha^2$$

$$= 0.16 \times (3.486 \times 10^{-3})^2$$

$$\boldsymbol{K_a = 1.944 \times 10^{-6}moldm^{-3}}$$

2. **(a) (i) Define the term "molar conductivity at infinite dilution, Λ_o".**
   (ii) State how you would expect the molar conductivity of sodium chloride solution to vary as the dilution of the solution is increased. Give a reason for your answer.

   (b) The values of Λ_o at 25℃ for some electrolytes are as follows;

Electrolyte	$\boldsymbol{\Lambda_o(Sm^2mol^{-1})}$
$\boldsymbol{HCOONa}$	**104.7**
$\boldsymbol{NaCl}$	**126.5**
$\boldsymbol{HCl}$	**426.2**

   (i) Calculate Λ_o at 25℃ for methanoic acid.

(ii) If the value of molar conductivity, Λ, for 0.01M methanoic acid is 50.5 $\boldsymbol{Sm^2mol^{-1}}$ at $\mathbf{25}$℃. Calculate the acid dissociation constant, $\boldsymbol{K_a}$, for methanoic acid.

(b) (i)

$$\Lambda_0(HCOOH) = \Lambda_0(HCOONa) + \Lambda_0(HCl) - \Lambda_0(NaCl)$$
$$\Lambda_0(HCOOH) = (104.7 + 426.2 - 126.5)Sm^2mol^{-1}$$
$$= \mathbf{404.4}\ \boldsymbol{Sm^2mol^{-1}}$$
$$\Lambda_c = 50.5\ Sm^2mol^{-1}, c = 0.16M$$
$$\alpha = \frac{\Lambda_c}{\Lambda_o} = \frac{50.5}{404.4} = \mathbf{0.1249}$$

(ii) The value of α is not very small as compared to one(12.49%) so $K_a = c\alpha^2$ cannot be used in the calculation.

$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{0.16 \times 0.1249^2}{(1-0.1249)}$$
$$\boldsymbol{K_a = 2.852 \times 10^{-3} moldm^{-3}}$$

---

3. The molar conductivity of a 0.093M solution of ethanoic acid at $\mathbf{25}$℃ is $\mathbf{5.34 \times 10^{-4}}\boldsymbol{Sm^2mol^{-1}}$. The molar conductivity at infinite dilution of hydrogen ion and ethanoate ion are $\mathbf{3.15 \times 10^{-2}}\boldsymbol{Sm^2mol^{-1}}$ and $\mathbf{0.4 \times 10^{-2}}\boldsymbol{Sm^2mol^{-1}}$respectively. Calculate the:

(i) molar conductivity of ethanoic acid at infinite dilution.

(ii) degree of dissociation , $\boldsymbol{\alpha}$ of ethanoic acid.

(iii) acid dissociation constant, $\boldsymbol{K_a}$, at $\mathbf{25}$℃.

(iv) $\boldsymbol{pH}$ of the acid.

(i)
$$\Lambda_0(CH_3COOH) = \Lambda_0(CH_3COO^-) + \Lambda_0(H^+)$$
$$\Lambda_0(CH_3COOH) = (0.4 \times 10^{-2}) + (3.15 \times 10^{-2})$$
$$= \mathbf{3.55 \times 10^{-2}}\Omega^{-1}\boldsymbol{m^2mol^{-1}}$$

(ii)
$$\Lambda_c = 5.34 \times 10^{-4}Sm^2mol^{-1}$$
$$\alpha = \frac{\Lambda_c}{\Lambda_o} = \frac{5.34 \times 10^{-4}}{3.55 \times 10^{-2}} = \mathbf{0.015}$$

(iii) **The value of $\boldsymbol{\alpha}$ very small as compared to one(1.5%) so $\boldsymbol{K_a = c\alpha^2}$ can be used in the calculation.** $K_a = c\alpha^2$

$$K_a = 0.093 \times 0.015^2 = \mathbf{2.093 \times 10^{-5}}\boldsymbol{moldm^{-3}}$$

(iv)
$$[H^+] = c\alpha = (0.093 \times 0.015)$$
$$= 1.395 \times 10^{-3}M$$
$$pH = -\log_{10}[H^+]$$
$$= -\log_{10}(1.395 \times 10^{-3}) = \mathbf{2.86}$$

---

4. The conductivity of a 0.063M solution of 2-hydroxypropanoic acid was found to be $\mathbf{0.001138}\ \boldsymbol{Scm^{-1}}$. The molar conductivity of the acid at infinite dilution at $\mathbf{25}$℃ is $\mathbf{388.5}\ \boldsymbol{Scm^2mol^{-1}}$. Calculate the $\boldsymbol{pH}$ of the solution and the acid dissociation constant.

$$c = 0.063M \qquad \mathcal{K} = 0.001138\ Scm^{-1}$$
$$\Lambda_0\left(\begin{matrix} CH_3\underset{|}{C}HCOOH \\ OH \end{matrix}\right) = 388.5\ Scm^2mol^{-1}$$
$$\Lambda_c = \frac{1000\mathcal{K}}{c} = \frac{1000 \times 0.001138}{0.063}$$
$$= \mathbf{18.06}\boldsymbol{Scm^2mol^{-1}}$$
$$\alpha = \frac{\Lambda_c}{\Lambda_o} = \frac{18.06}{388.5} = \mathbf{0.0465}$$

$$[H^+] = c\alpha = (0.063 \times 0.0465) = 2.93 \times 10^{-3}$$
$$pH = -\log_{10}[H^+] = -\log_{10}(2.93 \times 10^{-3})$$
$$= \mathbf{2.53}$$
$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{0.063 \times 0.0465^2}{(1-0.0465)}$$
$$\boldsymbol{K_a = 1.43 \times 10^{-4} moldm^{-3}}$$

5. **The molar conductivities at infinite dilution of the ammonium ion and the chloride ion are $73.5\,Scm^2mol^{-1}$ and $76.2\,\Omega^{-1}cm^2mol^{-1}$ respectively. The electrolytic conductivity of a 0.1M ammonium chloride is $1.288\times10^{-2}Scm^{-1}$. Calculate the hydrolysis constant of ammonium chloride.**

$$c = 0.1M \qquad \mathcal{K} = 1.288\times10^{-2}\ Scm^{-1}$$

$$\Lambda_0(NH_4Cl) = \Lambda_0(NH_4^+) + \Lambda_0(Cl^-)$$

$$\Lambda_0(NH_4Cl) = 73.5 + 76.2$$

$$= \mathbf{149.7\ Scm^2mol^{-1}}$$

$$\Lambda_c = \frac{1000\mathcal{K}}{c} = \frac{1000\times1.288\times10^{-2}}{0.1}$$

$$= \mathbf{128.8\ Scm^2mol^{-1}}$$

$$\alpha = \frac{\Lambda_c}{\Lambda_o} = \frac{128.8}{149.7} = \mathbf{0.86}$$

The value of α is not very small as compared to one(86%) so $K_a = c\alpha^2$ cannot be used in the calculation.

$$K_h = \frac{c\alpha^2}{(1-\alpha)} = \frac{0.1\times0.86^2}{(1-0.86)}$$

$$\boldsymbol{K_h = 0.063\ moldm^{-3}}$$

Questions

1. Calculate the molar conductivity of water at infinite dilution at 25℃ if at the same temperature, $\Lambda_o(NaOH) = 129.2\ \Omega^{-1}cm^2mol^{-1}$, $\Lambda_o(HNO_3) = 212.8\ \Omega^{-1}cm^2mol^{-1}$ and $\Lambda_o(NaNO_3) = 117.1\ \Omega^{-1}cm^2mol^{-1}$.
2. Calculate the molar conductivity at infinite dilution of ethanoic acid from the following data.

Compound	$\Lambda_o(Scm^2mol^{-1})$
Hydrochloric acid	426
Sodium chloride	126
Sodium ethanoate	91

3. The molar conductivity at infinite dilution of sodium ion and the carbonate ion respectively are 50.11 and 144 $\Omega^{-1}cm^2mol^{-1}$ respectively. Calculate the molar conductance at infinite dilution of sodium carbonate.
4. (a) State Kohlrausch's law of independent conductivity of ions.

   (b) Some ionic conductivity at infinite dilution at 25℃ are shown below:

Ion	**Ionic conductivity** ($\Omega^{-1}cm^2$)
$\bar{O}H$	198.6
Cl^-	76.4
NH_4^+	73.6
Na^+	50.1

Calculate the molar conductivity at infinite dilution of:

(i) Sodium hydroxide
(ii) Ammonium chloride

5. The electrolytic conductivity of a saturated solution of silver chloride at 18℃ after deducting the electrolytic conductivity of water is $1.22 \times 10^{-4} Sm^{-1}$.The molar conductivities at infinite dilution of silver and chloride ions are 0.0054 and 0.00652 Sm^2mol^{-1} respectively at 18℃. Calculate the:
   (a) solubility of silver chloride at 18℃
   (b) solubility product of silver chloride 18℃.
6. (a) Explain what is meant by solubility product
   (b) The electrolytic conductivity of a saturated solution of silver chloride in pure water at 25℃ is $3.41 \times 10^{-6} ohm^{-1}cm^{-1}$ and the electrolytic conductivity of pure water is $1.6 \times 10^{-6} ohm^{-1}cm^{-1}$. The molar conductivities at infinite dilution of the following salts are given as:

Salt	$AgNO_3$	KNO_3	KCl
Molar conductivity($\boldsymbol{ohm^{-1}cm^2mol^{-1}}$)	133.4	145.0	149.9

   Calculate the solubility product of a saturated solution of silver chloride at 25℃.

7. (a) Define the following terms in relation to an aqueous solution of an electrolyte;
   (i) specific conductance
   (ii) molar conductance
   (b) The electrolytic conductivity of an aqueous saturated solution of XCl at 25℃ is $2.40 \times 10^{-3} ohm^{-1}cm^{-1}$. The molar conductivities at infinite dilution of XOH, sodium hydroxide and sodium chloride are 273, 248 and 126 $ohm^{-1}cm^2mol^{-1}$ respectively. Calculate the:
   (i) molar conductivity at infinite dilution of XCl
   (ii) the solubility of XCl in water at 25℃ in $moldm^{-3}$
8. The conductivity of dichloroethanoic acid at a dilution of 8 dm^3 is 0.0238 Scm^{-1}. The molar conductivity at infinite dilution for the acid is 385 Scm^2mol^{-1} . Calculate the degree of ionization of the acid at a concentration of 0.125 $moldm^{-3}$.
9. The conductivity of a 0.01M ethanoic acid at is $1.43 \times 10^{-4} Scm^{-1}$. The molar conductivities of hydrogen ion and ethanoate ion at infinite dilution are 349.8 Scm^2mol^{-1} and 40.9 Scm^2mol^{-1}respectively. Calculate the acid dissociation constant, K_a, of ethanoic acid.
10. The electrolytic conductivity of a solution containing 6.66g of ethanoic acid per litre is $5.21 \times 10^{-2} Sm^{-1}$ at 25℃. The molar conductivity of the acid at infinite dilution at this temperature is 3.91×10^{-2} Sm^2mol^{-1}. Calculate the degree of dissociation of ethanoic acid.

11. (a) Write an equation for the:
    (i) acid dissociation constant, K_a, for ethanoic acid
    (ii) relationship between acid dissociation constant, K_a, and degree of ionisation of an acid.

    (b) The electrolytic conductivity of a $1.6 \times 10^{-2}\ M\ CH_3COOH$ at 20℃ is $1.96 \times 10^{-2}\ Sm^{-1}$ and its molar conductivity at infinite dilution is $3.5 \times 10^{-2} Sm^2 mol^{-1}$. Calculate:
    (i) the molar conductivity of the ethanoic acid at 20℃
    (ii) the degree of ionisation of the acid at 20℃
    (iii) the pH of the acid

    (c) Besides concentration, state one other factor that can affect the pH of the acid.

12. (a) State factors that can affect molar conductivity of an electrolyte.

    (b) The molar conductivities at infinite dilution at 25℃ for some electrolytes are given in the table below.

Electrolyte	$\mathbf{\Lambda_\infty (Scm^2 mol^{-1}) at\ 25}$℃
Sodium nitrate	122
Nitric acid	421
Sodium ethanoate	91

Calculate the molar conductivity at infinite dilution for ethanoic acid.

    (c) The molar conductivity of a $0.016M\ CH_3COOH$ aqueous solution at 25℃ is $13.0\ Scm^2 mol^{-1}$. Calculate the acid dissociation constant (K_a for ethanoic acid).

13. (a) Explain why hydrogen fluoride is a weaker acid than hydrogen chloride.

    (b) Molar conductivities at infinite dilution at 25℃ for some compounds are shown in the table below.

Compound	$\mathbf{\Lambda_o (ohm^{-1} m^2 mol^{-1}) at\ 25}$℃
Nitric acid	0.0421
Potassium nitrate	0.0145
Potassium fluoride	0.0129

The conductivity of a $0.1\ moldm^{-3}$ aqueous solution of hydrogen fluoride is $3.15 \times 10^{-3}\ ohm^{-1}\ m^{-1}$. Calculate the:
(i) molar conductivity of solution
(ii) degree of ionization of hydrogen fluoride.

14. (a) Explain the molar conductivity of an electrolyte.

    (b) Sketch a graph to show the variation of conductivity of a strong electrolyte with dilution.

    (c) Briefly explain the shape of the graph in (b) above.

(d) The molar conductivities of nitric acid, potassium nitrate and potassium fluoride are 421, 145 and 129 $\Omega^{-1}cm^2mol^{-1}$ respectively at infinite dilution. Calculate the:

(i) molar conductivity of hydrofluoric acid at infinite dilution

(ii) dissociation constant of K_a, of 0.1M hydrofluoric acid solution. (Electrolytic conductivity of hydrofluoric acid is $3.15 \times 10^{-5}\ \Omega^{-1}cm^{-1}$)

15. (a) Define the terms:

(i) conductivity

(ii) molar conductivity

(iii) conductance

(b) The table below shows the molar conductivities of aqueous potassium hydroxide at given dilutions.

Dilution($mol^{-1}dm^3$)	100	25	11.11	6.25	4.0	2.8
Molar conductivity($ohm^{-1}cm^2mol^{-1}$)	239	228	224	215	210	201

(i) Plot a graph of molar conductivity against dilution

(ii) Use the graph to determine molar conductivity of potassium hydroxide at infinite dilution.

(iii) Explain the shape of the graph

(c) (i) Draw a sketch graph to show change in conductivity with volume of aqueous sodium hydroxide when $25cm^3$ of a 0.1M propanoic acid is titrated with 0.1M sodium hydroxide solution.

(ii) Explain the shape of the graph.

(d) The conductivity of a saturated solution of silver phosphate at 25℃ is $2.65 \times 10^{-6}ohm^{-1}cm^{-1}$ and that of pure water is $1.52 \times 10^{-6}ohm^{-1}cm^{-1}$. If the molar ionic conductivities of phosphate ions and silver ions are 240 and 62 $ohm^{-1}cm^2mol^{-1}$ at infinite dilution at 25℃ respectively, calculate the:

(i) solubility of silver phosphate at 25℃

(ii) solubility product of silver phosphate at 25℃ and give its units.

Application of conductance (conductivity measurements)

The applications of conductivity measurements include:

(i) ***To determine solubility of sparingly soluble salts***

(ii) ***To determine solubility product of sparingly soluble salts***

(iii) ***To determine degree of dissociation of weak electrolytes***

(iv) ***To determine the ionisation constant of a weak electrolyte***

(v) ***To determine ionic product of water***

(vi) ***To determine formulae of complexes***

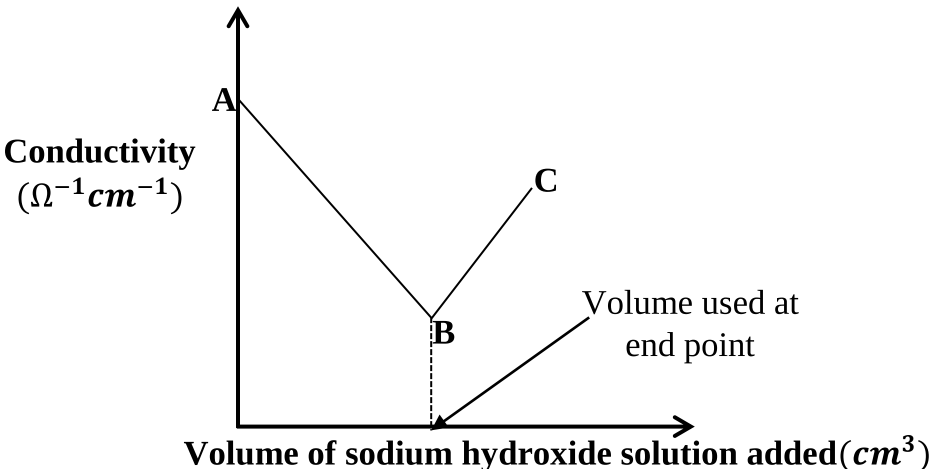
(vii) ***Conductimetric titrations***

Conductimetric titrations

The conductivity of a solution changes during an acid-base titration. The change in conductivity of the solution can be measured. There is a sharp change in conductivity at the end point. Such a titration is called a conductimetric titration.

The different velocities of the ions are used to ascertain the end point of a titration.

1. ***Titration of a strong base against a strong acid (sodium hydroxide solution against hydrochloric acid)***



Explanation of shape of the graph

Initially, ***conductivity is high at A*** due to ***very many fast moving*** and ***highly conducting hydrogen ions*** from the ***strong completely ionized hydrochloric acid***.

Conductivity ***decreases along AB*** as ***sodium hydroxide solution is added*** because the ***fast moving highly conducting hydrogen ions are being neutralized*** to form water and being ***replaced by the slow moving less conducting sodium ions***.

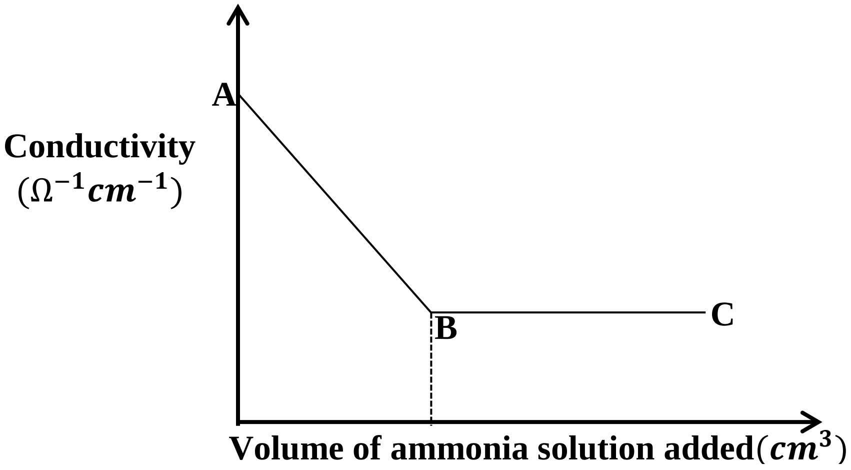
$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$
$$NaCl(aq) \longrightarrow Na^+(aq) + Cl^-(aq)$$

At B, the end point is reached. ***Conductivity is low*** and is due to ***the sodium ions and chloride ions*** from the sodium chloride salt formed.

Along BC, conductivity increases because the ***concentration of sodium ions is being increased*** and ***also the fast moving hydroxyl ions are being added***.

Note: The volume at end point is usually obtained by extrapolation since the minimum point from plotted graphs is not usually as shown on the sketch above. The point where two extrapolated lines meet gives the end point.

2. ***Titration of a weak base against a strong acid (ammonia solution against sulphuric acid or hydrochloric acid)***



Explanation of shape of the graph

Initially, ***conductivity is high at A*** due to ***very many fast moving*** and ***highly conducting hydrogen ions*** from the ***strong completely ionized sulphuric acid***.

Conductivity ***decreases along AB*** as ***ammonia solution is added*** because the ***fast moving highly conducting hydrogen ions are being replaced by the slow moving less conducting ammonium ions***.

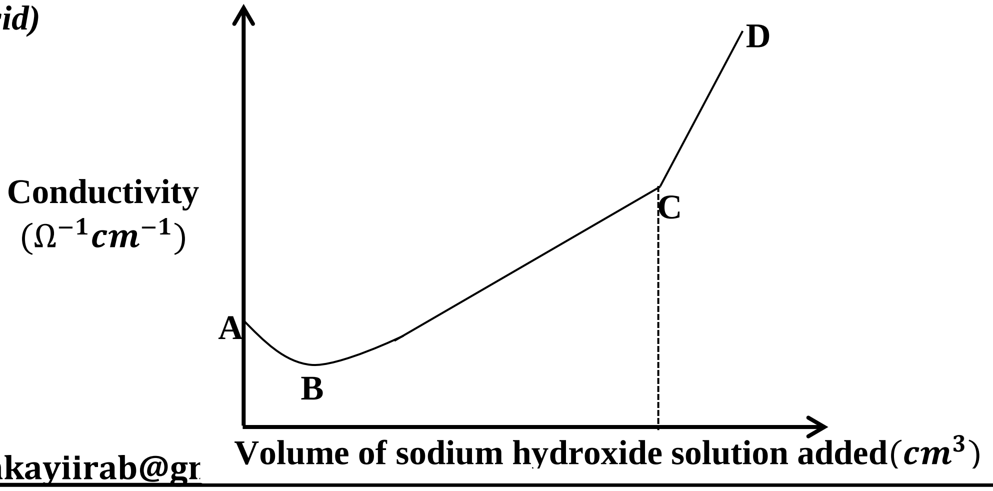
$$H_2SO_4(aq) + 2NH_3(aq) \longrightarrow (NH_4)_2SO_4(aq)$$
$$(NH_4)_2SO_4(aq) \longrightarrow 2NH_4^+(aq) + SO_4^{2-}(aq)$$

At B, the end point is reached. ***Conductivity is low*** and is due to ***the ammonium ions and sulphate ions*** from the ammonium sulphate salt formed.

Along BC, conductivity remains almost constant because the ***ionization of the excess weak ammonia solution added is suppressed*** by ***the ammonium ions from the completely ionized ammonium sulphate salt formed***. This makes the ***conductivity of hydroxyl ions negligible***.

Note: Using data obtained practically, when a graph is plotted, the conductivity may slightly increase along BC but the explanation still holds.

3. ***Titration of a strong base against a weak acid (sodium hydroxide solution against ethanoic acid)***



Explanation of shape of the graph

Initially, ***conductivity is low at A*** due to ***very few fast moving, conducting hydrogen ions*** from the ***weak partially ionized ethanoic acid***.

Conductivity ***slightly decreases along AB*** as ***sodium hydroxide solution is added*** because the ***few fast moving highly conducting hydrogen ions are being neutralized*** to form water and being ***replaced by the slow moving less conducting sodium ions***.

Also the ***ethanoate ions from completely ionised sodium ethanoate salt formed suppress the ionisation of the weak ethanoic acid***.

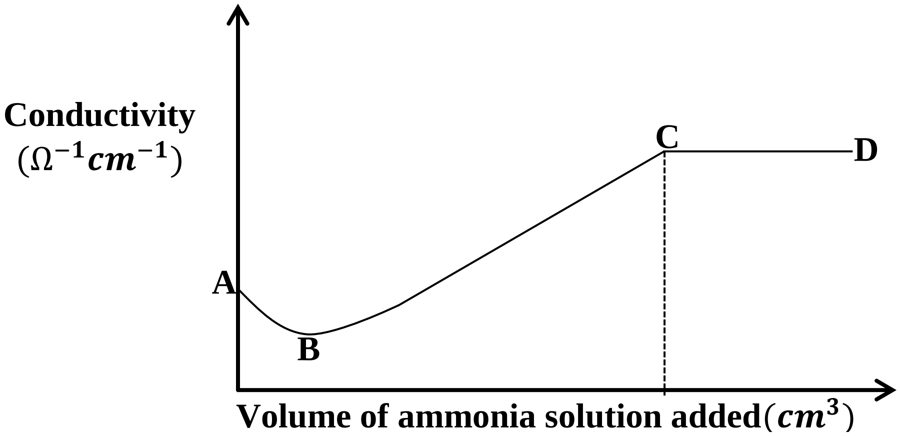
$$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)$$
$$CH_3COONa(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq)$$

Conductivity gradually increases along BC due to increase in number of conducting ethanoate ions and sodium ions from completely ionized sodium ethanoate formed.

At C, the end point is reached. ***Conductivity*** is ***only due to the sodium ethanoate*** salt formed.

Along CD, conductivity rapidly increases because ***excess fast moving hydroxyl ions are being added***.

4. ***Titration of a weak base against a weak acid (ammonia solution against ethanoic acid)***



Explanation of shape of the graph

Initially, ***conductivity is low at A*** due to ***very few highly conducting hydrogen ions*** from the ***weak partially ionized ethanoic acid***.

Conductivity ***slightly decreases along AB*** as ***ammonia solution is added*** because the ***ethanoate ions from ammonium ethanoate formed suppress the ionisation of the weak ethanoic acid***.

$$CH_3COOH(aq) + NH_3(aq) \longrightarrow CH_3COONH_4(aq)$$
$$CH_3COONH_4(aq) \longrightarrow CH_3COO^-(aq) + NH_4^+(aq)$$

Conductivity gradually increases along BC due to increase in number of conducting ethanoate ions and ammonium ions from completely ionized ammonium ethanoate formed.

At C, the end point is reached. ***Conductivity*** is ***only due to the ammonium ethanoate*** salt formed.

Along CD, conductivity remains almost constant because the ***ionization of the excess weak ammonia solution added is suppressed*** by ***the ammonium ions from the completely ionized ammonium ethanoate salt formed***.

However, conductimetric titration is not only confined to acids and bases. Copper(II) sulphate can be titrated with sodium hydroxide, sodium ethanoate with hydrochloric acid, etc.

Explain why in the conductimetric titration of aluminium nitrate solution against sodium hydroxide solution, the conductivity of the mixture decreases to a minimum value, then increases gradually and finally increases rapidly with excess base.

Aluminium ions react with hydroxide ions to form ***insoluble aluminium hydroxide***.

$$Al^{3+}(aq) + 3\bar{O}H(aq) \longrightarrow Al(OH)_3(s)$$

The reaction ***reduces the concentration of aluminium ions in solution*** and conductivity decreases to a minimum ***on complete precipitation***.

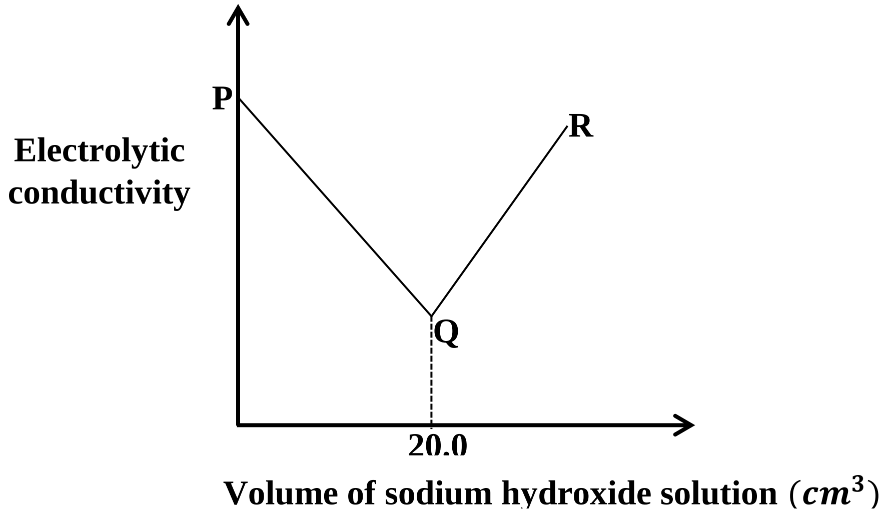
The ***aluminium hydroxide reacts with more hydroxide ions*** to form a ***soluble complex of tetrahydroxoaluminate(III) ions*** hence a gradual increase in conductivity.

$$Al(OH)_3(s) + \bar{O}H(aq) \longrightarrow Al(OH)_4^-(aq)$$

The conductivity then increases rapidly due to ***excess mobile highly conducting hydroxide ions***.

Questions

1. The conductivity of $25cm^3$ of copper(II) sulphate solution varies with the volume of 0.1M sodium hydroxide solution added as shown by the graph below;



(a) Define the term electrolytic conductivity

(b) Give a reason why:

  (i) conductivity is high at point P.

  (ii) conductivity increases along QR

(c) Calculate the initial concentration of copper(II) sulphate solution

(d) (i) The electrolytic conductivity at P was $1.536 \times 10^{-2}\Omega^{-1}cm^{-1}$ at $25°C$. Determine the molar conductivity of the copper(II) sulphate solution.

  (ii) State and explain the effect of dilution on the answer in d(i) above.

2. The molarity of a sample of hydrochloric acid about 0.1M was determined accurately by measuring the conductivity of the solution as 1.0M sodium hydroxide solution was added to $50cm^3$ of the acid. The results were as shown below:

Conductivity($\Omega^{-1}\boldsymbol{cm^{-1}}$)	4.1	3.3	2.4	1.7	1.5	1.8	2.2	2.5
Volume of 1.0M sodium hydroxide($\boldsymbol{cm^3}$)	1	2	3	4	5	6	7	8

(a) Plot a graph of conductivity against volume of 1.0M sodium hydroxide

(b) Determine from the graph, the volume of sodium hydroxide used to reach end point

(c) Calculate the molarity of hydrochloric acid

(d) Explain the shape of the graph

(e) (i) Distinguish between solubility and solubility product.

  (ii) Describe an experiment to determine the solubility product of calcium phosphate in the laboratory.

3. The table below shows the conductivity of a solution of when a small volume of sodium hydroxide solution was added to $50cm^3$ of 0.1M hydrochloric acid.

Volume of sodium hydroxide($\boldsymbol{cm^3}$)	0	1	2	3	4	5	6	7	8	9	10
Conductivity ($\Omega^{-1}\boldsymbol{cm^{-1}}$)	3.90	3.35	2.80	2.27	1.72	1.11	0.62	0.76	1.19	1.62	2.0

(a) (i) Plot a graph of conductivity against volume of sodium hydroxide

  (ii) Use your graph to determine the volume of sodium hydroxide used to neutralize the acid

  (iii) Calculate the molarity of sodium hydroxide

  (iv) Explain the shape of the graph

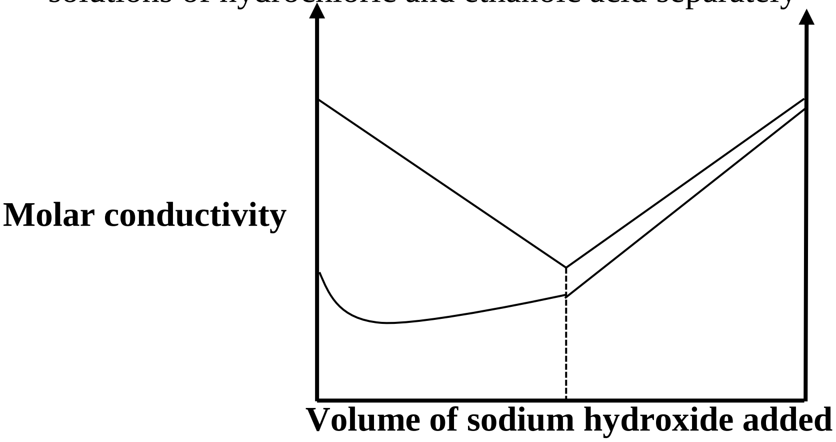
(b) State one other application of conductivity measurements.

4. (a) The ionic radii and ionic conductivities at infinite dilution of some ions are shown in the table below:

Ion	**Ionic radius**(nm)	**Ionic conductivity**$(\Omega^{-1}cm^{2})$
Li^{+}	0.060	38.7
Na^{+}	0.095	50.1
K^{+}	0.133	73.5

Explain the results in the table

(b) The diagram below shows curves A and B obtained when aqueous sodium hydroxide was gradually added separately to equimolar solutions of hydrochloric and ethanoic acid separately

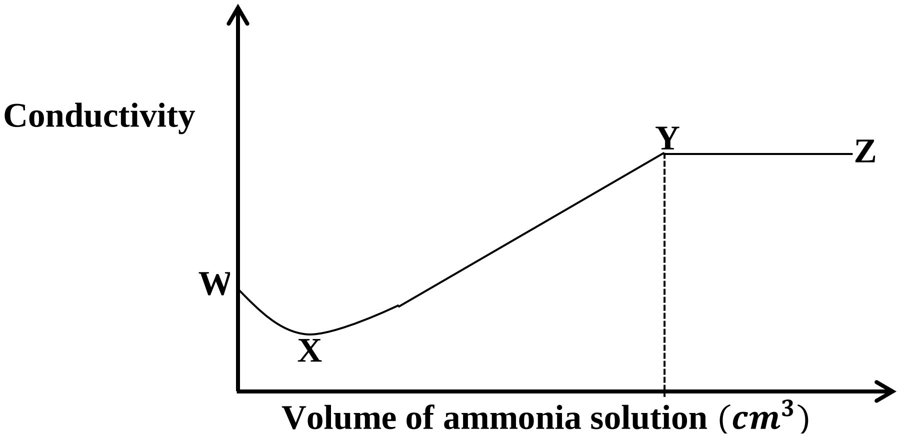


Explain the shape of the curves.

(i) Curve A

(ii) Curve B

5. (a)The conductimetric curve for titration of ethanoic acid and ammonia solution is given below:



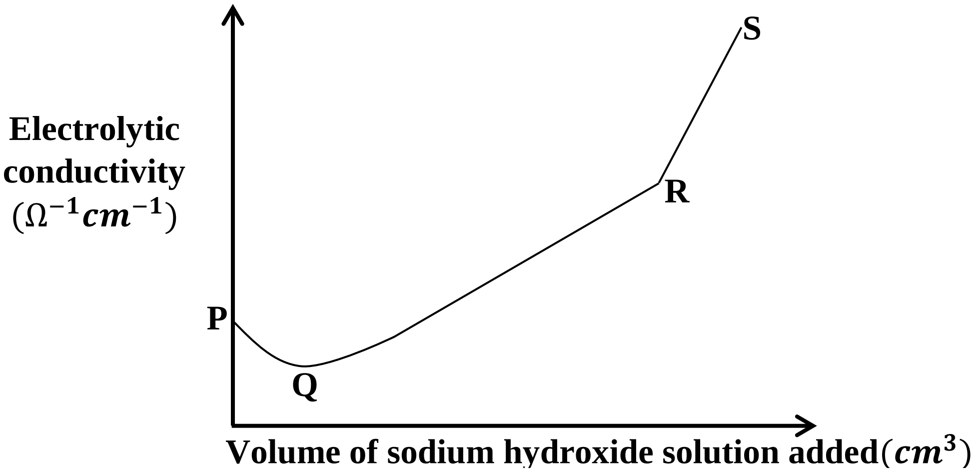
Explain the shape of the graph.

(b) The molar conductivities of nitric acid, sodium bromoethanoate and sodium nitrate are $421, 89.3$ and $121.3\Omega^{-1}cm^{2}mol^{-1}$ respectively at infinite dilution at 25℃. Calculate the:

(i) molar conductivity of bromoethanoic acid at infinite dilution

(ii) dissociation constant, K_a, of a 0.1M bromoethanoic acid solution. (Electrolytic conductivity of bromoethanoic acid is $4.38 \times 10^{-3}\Omega cm^{-1}$

6. (a) The conductimetric curve for the titration of ethanoic acid and sodium hydroxide is given below.



Explain the shape of the curve PQRS

(b) The molar conductivity of silver nitrate, potassium nitrate and potassium chloride are 134.0, 143.2 and 140.8 $Scm^{2}mol^{-1}$ respectively at infinite dilution and 25℃. Calculate the:

(i) molar conductivity of silver chloride at infinite dilution at 25℃

(ii) solubility product, Ksp of silver chloride at 25℃ .(The electrolytic conductivity of water and that of a saturated solution of silver chloride are 5.5×10^{-8} *and* $1.934 \times 10^{-6}Scm^{-1}$ respectively)

(c) The molar conductivities of sodium bromoethanoate, hydrochloric acid and sodium chloride are $89, 326$ and $126\Omega^{-1}cm^{2}mol^{-1}$ respectively at infinite dilution at 25℃. Calculate the:

(i) degree of ionization of 0.1M bromoethanoic acid solution at 25℃.
(The molar conductivity of 0.1M bromoethanoic acid solution is $43.7\ \Omega^{-1}cm^{2}mol^{-1}$)

(ii) ionisation constant, K_a, of a 0.1M bromoethanoic acid solution at 25℃.

7. (a) Define the terms:

(i) electrolytic conductivity

(ii) molar conductivity

(b) Draw a sketch graph to show how molar conductivity varies with concentration for:
   (i) hydrochloric acid
   (ii) ethanoic acid

(c) Explain the shape of the curve in each case.

(d) $25cm^3$ of 0.1M ethanoic acid was titrated with sodium hydroxide solution.
   (i) Draw a sketch graph to show how conductivity of the solution changes when sodium hydroxide is added to the acid
   (ii) Explain the shape of the graph.

ELECTRODE POTENTIAL AND ELECTROCHEMICAL CELLS

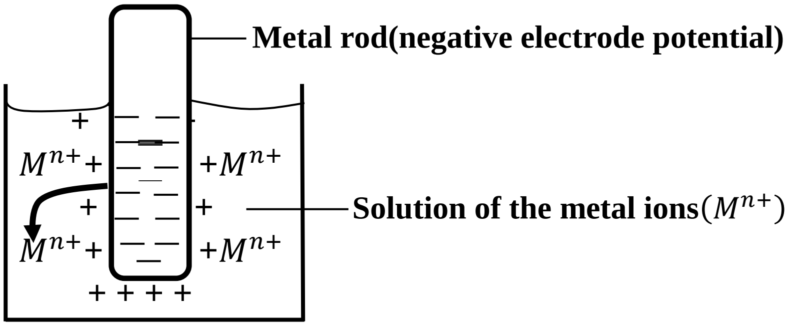
ELECTRODE POTENTIAL

A metal rod consists of metal ions and a cloud of delocalized valence electrons. If the metal is dipped in a solution of its ions, some of the cations dissolve leaving up an excess of electrons on the surface of the metal.

$$M(s) \longrightarrow M^{n+}(aq) + ne$$

The metal will become negatively charged with respect to the solution sorrounding it.

The tendency of the metal to lose ions to the sorrounding solution is known as ***electrolytic solution pressure.***

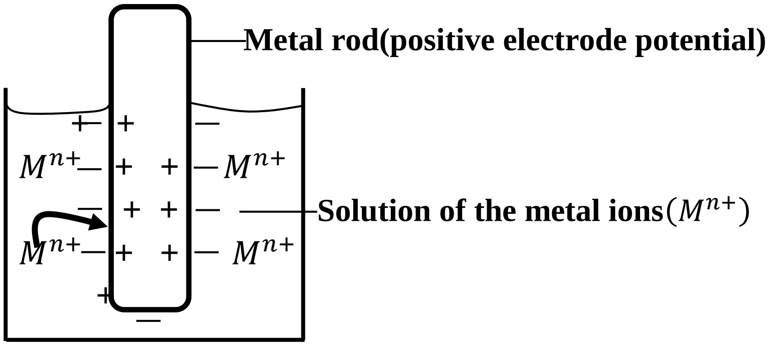


Alternatively, metal ions may take electrons from the strip of the metal and get discharged as metal atoms.

$$M^{n+}(aq) + ne \longrightarrow M(s)$$

In this case, the metal becomes positively charged with respect to the solution surrounding it.

The tendency of the ions to deposit on the metal from a solution is called the ***deposition pressure***.



The potential difference between the strip of the metal and the solution depends on the nature of the metal and on the concentration of the ions in equilibrium with the metal surface.

For a zinc rod dipped in a solution of zinc ions, the zinc has a ***negative electrode potential*** because it has a greater tendency to dissolve to form ions (greater electrolytic solution pressure) and a smaller tendency to be deposited as a metal (lower deposition pressure). The zinc rod is said to be a ***negative electrode***.

For a copper rod dipped in a solution of copper(II) ions, the copper has ***a positive electrode potential*** because it has a greater tendency to be deposited as a metal (higher deposition pressure) and a smaller tendency to dissolve to form ions (lower electrolytic solution pressure). The copper rod is said to be a ***positive electrode***.

An equilibrium is established when the rate at which electrons are gained is equal to the rate at which electrons are lost.

$$M(s) \rightleftharpoons M^{n+}(aq) + ne$$

The position of equilibrium differs for different combinations of metals placed in solutions of their ions.

Electrode potential is the potential difference developed between a metal placed in contact with a solution of its ions.

Its symbol is ***E*** (measured in volts, V).

By IUPAC convention, the term electrode potential means reduction electrode potential.

Therefore in most of the work hereafter we shall deal with reduction potentials.

Electrochemical series

The electrochemical series is an arrangement of elements in increasing order of their electrode potential. Reduction potentials are used in the arrangement.

Reduction equation	**Electrode potential, $\boldsymbol{E^{\theta}}(\boldsymbol{V})$**
$Li^{+}(aq) + e \rightleftharpoons Li(s)$	-3.04
$K^{+}(aq) + e \rightleftharpoons K(s)$	-2.92
$Ca^{2+}(aq) + 2e \rightleftharpoons Ca(s)$	-2.87
$Na^{+}(aq) + e \rightleftharpoons Na(s)$	-2.71
$Mg^{2+}(aq) + 2e \rightleftharpoons Mg(s)$	-2.38
$Al^{3+}(aq) + 3e \rightleftharpoons Al(s)$	-1.66
$Mn^{2+}(aq) + 2e \rightleftharpoons Mn(s)$	-1.18
$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s)$	-0.76
$Cr^{3+}(aq) + 3e \rightleftharpoons Cr(s)$	-0.51
$Fe^{2+}(aq) + 2e \rightleftharpoons Fe(s)$	-0.44
$Co^{2+}(aq) + 2e \rightleftharpoons Co(s)$	-0.28
$Ni^{2+}(aq) + 2e \rightleftharpoons Ni(s)$	-0.25
$Sn^{2+}(aq) + 2e \rightleftharpoons Sn(s)$	-0.14
$Pb^{2+}(aq) + 2e \rightleftharpoons Pb(s)$	-0.13
$\boldsymbol{2H^{+} + 2e \rightleftharpoons H_2(g)}$	$\boldsymbol{0.00}$
$Sn^{4+}(aq) + 2e \rightleftharpoons Sn^{2+}(aq)$	$+0.15$
$Cu^{2+}(aq) + e \rightleftharpoons Cu^{+}(aq)$	$+0.15$
$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$	$+0.34$
$Cu^{+}(aq) + e \rightleftharpoons Cu(s)$	$+0.52$
$I_2(s) + 2e \rightleftharpoons 2I^{-}(aq)$	$+0.54$
$Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq)$	$+0.77$
$Ag^{+}(aq) + e \rightleftharpoons Ag(s)$	$+0.80$
$Hg^{2+}(aq) + 2e \rightleftharpoons Hg(l)$	$+0.85$
$Br_2(l) + 2e \rightleftharpoons 2Br^{-}(aq)$	$+1.07$
$MnO_2(s) + 4H^{+}(aq) + 2e \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	$+1.23$
$Cr_2O_7^{2-}(aq) + 14H^{+}(aq) + 6e \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	$+1.33$
$Cl_2(g) + 2e \rightleftharpoons 2Cl^{-}(aq)$	$+1.36$
$Ce^{4+}(aq) + e \rightleftharpoons Ce^{3+}(aq) \quad (in\ H_2SO_4)$	$+1.45$
$MnO_4^{-}(aq) + 8H^{+}(aq) + 5e \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	$+1.52$
$Ce^{4+}(aq) + e \rightleftharpoons Ce^{3+}(aq) \quad (in\ HNO_3)$	$+1.61$
$MnO_4^{-}(aq) + 4H^{+}(aq) + 3e \rightleftharpoons MnO_2(s) + 2H_2O(l)$	$+1.69$
$H_2O_2(aq) + 2H^{+}(aq) + 2e \rightleftharpoons 2H_2O(l)$	$+1.77$
$F_2(g) + 2e \rightleftharpoons 2F^{-}(aq)$	$+2.87$

Note:

1. The elements with more negative values of electrode potential are highly electropositive metals i.e. Lithium, potassium, sodium and magnesium.
2. The elements with more positive values of electrode potential are strongly electronegative elements i.e. Bromine, chlorine and fluorine.
3. From the half-cell reactions, any reagent on the right is a reducing agent and any reagent on the left is an oxidizing agent.
4. Any species on the right for a reaction with a lower (more negative) electrode potential is a stronger reducing agent than a species with a higher(less negative or more positive) electrode potential. Lithium is the strongest reducing agent and the fluoride ion is the weakest reducing agent. On the other hand, fluorine, with a more positive electrode potential is the strongest oxidizing agent and the lithium ion is the weakest oxidizing agent.
5. The more positive (or less negative) the electrode potential, the easier it is to reduce the ions on the left. So the metal on the right is relatively unreactive and is a relatively poor reducing agent. For example: $Ag^{+}(aq) + e \rightleftharpoons Ag(s) \qquad E^{\theta} = +0.80V$
6. The more negative (or less positive) the electrode potential, the more difficult it is to reduce the ions on the left. So the metal/ species on the right is relatively reactive and is a relatively good reducing agent. For example:
   $Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s) \qquad E^{\theta} = -0.76V$
7. The Lithium electrode can as well be written as $Li^{+}(aq)/Li(s)$. The process is a reduction and the electrode potential is a reduction potential.

Question

The standard electrode potentials of some half-cell reactions are given below:

	$E^{\theta}(V)$
$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$	$+0.34$
$Co^{2+}(aq) + 2e \rightleftharpoons Co(s)$	-0.28
$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s)$	-0.76
$Ag^{+}(aq) + e \rightleftharpoons Ag(s)$	$+0.80$
$Pb^{2+}(aq) + 2e \rightleftharpoons Pb(s)$	-0.13

State which species is the:

(a) strongest reducing agent

(b) strongest oxidizing agent

(c) most difficult to reduce

(d) most reactive metal

(e) easiest to reduce

Absolute and relative electrode potential

Absolute electrode potential is the potential difference developed between a metal surface and the solution with which it is in contact.

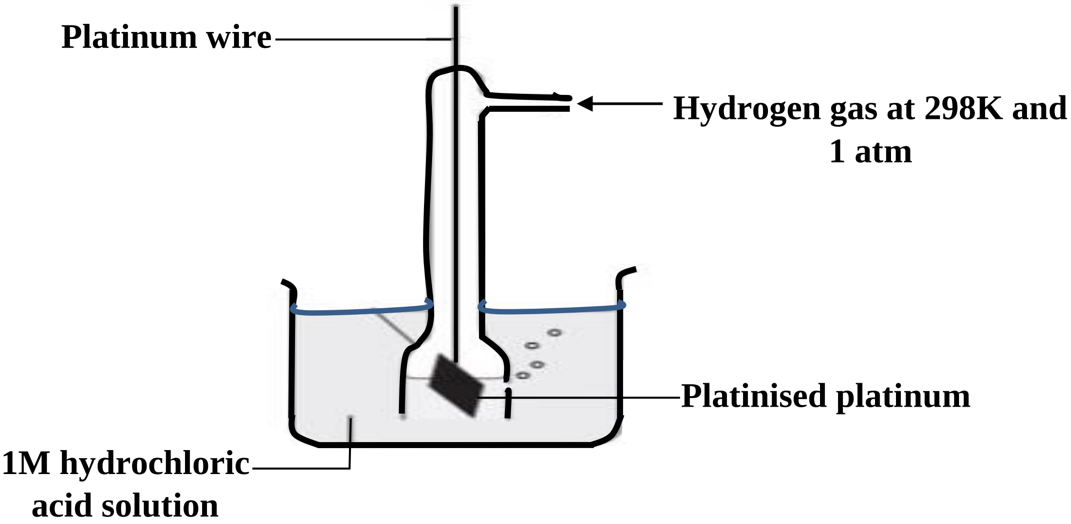
The relative electrode potential is the potential difference developed between a metal surface and the solution with which it is in contact relative to a reference electrode. The standard hydrogen electrode is the commonest reference electrode used.

Other reference electrodes include the saturated calomel electrode, the quinhydrone electrode, the silver/ silver chloride electrode and the glass electrode.

It is impossible to measure the absolute potential difference of a metal with respect to its solution because it is necessary to have a second electrode which also has its own potential difference with respect to its solution.

The structure and functioning of the Standard Hydrogen Electrode (SHE)

Structure



The standard hydrogen electrode consists ***pure hydrogen gas continuously bubbled over the surface of a platinum foil coated with platinum black*** at ***298K and 1 atmosphere***. The platinized platinum is dipped in ***1M solution of hydrogen ions***.

Functioning

The ***hydrogen is adsorbed on the platinum black*** and ***equilibrium is set up between the adsorbed layer of hydrogen and the hydrogen ions*** in the solution.

$$H_2(g) \rightleftharpoons 2H^+ + 2e$$

The platinum black is inert hence does not take part in the reaction and is finely divided platinum ***to catalyse the set up of this equilibrium***. There will be an ***electrode potential between the adsorbed hydrogen and the solution*** which is ***arbitrary taken as*** $\mathbf{0.00V}$.

This ***fixes a scale against which other standard electrode potentials are measured*** by ***combining the standard hydrogen electrode with other electrodes*** and ***measuring the emf of the cell formed***.

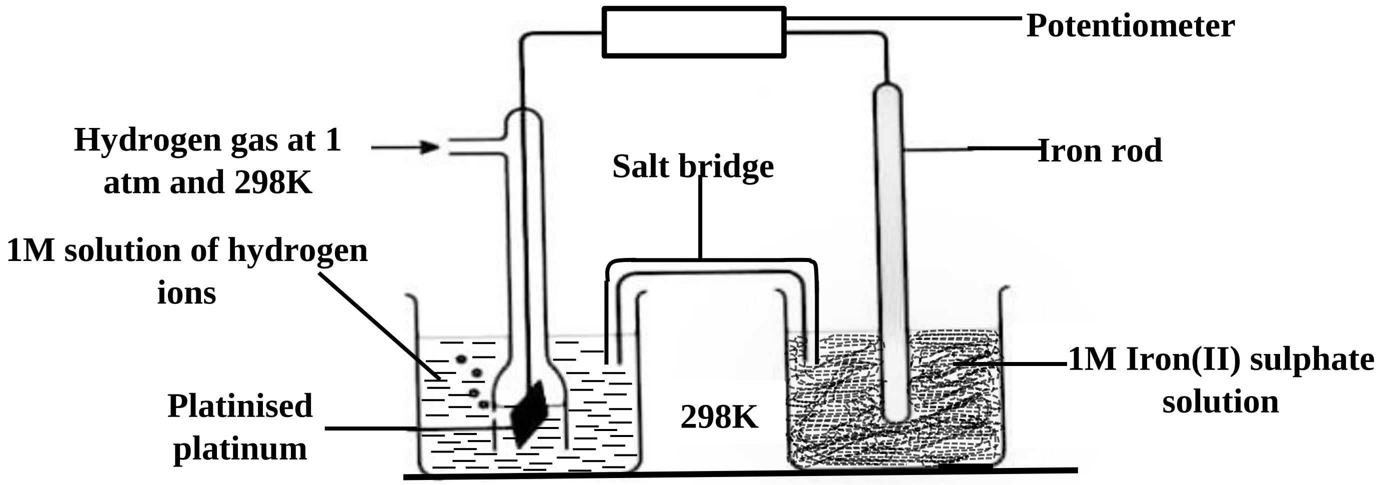
Standard electrode potential, $E^{\theta}(V)$

When the standard hydrogen electrode is used in conjunction with a metal electrode placed in a solution containing 1M of the ions of the metal at 298K and 1 atmosphere, the electromotive force (emf) obtained is called the ***standard electrode potential***.

Standard electrode potential is the potential difference or reduction potential established when a metal electrode is dipped in a 1 molar solution of its ions measured relative to the standard hydrogen electrode at 25 ^{o}C and 1 atmosphere.

Experiment to measure standard electrode potential of a metal

Considering an iron electrode;



An iron rod is dipped in a 1molar solution of iron(II) sulphate

The ***iron half-cell is connected externally by electric wires*** to ***a standard hydrogen electrode*** via a ***high resistance voltmeter or a potentiometer*** to ***measure the emf of the cell***.

The iron half-cell is connected to the standard hydrogen electrode ***internally by means of a salt bridge*** to ***allow exchange of ions without mixing of the two solutions*** in the half-cells.

The temperature of the solution is maintained at 298K

Since ***the standard hydrogen electrode has a standard electrode potential of $0.00V$, the reading on the voltmeter/ potentiometer is the standard electrode potential of the iron electrode.***

NOTE:

(i) ***The emf of the cell is measured without passing any current so that the composition of the chemicals in the cell is not changed.***

(ii) ***The salt bridge consists of a bent glass tube containing some inactive solution such as saturated potassium chloride or a folded filter paper saturated with potassium chloride.***

(iii) ***A standard hydrogen electrode is not easy to use because it is bulky, slow to reach equilibrium and susceptible to presence of impurities. It is also not easy to maintain a stream of hydrogen at 1 atmosphere.***

(iv) ***Electrode potentials of other metals are measured in the same way***

(v) ***A porous partition may be used instead of a salt bridge***

Factors affecting magnitude of electrode potential

When a metal rod is dipped or a gas is bubbled in/through a solution of its ions, it undergoes the energy changes. First, it's converted to free gaseous atoms. Electrons are then removed from the gaseous atoms to form gaseous ions. The gaseous ions then combine with water molecules to form hydrated ions. The energy changes involved are summarized below for a divalent metal, M;

$$\boldsymbol{M(s)} \xrightarrow[\text{}]{\substack{\textit{Atomisation}\\ \textit{or sublimation energy}}} \boldsymbol{M(g)} \xrightarrow{\textit{Ionisation energy}} \boldsymbol{M^{2+}(g)} \xrightarrow{\textit{Hydration energy}} \boldsymbol{M^{2+}(aq)}$$

Therefore the enthalpy change associated with the reaction;

$$M(s) \longrightarrow M^{2+}(aq) + 2e \qquad \Delta H = X\ kJmol^{-1}$$

$$X = (Enthalpy\ of\ atomisation + Ionisation\ enthalpy + Enthalpy\ of\ hydration)$$

Therefore the factors that affect the magnitude of electrode potential include;

(i) ***Atomization energy***
(ii) ***Ionization energy***
(iii) ***Hydration energy***
(iv) ***Concentration of the solution of the electrolyte***

Note that any endothermic process decreases the electrode potential (makes it less negative or more positive) and any exothermic process increases the electrode potential (makes it more negative or less positive.

(i) ***Atomization energy***

Atomisation energy is endothermic. The higher the atomisation energy, the lower (more positive) the electrode potential. This is because it becomes difficult to convert an element into its gaseous atoms.

(ii) *Ionization energy*

Ionization energy is endothermic. The higher the ionization energy, the lower (more positive) the electrode potential. This is because it becomes difficult to form gaseous ions from gaseous atoms.

(iii) *Hydration energy*.

Hydration is an exothermic reaction. The higher the hydration energy the higher(more negative) the electrode potential. This is because more energy is given off when gaseous ions are completely surrounded by water molecules.

Variation of electrode potential in group II and period 3

1. The table below shows the standard electrode potential values of Group II elements.

Element	*Be*	*Mg*	*Ca*	*Sr*	*Ba*
Standard electrode potential(E^{θ}) (Volts) for M^{2+}/M	-1.70	-2.37	-2.87	-2.89	-2.90

(a) Name with reasons;

(i) the strongest reducing agent

(ii) the weakest reducing agent

(b) Explain the general trend in standard electrode potential of the elements

(c) explain why beryllium has an abnormally less negative value

(a) (i) Barium (but not Ba) Because it has the most negative standard electrode potential

(ii) Beryllium (but not Be) Because it has the least negative standard electrode potential

(b) Standard electrode potential generally becomes more negative from beryllium to barium because ionic radius increases, ionisation energy decreases, atomisation energy decreases and hydration energy also decreases. However, the decrease in ionisation energy and atomisation energy is more rapid than decrease in hydration energy.

(c) Beryllium has an abnormally less negative value because the beryllium ion has the smallest ionic radius, highest charge density and highest polarising power, thus attracting many water molecules, giving off highest amount of hydration energy that counterbalances its high positive ionization energy and its high atomisation energy.

2. **The table below shows the standard electrode potential values of some of the elements in Period 3 of the Periodic Table.**

Element	***Na***	***Mg***	***Al***	***Cl***
Standard electrode potential(E^{θ}) (V) for $M^{n+/-}(aq)/M(s/g)$	-2.71	-2.37	-1.66	+1.36

(a) State;

- **(i)** **the factors that affect the magnitude of standard electrode potential**
- **(ii)** **with a reason, name the strongest reducing agent**
  sodium because it has the most negative standard electrode potential
- **(iii)** **with a reason, name the strongest oxidizing agent**
  chlorine because it has a positive standard electrode potential

(a) Explain the trend in standard electrode potential of the metallic elements

Standard electrode potential ***becomes less negative(decreases) from sodium to aluminium*** *because* ***ionic radius decreases, ionization energy increases****,* ***atomization energy increases*** *and* ***hydration energy also increases****. However, the increase in ionization energy and atomization energy* ***is more rapid*** *than increase in hydration energy.*

3. **Although standard electrode potentials of alkali metals and alkaline earth metals become more negative down the groups, the standard electrode potentials of Lithium and beryllium are most negative in the respective groups**.

ELECTROCHEMICAL CELLS

An electrochemical cell is a cell that converts chemical energy into electricity. Examples of electrochemical cells include a Daniel cell, dry cells, Lead-acid battery cell and fuel cells.

The cell consists two metal/ metal ion convention half cells.

Metal/ metal ion convention cells (RHE and LHE)

When a metal rod is dipped in a 1 molar solution of its ions, the cell generated is called a **half cell**.

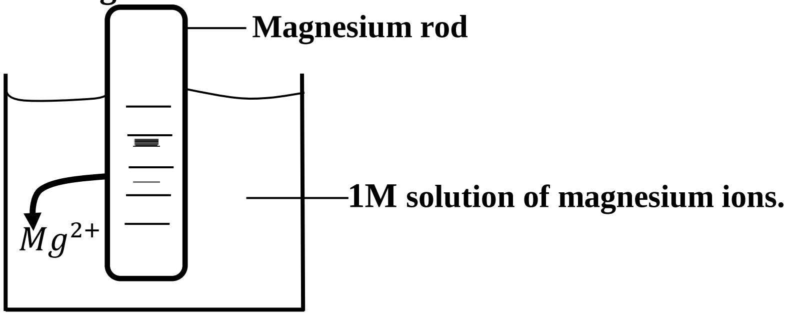
A magnesium half-cell is made by dipping a pure magnesium rod in a 1M solution of magnesium ions (for example a 1M magnesium sulphate solution) at 298K. The magnesium half-cell is represented as

$$Mg^{2+}(aq)/Mg(s)$$

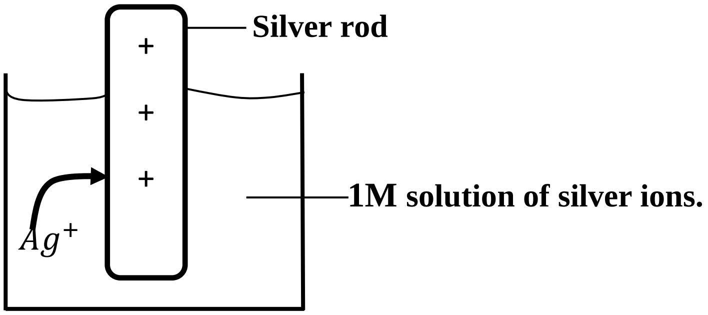
A silver half-cell is made by dipping a pure silver rod in a 1M solution of silver ions (for example a 1M silver nitrate solution) at 298K. The silver half-cell is represented as;

$$Ag^{+}(aq)/Ag(s)$$

The Magnesium half cell



The Silver half cell



To construct an electrochemical cell, the two half cells above are made by dipping the metal rods in 1 molar solution of their ions in separate beakers.

The two half cells are then connected using electric wires to connect the metal rods via a high resistance voltmeter.

A salt bridge is used to ***complete the internal circuit*** and ***allowing the movement of ions*** between the two half-cells so that ionic balance is maintained.

How do you come up with the conventional arrangement of the cell?

The reduction equations and reduction potentials for the half-cells can be represented by the following half-equations:

$$Mg^{2+}(aq) + 2e \rightleftharpoons Mg(s) \qquad E^{\theta} = -2.38V$$

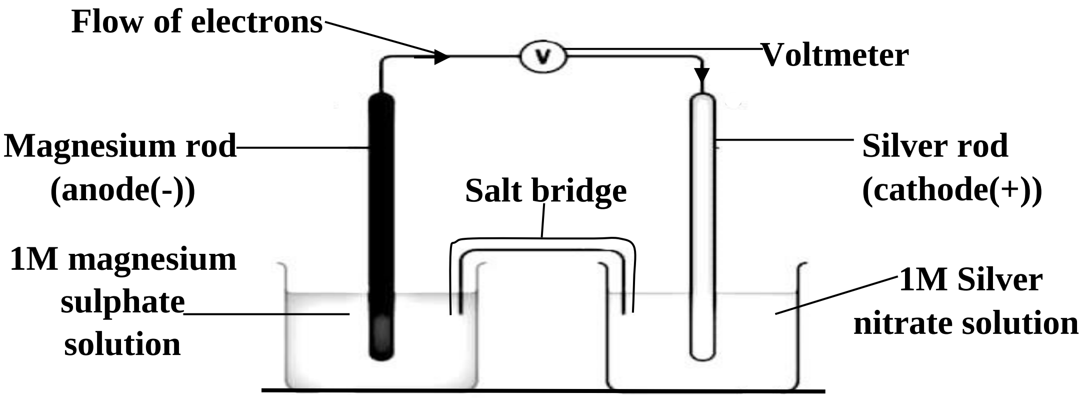
$$Ag^{+}(aq) + e \rightleftharpoons Ag(s) \qquad E^{\theta} = +0.80V$$

The relative values of these voltages show that Mg^{2+} ions are more difficult to reduce than Ag^{+} ions. So Ag^{+} ions will accept electrons from the $Mg^{2+}(aq)/Mg(s)$ half-cell and magnesium will lose electrons to the $Ag^{+}(aq)/Ag(s)$ half-cell.

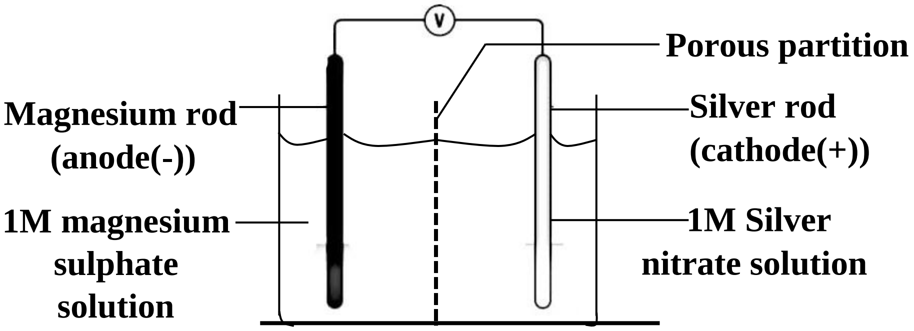
By convention, the electrode with **a negative standard electrode potential** constitutes the **Left Hand Electrode (LHE)**. This electrode is also called the **negative electrode** or the **anode.**

The electrode with **a positive standard electrode potential** constitutes the **Right Hand Electrode (RHE)**. This electrode is also called the **positive electrode** or the **cathode.**

The electrochemical cell can be drawn as shown below:



If a porous partition is used instead of a salt bridge, then the cell has the structure below:



Construction of a Daniel cell

A Daniel cell consists of a zinc half-cell made by dipping a pure zinc rod in a 1M solution of zinc ions and a copper half-cell made by dipping a pure copper rod in a 1M solution of copper(II) ions in separate beakers at 298K.

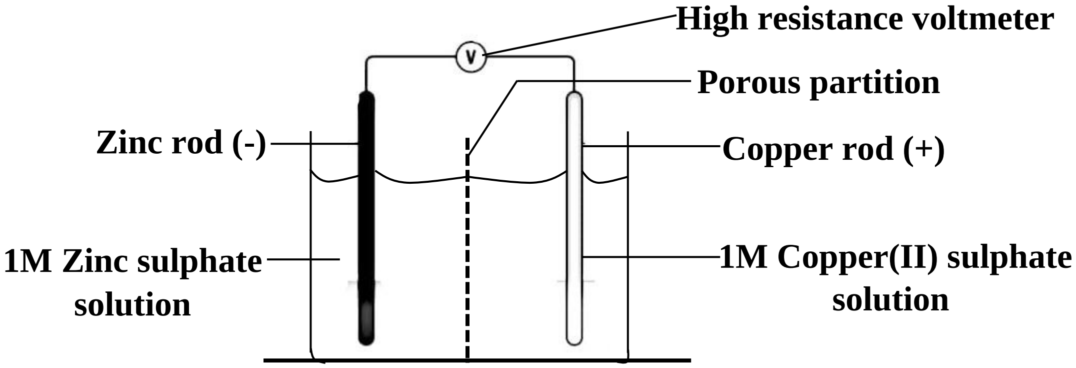
The two half cells are then connected using electric wires to connect the metal rods via a high resistance voltmeter.

A salt bridge is used to complete the internal circuit to allow the movement of ions between the two half-cells without the two solutions mixing.

The zinc electrode constitutes the Left Hand Electrode and the copper electrode constitutes the Right Hand Electrode.

Electrons move from zinc rod to copper rod. The sulphate ions move from the cathode to the anode to maintain the charge balance throughout the cell

The Structure of the Daniell cell:



The cell notation/cell convention

Symbolic representation used to represent an electrochemical cell is called the cell notation.

The following steps are followed to come up with a cell notation of any cell:

1. ***Make sure the electrode potentials given are reduction potentials. i.e. The equations show reduction(electrons on left hand side). If instead oxidation potentials are given, reverse the reactions to make them reduction equations and also the sign of electrode potential. For example;***

$$\boldsymbol{Zn^{2+}(aq)/\,Zn(s) \qquad -0.76V}$$
$$\boldsymbol{Ag^{+}(aq)\,/Ag(s) \qquad +0.80V}$$

The electrode potentials given above are reduction potentials and require no changes.

$$\boldsymbol{Sn^{2+}(aq) \rightleftharpoons Sn^{4+}(aq) + 2e \qquad -0.15V}$$
$$\boldsymbol{2Br^{-}(aq) \rightleftharpoons Br_2(l) + 2e \qquad -1.07V}$$

The electrode potentials given above are oxidation potentials and both equations and the values should be reversed to make them reduction reactions and potentials as shown below;

$$\boldsymbol{Sn^{4+}(aq) + 2e \rightleftharpoons Sn^{2+}(aq) \qquad +0.15V}$$
$$\boldsymbol{Br_2(l) + 2e \rightleftharpoons 2Br^{-}(aq) \qquad +1.07V}$$

Recall:

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)

In some cases, one electrode potential can be given as reduction and the other oxidation. In such a case, only one equation is reversed.

2. ***Identify the reaction that takes place at the anode (left hand electrode, negative electrode) and the cathode (right hand electrode, positive electrode). Use the table below to guide you.***
   Given two reduction potentials and equations;

One reduction potential positive and one negative	***Negative electrode potential***	***Represents reaction at anode(LHE)***
	Positive electrode potential	***Represents reaction at cathode(RHE)***
Both reduction potentials positive	***Less positive electrode potential***	***Represents reaction at anode(LHE)***
	More positive electrode potential	***Represents reaction at cathode(RHE)***
Both reduction potentials negative	***More negative electrode potential***	***Represents reaction at anode(LHE)***
	Less negative electrode potential	***Represents reaction at cathode(RHE)***

3. ***After step 2, write down the equation at the anode (negative electrode) and equation at the cathode (positive electrode). Equation at the anode should be oxidation (gain of electrons)and that at the cathode should be reduction(loss of electrons)***
   RED CAT and AN OX- Reduction occurs at the cathode, Anode is for oxidation.

Consider the reactions;

$$Sn^{4+}(aq) + 2e \rightleftharpoons Sn^{2+}(aq) \qquad +0.15V$$
$$Br_2(l) + 2e \rightleftharpoons 2Br^-(aq) \qquad +1.07V$$

Following step 2 shows that;

$$Sn^{4+}(aq) + 2e \rightleftharpoons Sn^{2+}(aq) \qquad +0.15V \longrightarrow \text{Anode(LHE)}$$
$$Br_2(l) + 2e \rightleftharpoons 2Br^-(aq) \qquad +1.07V \longrightarrow \text{Cathode(RHE)}$$

Equation at anode (oxidation reaction) is $Sn^{2+}(aq) \rightleftharpoons Sn^{4+}(aq) + 2e$

Equation at cathode (reduction reaction) is $Br_2(l) + 2e \rightleftharpoons 2Br^-(aq)$

4. ***Write cell notation following the following guidelines;***
   - ***(i)*** ***Use a vertical line*** $(/)$ ***to separate different phases e.g. (aq) from (s) , (s) from (l), (aq) from (g) or (s) from (g). However, (l) and (aq) are the same phase and cannot be separated by a line.***
   - ***(ii)*** ***Use a comma*** $(\, ,)$ ***to separate similar phases e.g (s) from(s) or (aq) from (l)***
   - ***(iii)*** ***Double vertical lines*** $(//)$ ***show the salt bridge***
   - ***(iv)*** ***The anode is written on the left and the cathode on the right***
   - ***(v)*** ***For half-cells that do not contain a solid metal electrode, platinum,*** $Pt(s)$ ***is introduced as an inert electrode.***

Using the equations above, the cell notation is:

$$\boldsymbol{Pt(s)/Sn^{2+}(aq), Sn^{4+}(aq)//Br_2(l), Br^-(aq)/Pt(s)}$$

The cell notation, if well written can guide you on how to draw a well labelled diagram of the electrochemical cell.

More examples

1. **The standard electrode potentials of two half cells are given below.**

$$\boldsymbol{Mg^{2+}(aq) + 2e \rightleftharpoons Mg(s) \qquad E^\theta = -2.38V}$$
$$\boldsymbol{Ag^{+}(aq) + e \rightleftharpoons Ag(s) \qquad E^\theta = +0.80V}$$

(a) Write ionic equation for the:

- **(i)** **reaction at the cathode**
- **(ii)** **reaction at the anode**
- **(iii)** **overall equation for the reaction**

(b) Write the cell notation for the cell made by combining the two half cells.

Hint: The negative electrode potential $(-2.38V)$ shows the reaction that will take place at the anode, where oxidation (loss of electrons) should occur. The other reaction obviously should occur at the cathode and should be reduction (gain of electrons)

(a) (i) *At cathode* $Ag^+(aq) + e \rightleftharpoons Ag(s)$

(ii) *At anode* $Mg(s) \rightleftharpoons Mg^{2+}(aq) + 2e$

~~$(Ag^+(aq) + e \rightleftharpoons Ag(s)) \times 2$~~

~~$Mg(s) \rightleftharpoons Mg^{2+}(aq) + 2e$~~

(iii) $2Ag^+(aq) + Mg(s) \longrightarrow 2Ag(s) + Mg^{2+}(aq)$

(b) $Mg(s)/Mg^{2+}(aq)//Ag^+(aq)/Ag(s)$

2. **The Daniell cell has copper and zinc half cells as shown below:**

$$\boldsymbol{Zn^{2+}(aq)/\,Zn(s) \qquad -0.76V}$$
$$\boldsymbol{Cu^{2+}(aq)\,/Cu(s) \qquad +0.34V}$$

(a) Write ionic equation for the:

- **(i)** **reaction at the negative electrode**
- **(ii)** **reaction at the positive electrode**
- **(iii)** **overall equation for the reaction**

(b) Write the cell notation for the Daniell cell.

Hint: The negative electrode potential $(-0.76V)$ shows the reaction that will take place at the negative electrode (anode), where oxidation (loss of electrons) should occur.

(a) (i) *At negative electrode* $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e$

(ii) $At\ positive\ electrode \quad Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$

~~$(Zn(aq) \longrightarrow Zn^{2+}(s) + 2e)$~~

~~$Cu^{2+}(s) + 2e \longrightarrow Cu(s)$~~

(iii) $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

(b) $Zn(s)/Zn^{2+}(aq)//Cu^{2+}(aq)/Cu(s)$

3. The electrode potentials of some half cells are given below.

	$\boldsymbol{E^{\theta}(V)}$
$\boldsymbol{Sn(s)/Sn^{2+}(aq)}$	$\boldsymbol{+0.14}$
$\boldsymbol{Mn^{2+}(aq), MnO_4^-(aq), H^+(aq)/Pt}$	$\boldsymbol{-1.52}$

(a) Write ionic equation for the:

(i) reaction at the cathode

(ii) reaction at the anode

(iii) overall equation for the reaction

(b) Write the cell notation for the cell made by combining the two half cells.

Hint: The electrode potentials given are oxidation potentials as there in increase in oxidation state in each case. Standard reduction potentials should be obtained first reversing the equations and the symbols of the electrode potentials too.

	$E^{\theta}(V)$
$Sn^{2+}(aq)/Sn(s)$	-0.14
$MnO_4^-(aq), H^+(aq), Mn^{2+}(aq)/Pt$	$+1.52$

(a) (i) $At\ anode \quad Sn(s) \longrightarrow Sn^{2+}(aq) + 2e$

(ii) $At\ cathode \quad MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$

(iii) $5Sn(s) + 2MnO_4^-(aq) + 16H^+(aq) \longrightarrow 5Sn^{2+}(aq) + 2Mn^{2+}(aq) + 8H_2O(l)$

(b) $Sn(s)/Sn^{2+}(aq)//MnO_4^-(aq), H^+(aq), Mn^{2+}(aq), H_2O(l)/Pt(s)$

$or\ Sn(s)/Sn^{2+}(aq)//MnO_4^-(aq), H^+(aq), Mn^{2+}(aq)/Pt(s)$

The platinum electrode $Pt(s)$ is introduced as an inert electrode in the cathode half-cell because there is no solid metal electrode.

4. The convention of a cell is given below $\boldsymbol{Pt(s)/Fe^{2+}(aq), Fe^{3+}(aq) \parallel MnO_4^-(aq), Mn^{2+}(aq), H^+(aq)/Pt(s)}$.

(a) Write equation for the half-cell reaction at the:

(i) anode

(ii) cathode

(b) Write the overall equation for the cell reaction

Hint: When the cell notation is already given, well balanced half-cell equations are written directly from it.

(a) (i) $At\ anode \quad Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e$

(ii) $At\ cathode \quad MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$

(b) $5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \longrightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$

Calculation of cell emf and prediction of spontaneity/feasibility of a reaction

The emf of a cell, E^{θ}_{Cell} is given by the expression;

$$\boldsymbol{E^{\theta}_{Cell} = E_{RHE} - E_{LHE}}$$

$$or\ \boldsymbol{E^{\theta}_{Cell} = E_{Cathode} - E_{Anode}}$$

The values substituted in the above expression ***must be reduction potentials***.

The final answer should have a charge which should never be a superscript or subscript.

Wrong answers	Correct answers
-1.20, $^{-}$1.20V, $_{-}$1.20V	$-1.20V$
+0.45, $^{+}$0.45V, $_{+}$0.45V	$+0.45V$

- ***If the calculated value of emf is positive, the reaction is spontaneous/ feasible***
- ***If the calculated value of emf is negative, the reaction is not feasible***

Examples

1. **The standard electrode potential for some half cells are shown below:**

$\boldsymbol{Fe^{3+}(aq)/Fe^{2+}(aq)} \qquad \boldsymbol{+0.76V}$

$\boldsymbol{I_2(aq)/I^-(aq)} \qquad \boldsymbol{+0.54V}$

(a) What is meant by the term standard electrode potential

(b) (i) Write the cell convention and the equation for the overall reaction that occurs when electrode potentials in (a) are combined.

(ii) Calculate the overall electrode potential for the cell

(iii) State whether the reaction in b(i) is feasible or not. Give a reason for your answer.

Hint: Electrode potentials are both positive. The less positive electrode potential $(+0.54V)$ shows the reaction that will take place at the anode, where oxidation (loss of electrons) should occur. The other reaction obviously should occur at the cathode and should be reduction (gain of electrons)

(b) (i) $Pt(s)/I^-(aq), I_2(aq)//Fe^{3+}(aq), Fe^{2+}(aq)/Pt(s)$

Overall equation; $2I^-(aq) + 2Fe^{3+}(aq) \longrightarrow I_2(aq) + 2Fe^{2+}(aq)$

(ii) $E^{\theta}_{Cell} = E_{RHE} - E_{LHE} = +0.76 - (+0.54) = \boldsymbol{+0.22V}$

(iii) ***The reaction is feasible, because the emf of the cell is positive.***

---

2. The standard electrode potential for some half cells are shown below:

$$\boldsymbol{Fe^{3+}(aq)/Fe^{2+}(aq) \qquad E^{\theta} = +0.77V}$$
$$\boldsymbol{S(s)/H_2S(g) \qquad E^{\theta} = +0.14V}$$

(a) Write the:

(i) cell convention

(ii) equation for the reaction that takes place at the anode and cathode

(iii) equation for the overall cell reaction

(b) (i) Calculate the emf of the cell.

(ii) State whether the reaction in a(iii) is feasible or not. Give a reason for your answer.

(a) (i) $Pt(s)/H_2S(g)/S(s)/H^+(aq)//Fe^{3+}(aq), Fe^{2+}(aq)/Pt(s)$

(ii) $At\ anode: H_2S(g) \longrightarrow S(s) + 2H^+(aq) + 2e$

$At\ cathode: Fe^{3+}(aq) + e \longrightarrow Fe^{2+}(s)$

(iii) $H_2S(g) + 2Fe^{3+}(aq) \longrightarrow S(s) + 2Fe^{2+}(aq) + 2H^+(aq)$

(b) (i) $E^{\theta}_{Cell} = E_{RHE} - E_{LHE} = +0.77 - (+0.14) = +\mathbf{0.63V}$

(ii) ***The reaction is feasible because the emf of the cell is positive.***

---

3. The standard electrode potential for some half cells are shown below:

$$\boldsymbol{Fe^{2+}(aq)/Fe(s) \qquad -0.44V}$$
$$\boldsymbol{Sn^{4+}(aq)/Sn^{2+}(aq) \qquad +0.15V}$$

(a) Write the cell notation

(b) Calculate the emf for the cell

(c) State whether the cell reaction in (a) is feasible or not. Give a reason for your answer.

Hint: The negative electrode potential $(-0.44V)$ shows the reaction that will take place at the anode. The other reaction obviously should occur at the cathode and should be reduction (gain of electrons)

(a) $Fe(s)/Fe^{2+}(aq)//Sn^{4+}(aq), Sn^{2+}(aq)/Pt(s)$

(b) $E^{\theta}_{Cell} = E_{RHE} - E_{LHE} = +0.15 - (-0.44) = +\mathbf{0.59V}$

(c) ***The reaction is feasible, because the emf of the cell is positive.***

---

4. A galvanic cell consists of the following electrodes.

$$\boldsymbol{Pb(s) \longrightarrow Pb^{2+}(aq) + 2e \qquad E^{O} = -0.13V}$$
$$\boldsymbol{VO^{2+}(aq) + 2H^+(aq) + e \longrightarrow V^{3+}(aq) + H_2O(l)}$$

At 25℃, the emf of the cell was found to be $+0.76V$.

(i) Write the overall cell equation

(ii) Calculate the standard electrode potential for the $VO^{2+}(aq)/V^{3+}(aq)$ electrode.

Note; The reactions given are already reactions at the electrodes. However for calculations, the electrode potential at the LHE should be made a reduction one.

(i) $Pb(s) + 2VO^{2+}(aq) + 4H^{+}(aq) \longrightarrow 2V^{3+}(aq) + Pb^{2+}(aq) + 2H_2O(l)$

(ii) $E^{\theta}_{Cell} = E_{RHE} - E_{LHE}$

$+0.76 = E_{RHE} - (+0.13)$

$\boldsymbol{E_{RHE} = +0.76 + 0.13 = +0.89V}$

Gibb's free energy, ΔG, as a measure of spontaneity

The Gibb's free energy, ΔG^{θ} ($in\ Joules$) of a cell is given by the expression;

$$\boldsymbol{\Delta G^{\theta} = -nFE^{\theta}_{Cell}}$$

where n is number of electrons taking part in the process
F is the Faraday's constant ($96500Cmol^{-1}$)
E^{θ}_{Cell} is the emf of the cell

- ***The value of n is simply the number of electrons involved in writing the overall reaction.***
- ***If the calculated value of ΔG^{θ} is negative, the reaction is spontaneous/ feasible***
- ***If the calculated value of ΔG^{θ} is positive, the reaction is not feasible***
- ***Gibb's free energy is also a measure of maximum useful work done by the cell.***

Examples

1. **The electrode potentials of $\boldsymbol{S_2O_8^{2-}(aq)/SO_4^{2-}(aq)}$ and $\boldsymbol{I_2(aq)/I^{-}(aq)}$ are $\boldsymbol{+2.01V}$ and $\boldsymbol{+0.54V}$ respectively.**
   (a) Write an equation for the reaction that occurs at the:
      (i) anode
      (ii) cathode
   (b) Write the:
      (i) cell notation
      (ii) overall cell reaction
   (c) Calculate the :
      (i) emf of the cell generated from the cell reaction in c(ii) above.
      (ii) Gibb's free energy for the cell ($\boldsymbol{Faraday's\ constant = 96500C}$)
      (iii) **State whether the above cell reaction is feasible or not. Give a reason for your answer**.

(a) (i) $At\ anode: \quad 2I^{-}(aq) \longrightarrow I_2(aq) + 2e$

(ii) $At\ cathode: S_2O_8^{2-}(aq) + 2e \longrightarrow 2SO_4^{2-}(aq)$

(b) (i) $Pt(s)/I^{-}(aq), I_2(aq)//S_2O_8^{2-}(aq), SO_4^{2-}(aq)/Pt(s)$

(ii) $2I^{-}(aq) + S_2O_8^{2-}(aq) \longrightarrow I_2(aq) + 2SO_4^{2-}(aq)$

(c) (i) $E^{\theta}_{Cell} = E_{RHE} - E_{LHE} = +2.01 - (+0.54) = \boldsymbol{+1.47V}$

(ii) $\Delta G^{\theta} = -nFE^{\theta}_{Cell} = -2 \times 96500 \times 1.47 = -283710J = -283.71kJ$

(iii) ***The reaction is feasible because the value of Gibb's free energy of the cell is negative.***

---

2. The convention of a cell was set up as shown below $Pt(s)/Mn^{2+}(aq), MnO_4^-(aq), H^+(aq)//O_2(g)/\ H^+(aq), H_2O_2(aq)/Pt(s)$.

(a) Write equation for the half-cell reaction at the:

(i) anode

(ii) cathode

(b) Write the overall equation for the cell reaction.

(c) **The reduction potentials for the reactions in (a)(i) and (ii) above respectively are $+1.52V$ and $+0.68V$ respectively. Predict the spontaneity of the cell reaction.**

(a) (i) $At\ anode$: $Mn^{2+}(aq) + 4H_2O(l) \longrightarrow MnO_4^-(aq) + 8H^+(aq) + 5e$

(ii) $At\ cathode$: $O_2(g) + 2H^+(aq) + 2e \longrightarrow H_2O_2(aq)$

(b) $2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g) \longrightarrow 2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2(aq)$

(c) $E^{\theta}_{Cell} = E_{RHE} - E_{LHE} = +0.68 - (+1.52) = \mathbf{-0.84V}$

$\Delta G^{\theta} = -nFE^{\theta}_{Cell} = \mathbf{-10} \times 96500 \times -0.84 = 810600J = +810.6kJ$

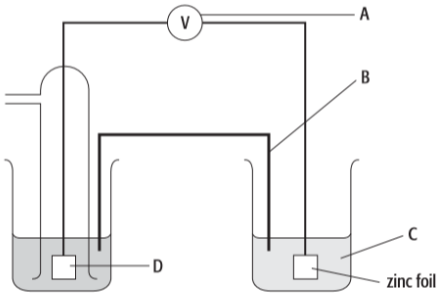
Since the emf of the cell is negative, giving a positive value of Gibb's free energy, the reaction is not spontaneous.

Applications of electrode potentials

- ***(i)*** ***Predicting feasibility of a reaction***
- ***(ii)*** ***Calculating emf of electrochemical cells***
- ***(iii)*** ***Determining equilibrium constant***
- ***(iv)*** ***Determining solubility of a sparingly soluble salt.***

Questions

1. The diagram below shows an electrochemical cell designed to calculate the standard electrode potential of zinc.



(a) Name the apparatus labeled A and state a characteristic it should have

(b) (i) Name B and state its purpose.

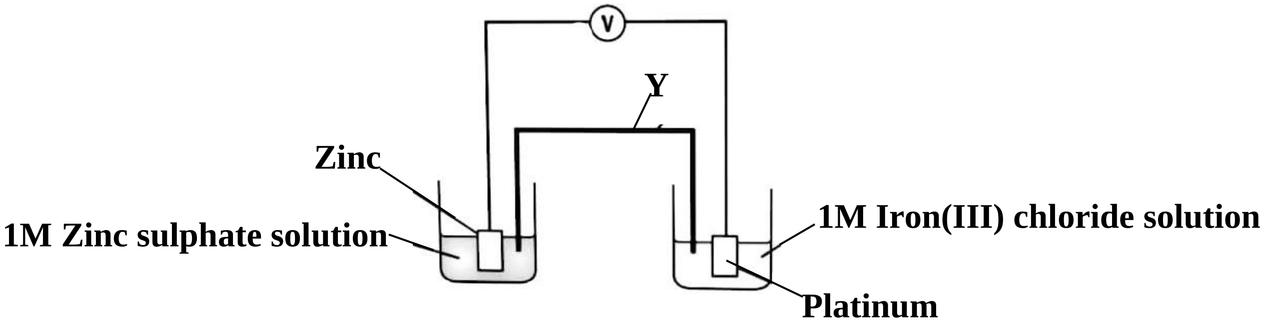
(ii) State how part B is prepared

(c) Identify C

(d) Name part D and explain its function.

(e) State three standard conditions for measuring of standard electrode potential.

2. The figure below shows a voltaic cell set up between two electrodes



(a) (i) Define the term voltaic cell

(ii) Name Y and state its role in the above set up

(b) The reading on the voltmeter above was +1.53 volts.

(i) Write the equation for the redox reaction that takes place

(ii) State whether the reaction in b(i) is feasible . Give a reason for your answer.

(c) Calculate the electrode potential of the left hand electrode if the electrode potential of the right hand electrode is $+0.77V$

(d) Write the cell convention of the voltaic cell above.

3. Calculate the emf, write the cell notation, equation at each electrode and overall equation for each of the following cells

(a) $Cu^{2+}(aq)/Cu(s)$ $E^{\theta} = +0.34V$

$Ag^{+}(aq)/Ag(s)$ $E^{\theta} = +0.80V$

(b) $Cr^{3+}(aq)/Cr(s)$ $E^{\theta} = -0.744V$

$Cu^{2+}(aq)/Cu(s)$ $E^{\theta} = +0.34V$

(c) $I_2(aq) + 2e \longrightarrow 2I^{-}(aq)$ $E^{\theta} = +0.54V$

$Br_2(l) + 2e \longrightarrow 2Br^{-}(aq)$ $E^{\theta} = +1.08V$

(d) $Cu^{2+}(aq)/Cu(s)$ $E^{\theta} = +0.34V$

$Fe^{2+}(aq)/Fe(s)$ $E^{\theta} = -0.44V$

(e) $Al^{3+}(aq)/Al(s)$ $E^{\theta} = -1.66V$

$Cu^{2+}(aq)/Cu(s)$ $E^{\theta} = +0.34V$

(f) $Li^{+}(aq) + e \rightleftharpoons Li(s)$ $E^{\theta} = -3.04V$

$\frac{1}{2}I_2(s) + e \rightleftharpoons I^{-}(aq)$ $E^{\theta} = +0.54V$

(g) $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e \qquad E^{\theta} = -0.74V$

$Mn_2O_3(s) + 2\bar{O}H \longrightarrow 2MnO_2(s) + H_2O(l) + 2e \qquad E^{\theta} = +0.76V$

(h) $Cd^{2+}(aq) + 2e \longrightarrow Cd(s) \qquad E^{\theta} = -0.44V$

$H_2O_2(aq) + 2H^+(aq) + 2e \longrightarrow 2H_2O(l) \qquad E^{\theta} = +1.77V$

4. (a) State factors that can affect standard electrode potential of an element.

   (b) The standard electrode potential for group II elements are given in the table below

Element	Be	Mg	Ca	Sr	Ba
Electrode potential	−1.85	−2.37	−2.87	−2.89	−2.91

   (i) State and explain the trend in variation of standard electrode potential

   (ii) Explain why the values of standard electrode potentials are negative

   (c) Electrode potentials for some half cells are given below:

Half cell	$\boldsymbol{E^{\theta}(V)}$
$Pt(s)/SO_4^{2-}(aq), SO_4^{2-}(aq)$	-0.90
$Cu^{2+}(aq)/Cu(s)$	$+0.34$

   (i) Write the equations for the reactions that take place at anode and cathode

   (ii) Write the overall cell reaction

   (iii) Calculate the emf of the cell

   (d) State whether the reaction in c(iii) is feasible or not. Give a reason for your answer.

5. Calculate the standard electrode potential of the $Cd^{2+}(aq)/Cd(s)$ electrode if the electrode potential of the cell given below is $+0.36V$. $E^{\theta}_{Zn^{2+}(aq)/Zn(s)} = -0.76V$.

$$Zn(s)/Zn^{2+}(aq)//\, Cd^{2+}(aq)/Cd(s)$$

6. Two half cells are given below where combined:

$$Co^{2+}(aq)/Co(s)$$

$$Cl_2(g)/Cl^-(aq)/Pt(s)$$

   (a) State which half-cell is suitable to make the:

   (i) negative electrode

   (ii) positive electrode

   (b) Write the equation for the cell reaction.

   (c) If the emf of the cell is $1.63V$ and $E^{\theta}_{Cl_2(g)/Cl^-(aq)} = +1.36V$. Calculate the standard electrode potential for the cobalt half-cell.

7. Equations for some half-cell reactions are given below.

$Hg_2Cl_2(s) + 2e \longrightarrow 2Hg(l) + 2Cl^-(aq) \qquad E^{\theta} = +0.334V$

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l) \qquad E^{\theta} = +1.33V$

   (a) Write the convention for the cell.

   (b) Write equation for the overall reaction.

   (c) Calculate the cell voltage.

8. Half equations for some cell reactions and the electrode potentials are given below:

$$Fe^{3+}(aq) + e \longrightarrow Fe^{2+}(aq) \qquad E^{\theta} = +0.76V$$

$$ClO_4^-(aq) + 2H^+(aq) + 2e \longrightarrow ClO_3^-(aq) + H_2O(l) \qquad E^{\theta} = +1.20V$$

(a) Write:

(i) the cell notation of the cell formed when the half cells are combined.

(ii) the overall cell reaction

(b) Calculate the emf of the cell

(c) Predict the feasibility of the reaction and give a reason for your answer.

9. The standard electrode potentials for some half cell reactions are given below:

$$Sn^{4+}(aq) + 2e \longrightarrow Sn^{2+}(aq) \qquad +0.15V$$

$$PbO_2(s) + 4H^+(aq) + 2e \longrightarrow Pb^{2+}(aq) + 2H_2O(l) \qquad +1.46V$$

(a) Write the overall equation for the cell reaction that occurs when the half cells are combined.

(b) (i) Calculate the Gibbs free energy for the cell reaction.

$$(Faraday's\ constant = 96500C)$$

(ii) State whether the cell reaction is feasible or not and give a reason for your answer.

10. (a) Explain what is meant by the terms

(i) standard electrode potential

(ii) standard hydrogen electrode

(b) The standard electrode potentials for some half-cells are shown below.

Half cell	$\boldsymbol{E^{\theta}}(\boldsymbol{V})$
$MnO_4^-(aq), H^+(aq)/Mn^{2+}(aq)$	$+1.52$
$I_2(aq)/I^-(aq)$	$+0.54$

State what is observed at the:

(i) positive electrode

(ii) negative electrode

(c) Write:

(i) the cell convention for the combined cell

(ii) the equation for the cell reaction that would take place if the half cells are combined.

(d) Calculate;

(i) the electrode potential for the cell

(ii) the work done by the cell

11. The following half-cell reactions are given:

	$E^{\theta}(V)$
$PbO(s) + 4H^+(aq) + 2e \longrightarrow Pb^{2+}(aq) + 2H_2O(l)$	$+0.52$
$Fe^{3+}(aq) + e \longrightarrow Fe^{2+}(aq)$	$+0.77$

(a) Write the cell notation for the cell formed by combining the two half cells.

(b) State what will be observed and write equations for the reactions that take place at:

(i) anode

(ii) cathode

(c) Calculate the emf of the cell.

12. The standard electrode potentials for some half cells, E^{θ} in volts are shown below:

A. $Zn^{2+}(aq) + 2e \longrightarrow Zn(s)$ $\quad -0.76V$

B. $SO_4^{2-}(aq) + 2H^+(aq) + 2e \longrightarrow SO_3^{2-}(aq) + H_2O(l)$ $\quad +0.20V$

C. $Fe^{3+}(aq) + e \longrightarrow Fe^{2+}(aq)$ $\quad +0.77V$

D. $Br_2(aq) + 2e \longrightarrow 2Br^-(aq)$ $\quad +1.07V$

E. $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ $\quad +1.33V$

F. $Cl_2(g) + 2e \longrightarrow 2Cl^-(aq)$ $\quad +1.36V$

G. $MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$ $\quad +1.52V$

H. $MnO_4^{2-}(aq) + 4H^+(aq) + 2e \longrightarrow MnO_2(s) + 2H_2O(l)$ $\quad +2.26V$

(a) State the species that is the most powerful oxidizing agent and give a reason for your answer.

(b) State what would be observed and write equation for the reaction that would take place if the half cells:

(i) A and E are connected

(ii) B and G are connected

(c) Calculate the emf of the cell in a(i)

(d) Write the cell notation for the cell in (b)(ii) above

(e) Explain why hydrochloric acid is not used to acidify titrants in volumetric analysis involving potassium manganate(VII) solution.

(f) Write the cell convention when half cells C and D are combined.

13. (a)(i) Distinguish between **electrolytic conductivity** and **molar conductivity** of a solution.

(ii) Write the equation to show the relationship between electrolytic conductivity and molar conductivity of a solution.

(b) The table below gives the molar conductivity of a solution of ethanoic acid at 298K.

$[\boldsymbol{CH_3CO_2H}](\boldsymbol{moldm^{-3}})$	0.001	0.01	0.1
Molar conductivity $(\Omega^{-1}\boldsymbol{cm^2mol^{-1}})$	50	16	5

(i) Give a reason for the decreasing values of molar conductivity of ethanoic acid with increase in concentration.

(ii) Calculate the pH and ionization constant, K_a of 0.01M ethanoic acid.

(The molar conductivity of ethanoic acid at infinite dilution is $390\Omega^{-1}cm^2mol^{-1}$)

(c) (i) Define the term **standard electrode potential**.

(ii) Discuss the factors that affect the value of standard electrode potential.

(iii) State **two** applications of standard electrode potential.

(d) The standard electrode potentials of systems, $Pt(s)/H_2(g)/HCl(aq)$ and $CuSO_4(aq)/Cu(s)$ are $0.00\ V$ and $+0.34\ V$ respectively.

(i) Write equation for the overall cell reaction.

(ii) Calculate the maximum energy obtained from the cell.

$(1F = 96500C)$

14. (a) State three factors which determine the magnitude of electrode potential of a metal

(b) The standard electrode potentials for the following reactions are given

$$
\begin{array}{lr}
 & E^{\theta}(V) \\
Cu^{+}(aq) + e \longrightarrow Cu(s) & +0.52 \\
Cu^{2+}(aq) + e \longrightarrow Cu^{+}(aq) & +0.16
\end{array}
$$

Write;

(i) the cell notation for the cell formed when the two half cells are connected.

(ii) the equation for the overall cell reaction

(c) (i) Calculate the emf of the cell.

(ii) What deduction do you make from your answer in (c)(i)?

(d) When dilute sulphuric acid is added to copper(I) oxide, a brown solid and a pale blue solution were formed. Explain the observation.

15. The standard redox potentials of $Fe^{3+}(aq)/Fe^{2+}(aq)$ and $Sn^{4+}(aq)/Sn^{2+}(aq)$ are $+0.76\ V$ and $+0.15V$ respectively.

(a) Write the cell convention for the combined cell

(b) Write an equation for the half-cell reaction at the:

(i) cathode

(ii) anode

(c) Write the overall cell reaction equation.

(d) State two conditions under which the electrode potentials above are measured

(e) Deduce if the overall reaction is feasible or not. Give a reason for your answer.

(f) State one application of electrode potentials

16. The standard electrode potentials for some systems are given below:

$$Ca^{2+}(aq) + 2e \longrightarrow Ca(s) \qquad E^{\theta} = -2.87V$$

$$Mg^{2+}(aq) + 2e \longrightarrow Mg(s) \qquad E^{\theta} = -2.37V$$

(a) Write the convention for the cell

(b) Write the equation for the overall reaction

(c) (i) Calculate the cell voltage

(ii) What conclusion can you draw from the emf value in c (i) above

17. The standard electrode potentials of lead and magnesium are given below:

$$Pb^{2+}(aq) + 2e \longrightarrow Pb(s) \qquad E^{\theta} = -0.13V$$

$$Mg^{2+}(aq) + 2e \longrightarrow Mg(s) \qquad E^{\theta} = -2.40V$$

(a) Write the convention for the cell that can be formed

(b) Write the equation;

(i) for the reaction taking place at each electrode

(ii) for the overall reaction

(c) Calculate the emf of the cell

18. (a) (i) Define the term standard electrode potential.

(ii) Give reasons why it is not possible to measure standard electrode potential absolutely.

(iii) Explain the factors that affect the value of standard electrode potential.

(b) Describe:

(i) the structure of a standard hydrogen electrode.

(ii) how you would measure standard electrode potential of magnesium in a solution of its ions.

(c) The standard electrode potential of copper and zinc are given below.

$$Cu^{2+}(aq) + 2e \longrightarrow Cu(s) \quad E = +0.34V$$

$$Zn^{2+}(aq) + 2e \longrightarrow Zn(s) \quad E = -0.76V$$

Write the cell notation for a zinc-copper cell and calculate the emf of the cell.

(d) State two ways by which an electrolytic cell differs from an emf cell.

19. Given the following electrode potentials.

$$Na^{+}(aq) + e \longrightarrow Na(s) \qquad -2.71V$$

$$Cu^{2+}(aq) + 2e \longrightarrow Cu(s) \qquad +0.337V$$

$$Zn^{2+}(aq) + 2e \longrightarrow Zn(s) \qquad -0.763V$$

$$Ag^{+}(aq) + e \longrightarrow Ag(s) \qquad +0.799V$$

(a) Arrange the electrodes in order of reducing power starting with the least reducing

(b) (i) Which two electrodes will form a cell of maximum emf ?

(ii) Write the cell notation for the cell you gave in b(i) above.

(iii) Write the overall cell reaction for the cell in b(i).

20. (a)(i) What is meant by the term "**standard electrode potential**"?

(ii) Write down the factors that affect the magnitude of standard electrode potential.

(b) (i) With the aid of a labeled diagram, describe how the standard electrode potential of a metal can be measured.

(ii) State two applications of standard electrode potentials.

(c) Some half equations and their standard electrode potentials are given below:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l) \quad E^\theta = +1.33V$

$Cl_2(g) + 2e \longrightarrow 2Cl^-(aq) \quad E^\theta = +1.36V$

$MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) + 4H_2O(l) \quad E^\theta = +1.52V$

(i) Name the species that is the strongest reducing agent. Give a reason for your answer.

(ii) Write the cell notation of the cell made by combining half cells of dichromate(VI) and chlorine and calculate the emf of the cell. Draw a well labeled diagram for the cell arrangement.

(iii) Calculate the energy given out by the cell in (c)(ii) above. Comment on your answer. ($1\ Faraday = 96500\ coulombs$)

(iv) Using the standard electrode potentials given, explain why hydrochloric acid cannot be used to acidify aqueous manganate(VII) solutions.

21. Draw a well labeled diagram of a half cell consisting of;

(a) a Cr^{3+}/Cr half-cell and a Cl_2/Cl^- half-cell.

(b) a Mn^{2+}/Mn half-cell and a Pb^{2+}/Pb half-cell.

22. (a) The molar conductivity of a carboxylic acid, $RCOOH$ at infinite dilution at 25℃ is $390.7\ \Omega^{-1}cm^2mol^{-1}$ and the acid dissociation constant, $K_a = 1.80 \times 10^{-5}M$.

(i) Define the term molar conductivity

(ii) Calculate the molar conductivity of a 0.01M solution of $RCOOH$.

(b) The zinc/ silver oxide cell used in hearing aids and electric watches has the following electrode potentials.

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e \quad E^\theta = +0.76V$

$Ag_2O(s) + H_2O(l) + 2e \longrightarrow Ag(s) + 2\bar{O}H \quad E^\theta = +0.344V$

(i) Calculate the emf of the zinc/silver oxide cell

(ii) Write the overall redox reaction that generates the emf calculate in b(i) above

(iii) Draw a well labeled diagram to show the zinc/ silver oxide cell can be set up and the emf measured.

23. (a) State and discuss three factors that affect the value of standard electrode potential

(b) Draw a well labeled diagram to show how the standard electrode potential of the zinc electrode can be determined.

(c) The electrode potentials of some half cells are given below;

	$E^\theta(Volts)$
$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e$	$-0.771V$
$2Cr^{3+}(aq) + 7H_2O(l) \longrightarrow Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e$	$-1.33V$

Write the:

(i) cell notation for the cell formed when the two half cells are combined.
(ii) equation at the anode, cathode and overall cell reaction.

(d) Calculate the emf of the cell in (c)(i)

(e) (i) State Faraday's law of electrolysis.
(ii) How long will it take $48\,cm^3$ of hydrogen at room temperature and pressure when acidified water is electrolyzed using a current of $0.25A$.

Assignment:

Batteries

- ***Research, read and make notes about batteries (dry cells, mercury cell, Nickel-Cadmium cell and fuel cells)***
- ***Uses of batteries***
- ***Explain the functioning of a battery***
- ***Explain the conversion of one form of energy to another***