Teach yourself

A-LEVEL INORGANIC CHEMISTRY

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To my parents, of course

ACKNOWLEDMENTS

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Mr. Tukesiga David offered unwavering support towards the technical review of Chapter 2. David has a very long history of teaching and examining chemistry at various levels of education. He is currently teaching at Old Kampala S. S., in addition to other responsibilities. I am really grateful for his dedicated support and kind comments.

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Of course, a big thanks to all my readers, you have kept me moving over the years.

A sincere thank you is also in order for my family and friends just for being there, and for dragging me away from the laptop on occasion.

Any errors in this book are mine and mine alone.

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CONTENTS

PREFACE

It's here; the long awaited **"Teach Yourself A-Level Inorganic Chemistry"**, is now on the book shelves. I thank my readers that have always called me and patiently waited for this book ever since I announced it back in 2012. I want to assure you all that it's been worth the wait.

Textbooks are often too detailed and complex to be understood by an average student; pamphlets are too simplified to the exclusion critical details. "Teach Yourself A-level Inorganic Chemistry" stands in the middle of the two non-overlapping worlds of textbooks and pamphlets. At the heart of this book's presentation is the belief that chemistry is for everyone. With straight forward illustrations and seamless integration with "**Concise Solutions to A-Level chemistry paper one and two –** a book by the same author", I am convinced that this book will deliver the anticipated success to its readers. This book presents an approach to inorganic chemistry where understanding from first principles and simplicity are front and central. My empirical analyses confirm that learning from first principles is permanent and pleasant.

Nobody likes to wait, so we have made this book brief and straight to the point; you will find explanations in this book simple and straight forward. Great effort has been taken use examples and illustrations taken from the local environment of the reader. We understand that searching for information from cluttered text can be a tad inconveniencing and frustrating; while designing this book, we kept the ease of finding information at the forefront. With features like tables of content, lists of figures and tables, index, interlinks to various parts of the book, and a summary of objectives at the beginning of each chapter, we are sure that your reading experience will be pleasurable. Once again, thank you for choosing this book and enjoy using your book

Ntanda Moses

HOW TO USE THIS BOOK

Who should read this book?

This book is especially suitable for students preparing for Uganda Advanced Certificate of Education (UACE) examinations. Because of its simplified explanations, the book is suitable for both students starting their advanced level course in S.5 as well as those finalizing their course in S.6. Explanations in this book can easily be understood without external assistance.

How this book is organised?

The chapters in this book can be read independent of each other. Where knowledge from another chapter is required, it is always pointed out through cross references. However, we recommend reading Chapters 1 and 2 before reading other chapters. These two first chapters contain several foundational principles. For beginners, we recommend reading the book cover to cover.

Conventions used in the book

This book uses the following conventions:

Effort has been taken to include alternative explanations or equations where appropriate. In cases, we use the convention "**OR**" to represent these two equivalent alternatives.

Example:

Factors that affect ionisation energy include screening (or *shielding*) effect....

The above example illustrate that screening and shield are equivalent terms and **you choose only one** of them when answering questions but not both.

References to other sections of the book are written in italics

Example:

Melting point depends on number of valence electrons and metallic radius – *Section 4.2.2*

The above example directs the reader to section 4.2.2 for a more detailed explanation on factors that affect melting point.

Some references in the further section are written as **P1 2004 Q4** which means go to paper one 2004 question 4 in another book by this author called Concise solutions to UACE Chemistry Paper One and Two.

Errata

Although I have taken every care to ensure the accuracy of contents of this book, mistakes do happen. If you find a mistake in this book—maybe a typing or technical error—I would be grateful if you would report this to me. By doing this you can save other readers from frustration, and help to improve subsequent versions of this book. If you find any errata, report them by visiting http://www.concisebooks.info/errata Once your errata have been verified, your submission will be accepted and the errata corrected in subsequent editions of this book. Existing errata, if any, can be viewed by visiting http://www.concisebooks.info/errata/view.php

Join our discussion forum

Besides the usual social fads like Facebook and Twitter, there is need for a special forum where serious scientific academic work can be discussed and ideas shared. I welcome you to our forum where you get to share chemistry knowledge with experienced chemistry scholars. At this forum, you get to ask questions and get answered by experienced science teachers and students. Come share ideas at http://www.concisebooks.info/forums/

We want to hear from you

As a reader of this book, you are our most important critic and commentator. We value your opinion and want to know what we're doing right, what we could do better, what areas you'd like to see us publish in, and any other words of wisdom you're willing to pass our way. Give us your feedback at http://www.concisebooks.info/feedback/

What a few others say about this book?

The book discusses the detailed chemistry of group(IV) elements and is in line with UACE syllabus. It's a work well-done and I highly recommend it – *Nathan Bakebwa, Gayaza High School.*

I am confident sure that the book will help learners acquire the required skills of the subject. Thank you for the great deal of work – *Nalumansi Irene, Kitante High School.*

I highly recommend this book – *Tukesiga David, Old Kampala S. S.*

Thanks for the effort. I highly recommend this book – *Kigozi Hassan, Kawempe Muslim S.S.*

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CHAPTER

1

ATOMIC STRUCTURE

Learning Objectives

After reading this chapter and completing the exercises you should be able to;

- Describe the structure of an atom and the nature of sub atomic particle.
- Appreciate the existence of unstable nuclei and name the particle emitted during radioactive decay.
- Understand the importance of radioactive isotopes in chemistry.
- Explain how the hydrogen spectrum is formed.
- Appreciate the use of atomic number as basis for periodic classification of elements.
- Explain factors that affect the magnitude of ionisation energy.

1.1 Introduction

As a result of early experiments in physics and chemistry, it is now known that an atom consists of three fundamental sub-atomic particles – the electron, proton, and the neutron. Table 1.1 summaries the characteristics of these particles.

Table 1.1 Subatomic particles

Particle	**Mass**	**Charge**	**Symbol**
Proton	1unit	+1	P
Electron	$\frac{1}{1837}$ unit (*negligible*)	-1	e
Neutron	1 unit	Neutral	n

The history of the discovery of the atom's structure is interesting but outside the scope of this book. However, evidence on which atomic theories are based will be discussed in subsequent sections of this chapter.

1.2 Dalton's Atomic theory

Dalton, in his atomic theory, proposed that;

- All matter is composed of atoms.
- Atoms cannot be created, divided, or destroyed.
- All atoms of one element are alike and different from those of any other element.

- Atoms combine together in a ratio of small whole numbers, and the compounds formed are held together by forces of chemical affinity.

However, Dalton's atomic theory has since been modified to embrace new findings. The modifications include, but are not limited to;

- Atoms can be created, divided, or destroyed in nuclear changes but not in chemical changes.
- All atoms of any one element are not the same (*as in the case of isotopes*) but are different from atoms of any other element.

1.3 Discovery of cathode rays

Crookes discovered that when a high voltage is applied to a gas at a low pressure in a discharge tube, luminous rays are observed to move from the cathode to the anode; it did not matter what gas was used, giving a strong evidence that these rays/particles were common to all elements. He called these **cathode** rays since they move from the cathode.

Cathode rays have the following properties;

- When they fall on glass at the end of the discharge tube, they cause it to fluoresce with green light. These rays also cause many other substances to fluoresce for example zinc sulphide coated in television tubes.
- When a solid obstacle is placed in their path, they cast a sharp shadow at the end of the tube, showing that they travel in straight lines.
- They are deflected by electric fields towards the positive plate showing that they are negatively charged.
- They are deflected by magnetic fields in a direction which would be expected for negatively charged particles.

- A freely moving paddle wheel, placed in their path, is set in motion showing that they posses momentum.
- They can penetrate thin sheets of metal such as aluminium, showing that they are smaller than atoms.

Later, J. J. Thompson was able to determine the velocity of these particles and their mass/charge ratio using the apparatus shown in figure 1.1.

It can therefore be concluded that gases are good conductors of electricity at low pressures. Discharge tubes are commonly used in fluorescent lights and neon advertising signs.

Figure 1.1. Thompson's apparatus for determining e/m for the electron

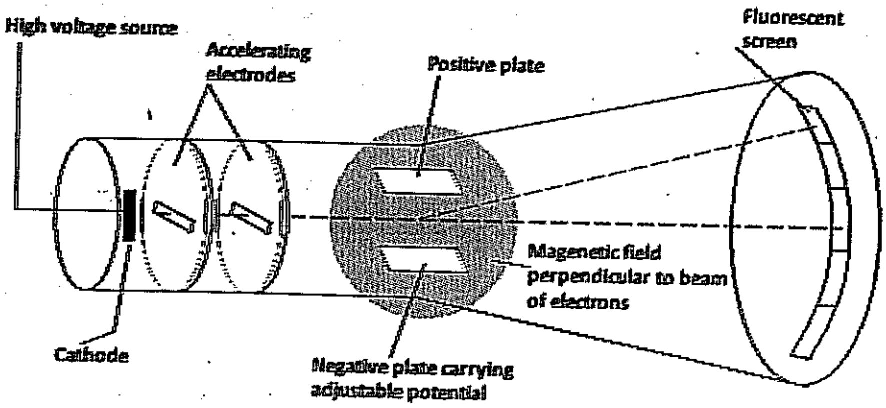


Figure 1.2 shows neon advertising signs taken from Kampala city.

Figure 1.2 Some neon advertising signs at Garden City, Communications house and Fairway Hotel

Electrons can be produced by other means, besides discharge tubes. They are given off when metal filaments are heated, when metals are exposed to light (*for example in photoelectric cells*), and when two materials are rubbed together. Production of electrons from so many substances gives evidence that electrons are one of the basic constituents of atoms.

1.4 Discovery of protons and neutrons

Since atoms are electrically neutral, they must contain an equal amount of positive charges to counter the negatively charged electrons in an atom. For a long time, atoms were thought to consist of electrons and protons. Later, it was found that when beryllium is bombarded with x-rays, particles were given off which had properties quite different from those of protons and electrons. They were not deflected by electric fields or magnetic fields. They therefore possessed no charge. Chadwick showed that the new particles had almost the same mass as protons. They were named **neutrons,** since they were neutral. Later experiments showed that all atoms contained neutrons except hydrogen.

1.5 Discovery of x-rays, α-particles, β-particles and γ-rays

Rontgen (1895) discovered a penetrating radiation emitted from discharge tubes, which appeared to originate from the anode. The radiation had the following properties;

- It blackened wrapped photographic film.
- It ionised gases allowing them to conduct electricity.
- It made certain substances to fluoresce e.g. zinc sulphide.
- It had no charge.

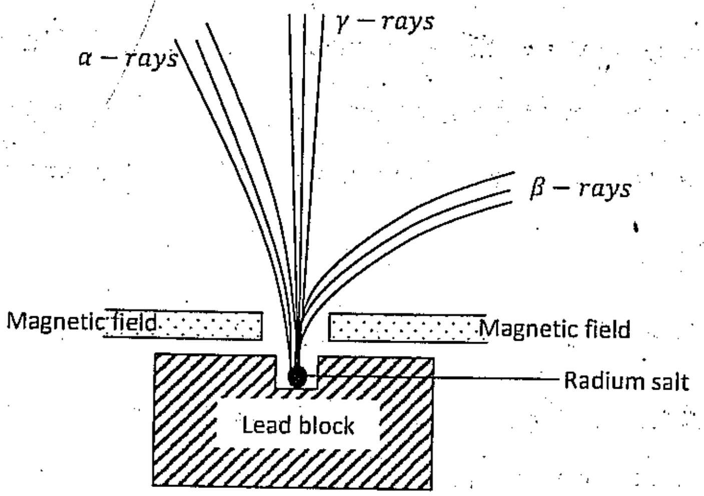
This radiation was named **x-ray,** and is now known to be produced whenever fast-moving electrons are stopped by impinging on a target. The excess energy appears mainly in form of x-radiation.

In 1886, Bacquerel found that a crystal of Uranium salt blackened a photographic plate, even in complete darkness. This suggested that some rays were emitted by Uranium.

Later on, two new elements; Radium and Polonium were discovered to give off more rays, thus more radioactive than Uranium.

Curies and Rutherford investigated the rays given off by Radium and were established to be of three kinds. These were labeled $\alpha, \beta,$ and γ according to their penetrative power. Figure 1.3 shows a diagrammatical representation of the apparatus used in the discovery of these rays.

Figure 1.3 Effect of magnetic field on radiation emitted by radium



α-rays

- These have the least penetrating power. They can be stopped by a sheet of paper.
- They are deflected in a direction expected for positively charged particles.
- They are a helium nucleus having a charge of +2 and a mass of 4 units i.e. ^4_2He

β-particles

- These are more penetrative than α-particles. They can penetrate a thin sheet of aluminum.
- A magnetic field deflects them much more strongly than α-particles, showing that they are lighter than α-particles. They are deflected in a direction expected for negative particles.

- They have a charge of -1 and negligible mass, thus they are identical to electrons i.e. $^{0}_{-1}e$

γ-rays

- These are the most penetrative.
- They are not deflected by a magnetic field, thus they are neutral.
- They are extremely dangerous to living creatures.

1.6 Radioactivity

1.6.1 Introduction

Rutherford put forward a theory of radioactivity in which he suggested that **radioactivity** is the disintegration (*or decay*) of heavy unstable atoms to form simpler stable atoms with emission of radiations. Types of radiations emitted during radioactivity include α,β, and γ rays. Examples of radioactive atoms include radium, uranium, bismuth, and all other atoms of atomic mass higher than that of bismuth.

Examples

$^{207}_{81}Ti \longrightarrow {}^{207}_{82}Pb + {}^{0}_{-1}e$

$^{223}_{88}Ra \longrightarrow {}^{219}_{86}Rn + {}^{4}_{2}He$

$^{214}_{83}Bi \longrightarrow 3\beta + 2\alpha + {}^{206}_{82}Pb$

Note

- The above equations are completed by ensuring that sum of atomic numbers and sum mass numbers on both sides of each equation balance. e.g. in the first equation atomic number on left hand side is 81 while sum of atomic numbers on right hand side is also 81 ($82 + {}^{-}1$)
- An element is uniquely indentified by atomic number but not atomic mass e.g. both $^{207}_{82}Pb$ and $^{206}_{82}Pb$ represent the same element, which is lead.

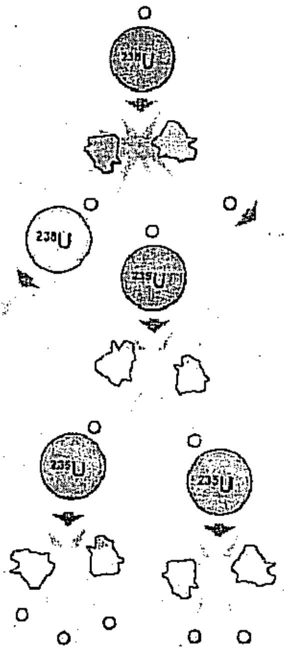
1.6.2 Nuclear fission and nuclear fusion

Nuclear Fission

This is a nuclear reaction in which the nucleus of an atom splits into lighter nuclei with emission of large amount of energy and radiations such as neutrons and photons. Fission is usually induced by a neutron. The composition of the products of fission is usually unpredictable, which distinguished it from reactions like alpha-decay that produce the same products consistently. An example is the fission of Uranium which may produce Barium and Krypton in one case or Xenon and Strontium in another case. Nuclear fission is accompanied by shooting out of two or more fresh neutrons; the fresh neutrons may also induce another nuclear fission causing a chain reaction. The equation below shows fission of Uranium and its chain effect is shown in figure 1.4.

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{236}_{92}U \longrightarrow ^{92}_{36}Kr + ^{141}_{56}Ba + 3^{1}_{0}n$$

Figure 1.4. Induced fission of Uranium



Energy obtained from nuclear fission has been applied in atomic bombs and atomic power plants. The first atomic bomb dropped on Japan in 1945 derived its energy from an extremely rapid chain reaction of a few kilograms of Uranium. Atomic power plants produce tremendous quantity of electricity

Nuclear Fusion

This is the joining together of two or more nuclei to form a single heavier nucleus, usually accompanied by absorption of energy.

$${}^{2}_{1}D + {}^{3}_{1}T \longrightarrow {}^{4}_{2}He + {}^{1}_{0}n + energy$$

Fusion is the process that powers hydrogen bombs. Since nuclear fusion requires very high temperatures to occur, it is often described as a thermonuclear reaction. Thermonuclear reactions occur in the sun and other stars, producing very high temperatures.

1.6.3 Stability of a nucleus

Nuclei of radioactive atoms are unstable. Unstable nuclei have a tendency of emitting radiations. There are no concrete theories to explain why some nuclei are unstable whereas others are stable. However, general observations based on available stable isotopes indicate that neutron to proton (n/p) ratio is a dominant factor in nuclear stability.

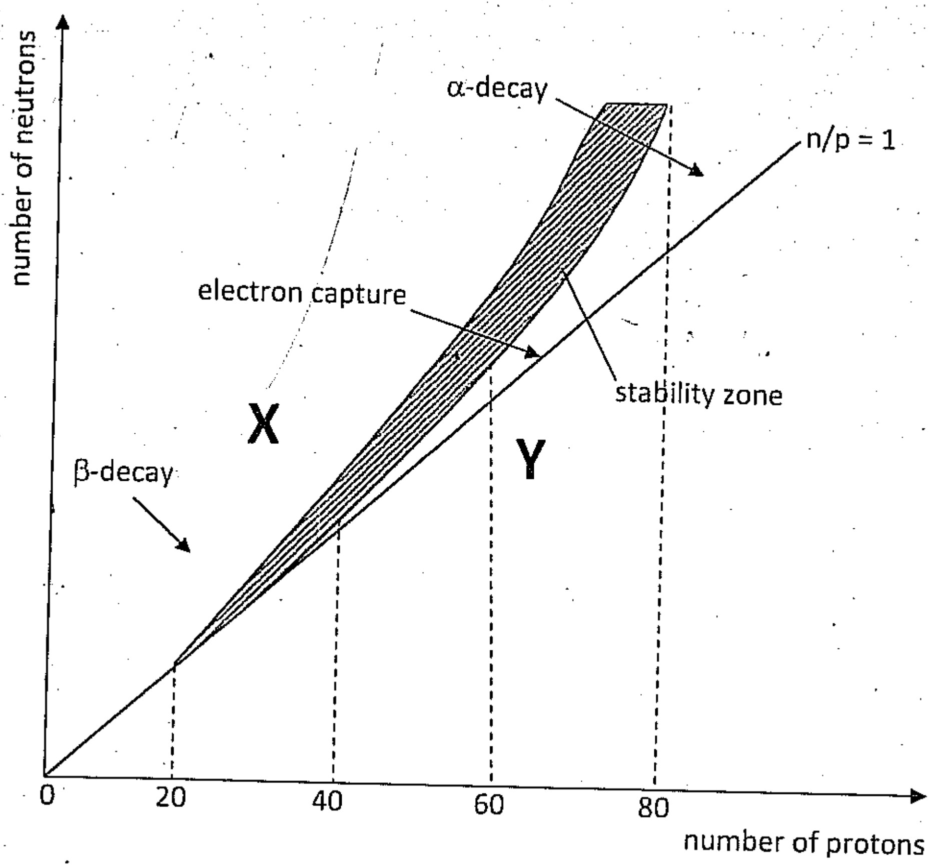
Some nuclei are unstable because they have a higher neutron to proton ratio than required for stability; others are unstable simply because they are too heavy for stability. Figure 1.5. shows a plot of number of neutrons against number of protons for known stable nuclei. All stable nuclei lie within a definite area called Zone of stability (or stability belt)

The figure indicates that nuclei with low atomic numbers are stable when their n/p ratio is very close to 1. As atomic number increases, the stability zone corresponds to a gradually increasing n/p ratio.

Gaining Stability

In an attempt by an unstable nucleus to reach a stable arrangement of its protons and neutrons, the nucleus spontaneously decomposes to form different nuclei with emission of particles. In the process, its number of neutrons or protons will change forming a different isotope or element respectively. This decomposition of the nuclei is known as radioactive decay. Nuclei gain stability by beta decay, electron capture or alpha decay.

Figure 1.5 Neutron to proton ratio for nuclear stability



Beta decay

An unstable isotope that lies to the left of the stability belt (position X) is neutron rich and undergoes beta decay to gain stability.

Through beta decay, a neutron from the nucleus splits to convert into a proton with emission of a beta particle; the proton remains in the nucleus but the beta particle (electron) is ejected. This increases the number of protons in the nucleus by 1 and reduces the number of neutrons by 1 thus moving the isotope towards the stability zone. In this case, scientists say that a new element has been formed and call this transformation.

$${}^{1}_{0}n \longrightarrow {}^{0}_{-1}e + {}^{1}_{1}P$$

Example

$^{32}_{15}P \longrightarrow {}^{0}_{-1}e + {}^{32}_{16}S$

Electron capture (also known as positron emission)

An unstable nucleus located at the right of the stability zone is proton rich and undergoes electron capture to gain stability.

By this process, the nucleus captures an electron from its innermost shell. The captured electron combines with a proton to form a neutron. This increases the number of neutrons by 1 and reduces the number of protons by 1 thus shifting the isotope towards the stability zone.

$^{1}_{1}P + {}^{0}_{-1}e \longrightarrow {}^{1}_{0}n$

Example

$^{23}_{11}Na + {}^{0}_{-1}e \longrightarrow {}^{23}_{10}Ne$ -- *

Note that equation * can alternatively be written as

$^{23}_{11}Na \longrightarrow {}^{0}_{1}e + {}^{23}_{10}Ne$

The particle ${}^{0}_{1}e$ is called a positron thus beta decay is also known as positron decay/emission.

Note that a positron is an antielectron having a charge of +1; it is usually represented as e^{+} or β^{+}.

Alpha decay

Almost all isotopes with atomic number greater than 83 are unstable. Very heavy isotopes gain stability by alpha decay. By alpha decay, atomic number of the isotope reduces by 2 while atomic mass reduces by 4.

Example

$^{238}_{92}U \longrightarrow {}^{4}_{2}He + {}^{234}_{90}Th$

Uses of radioactive isotopes

- Treatment of cancer

Penetrating gamma-radiation from cobalt-60 is used in treating inaccessible cancerous cells. Superficial cancers such as skin cancer can be treated by less penetrating radiations from phosphorous-32.

- Studying metabolic pathways

  Radioactive isotopes are used to trace the uptake and metabolism of various elements by animals and plants; the metabolism of phosphorous by plants can be studied using a fertilizer containing phosphorous-32. Iodine-131 has been used in the diagnosis and treatment of thyroid diseases.

- Determination of thickness of gauges and empty packet detection

  The radiation that goes through a material decreases as the material gets thicker thus, the amount of penetrating beta or gamma-radiation can be used to estimate the thickness of various materials such as paper, metal, or plastic.

- Carbon-14 dating

  Living plants and animals have an almost constant amount of carbon-14. On death, carbon-14 of the plant or animal begins to decay. The remaining carbon-14 at any time can be used to calculate the age of the plant or animal.

- Sterilisation of surgical instruments

  Radioactivity is more effective than boiling in sterilising surgical instruments.

- Detection of leakages in underground fuel pipes and water pipes.

  Underground pipe leaks are detected by introducing a short-lived isotope into the pipe. The level of radiation on the surface is monitored. A sudden increase of surface radioactivity shows the location of the leakage.

1.6.4 Radioactive decay equation

Suppose N_o is the initial amount of a radioactive sample and let N_t be the amount of the sample remaining after time t.

The rate of radioactive decay is proportional to the amount of the sample remaining at any time. Mathematically, this is expressed as;

$-\frac{dN_t}{dt} \propto N$ ($\frac{dN_t}{dt}$ means the rate of change of N_t with time t)

Note that since the amount is decreasing (decay), we precede the rate by a negative (-) sign.

We can eliminate the proportionality sign by introducing a constant, thus;

$-\frac{dN_t}{dt} = kN$ where k is the decay constant.

We integrate the above equation to yield the radioactive decay equation as shown below.

$-\int \frac{dN_t}{N} = \int kdt$

$\ln N_t = -kt + c$ where c is a constant of integration.

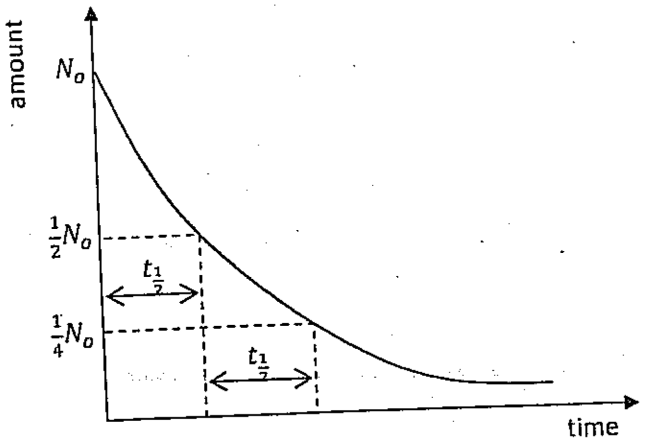
But at $t = 0$, $N_t = N_o$ $\therefore \ln N_o = -k \times 0 + c$; $c = \ln N_o$

$\therefore \ln N_t = -kt + \ln N_o$ -- **

Equation ** is known as the radioactive decay equation.

Half life $\left(t_{\frac{1}{2}}\right)$

This is the time taken by half the original amount of a radioactive sample to decay. It is usually denoted by $t_{\frac{1}{2}}$.



Consider the radioactive decay equation below

$\ln N_t = -kt + \ln N_o$

At $t_{\frac{1}{2}}$, $N_t = \frac{1}{2}N_o$

$\therefore \ln \frac{N_o}{2} = -kt_{\frac{1}{2}} + \ln N_o$

$kt_{\frac{1}{2}} = \ln N_o - \ln \frac{N_o}{2}$

$= \ln\left(N_o \times \frac{2}{N_o}\right) = \ln 2$

$\therefore t_{\frac{1}{2}} = \frac{\ln 2}{k}$

Examples

1. The initial count of a radioactive nucleus was 680 per second. After 350 seconds, the count rate was 125 per second. Calculate the;

   (a) decay constant.

   (b) half life of the nucleus.

   Solution

   (a) Using $\ln N_t = -kt + \ln N_o$,

   $N_o = 680,\ \ N_t = 125,\ \ t = 350\ \ thus$

   $\ln 125 = -350k + \ln 680$; $k = \frac{1}{350}\ln\frac{680}{125} = 4.839 \times 10^{-3}$ per second

   (b) $t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{4.839 \times 10^{-3}} = 1.432 \times 10^{2}$ seconds

2. When a radioactive isotope was stored for 42 days, it retained $\frac{1}{8}th$ of its original activity. Calculate the half life of the isotope.

   Solution

   Using $\ln N_t = -kt + \ln N_o$; $N_t = \frac{1}{8}N_o$, $t=42\ days$

   $\therefore \ln\frac{1}{8}N_o = -42k + \ln N_o$; $k = \frac{1}{42}\ln\frac{N_o \times 8}{N_o} = 4.951 \times 10^{-2}$ per day

   $t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{4.951 \times 10^{-2}} = 14$ days

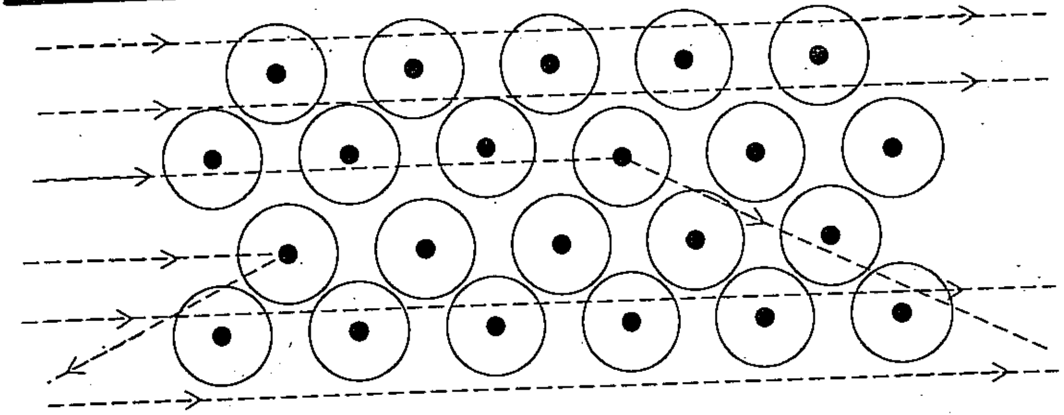
1.7 Rutherford's nuclear model of the atom

Rutherford found out that when alpha particles are directed towards a very thin sheet of gold, the majority of the particles passed through straight with no change in direction. A few, however, were deflected through angles as great as higher than 90°. Figure 1.6 illustrates Rutherford's observations.

Rutherford made the following conclusions;

- Since alpha particles were positively charged, the deflection could have been caused by a positive charge in the atoms of gold.
- Since just a few particles were deflected, the positive charge forms the smallest part of the atom.

Figure 1.6 Scattering of α –particles by nuclei of metal



To explain the above conclusions, Rutherford suggested an atomic model in which all protons were collected in a small central nucleus. Electrons were pictured to rotate around the nucleus so as to make the atom neutral.

- Since most of the alpha particles were not deflected at all, Rutherford concluded that a vast part of the atom consists of an empty space.
- He further suggested that electrons were prevented from falling into the oppositely charged nucleus by a centrifugal force.

Later on, neutrons were discovered. It was necessary to incorporate the neutrons in the nucleus as well.

1.8 Electronic structure of an atom

1.8.1 Introduction

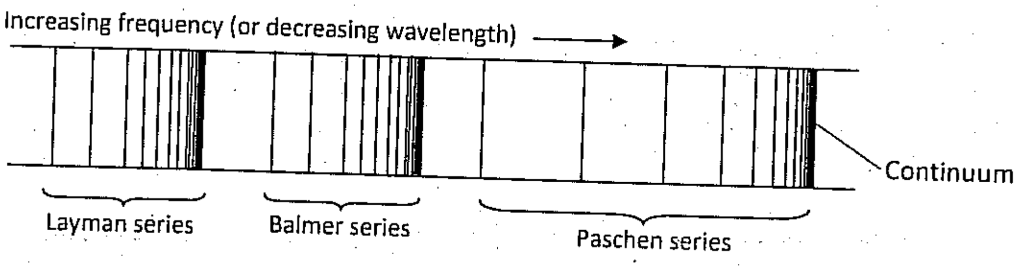
So far, little has been discussed about the arrangement of electrons in an atom. This section will focus on the evidence for existence of energy levels within an atom. Electrons occupy energy levels in atoms.

Rutherford's model of the atom suggests that electrons rotate around the nucleus. The electrons are prevented from falling into the nucleus by a centrifugal force. However, since moving particles radiate energy, then we would expect the velocity of electrons to decrease. Decrease in velocity would decrease the centrifugal force, eventually drawing the electron to the nucleus. However, this does not happen thus the electron part of Rutherford's model was discarded soon. The concept of the nucleus however remained.

1.8.2 The emission spectrum of the hydrogen atom

The hydrogen spectrum is a series (*or group*) of lines, some in the visible region and others in the invisible region. In each series, the spacing between the adjacent lines decreases as the frequency of the waves giving the lines increases (*or as wavelength decreases*). The decrease in the spacing is caused by decreased nuclear attraction on the electrons resulting into a continuum in each series.

Figure 1.7 The hydrogen spectrum



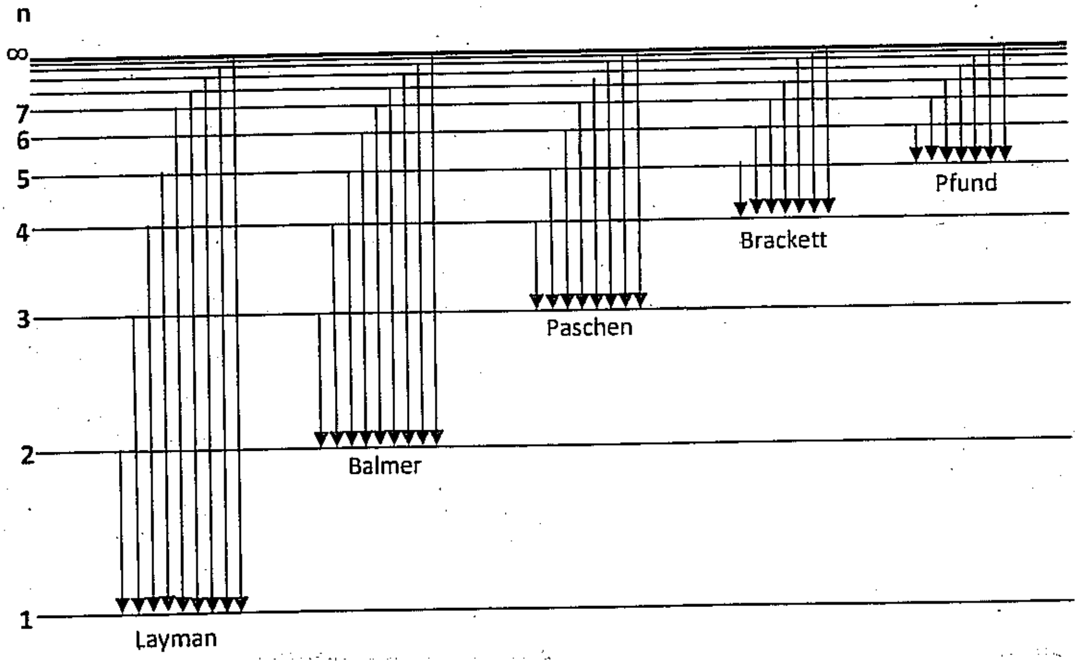
Formation of the hydrogen spectrum

When electricity is passed through a discharge tube containing hydrogen gas at low pressure, the molecules break up into single hydrogen atoms. The single electron of the hydrogen atom absorbs energy and is promoted from ground state (*energy level n=1*) to higher energy levels where it becomes unstable. When the electron falls back to the ground state, energy is given out in form of radiations of particular wavelength. This gives rise to the emission spectrum of hydrogen recorded on a photographic plate.

The electron may fall back directly to ground state or it may fall in steps through different energy levels (*n*=2, *n*=3, *etc*). To each energy level the electron falls, a different series of line is formed for example the Balmer series are formed when the electron fall back to energy level n=2.

The frequency of the radiation depends on the energy emitted. Therefore the size of the fall will determine the frequency of the radiation.

Figure 1.8 Energy levels for the hydrogen atom and transitions giving rise to various series



The Balmer series was the first to be discovered since it lies in the visible region. Later on, Layman (*in ultra violet region*), Paschen, Brackett, and Pfund series were also discovered.

The wavelength of the lines and the series to which they belong are related by the equation;

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

Where λ = wave length of a particular line

R_H = Rydberg's constant (109678 cm^{-1})

n = energy level to which the electron has fallen

m= energy level from which the electron has fallen

Table 1.2. shows the values of m and n for the different line series.

Table 1.2. Emission line series and their regions

Series	n	m	Region of the series
Layman	1	2, 3, 4, etc	Ultra violet
Balmer	2	3, 4, 5, etc	Visible
Paschen	3	4, 5, 6, etc	Infra red
Brackett	4	5, 6, 7, etc	Infra red
Pfund	5	6, 7, 8, etc	Infra red

Example

Find the wavelength of the line formed in the Balmer series when an electron falls from the third energy level.

$\frac{1}{\lambda} = R_H\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \Rightarrow \frac{1}{\lambda} = 109678\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$; λ = 0.00006565 cm

When an electron drops from energy level E_2 to energy level E_1, the frequency of the radiation emitted is related to the energy change by;

$E = h\upsilon$ where E is the energy change ($E_2 - E_1$)

h is Planck's constant (6.6256 x 10^{-34} JS)

ν is frequency of the radiation.

Note that $\nu = \frac{1}{\lambda}$

Evidence of existence of energy levels in atom

The hydrogen spectrum provides an evidence for existence of energy levels within an atom. This is because;

- Hydrogen has one electron yet it produces a spectrum containing many lines.
- There are several series of lines e.g. Balmer series, Layman's series, Pfund etc. Each series represents a particular energy level to which an electron returns.
- The spacing between adjacent lines in each series differs.
- There is a continuum in each series of lines
- The light giving each line is of definite energy or frequency.

1.8.3 Bohr's explanation of the hydrogen spectrum

The origin of the hydrogen spectrum was explained by Bohr, applying Planck's quantum theory.

The quantum theory postulates that matter cannot absorb or emit energy in continuous amounts, but only in small discrete units called **quanta**.

Using the quantum theory, Bohr made the following suggestions;

- The electron moves in an orbit around the central nucleus and only certain orbits are allowed.
- No energy is radiated by the electron while it is rotating in a permissible orbit (energy level). The energy levels were designated using quantum numbers 1, 2, 3, etc.
- Under normal circumstances, the electron occupies the energy level nearest to the nucleus (n=1). It is then said to be in ground state.

- When an atom is given energy in form of heat, electricity or light, the electron jumps to one of the higher energy levels hence getting excited.
- The excited state is unstable and there is a strong tendency for the electron to return to ground state.
- The return may occur in one step or in stages. To whatever level the electron returns, it emits some or all of its surplus energy in form of radiations. The frequency of the radiation depends on the energy difference between the two energy levels. This is illustrated by figure 1.8.

Since the discharge tube contains millions of hydrogen atoms, the atoms may be excited to different extents. Therefore electron transitions of many kinds may take place thus the different series of lines in the hydrogen spectrum.

The differences in energy levels become smaller with increasing distance of the energy levels from the nucleus. The convergence limit is reached when $n = \infty$, as illustrated by figure 1.8.

When an electron jumps from $n = 1$ to $n = \infty$, the electron is said to be completely removed from the atom. The atom is said to be ionised and the energy required for this change is called **ionisation energy.**

1.8.4 Electron distribution in atoms

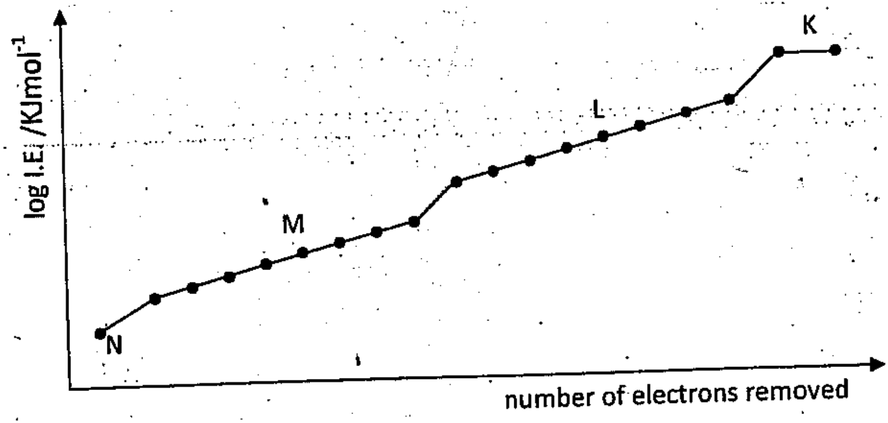
Within an atom, electrons occupy energy levels. Electrons occupying the same energy level are said to belong to the same quantum shell. The energy levels are denoted by numbers 1, 2, 3, etc or letters K, L, M, etc.

A graph of ionisation energy against number of electrons removed from an atom gives evidence for existence of energy level.

Ionisation energy is the minimum amount of energy required to remove an electron from a gaseous atom or gaseous cation to form a gaseous cation.

If the electron removed is the first to be removed from that atom, then the energy is referred to as first ionisation energy. If it is the second electron, then it is second ionisation energy and so on. Figure 1.8 shows a plot of log ionisation energy (I.E.) against number of electrons removed from a gaseous atom of potassium.

Figure 1.8 Graph of ionisation energies against number of electrons removed



It should be noted that;

- the electron with the lowest ionisation energy is one which is far-most from the nucleus. Therefore the electron in energy level N is the outermost.
- after removal of the first electron, there is a sudden very big increase in energy required to remove the second electron. This shows that the second electron is being removed from a new inner energy level (shell).
- from the second up to the ninth electron, increase in ionisation is gradual. However, the tenth ionisation energy is abnormally higher than the ninth. This shows that the tenth electron is being removed from a new shell.
- from the 10th to the 17th electron, increase in ionisation energy is gradual. However, there is a steep increase in energy required to remove the 18th electron showing that the 18th electron is being removed from a new shell.
- the atom has four energy levels, thus it belongs to period four.
- the atom belongs to group one since the outermost shell has only one electron.

- the atomic number is 19 since a total of 19 electrons have been removed.

Example

The table below shows the ionisation energies (in $KJmol^{-1}$) of five elements lettered A, B, C, D and E.

Element	1st ionisation energy	2nd ionisation energy	3rd ionisation energy	4th ionisation energy
A	500	4600	6900	9500
B	740	1500	7700	10500
C	630	1600	3000	4800
D	900	1800	14800	21000
E	589	1800	2700	11600

(a) Which one of these elements is most likely to form an ion with a charge of +1? Give a reason for your answer.

(b) To which group does B belong? Give a reason for your answer.

(c) State two elements which belong to the same group in the Periodic Table and the group to which they belong.

Solution

(a) A: The difference between the first and second ionisation energies is very high compared to the difference between the second and third ionisation energies as well as third and fourth ionisation energies.

(b) B belongs to group II. This is because there is a very big difference between the 2nd and 3rd ionisation energy as compared to the difference between the 1st and 2nd ionisation energy as well as to the 3rd and 4th ionisation energy.

(c) B and D belong to the same group which is group II.

The major energy levels are subdivided into sub energy levels (or sub shells) and are designated as s, p, d, and f. The sub-energy levels also differ in energy. The sub-energy levels contain orbitals into which electrons are located. Each orbital takes a maximum of two electrons.

- The s sub-energy level has one orbital and therefore takes a maximum of two electrons.
- The p sub-energy level has 3 orbitals and therefore takes a maximum of six electrons.
- The d sub-energy level has 5 orbitals and takes ten electrons.
- The f sub-energy level has seven orbitals and takes a maximum of fourteen electrons.

An orbital is that volume of space around the nucleus where there is a high probability of finding electrons.

Energy level	**Sub-energy levels**
1	1s
2	2s 2p
3	3s 3p 3d
4	4s 4p 4d 4f
5	5s 5p 5d 5f

Rules governing electron distribution in atoms

Pauli's exclusion principle

This states that an orbital can take a maximum of two electrons only and only on condition that the two electrons occupy it with opposite spins i.e. $\boxed{\uparrow\downarrow}$

Hund's rule

If electrons are present in a number of degenerate (equal energy) orbitals, they occupy them singly with parallel spins before any pairing occurs.

Consider the nitrogen atom whose atomic number is seven (therefore it has seven electrons). We use the above rules to write its configurations shown below;

- We start by filling the first energy level which has only 1s sub-energy level. Therefore the first shell will take only 2 electrons and is written as $1s^2$. Diagrammatically, this is shown as $\boxed{\uparrow\downarrow}$

- After filling the first shell, we remain with 5 electrons (7-2). We then move on to the second shell that has two sub-energy levels – 2s and 2p. 2s is of lower energy than 2p and is filled first. Since s orbitals take a maximum of 2 electrons, the 2s sub-energy level will also take two electrons leaving us with a balance of 3 electrons (5-2). The electron configuration is further written as $1s^2 2s^2$. Diagrammatically, this is shown as $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}$.
- We now move on to the 2p sub-energy level. The p sub-energy level has three orbitals which are of equal energy (degenerate). It can take six electrons but we are remaining with 3. Since these orbitals are degeneration, the electrons will occupy them singly with parallel spins before any paring can occur. The electronic configuration thus becomes $1s^2 2s^2 2p^3$ which is diagrammatically represented as $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \boxed{\uparrow\,|\,\uparrow\,|\,\uparrow}$.

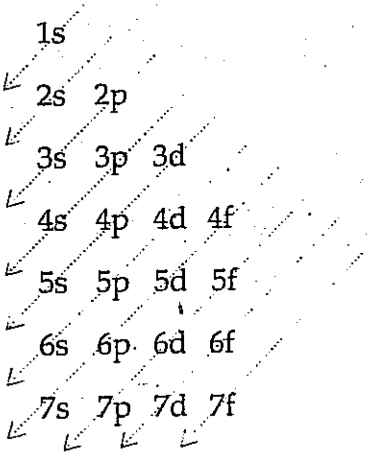
Similarly, we can come up with electronic configurations of the following elements.

Element	**Atomic no.**	**Electronic configuration (in major energy levels)**	**Electronic configuration and diagrammatic representation**
Lithium	3	2:1	$1s^2\ 2s^1$ $\boxed{\uparrow\downarrow}\ \boxed{\uparrow}$
Beryllium	4	2:2	$1s^2\ 2s^2$ $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}$
Carbon	6	2:4	$1s^2\ 2s^2\ 2p^2$ $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \boxed{\uparrow\,|\,\uparrow\,|\,}$
Nitrogen	7	2:5	$1s^2\ 2s^2\ 2p^3$ $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \boxed{\uparrow\,|\,\uparrow\,|\,\uparrow}$
Oxygen	8	2:6	$1s^2\ 2s^2\ 2p^4$ $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow\,|\,\uparrow\,|\,\uparrow}$
Fluorine	9	2:7	$1s^2\ 2s^2\ 2p^5$ $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow\,|\,\uparrow\downarrow\,|\,\uparrow}$

Sub-energy levels are filled in the order 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s etc.

Note that after filling the 2nd energy level, an overlap occurs between the 3rd and 4th energy level such that the 4s sub-energy level is filled before 3d. Similar overlaps occur as the electronic configuration grows bigger. The electronic configuration of scandium, whose atomic number is 21, is thus $1s^22s^22p^63s^23p^64s^23d^1$

The illustration below may be useful in memorizing the order.



1.8.5 Ionisation energy

Ionisation energy is the minimum amount of energy required to completely remove an electron from a gaseous atom or gaseous cation to form a gaseous cation e.g.

$M(g) \longrightarrow M^+(g) + e$ ΔH = 1st ionisation energy of M

$Na(s) \longrightarrow Na^+(g) + e$ ΔH = 1st ionization energy of sodium

First ionisation energy is the minimum amount of energy required to remove an electron from a free gaseous atom to form a uni-positively charged gaseous cation e.g.

$Mg(s) \longrightarrow Mg^+(g) + e$ ΔH = 1st ionisation energy of magnesium.

Similarly, energy required to remove the second electron is called second ionisation energy and so on.

$M^+(g) \longrightarrow M^{2+}(g) + e$ ΔH = 2nd ionisation energy of M

The process of removing an electron from an atom requires energy since the electron is being removed against the attractive force of the nucleus. Therefore the process is endothermic.

Factors that affect the magnitude of ionisation energy

Ionisation energy gives a measure of how firmly the nucleus of a gaseous atom or gaseous ion holds on to its outer electrons. The oppositely charged nucleus attracts electrons towards its self. The charge/attraction which a particular electron feels from the nucleus is called **effective nuclear charge**. The effective nuclear charge is influenced by several factors and these factors also affect the ionisation energy. They factors include;

- The net charge on the atom or ion.
- The screening effect of inner electrons.
- Nuclear charge.
- The penetrating power of the valence electrons.
- Electronic configuration of the atom or ion

Before we can explain these factors, it is essential to understand that outermost electrons (valence electrons) are removed first when ionising an atom.

Net charge on the atom or ion

Ionisation energy increase with increase in charge on the atom or ion. consequently, ionisation energies increase in the order 1st < 2nd < 3rd < 4th and so on.

As electrons are removed, the nuclear charge remains constant but the number of electrons reduce. The nucleus therefore attracts the remaining fewer electrons more strongly thus increasing the effective nuclear charge.

Examples

1. The 1st, 2nd, and 3rd ionisation energies (in $KJmol^{-1}$) of aluminium are 577, 1816, and 2745 respectively. Explain this trend.

The ionisation energies increase from the 1st to the 3rd through the 2nd. This is because as electrons are removed, the nuclear charge remains constant. This increases the effective nuclear charge thus the outer electrons become more strongly attracted by the nucleus. Ionisation energy therefore increases.

2. The ionisation energies of Na^+, Mg^{2+}, and Al^{3+} are in the order $Na^+ < Mg^{2+} < Al^{3+}$. Explain this observation.

From Na^+ through Mg^{2+} to Al^{3+}, nuclear charge increases (*since protons are 11, 12, and 13 respectively*). However, the number electrons remain constant (*all the ions have 10 electrons*). Therefore the nuclear attraction for the electrons (effective nuclear charge) increase from Na^+ to Mg^{2+} to Al^{3+}. This causes an increase in ionisation energy in the same direction.

The screening effect of the inner electrons

Shielding (*or screening*) of outer electrons by inner electrons reduces the attraction of outer electrons by the nucleus. Therefore increase in screening effect causes a decrease in effective nuclear charge and thus a decrease in ionisation energy.

Within a given shell, the screening efficiency of the inner electrons decreases in the order s > p > d > f. Therefore s-electrons are more screening than p-electrons and so on.

Nuclear charge

Increase in nuclear charge causes an increase in attraction of outer electrons by the nucleus. Therefore keeping other factors constant, increase in nuclear charge causes an increase in ionisation energy.

Penetrating power of valence electrons

In a given shell, the penetrating power of electrons towards the nucleus decreases in the order s > p > d > f; therefore the s-electrons are more penetrating and more firmly held than p-electrons and so on. Consequently in a given shell, ionisation energies increase in the order s > p > d > f.

Electronic configuration of the atom or ion

Electronic configurations with half-filled sub energy levels or fully-filled sub energy levels are relatively stable. For example, first ionisation energy of nitrogen ($1s^2 2s^2 2p^3$) is higher than that of oxygen ($1s^2 2s^2 2p^4$) although oxygen has a higher nuclear charge than nitrogen. This is because nitrogen has a half filled $2p^3$ sub-energy level which is more stable than the partially filled $2p^4$ sub energy level of oxygen. Similarly, the first ionisation energy of helium (with s fully filled $2s^2$ sub-energy level) is higher than that of lithium.

The concept of ionisation energy is very essential in understanding the chemistry of elements. Section 4.2.6 gives a detailed discussion of how the above factors affect ionisation energy down groups and across periods. It also explains how ionisation energies affect the chemistry of the groups and periods.

1.9 Summary

This chapter has focused on the structure of an atom and the discovery of sub-atomic particles. Knowledge gained from this discussion is essential in understanding material covered in the subsequent chapters.

1.10 Suggested further reading on chapter 1

G. F. Liptrot, *Modern Inorganic Chemistry*, Mills & Boon Ltd, Fourth Edition, 1984.

E. N. Ramsden, *Calculations For A-level Chemistry*, Nelson Thornes, Fourth Edition 2001.

H. L. Heys, *Physical Chemistry*, Nelson Thornes, Fourth Edition 1985.

C. H. Graham and J. S. Holman, *Chemisty in Context*, Thomas Nelson and Sons Ltd, 4th Edition 1995.

W. R. Kneen, *Chemistry, Facts, Patterns and Principles*, Addison-Wesley Pub (Sd), 1972

1.11 Questions on chapter one

1. (a) Derive the expression for half life of a first order reaction; $2.303\log\left(\frac{a_0}{a_0-x}\right) = kt$ where a_0 is the initial concentration of the reactant and $(a_0 - x)$ is the concentration after time t.

   (b) The half life of a first order reaction is 100 s.

   (i) Calculate the rate constant.

   (ii) Determine the percentage of the reactant that reacted after 250 s.

   (Hint: All radioactive decay reactions are first order reactions. Rate constant is similar to decay constant)

2. (a) Complete the following equation for radioactive decay of bismuth.

   $^{214}_{83}Bi \longrightarrow {}^{0}_{-1}e + \_\_\_\_\_\_$

   (b) The half life of bismuth is 19.7 minutes. Determine the time taken for 43% by mass of bismuth to decay.

3. The activity of $^{234}_{90}Th$ was reduced to 25% in 50 days. Determine the half life of $^{234}_{90}Th$.

4. The table below shows the activity of krypton with time. Plot a suitable graph and use it to find the half life and hence decay constant for krypton.

Time/minutes	0	20	40	60	80	100	120
Activity/counts per second	100	92	85	78	72	66	61

5. Actinium B has a half life of 36.0 min. What fraction of the original quantity of actinium B remains after;

   (a) 180.0 min (b) 1080.0 min

CHAPTER 2

BONDING AND STRUCTURE

Learning Objectives

After reading this chapter and completing the exercises, you should be able to:

- Explain how ionic, covalent, metallic, and hydrogen bonds are formed and give examples of each.
- Discuss the properties, and relative strengths of the above bonds.
- Appreciate the existence of polar and non-polar covalent bonds.
- Predict shapes of simple molecules using the Valence Shell Electron Pair Repulsion theory.
- Discuss the formation and properties of giant ionic structures, giant covalent structures and giant molecular structures.

2.1 Introduction

Why atoms combine?

Atoms combine with others in order to complete their octet. Completion its octet enables an atom to acquire a noble gas electronic configuration, which is highly stable. Atoms complete their octet by either transfer or sharing of electrons. Loss and gain (*transfer*) of electrons by atoms results into ionic bonds; sharing of electrons between atoms results into covalent bonds. Besides ionic and covalent bonds, other bond types exist which include metallic and hydrogen bonds. These bond types are discussed, in details, in the following section.

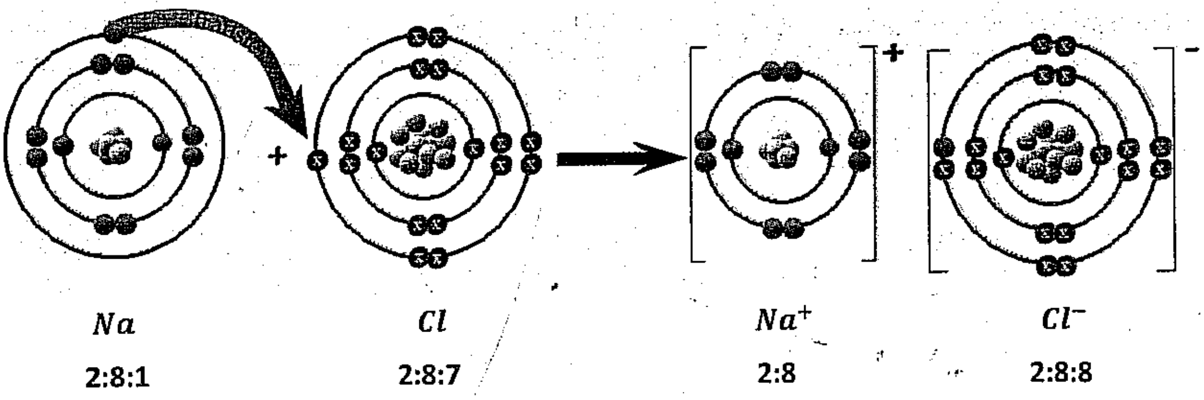
2.2 Types of bonds

2.2.1 Ionic bonding

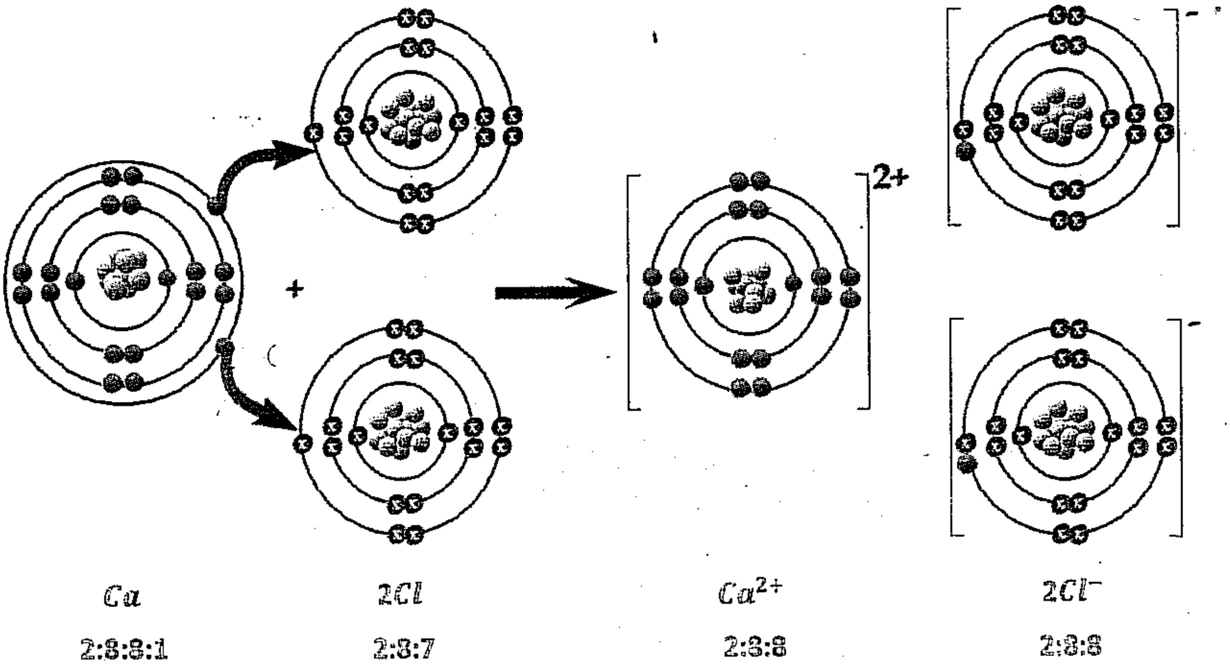
An ionic bond is formed as a result of transfer of one or more electrons from one atom to another. It is also known as an **electrovalent bond.**

On losing an electron, an atom acquires a positive charge and becomes a cation.

The atom that gains the electron acquires a negative charge and becomes an anion. Strong electrostatic attractions exist between oppositely charged positive and negative ions thus an **ionic bond**. Examples of ionic compounds include Na^+Cl^-, $Zn^{2+}O^{2-}$, $Cu^{2+}SO_4^{2-}$ and many more. The figures below illustrate formation of sodium chloride and calcium chloride through ionic bonding.

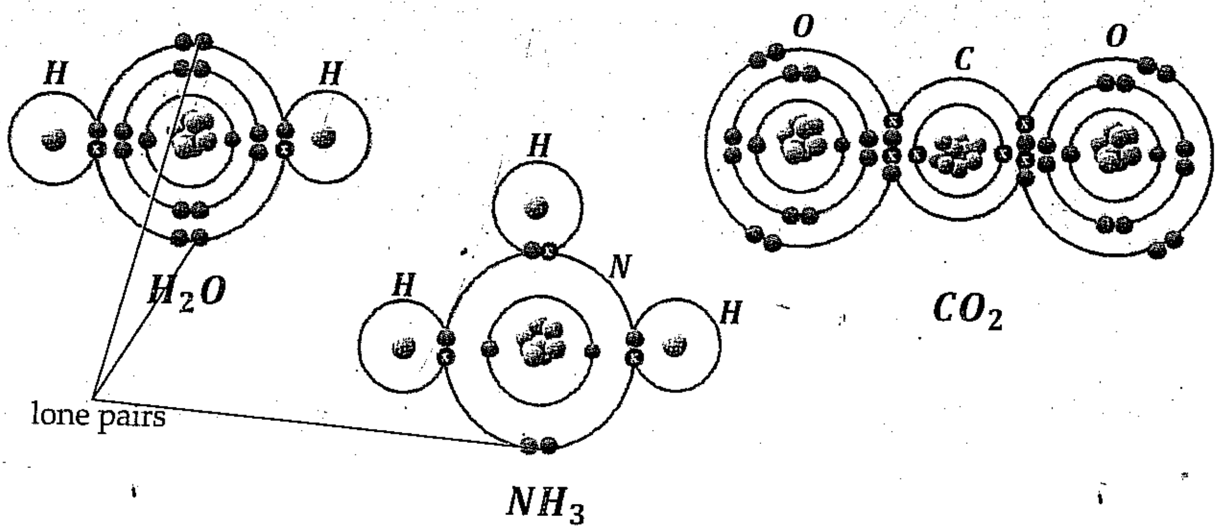


Calcium has two electrons in its valence cell and therefore requires two chlorine atoms



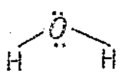
2.2.2 Covalent bonding

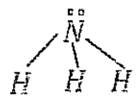
A covalent bond is formed as a result of sharing one or more electron pairs between two atoms. The diagrams below illustrate the formation of water, ammonia, and carbon dioxide through covalent bonding.



It's worth noting that;

- After bonding, all the atoms acquire a fully filled valency (outermost) shell. Each of the atoms acquires the configuration of the closest noble gas.
- Any electron pair on the central atom not being used for bonding is called a **lone pair**.
- A covalent bond is represented by a dash (–) which indicates a pair of electrons being shared. Therefore water, ammonia, and carbon dioxide molecules can be represented as;





$O=C=O$

2.2.2.1 Comparison of properties of ionic compounds and covalent compounds

- Ionic compounds are usually solids at room temperature as opposed to covalent compounds that are normally liquids or gases at room temperature.

  The ions in ionic compounds are held by very strong electrostatic attractions thus resulting into solids. However, the molecules of most covalent compounds are held by weak Van der Waals thus resulting into liquids or gases. It is important to note that not all covalently bonded compounds are liquids or gases, as will be discussed in subsequent sections.
- Ionic compounds have very high melting points and boiling points as opposed to covalent compounds whose boiling points and melting points are usually low. This can still be attributed to the strong electrostatic forces binding the ions in ionic compounds in comparison to the weak Van der Waals forces binding molecules of covalent compounds.
- Ionic compounds contain mobile ions when dissolved or molten and therefore they are good conductors of electricity both in molten and dissolved state. However, covalent compounds contain no ions and thus don't conduct electricity.
- Ionic compounds are soluble in polar solvents such as water and are insoluble in organic solvents such as benzene and chloroform. Covalent compounds are insoluble in polar solvents but soluble in organic solvents.

  Solubility of an ionic compound involves two major energy changes; separation of the ionic lattice into constituent gaseous ions (energy required is called **lattice energy**) and surrounding of the separated gaseous ions by water molecules (this gives out energy called **hydration energy**). A compound will dissolve only if the magnitude of hydration energy is high enough to offset lattice energy.

Ionic compounds are soluble in water because the hydration energy released when the separated ions are surrounded by the polar water molecules recoups the lattice energy required to break up the ionic lattice.

However, some ionic compounds such as barium sulphate are virtually insoluble in water because of their very high lattice energy which cannot be offset to any great extent by hydration energy.

Ionic compounds are insoluble in non-polar solvents since there can be little or no interaction between the ions and solvent molecules thus no way of offsetting the lattice energy.

Some covalent compounds may dissolve in water and this may be because a chemical reaction occurs which changes their structure, e.g. the ionisation of hydrogen chloride in water, or because of a similar grouping, e.g. ethanol is completely soluble in water since they both contain hydroxyl groups.

2.2.2.2 Polarisation and its effects on ionic and covalent bonds

Electronegativity is the tendency of an atom to attract bonding electrons towards its self so as to become negatively charged in a covalent bond.

Purely ionic bonds cannot exist, as the proximity of the ions involved in the bond allows some degree of sharing electron density between them. If the positive ion is small and/or highly charged, it will distort the electron cloud of the negative ion.

The electrons tend to be more less shared hence a purely ionic bond gains some degree of covalency. This distortion of the electron cloud of the negative ion is called **polarisation.**

Therefore, all ionic bonds have some covalent character. Thus, an ionic bond is considered a bond where the ionic character is greater than the covalent character. The larger the difference in electronegativity between the two atoms involved in the bond, the more ionic (polar) the bond is. Polarisation induces some covalent character within an ionic compound thus affecting the physical properties (e.g melting point and boiling point) of the compound.

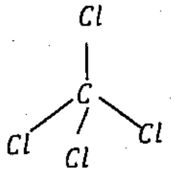
Larger negative ions are more easily polarized, but the effect is usually only important when positive ions with charges of 3+ (e.g., Al^{3+}) are involved. However, 2+ ions (e.g., Be^{2+}) or even 1+ (e.g., Li^{+}) show some polarizing power because their ionic radii are so small.

Conversely, when a covalent bond is formed between two atoms of different electronegativity, the bonding electrons are not equally shared. This brings about electrical dipoles within the bond. The molecule is said to be polar e.g.

$$H^{\delta+} - F^{\delta-};\quad CH_3CH_2O^{\delta-} - H^{\delta+}$$

Other examples of polar molecules include water, hydrogen chloride, sulphur dioxide, phosphorous trichloride and ammonia among others.

Because of the dipoles, polar molecules posses some ionic character. However, some molecules have polar bonds but they are not polar themselves. An example of such molecules is carbon tetrachloride (CCl_4). In carbon tetrachloride, although the $C - Cl$ bond is polar, $C - Cl$ bonds are symmetrical arranged tetrahedrally leading to the cancellation of the polar effect.



Also the carbon-oxygen bonds in carbondioxide are polar but the carbondioxide molecule is non-polar. The carbon dioxide molecule is linear which cancels out the dipole moments of the carbon-oxygen bonds. i.e. $O = C = O$

Factors that favour polarisation

Degree of polarisation is affected by ionic radius and ionic charge both of which give a combined effect called charge density.

Ionic radius

Polarising power of a cation increases with a decrease in ionic radius. For anions, polarisability increases with increase in ionic radius.
This is because for cations, a decrease in ionic radius leads to an increase in charge density. Due to high charge density, the electrostatic attraction of the anion's electron cloud by the cation increases leading to high polarising power of the cation.

For anions, an increase in ionic radius implies that valence electrons are very far away from the nucleus. These electrons are therefore easily polarized by the cation.

Melting points of the following chlorides of group(I) elements increase in the order $LiCl < NaCl < KCl$. This is because the ionic radii of the cations increase in the order $Li^+ < Na^+ < K^+$. Due high charge density, Li^+ is the most polarising followed by Na^+ while K^+ is the least polarising. Covalent character of the chlorides therefore reduces in the order $LiCl > NaCl > KCl$. Melting point increases with decrease in covalent character.

Ionic charge

Polarisation increases with increase in ionic charge. This is because an increase in ionic charge leads to a high charge density which makes the cation more polarising. Consequently, aluminium chloride has a lower melting point than calcium chloride.

To further explain the effect of ionic charge and ionic radius, we consider the melting points of a few compounds below

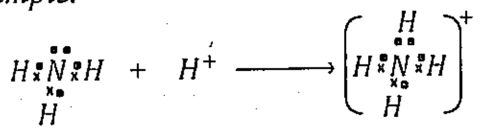
Compound	melting point (K)
Al_2O_3	2290
$AlCl_3$	451
CaO	2850
$CaCl_2$	1051

We note that the melting point of aluminium chloride is lower than that of aluminium oxide. This is explained by the fact that the chloride ion has a bigger ionic radius than the oxide ion. Aluminium chloride is thus more covalent than aluminium oxide. It can also be argued that aluminium chloride is more covalent than calcium chloride due to a very high charge density of the aluminium ion compared to that of the calcium ion.

2.2.2.3 The coordinate covalent (dative) bond

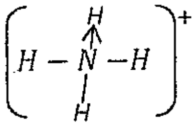
This is a covalent bond in which only one atom provides the pair of electrons being shared. The donor atom must have atleast one lone pair of electrons (*a pair of non-bonding electrons*). The acceptor must possess at least a vacant orbital to accommodate the lone pair.

Example:



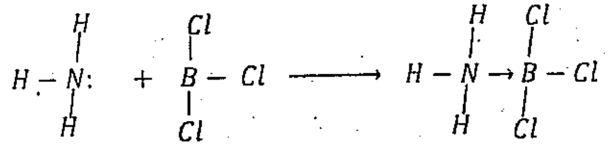
A dative bond is represented by an arrow (→), pointing from the donor atom to the acceptor thus;

The ammonium ion can be represented as



$$\left[H - \overset{\displaystyle H \atop \displaystyle \uparrow}{N} - H \right]^+$$

Reaction between ammonia and boron trichloride can be represented as



$$H_3N: + BCl_3 \longrightarrow H_3N \rightarrow BCl_3$$

In the above equation, the boron atom in boron trichloride is surrounded by only six electrons (only three bonds) instead of eight. The boron atom therefore has an incomplete octet and hence vacant orbitals.

2.2.3 The metallic bond

In metallic bonding, each metal pools (loses) its valency electrons forming metal cations. The metal cations are attracted together by the cloud of lost electrons resulting into strong metallic bonds. Thus a metallic bond can be defined as an electrostatic force of attraction between positively charged metal ions and a cloud of negatively charged electrons lost by the metal atoms.

The lost electrons are delocalised and free to move throughout the entire metal lattice thus metals conduct electricity and heat.

When metal atoms approach each other closely, their outer shell orbitals overlap forming molecular orbitals. Because of a large number of outer shell orbitals, many molecular orbitals are formed which are non-degenerate (i.e. they are at different energy levels). When light is shone on the metal, the electrons absorb energy and transitions occur from low energy molecular orbitals to higher energy molecular orbitals. When electrons return to low energy molecular orbitals, they emit energy in form of light. This explains why metals appear shiny.

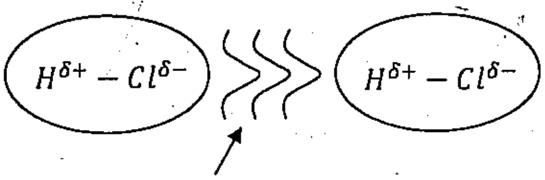
2.2.4 Intermolecular forces

Covalent bonds have directional properties (*they are polar*). Therefore intermolecular forces exist between opposite dipoles of covalent molecules. The magnitude of the intermolecular forces will determine whether the molecules are bound into solid, liquid or gaseous state.

Common intermolecular forces present in covalent molecules include dipole-dipole interactions, van der waals forces (bonds) and hydrogen bonds. Intermolecular forces are relatively weaker compared to other bonds. Van der Waals forces are the weakest among the intermolecular forces.

2.2.4.1 Dipole-dipole interactions

In solid state, polar molecules arrange themselves in such a way that opposite charges are adjacent to each other. This results into permanent dipole-dipole attractions between the molecules.



permanent dipole-dipole attractions

Consequently, ionic compounds dissolve in polar solvents because the energy required to break up the ionic lattice is recouped (recovered) by the energy released when dipole-dipole interactions occur between polar solvent molecules and ions from the ionic compound-*section* 2.2.2.1.

2.2.4.2 Van der Waals forces

Non-polar molecules also have temporary induced dipoles resulting from random movement of electrons in the atoms of the molecules. These dipole moments are temporarily created when the non-polar molecules approach each other. Forces of attraction exist between the induced electrical dipoles of the different molecules resulting into Van der Waals forces (*also known as molecular bonds*). These forces also exist between noble gases.

The magnitude of Van der Waals forces increase with increasing molecular mass (*since number of electrons increases with molecular mass*). This explains why fluorine and chlorine are gases are room temperature while bromine is a liquid and iodine is a solid at room temperature.

For the same reason, boiling points of alkanes increase with increasing formula mass.

2.2.4.3 Hydrogen bonds

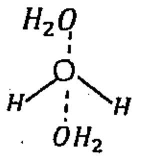
A hydrogen bond is dipole-dipole attraction between a hydrogen atom attached to a strongly electronegative atom and another highly electronegative atom.

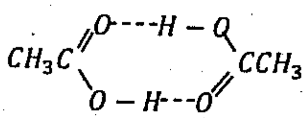
Hydrogen bonds are characteristic of compounds containing highly electronegative atoms such as fluorine, oxygen, and nitrogen. Therefore hydrogen fluoride(HF), ammonia(NH_3), and water(H_2O).

Hydrogen bonds are stronger than other intermolecular forces thus compounds having hydrogen bonds are characterized by unanticipated physical properties such as melting point, boiling point, density etc.

A hydrogen bond is represented by a dotted line as shown in the compounds below.

$$-----H^{\delta+} - F^{\delta-}---H^{\delta+} - F^{\delta-}--- H^{\delta+} - F^{\delta-}--$$





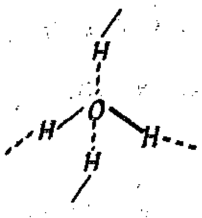
Presence of hydrogen bonds is responsible for the unpredicted physical properties of the following compounds.

- The boiling point of hydrogen fluoride is abnormally higher than that of other hydrides of group(VII) i.e. HCl, HBr and HI.

  HCl, HBr and HI molecules are held by weak Van der Waals. Boiling point increases with increase in magnitude of the Van der Waals forces. The magnitude of Van der Waals forces increase with increasing formula mass. Molecular mass of the hydrides increase in the order $HCl < HBr <$ HI. Hydrogen fluoride has an abnormally high boiling point because its molecules associate through hydrogen bonds due to the high electronegativity of fluorine.

- Ammonia has a higher melting point and boiling point than other hydrides of group(V) i.e. PH_3 and AsH_3.
- Water is a liquid and has higher boiling point than hydrides of group(VI), which are gases i.e. H_2S and H_2Se.
- Ice floats on water due to having a lower density than water.

In ice, the water molecules are held by hydrogen bonds. Each oxygen atom is covalently bonded to two hydrogen atoms and then also to two other hydrogen atoms through hydrogen bonds. This gives ice an extremely open tetrahedral structure with low density.



In liquid water, the hydrogen bonds are constantly broken and reformed due to thermal movement of water molecules. This leads to close packing of water molecules thus a higher density than ice. Figure 2.1 shows a big mass of ice floating on water.

- The formula mass of ethanoic acid as determined by freezing point depression method in benzene is twice the theoretical formula mass. This is because ethanoic acid associates in benzene through hydrogen bonding to form dimmers.
- Alcohol molecules are held by strong hydrogen bonds while alkane molecules are held by weaker Van der Waals forces. Intermolecular forces in alcohols are therefore stronger than those in alkanes thus alcohols require more energy for these forces to be broken.

Evidence for existence of hydrogen bonds

We are surrounded by substances that exhibit presences of hydrogen bonds. Notable among these includes the following facts;

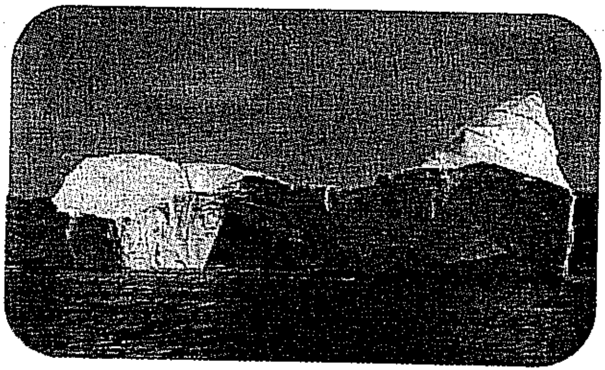
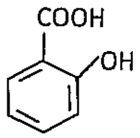
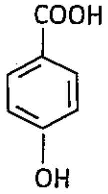


Figure 2.1 A big mass of an iceberg floating on water

- Ice has a lower density than water.
- Boiling points of carboxylic acids and alcohols are higher than those of other hydrocarbons of comparable formula mass.
- Amines have higher boiling points than alkanes of approximately the same molecular mass. Also since primary amines form more hydrogen bonds than secondary amines, primary amines have higher boiling points than secondary amines.
- Molecular masses of carboxylic acids determined by cryoscopic method in organic solvents are observed to be twice the theoretical ones. This is because carboxylic acids dimerise in organic solvents through hydrogen bonding.
- Ammonia, water and hydrogen fluoride have higher boiling points than hydrides of group V, VI and VII respectively.
- 2-hydroxybenzoic acid has a lower boiling point than 4-hydroxybenzoic acid. This can be explained by first considering their structures below;



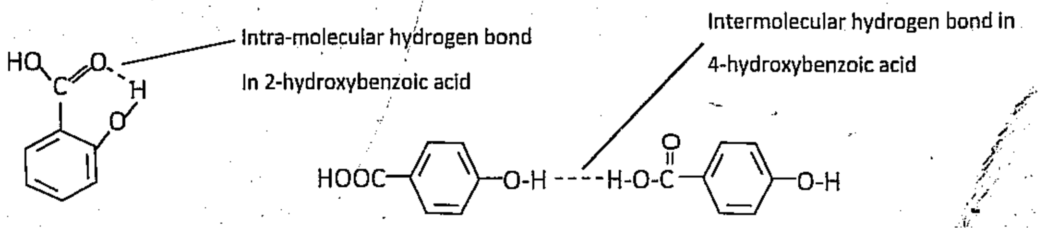
2-hydroxybenzoic acid



4-hydroxybenzoic acid

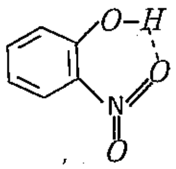
In 2-hydroxybenzoic acid, the functional groups are very close to each other hence molecules form more intra-molecular hydrogen bonds than inter-molecular hydrogen bonds. Therefore very few inter-molecular hydrogen bonds need to be broken thus low boiling point.

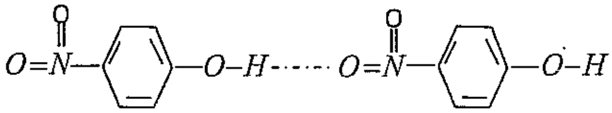
In 4-hydroxybezoic acid, the functional groups are very far apart thus 4-hydroxybenzoic acid forms more inter-molecular hydrogen bonds than intra-molecular hydrogen bonds. Therefore very many inter-molecular hydrogen bonds have to be broken for 4-hydroxybenzoic acid to boil. This requires a lot of energy hence a high boiling point.



Note

Intra-molecular hydrogen bonds are formed within the same molecule and have no effect on boiling point. Similarly, 2-nitrophenol has a lower boiling point than 4-nitrophenol.





2.3 Shapes of simple covalent molecules

2.3.1 Introduction

The arrangement of covalent bonds in space around the central atom or ion gives the shape of the molecule. Within a molecule, orbitals contain bonding and non-bonding electron pairs. Non-bonding electron pairs located on a central atom are commonly referred to as **lone pairs** of electrons.

Electron pairs repel themselves as far as possible so as to make the angle between them maximum. This is so to reduce stress on the molecule.

In order to determine the number of electron pairs (*both bonding and non-bonding*) within a molecule, Lewis structures are constructed. Lewis structures are named after Gilbert N. Lewis, who described them in his 1916 article entitled *"The Atom and the Molecule"*. Lewis structures depict the bonds between atoms of a molecule as well as any un-bonded electron pairs. You can draw a Lewis dot structure for any covalent molecule or coordination compound.

2.3.2 Lewis structures

A Lewis structure uses dots to represent electrons. Only valence electrons are considered when constructing Lewis structures since only valence electrons take part in bonding.

When constructing Lewis structures, the octet rule is applied. By this rule, bonded atoms have eight (*octet*) electrons in their outer shells. The octet rule is sometimes broken; hydrogen for example conforms to the duet rule where it reacts by either filling its outer (first) shell with two electrons or emptying it completely.

Examples

We follow the steps below to construct Lewis structures for the given molecules.

Chlorine gas (Cl_2)

Step 1:

Determine the total number of valence electrons for all the atoms in the molecule or ion. You can use the periodic table to determine the group of an element. The group corresponds to the valence electrons of the atom.

2 Cl atoms have (2 x 7) valence electrons = 14 electrons.

Step 2:

Determine the number of electron pairs

$\Rightarrow \quad \frac{14}{2} = 7\ electron\ pairs$

Step 3:

Bond all the atoms to the **central atom** using one electron pair for each atom. The central atom is in most cases the atom with least electronegativity. Atoms attached to the central atom are called **ligands.** In this case, we have only two atoms therefore we use one electron pair to bond both of them.

$Cl : Cl$

Step 4:

Use the remaining electron pairs to complete the octet for all the atoms, starting with the ligands and finally the central atom. In this case, we shall use the remaining six electron pairs to complete octets for the two chlorine atoms. By completing octet, we mean that each atom should be surrounded by a total of eight electrons.

$: \ddot{\underset{..}{Cl}} : \ddot{\underset{..}{Cl}} :$

If the molecule is charged, place the molecule in brackets and write the charge in the upper right hand corner outside brackets as a superscript.

The electron pair used to bond the atoms an also be represented using a dash (—)

The result of step 4 is the Lewis structure. In this case, the chlorine molecule has one bonding electron pair.

Water (H_2O)

From O we get 6 valence electrons

$2H$ we get (1x2) = 2 electrons

Total electrons = (6 + 2) = 8; $\Rightarrow \frac{8}{2} = 4\ electron\ pairs$

We use two electron pairs to bond the two hydrogen atoms to the central atom (oxygen)

$$H : O : H$$

We then use the remaining two electron pairs to complete the octet for all the atoms. However, the hydrogen atom conforms to the duet rule so its outermost shell must contain only **two** electrons.

$H : \underset{\cdot\cdot}{\ddot{O}} : H$ Therefore a water molecule has two bonding pairs and two lone pairs of electrons on the oxygen atom.

Nitrogen (N_2)

We get 5 electrons from each of the two nitrogen atoms, resulting into 5 electron pairs. We use one electron pair to bond the two nitrogen atoms.

$$N : N$$

Efforts to complete octets for both atoms using the remaining four electron pairs are futile. Therefore the logical way forward is to have 3 pairs shared between the two nitrogen atoms and then a lone pair to each nitrogen atom.

$$: N ::: N :$$

A molecule of nitrogen can therefore be represented as $: N \equiv N :$ since each bonding electron pair is a covalent bond represented by a dash.

Cyanide ion (CN^-)

From C we get 4 electrons

N we get 5 electrons

The negative charge on the ion gives us 1 extra electron

⇒ 10 electrons and therefore 5 electron pairs

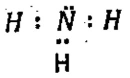
Using the 5 electron pairs, we come up with the following Lewis structure

$$[: C ::: N :]^-$$

Ammonia (NH_3)

From the nitrogen we get five electrons and three electrons from the three hydrogen atoms, giving us a total of eight electrons and therefore 4 electron pairs.

We use three electron pairs to bond the three hydrogen atoms to the central atom (nitrogen). The remaining electron pair is used to complete the octet for nitrogen.



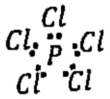
$H : \underset{\underset{H}{\cdot\cdot}}{\dot{\dot{N}}} : H$

Therefore ammonia has 3 bonding pairs and 1 lone pair

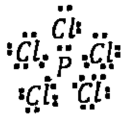
Phosphorous pentachloride (PCl_5)

We get seven electrons from each of the five chlorine atoms and five electrons from the phosphorous atom, giving a total of 40 electrons thus 20 electron pairs.

We use 5 electron pairs to bond the 5 chlorine atoms to the central atom.



We use the remaining 15 electron pairs to complete octets for all the ligands (chlorine atoms)



No lone pair on central atom

It is important to note that in this case the phosphorous atom has five electron pairs surrounding it. It is said to have expanded its octet. Some atoms (*most especially those with principal quantum shell* $n \geq 3$) have available d-orbitals which can accommodate extra electrons up to a maximum of 18.

Sulphate ion (SO_4^{2-})

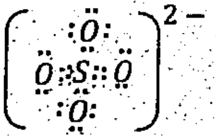
From S we get 6 electrons

4 O we get 24 electrons

(2-) we get 2 electrons

⇒ 32 electrons and therefore 16 electron pairs

Using the 16 electron pairs, we come up with the following Lewis structure



$$\left[\begin{array}{c} :\ddot{O}: \\ \ddot{O}::\ddot{S}::\ddot{O} \\ :\ddot{O}: \end{array}\right]^{2-}$$

No lone pair on central atom

Note that sulphur has also expanded its octet to accommodate six bonding electron pairs around it.

Hydroxonium ion (H_3O^+)

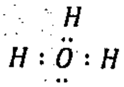
From 3H we get 3 electrons

O we get 6 electrons

(+) we get -1 electron (a positive charge on the ion implies an electron less)

⇒ 8 electrons and therefore 4 electron pairs

Using the 4 electron pairs, we come up with the following Lewis structure



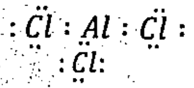
$$\begin{array}{c} H \\ H:\ddot{O}:H \end{array}$$

One *lone pair on central atom*

Aluminium trichloride ($AlCl_3$)

From the 3 chlorine atoms and 1 aluminium atom, we get 12 electron pairs.

Using the 12 electron pairs, we come up with the following Lewis structure



$$\begin{array}{c} :\ddot{Cl}:Al:\ddot{Cl}: \\ :\ddot{Cl}: \end{array}$$

No lone pair on central atom and 3 bonds on central atom

It is important to note that aluminium in the above molecule has an incomplete octet. Such molecules can accept lone pairs of electrons to complete their octet thus acting as **Lewis acids**. In this case, such molecules form dative bonds with the electron donor.

A Lewis acid is a compound which can accept a lone pair of electrons from a Lewis base to form a dative bond.

In the following reaction between ammonia and aluminium chloride, ammonia is acting as the Lewis base while aluminium chloride is acting as the Lewis acid.

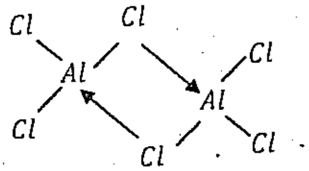
$$\ddot{N}H_3(g) + AlCl_3(g) \longrightarrow H_3N \rightarrow AlCl_3(s)$$

A similar reaction takes place between ammonia and boron trichloride. It should be noted that a Lewis base must possess at least a lone pair of electrons.

Also molecules with central atom which have incomplete octet can combine with themselves to form polymeric compounds e.g.

$$AlCl_3 + AlCl_3 \longrightarrow Al_2Cl_6$$

The structure of Al_2Cl_6 can be represented as shown below. It should be noted that the chlorine atoms use their non-bonding electrons to form dative bonds with aluminium atoms whose octet is incomplete.



Exercise

Construct Lewis structures for the following molecules and ions. In each case, indicate the number of appropriate electron pairs.

(a) SO_2 (b) PCl_3 (c) CO_3^{2-} (d) ClO_4^- (e) H_2S (f) NH_4^+

(g) $BeCl_2$ (h) BCl_3 (i) CH_4 (j) CrO_4^{2-} (k) PO_4^{3-} (l) ClO_2^-.

(m) NO_3^-

2.3.3 The Valency Shell Electron Pair Repulsion theory (VSEPR)

Shapes of molecules can be predicted from Lewis structures using the VSEPR.

The theory postulates that electron pairs around the central atom repel each other to make the angle between them maximum. Lone pair-lone pair (L.P-L.P) repulsion is greater than bond pair-lone pair (B.P-L.P) repulsion which is in turn greater than bond pair-bond pair (B.P-B.P) repulsion.

i.e L.P-L.P > B.P-L.P > B.P-B.P

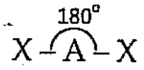
Molecules with only two atoms always adopt a linear shape like in cases of $O = O\ (O_2)$, $Cl - Cl\ (Cl_2)$, $N \equiv N\ (N_2)$, and $H - Cl\ (HCl)$.

2.3.3.1 Shapes of molecules with no lone pairs of electrons on the central atom

Let **A** be the central atom and **X** the ligand.

AX2 (2 ligands and no lone pair)

Such molecules attain a linear structure as shown below. Bond angle is 180°.

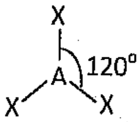


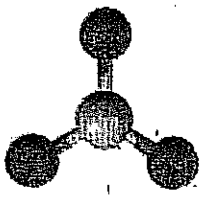
Examples of linear molecules

Molecule	**Structure**
$BeCl_2$	$Cl - Be - Cl$
HCN	$H - C \equiv N$
CO_2	$O = C = O$

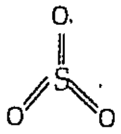
AX3 (3 ligands, no lone pair)

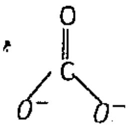
Such molecules attain a trigonal planar shape. Bond angle is 120°.





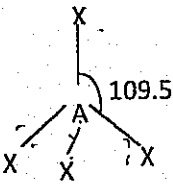
Examples

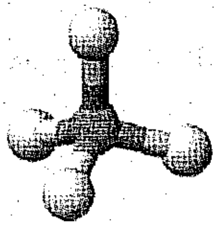
SO_3 

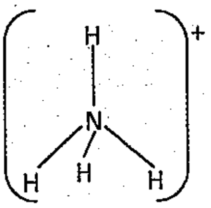
CO_3^{2-} 

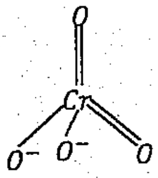
AX4(4 ligands, no lone pair)

These attain a tetrahedral shape. Bond angle is 109.5°. Examples include CH_4, NH_4^+, CCl_4, CrO_4^{2-}, $POCl_3$, ClO_4^- *etc.*



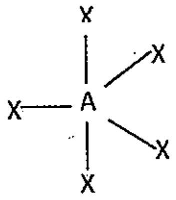


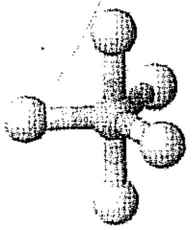


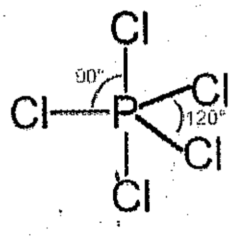


AX5(5 ligands, no lone pair)

These attain a trigonal bipyramidal shape. Bond angles are 120° and 90°. Examples include phosphorous pentachloride

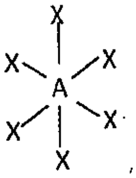


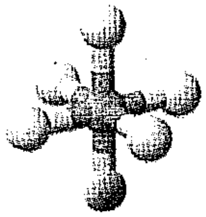


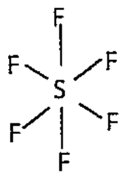


AX6(6 ligands, no lone pair)

Such molecules attain an octahedral structure. Examples include SF_6.







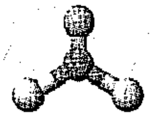
2.3.3.2 Shapes of molecules with lone pairs of electrons on the central atom

A stronger repulsion occurs between a lone pair of electrons and another lone pair than between a lone pair of electrons and a bonding pair of electrons (L.P-L.P > B.P-B.P). As a consequence, lone pairs of electrons will repel bonds within a molecule as far as possible. Therefore presence of lone pairs of electrons on the central atom distorts the expected shape of the molecule.

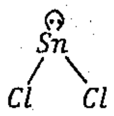
Let A be the central atom, X the ligand, and E the lone pair.

AX2E1 (2 ligands and 1 lone pair)

Molecules conforming to the general formula AX_2E_1 adopt a V-shape (or bent shape). Examples include sulphur dioxide (SO_2), and tin(II) chloride ($SnCl_2$)



Examples



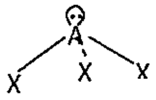
AX_2E_2 (2 ligands and 2 lone pairs)

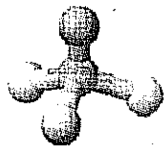
These also attain a V-shape. Examples include water, and hydrogen sulphide

Example

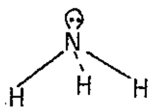
AX3E1 (3 ligands and 1 lone pair)

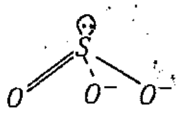
These attain a trigonal pyramidal shape. Examples include ammonia, phosphorous trichloride and a sulphite ion.





Examples NH_3 SO_3^{2-}

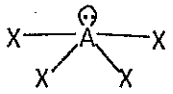


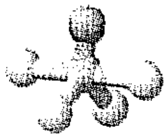


The bond angle in ammonia is 107°

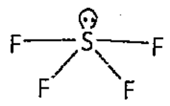
AX4E1 (4 ligands and 1 lone pair)

These molecules attain a distorted (*or irregular*) tetrahedral structure. Some old literature still refers to this shape as a seesaw; however, this name is strongly discouraged. Sulphur tetrafluoride is one of the molecules that attain this shape.



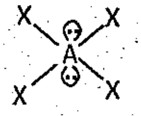


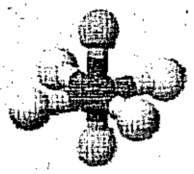
Example SF_4



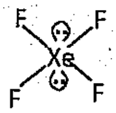
AX4E2 (4 ligands and 2 lone pairs)

These attain a square planar shape. Xenon tetrafluoride is an example of such molecules.





Example XeF_4



2.3.3.3 Effect of electronegativity of atoms on the bond angle

Bond angles within a molecule increase with increase in electronegativity of the central atom. This is because the highly electronegative central atom withdraws electrons towards its self; this increases the repulsion between the bonds. Consequently, bond angles of group(VI) hydrides reduce in the order $H_2O > H_2S > H_2Se > H_2Te$ owing to decrease in electronegativity of the central atom in the order $O > S > Se > Te$. Not surprisingly, however, bond angles within a molecule reduce with increase in electronegativity of the ligands. Thus bond angles of the halides of phosphorus increase in the order $PF_3 < PCl_3 < PBr_3$. Table 2.1 shows the actual bond angles in hydrides of group(VI) and halides of phosphorous.

Table 1.2 Bond angles in hydrides of group(VI) and halides of phosphorous

Compound	PF_3	PCl_3	PBr_3	H_2O	H_2S	H_2Se	H_2Te
Bond angle /°	96.3	100	101	104.5	92.2	91.0	89.5

Exercise

1. Sketch and name the shape attained by the following molecules. In each case, explain why the molecule attains the named shape.
   (a) H_2S (b) NH_3 (c) H_3O^+ (d) PCl_4^- (e) PCl_6^-
2. Explain the following observations.

(a) At room temperature, chlorine is a gas but iodine is a solid.

(b) At room temperature, hydrogen chloride consists of HCl molecules but hydrogen fluoride mainly consists of H_2F_2 and H_3F_3 molecules.

(c) In vapour phase, aluminium chloride exists as Al_2Cl_6 but not as $AlCl_3$.

(d) Bond angles in the halides of phosphorous increase in the order $PF_3 < PCl_3 < PBr_3$.

(e) The bond angles in NH_3, NH_3,, and NH_3 are 106.6°, 93.8°, and 91.83° respectively.

3. (a) What is meant by the term hydrogen bonding?

(b) Explain how hydrogen bonding occurs in;

(i) hydrogen fluoride (ii) ice (iii) methylamine

(c) What practical evidence is there for there for the existence of hydrogen bonds in;

(i) ice (ii) Ethanoic acid

2.4 CRYSTAL LATTICES

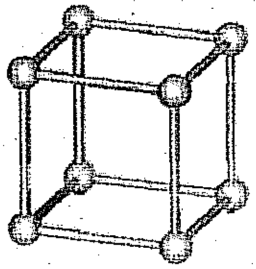
2.4.1 Introduction

In section 2.2.3, we have noted that molecular geometry around the central atom in simple covalent compounds is determined by VSEPR rules; however, in ionic compounds, metals, and giant covalent compounds, the geometry follows maximum packing rules.

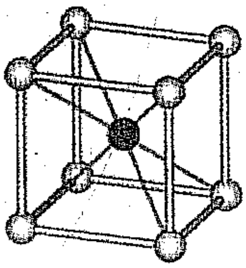
Ionic compounds, metals, and giant covalent compounds are capable of forming solid structure with closely packed atoms or ions. This is due to very strong bonds between atoms or ions in these lattices.

The ions or atoms may be arranged in shape of a cube giving rise to a Cubic Close Packed structure (CCP); they may also be arranged in shape of a hexagon giving rise to Hexagonal Close Packed (HCP) structure.

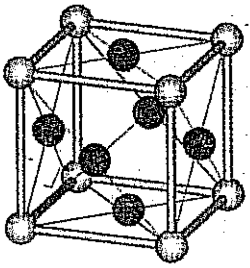
In all CCP lattices, the atoms or ions occupy all the corners of a regular cube. CCP lattices are subdivided into three variants; **simple cube** where the atoms or ions occupy the corners of a regular cube , **body centered** cube where the atoms or ions occupy the corners of a regular cube in addition to the centre of the cube, and face centered cube where the atoms or ions occupy the corners of a regular cube in addition to the centre of the faces of the cube.



Simple cube

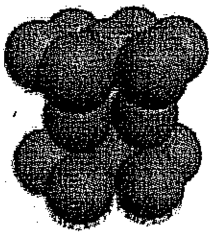


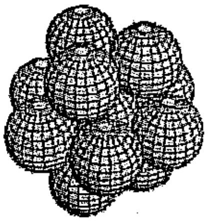
Body centered cube

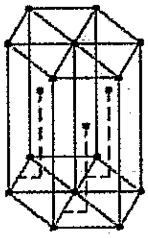


Face centered cube

In HCP, a unit consists of three layers of atoms. The top and bottom layers contain six atoms at the corners of a regular hexagon, and one atom at the center of the hexagon. The middle layer consists of three atoms. Figures below show how atoms are arrange in an HCP lattice.







Most metals adopt hexagonal close packing.

2.4.2 Giant Ionic Lattices

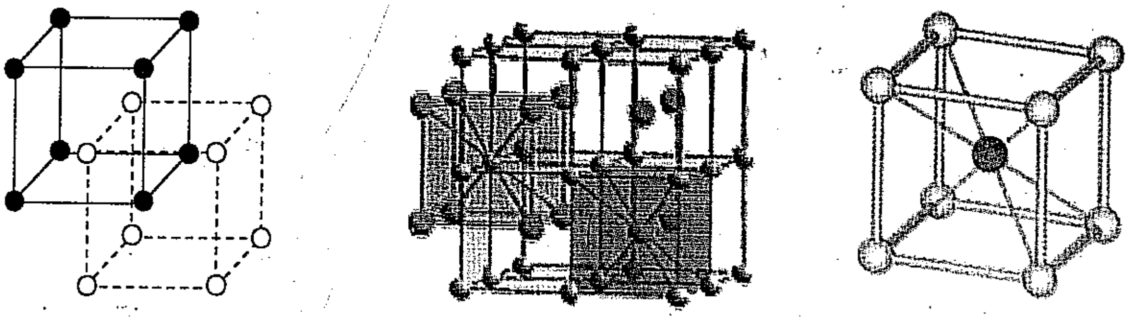
When drawing ionic lattices, we assume the ions that make up the lattice to be spherical. The type of close packing attained by a compound largely depends on the size and relative number of ions involved.

Ionic compound are characterized by high melting point, and conduction of electricity in molten or aqueous state.

Examples

Caesium chloride (CsCl)

In caesium chloride, each chloride ion is surrounded by 8 caesium ions and each caesium ion is also surrounded by 8 chloride ions. Coordination number is 8:8. Both the caesium ions and the chloride ions each form a simple CCP structures which interpenetrate each other.



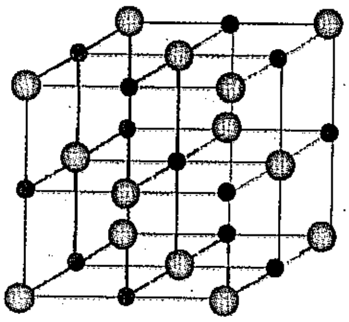
Caesium chloride lattices

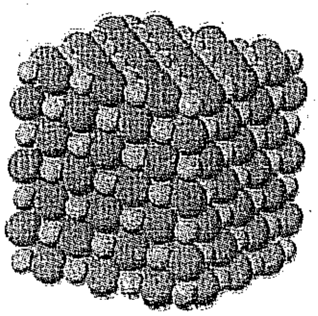
Other compounds that have similar lattice with caesium chloride include caesium bromide and caesium iodide.

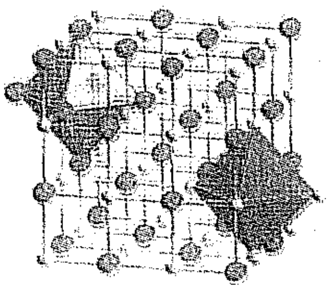
Sodium chloride (NaCl)

Sodium chloride forms a giant ionic crystal lattice with face centered close packing. Coordination number is 6:6. With exception of caesium halides, the rest of group I halides have a similar structure to sodium chloride.

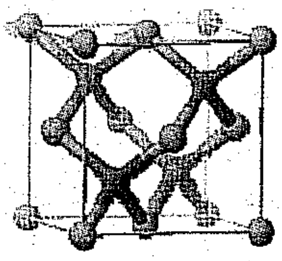
Figures below show the structure of sodium chloride lattice using different models.







Zinc blende (ZnS)



This forms a giant ionic lattice with face centered cubic close packing. Each zinc ion is in contact with four sulphide ions thus coordination number is 4. Both the zinc and sulphide ions are arranged tetrahedrally with regard to each other.

2.4.3 Metallic lattices

Metals are characterized by their high melting points and conduction of electricity both in solid and molten state. Melting point of metals increase with increase in the number of valence electrons that each metal atom contributes during metallic bond formation – *section 4.2.2.*

Melting points of some metals like sodium are relatively low, even much lower than those of ionic compounds. However, melting points of most metals are higher than those of ionic compounds.

Most metallic lattices attain hexagonal close packing while some few attain cubic close packing. In body centered cubic close packing, 68% of the space is occupied by metal atoms; in simple cubic close packing and hexagonal close packing 52% and 74% of the space respectively is filled by metal atoms.

Group I metals adopt body centered cubic close packing and this explains their low density. Iron and manganese also adopt a similar structure to group I metals.

Zinc and magnesium exhibit hexagonal close packing with coordination number of 12.

Copper exhibits face centered cubic close packing with coordination number of 12.

Other metals that exhibit a similar close packing to copper include aluminium, gold, silver, lead, and platinum.

2.4.4 Giant molecular and giant atomic lattices

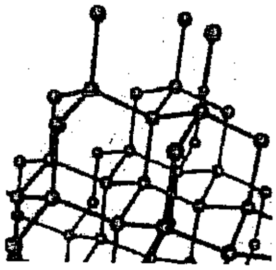
Covalent compounds are characterized by low melting point, poor conduction of electricity and, in most cases, being liquids or gases at room temperature. However, some covalent compounds form giant atomic lattices resulting into very high melting points; such covalent compounds are solids. Giant atomic lattices are normally formed by atoms with four valence electrons such as carbon and silicon

Examples

Iodine (I_2)

Iodine forms a simple molecular solid with molecules of iodine held by weak van der waals forces. Iodine sublimes at 30°C. Although the molecules of iodine are held by Van der waals forces, the atoms are covalently bonded forming diatomic molecules (I_2). Iodine adopts a face centered cubic close packing with iodine molecules occupying the corners of a regular cube. Solid carbon dioxide has a similar close packing to iodine.

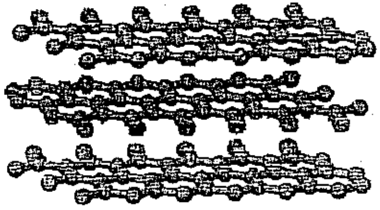
Diamond



Diamond structure

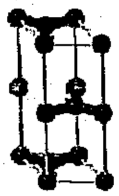
Diamond forms a giant molecular (macromolecular) structure with very high melting point. In diamond, each carbon atom is covalently bonded to four others. Carbon, therefore, uses all the four valency electrons in bonding thus it does not conduct electricity. The coordination number is four since each carbon atom is surrounded by four others. Silicon(IV) oxide has a similar structure to diamond.

Graphite



Layers of graphite

Graphite forms a simple molecular structure. In graphite, each carbon atom uses three of its four



A unit of graphite

A block of graphite

valency electrons to form covalent bonds with three other carbon atoms. This forms a hexagonal layer. Weak van der waals forces exist between the layers thus the layers can slide over each other. This makes graphite soft and slippery.

The unused fourth electron from each atom form a cloud of delocalized electrons. These electrons can move along the layers of graphite, thus graphite conducts electricity.

2.5 Summary

Type of bonding has a very great influence on both the chemical properties and physical properties of a compound. In this chapter, we has discussed three major types of bonds; ionic, covalent, and metallic. We have also covered intermolecular forces that normally exist between molecules of covalently bonded compounds. We have discussed the effects of bonding on both melting point and boiling point. We have learnt how to predict shapes of simple molecules basing on the Valence Shell Electron Pair Repulsion theory. We have concluded the chapter by discussing crystal lattices formed by ionic compounds, metals, and giant atomic covalent compounds. The concepts covered in this chapter will be very essential in understanding the chemistry of the periods and groups that will be covered in subsequent chapters.

2.6 Suggested further reading on chapter 2

E. N. Ramsden, *A level Physical Chemistry*, Nelson Thornes, Third Edition.

W. R. Kneen, *Chemistry, Facts, Patterns and Principles*, Addison-Wesley Pub (Sd), 1972

David Arthur Johnson, *Metals and Chemical Change*, Open University, Royal Society of Chemistry, 2002, ISBN 0-85404-665-8

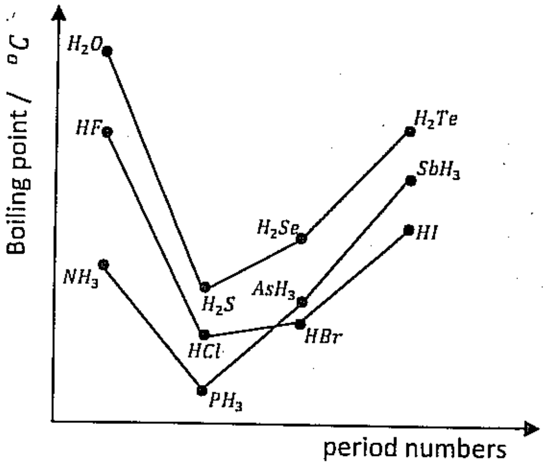
M. Ntanda, *Concise Solutions to U.A.C.E Chemistry paper one and two;*

Questions:

P1 2007 Q5, P1 2006 Q8, P1 2004 Q4, P2 2005 Q5(c), P2 2004 Q6, P1 2002 Q13, P1 2000 Q5, P2 2000 Q1(d), P2 2000 Q4(a), P2 2000 Q5, P2 2000 Q8, P1 1998 Q2, P2 1998 Q2, P1 1996 Q10, P1 1996 Q17, P1 1993 Q2, P1 1992 Q1, P1 1988 Q12, P1 1987 Q15, P2 1987 Q3(d), P2 1986 Q3, P2 1986 Q7, P1 1985 Q10, P1 1985 Q17, P2 1985 Q3(a), P2 1985 Q5

2.7 Questions on chapter 2

1. (a) Define the term hydrogen bonding.
   (b) Giving examples, discuss the effects of hydrogen bonds on physical properties of some compounds.
   (c) Explain why ice has a lower density than water.
2. The graph below shows the boiling points of hydrides of groups V, VI and VII. Explain the shape of each curve.



3. Explain the following observations

Chapter 2 Bonding and Structure

Most ionic compounds are soluble in water but insoluble in non-polar solvents.

4. Discuss the bonding in;
   (a) Calcium oxide
   (b) Tetrachloromethane
   (c) Aluminium chloride
   (d) Ammonium ion.

CHAPTER
3
OXIDATION AND REDUCTION

Learning Objectives

After reading this chapter and completing the exercises you should be able to:

- Define oxidation and reduction in terms of electron transfer.
- Work out oxidation numbers of elements in a given compound.
- Write have equations.
- Balance redox reactions using half reactions.
- Explain factors that affect electrode potentials.
- Determine percentage purity of substances basing on redox titrations.

3.1 Introduction

Oxidation, at lower levels of chemistry study, was limited to ***addition*** of oxygen to a substance or removal of hydrogen from a substance. Reduction was limited to ***removal*** of oxygen from a substance. In the following equation, zinc is said to be oxidised to zinc oxide.

$$2Zn(s) + O_2(g) \longrightarrow 2ZnO(s)$$

Similarly, the following equation shows reduction of copper(II) oxide by hydrogen.

$$CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(l)$$

The concepts of oxidation and reduction have gone through several stages, during which broader definitions have been adopted.

Many reactions now do not involve addition or removal of oxygen (or hydrogen) but are classified as oxidation or reduction reactions.

A substance that which oxidises another is called an **oxidising agent** or **oxidant**. On the other hand, a substance that reduces another is called a **reducing agent** or **reductant**.

Consider the oxidation of zinc below;

$$Zn(s) + ½\,O_2(g) \longrightarrow ZnO(s) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (i)$$

Zinc oxide formed is an ionic compound. It contains Zn^{2+} ions and O^{2-} ions. Therefore zinc has undergone the following change in equation (i)

$$Zn\,(s) \longrightarrow Zn^{2+}(s)$$

To balance the above equation, electrically, we need to add two electrons on the right hand side (R.H.S).

Chapter 3 Oxidation and Reduction

$$Zn(s) \longrightarrow Zn^{2+}(s) + 2e$$

In the equation above, it is clear that zinc has lost two electrons to get oxidised to Zn^{2+}. Oxidation can therefore be defined as a process of removal of electrons from a substance during a redox reaction.

Any substance that can remove electrons from another substance is therefore an oxidising agent. An oxidising agent is therefore an electron acceptor.

On the other hand, oxygen has been converted to O^{2-} in equation (i) above according to the following balanced equation;

$$½\, O_2(g) + 2e \longrightarrow O^{2-}(s)$$

In the above equation, oxygen has gained two electrons thus getting reduced to the oxide ion, O^{2-}.

Reduction is therefore defined as a process of addition of electrons to a substance during a redox reaction. Any substance that can add electrons to another substance is called a reducing agent. A reducing agent is therefore an electron donor.

Defining oxidation and reduction in terms of electron transfer widens the concept to include reactions that would otherwise be left out by the simplistic original definitions. The reactions below are therefore also regarded as oxidation/reduction reactions.

$$4FeS(s) + 2S(l) \longrightarrow 2Fe_2S_3(s)$$

$$MnO_2(s) + 4HCl(aq) \longrightarrow MnCl_2(aq) + 2H_2O(l) + Cl_2(g)$$

$$2Fe(s) + 3Cl_2(g) \longrightarrow 2FeCl_3(s)$$

$$H_2S(g) + 2FeCl_3(aq) \longrightarrow S(s) + 2FeCl_2(aq) + 2HCl(aq)$$

Under normal circumstances, electrons cannot exist independently. Therefore whenever electrons are lost by one species, they are gained by another species – much in the same way as whenever you lose money, someone gets richer by an equal amount! It so happens that oxidation and reduction are complementary and usually occur together. A reaction in which oxidation and reduction take place simultaneously is called a **redox reaction.**

Examples of common oxidising agents include oxygen, chlorine, hydrogen peroxide, manganese(IV) oxide, lead(IV) oxide, potassium dichromate(VI), potassium permanganate(VII) etc.

Examples of common reducing agents include hydrogen, carbonmonoxide, hydrogen sulphide, carbon etc.

Some compounds e.g. hydrogen peroxide can act as oxidising agents or reducing agents, depending on conditions available.

3.2 Oxidation numbers

Oxidation numbers are very essential in balancing redox reactions. Oxidation number is 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. The oxidation number of oxygen in water (H_2O) is -2 while its oxidation number in hydrogen peroxide (H_2O_2) is -1.

Rules for assigning oxidation numbers

When assigning oxidation numbers, all the compounds (*including covalent compounds)* are considered to be ionic; though we know that no compound is completely ionic. The following rules are used in assigning oxidation numbers (*or oxidation states*) to elements.

- The sign of the oxidation number is put before the number to distinguish it from valency e.g. the oxidation state of sodium in sodium hydroxide is +1 while its valency is 1.
- Atoms of elements in uncombined elementary state e.g. O_2, H_2, N_2 etc are given oxidation number zero.
- Oxygen has oxidation number of -2 except in peroxides where it is –1 and in compounds with fluorine
- The oxidation number of an ion is similar to its ionic charge e.g. that of Zn^{2+} is +2.
- Oxidation number of metals is usually positive, corresponding to the valency of the metal.
- The oxidation number of hydrogen is always +1 in most of its compounds except when bonded to metals e.g. in NaH where it is -1
- The oxidation number of chlorine is -1 except in its compounds with oxygen and fluorine.
- F, Cl, Br, I when present in halides have an oxidation number of -1.
- In any neutral compound, the sum of the oxidation numbers of all the elements is zero.
- The sum of oxidation numbers of all atoms in an ion is equal to the charge on the ion.

- When two or more atoms of the same element are present in the same compound, the oxidation number of the element is the average of the oxidation numbers of the group of the atoms.
- When the oxidation number of an element in a compound is not known, it can be calculated by following the steps below.
  - (a) The unknown oxidation state is assigned an arbitrary letter such as x or y.
  - (b) All the other elements are assigned their normal oxidation states e.g. Cl = -1, O = -2, Na = +1.
  - (c) The sum of the oxidation states is equivalent to the overall charge on the compound or ion.

Examples

Determine the oxidation states of the following;

(a) sulphur in H_2SO_4

let the oxidation state of sulphur be **m**

$(2 \times +1) + \mathbf{m} + (4 \times -2) = 0$

$m = 8 - 2$

$= +6$

(b) chlorine in $HClO_3$

let the oxidation state of chlorine be y

$+1 + y + 3(-2) = 0$

$y = -1 + 6$

$= +5$

(c) manganese in MnO_4^-

let the oxidation state of manganese **m**

$\mathbf{m} + (4 \times -2) = -1$

$m = +7$

(d) chromium in $Cr_2O_7^{2-}$

let the oxidation state of chromium be y

$2y + 7(-2) = -2$

$y = +6$

3.3 Balancing redox reactions

Redox reactions take place between oxidising agents and reducing agents. The oxidising agent accepts electrons and gets reduced. The reducing agent loses electrons and gets oxidised. To tell whether a compound has been reduced or oxidised, we work out its oxidation number in reactants and in products. If the reaction proceeds with a reduction in oxidation number of a given element, then it is a reduction process e.g. In the reaction below, the oxidation number of manganese reduces from +7 (in MnO_4^-) to +2 (in Mn^{2+}) hence it is a reduction process. MnO_4^- has been reduced to Mn^{2+}.

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

On the other hand, an oxidation process is followed by an increase in oxidation state of an element. In the following reaction, the oxidation state of iodide ion increases from -1 to 0 (in I_2). Therefore oxidation has occurred.

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

A reaction in which an oxidising agent accepts electrons is called a half equation. Similarly, a reaction in which a reducing agent loses electrons is also called a half equation. Therefore both equations (i) and (ii) above represent half equations (also known as half cell reactions).

To get an overall reaction between an oxidising agent and a reducing agent, we combine the half equations for the reducing agent and oxidising agent – *section 3.3.2.*

3.3.1 Half equations

Before we can write half equations, it is essential to know the product species to which the oxidising agent will be reduced or to which the reducing agent will be oxidised. Table 3.1 shows common oxidising agents, active oxidising species, and species to which they are usually reduced.

Table 3.1 Common oxidising agents

Oxidising agent		Oxidising species	Species is reduced to
Name	**Formula**		
Potassium manganate(VII)	$KMnO_4$	MnO_4^-	Mn^{2+}
Potassium dichromate(VI)	$K_2Cr_2O_7$	$Cr_2O_7^{2-}$	Cr^{3+}
Potassium iodate	KIO_3	IO_3^-	I_2
Manganese(IV) oxide	MnO_2	MnO_2	Mn^{2+}
Lead(IV) oxide	PbO_2	PbO_2	Pb^{2+}
Hydrogen peroxide	H_2O_2	H_2O_2	H_2O

As we shall soon find out, using half equations is a convenient way of writing redox reactions. The following examples illustrate ways of writing half equations for the above oxidising agents.

Examples

1. To write the half equation for potassium permanganate, we follow the following steps.

   Step 1:

   Write the formula of the active oxidising species and the species to which it is reduced.

   $$MnO_4^-(\text{aq}) \longrightarrow Mn^{2+}(\text{aq})$$

   Step 2:

   Since Mn^{2+} does not need oxygen atoms for stability, the four oxygen atoms from MnO_4^- will combine with hydrogen ions to form four molecules of water. Therefore we add four molecules of water on the R.H.S. of the equation.

   $$MnO_4^-(\text{aq}) \longrightarrow Mn^{2+}(\text{aq}) + 4H_2O(\text{l})$$

   Step 3:

   Introduction of water adds eight hydrogen atoms on the R.H.S. To balance the equation, we add eight hydrogen ions on the left hand side (L.H.S.) of the equation.

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

   Step 4:

   The equation is now balanced in terms of atoms but not electrically. A quick count shows an overall charge of +2 (due to Mn^{2+}) on the R.H.S. and +7 (due to MnO_4^- and $8H^+$) on the L.H.S.

   Therefore we need to add five electrons (five negative charges) on the L.H.S. to balance charge.

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

   The above equation represents the half equation for potassium manganate(VII). The following points are worthy noting about the equation;

   - The oxidation state of Mn in MnO_4^- is +7 while its oxidation state in Mn^{2+} is +2. This shows that MnO_4^- has been reduced (since oxidation state has reduced from +7 to +2).

- Since there is a change from +7 oxidation state to +2, there is need of 5 electrons (7-2) to accomplish this. For this reason, we added five electrons on the L.H.S.
- We needed to add hydrogen ions on the L.H.S. to take up oxygen atoms from MnO_4^-. These hydrogen ions are usually provided by an acid. The acid usually used is sulphuric acid. Nitric acid cannot be used for this purpose because the acid is also an oxidising agent itself and therefore will interfere with the reaction. Potassium permanganate oxidises hydrochloric acid to chlorine. For this reason, hydrochloric acid cannot also be used to acidify potassium permanganate.

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

2. Half equation for reduction of potassium dichromate $(K_2Cr_2O_7)$

Step 1:

$$Cr_2O_7^{2-}(aq) \longrightarrow Cr^{3+}(aq)$$

Step 2:

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

Step 3:

Since we added seven molecules of water on the R.H.S., we need to add fourteen hydrogen ions on the left so as to balance hydrogen.

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

Step 4:

Balance number of atoms on either side.

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

Step 5:

Balance charge on either side:

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

3. Half equation for manganese(IV) oxide (MnO_2)

Steps 1, 2, and 3:

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

Step 4:

Balance charge.

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

Exercise 3.1

By going through the steps above, come up with half equations for potassium iodate, lead(IV) oxide, iodine, and hydrogen peroxide shown below;

$$2IO_3^-(aq) + 12H^+(aq) + 10e \longrightarrow I_2(aq) + 6H_2O(l)$$

$$PbO_2(s) + 4H^+(aq) + 2e \longrightarrow Pb^{2+}(aq) + 2H_2O(l)$$

$$H_2O_2(aq) + 2H^+(aq) + 2e \longrightarrow 2H_2O(l)$$

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

Table 3.2 Common reducing agents and species to which they are oxidised

Reducing agent		Active species	Oxidised to
Name	**Formula**		
Potassium iodide	KI	I^-	I_2
Oxalates e.g. Sodium oxalate and Oxalic acid	$Na_2C_2O_4$ $H_2C_2O_4$	$C_2O_4^{2-}$	CO_2
Hydrogen peroxide	H_2O_2	H_2O_2	O_2 and H^+
sulphites e.g. sodium sulphite	Na_2SO_3	SO_3^{2-}	SO_4^{2-}
Thio sulphates e.g. Sodium thiosulphate	$Na_2S_2O_3$	$S_2O_3^{2-}$	$S_4O_6^{2-}$

Writing half equations for reducing agents involves balancing charge, usually by addition of electrons to the appropriate side.

Examples

1. Half equation for potassium iodide.

Step 1:

$$I^-(aq) \longrightarrow I_2(aq)$$

Step 2:

Balance atoms and charge.

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

2. Half equation for sodium oxalate ($Na_2C_2O_4$).

Step 1:

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

Step 2:

Balance atoms.

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

Step 3:

Balance charge.

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

3. Half equation for sodium sulphite, (Na_2SO_3).

Step 1:

$SO_3^{2-}(aq) \longrightarrow SO_4^{2-}(aq)$

Steps 2 and 3:

Since we have 3 atoms of oxygen on L.H.S. but 4 on the R.H.S. , we need to add a molecule of water on the L.H.S. in order to balance oxygen. However, addition of water introduces hydrogen atoms on the L.H.S. Therefore we add 2 hydrogen ions on the R.H.S. in order to balance hydrogen.

$SO_3^{2-}(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq)$

Step 4:

Balance charge.

$SO_3^{2-}(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e$

Exercise 3.2

Come up with half equations shown below.

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

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

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

$$H_2O_2(aq) \longrightarrow 2H^+(aq) + O_2(g) + 2e$$

Tip:

As you become familiar with writing half equations, you will realise that the above steps can be carried out once.

3.3.2 Redox reactions

To come up with a redox reaction from half equations, we merely balance the number of electrons in both equations. This is usually done by multiplying the half equations by appropriate numbers.

Examples:

Write overall reactions between the following compound.

(a) Iron(II) sulphate and potassium permanganate.

Half equations are

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

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

To balance electrons in both equations, we need to multiply the second equation by 5.

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

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

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

Note that electrons do not appear in the overall reaction since the same number of electrons appears on both sides.

(b) Potassium dichromate and sodium sulphite.

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

$$SO_3^{2-}(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e$$

To balance electrons in both equations, we multiply the second equation by 3.

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$
$$2SO_3^{2-}(aq) + 2H_2O(l) \longrightarrow 2SO_4^{2-}(aq) + 4H^+(aq) + 6e$$

Overall equation: $Cr_2O_7^{2-}(aq) + 8H^+(aq) + 3SO_3^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + 4H_2O(l)$

Note that H^+ and H_2O would have appeared on both sides of the overall equation. By appropriate subtraction, we ensure that each appears only on one side.

(c) Hydrogen peroxide and potassium permanganate.

Hint:

Hydrogen peroxide can act both as an oxidising agent or a reducing agent. In this case, since potassium permanganate is a strong oxidising agent, hydrogen peroxide will assume the role of a reducing agent.

$$MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) + 4H_2O(l) \qquad \times 2$$
$$H_2O_2(aq) \longrightarrow O_2(g) + 2H^+(aq) + 2e \qquad \times 5$$

Overall reaction: $2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2(aq) \longrightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(l)$

(d) Potassium permanganate and hydrochloric acid.

$$MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) + 4H_2O(l) \qquad \times 2$$
$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e \qquad \times 5$$
$$2MnO_4^-(aq) + 16H^+(aq) + 10Cl^-(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Cl_2(g)$$

The above equation is the basis for preparation of chlorine gas from potassium permanganate and concentrated hydrochloric acid. Balancing it is a nightmare for many Ordinary Level students. It is amazing how simple it becomes with knowledge of half equations.

Redox reactions are applied in volumetric analysis. However, detailed treatment of their application in volumetric analysis is beyond the scope of this book. Readers interested in these details are referred to Chapter 4 of Quantitative and Qualitative Analysis in A-Level Chemistry by the same author. The following examples will illustrate, theoretically, the application of redox reactions in volumetric analysis.

Chapter 3 Oxidation and Reduction

Examples

1. In an experiment to standardise potassium permanganate, 25.0cm³ of a solution containing 6.8 g/l of anhydrous sodium oxalate required exactly 10.00cm³ of potassium permanganate solution for complete reaction. Determine the molarity of potassium permanganate.
   ($Na = 23$, C=12, O=16)

   Solution

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

   Formula mass of $Na_2C_2O_4$ = (23 x 2) + (12 x 2) + (16 x 4) = 134

   134g of sodium oxalate contain 1 mole

   6.8 g contain $\left(\frac{1}{134} \text{ x } 6.8\right)$ moles

   = 0.05075 moles

   ∴ molarity of sodium oxalate solution is 0.05M

   Moles of sodium oxalate reacted = $\left(\frac{25 \text{ x } 0.05075}{1000}\right)$

   = 1.269 x 10^{-3}

   Mole ratio $C_2O_4^{2-} : MnO_4^- = 2 : 5$

   ∴ moles of potassium permanganate = $\frac{2}{5}$ x 1.269 x 10^{-3}

   = 5.075 x 10^{-4}

   ∴ 10cm³ of potassium permanganate solution contain 5.075 x 10^{-4} moles

   1000cm³ of the solution contain $\left(\frac{5.075 \text{ x } 10^{-4}}{10} \text{ x } 1000\right)$

   = 0.05 moles

   Molarity of potassium permanganate is 0.05M.

2. During the titration of sodium ethane dioate (sodium oxalate) with potassium dichromate solution, 47.00cm³ of potassium dichromate solution reacted completely with 25.0 cm³ of 0.0925M sodium ethanedioate solution. Determine the concentration of potassium dichromate.

   Solution

25cm^3 of solution contained 1.5 x 10^{-3} moles of iron(II) sulphate

1000cm^3 contain $\left(\frac{1.5 \times 10^{-3}}{25} \times 1000\right)$ = 0.06 moles

Concentration of iron(II) sulphate in solution = 0.06M

(ii) moles of potassium permanganate used in second titration = $\left(\frac{19 \times 0.02}{1000}\right)$ = 3.8 x 10^{-4}

Mole ratio $e^{2+} : MnO_4^-$ = 5 : 1

moles of Fe^{2+}= (5 x 3.8 x 10^{-4}) = 1.9 x 10^{-3}

25.0cm^3 of reduced solution contained 1.9 x 10^{-3} moles of iron(II) ions

1000cm^3 contain $\left(\frac{1.9 \times 10^{-3}}{25} \times 1000\right)$ = 0.076 moles

∴ total concentration of iron(II) sulphate and iron(III) sulphate in original solution = 0.076M

Concentration of iron(III) sulphate = 0.076 – 0.06 = 0.016M

4. A solution contains both oxalic acid ($H_2C_2O_4.2H_2O$) and sodium oxalate ($Na_2C_2O_4$). 25.0 cm^3 of the solution required 10.00cm^3 of 0.1M sodium hydroxide solution for complete reaction. Another 25.0cm^3 of the same solution required 20.00 cm^3 of 0.02M potassium permanganate solution for complete reaction. Determine the concentration of the solution with respect to;
(i) oxalic acid in grams per litre.
(ii) sodium oxalate in moles per litre.

Solution

Hint:

Sodium hydroxide reacts with oxalic acid but not sodium oxalate. Potassium permanganate reacts with both sodium oxalate and oxalic acid since they both contain oxalate ions ($C_2O_4^{2-}$)

(i) moles of sodium hydroxide reacted = $\left(\frac{10 \times 0.1}{1000}\right)$ = 1 x 10^{-3}

mole ratio $NaOH : H_2C_2O_4$ = 1 : 2

∴ moles of oxalic acid reacted = $\left(\frac{1}{2} \times 1 \times 10^{-3}\right)$ = 5 x 10^{-4}

25cm^3 of solution contained 5 x 10^{-4} moles of oxalic acid

1000cm³ contained $(\frac{5 \times 10^{-4}}{25} \times 1000) = 0.02$ moles

Formula mass of $H_2C_2O_4.2H_2O = (2 \times 1) + (12 \times 2) + (16 \times 4) + (2 \times 18) = 126$
Concentration of solution in g/l of oxalic acid = (0.02 x 126)
= 2.52 g/l

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

moles of potassium permanganate = $\left(\frac{0.02 \times 20}{1000}\right) = 4 \times 10^{-4}$

mole ratio $MnO_4^- : C_2O_4^{2-} = 2 : 5$

moles of $C_2O_4^{2-} = \left(\frac{5}{2} \times 4 \times 10^{-4}\right) = 1 \times 10^{-3}$

∴ 25.0 cm³ of solution contained 1×10^{-3} oxalate ions
1000cm³ contain $\left(\frac{1 \times 10^{-3}}{25} \times 1000\right) = 0.04$ moles

∴ moles of sodium oxalate = total oxalate moles – moles of oxalic acid
= 0.04 – 0.02 = 0.02 moles

Concentration of solution with respect to sodium oxalate = 0.02M

Exercise 3.3

1. (a) Determine the oxidation state of iodine in IO_3^- ion.
   (b) Write down half equations for the iodate ion and iodide ion (I^-) and hence write the overall reaction between the two ions.
   (c) An unknown mass of KIO_3 was treated in aqueous solution with excess iodide ions and acidified. The resulting solution on titration required 53.70cm3 of 0.20M sodium thiosulphate solution for complete reaction. Find the mass of KIO_3 used. (K=39.10, I=126.90, O=16.0)

2. (a) Write an equation for the reaction between acidified potassium dichromate(VI) and iron (II) ions.
   (b) A sample of steel weighing 0.20g is dissolved in aqueous sulphuric acid. The resulting solution requires 34.0cm³ of 0.02M $KMnO_4$ for complete reaction. Steel contains iron which reacts with an acid as below.

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

   Calculate the percentage of iron in steel.

3. 8.492g of ammonium iron sulphate, ($(NH_4)_2SO_4.FeSO_4.nH_2O$) Were dissolved in water to make 250cm³ of solution. 25.0 cm³ of this solution required 22.50 cm³ of 0.015M potassium permanganate in presence of an acid for complete reaction.
   (a) Write an equation for the reaction of iron(II) ions and potassium permanganate.
   (b) Determine the value of n in the salt. (Fe=56, S=32, N=14, O=16, H=1)

4. 13.2 g of iron(III) alum were dissolved in water and reduced to an iron(II) ion solution by zinc and dilute sulphuric acid. The mixture was filtered and the filtrate and washings made up to 500 cm³ in a standard volumetric flask. 20.0 cm³ of this solution required 26.5 cm³ of 0.01 moldm⁻³ $KMnO_4$ for oxidation.
   (a) Give the ionic equation for the reduction of iron(III) ions by zinc metal.
   (b) Calculate the percentage by mass of iron in iron alum.

5. The half equation for oxidation of a nitrite ion to a nitrate is shown below.

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

   (a) Give the ionic equation for potassium manganate(VII) oxidising nitrite ion to nitrate ion.
   (b) 24.20 cm³ of sodium nitrite solution, added from a burette were needed to discharge the colour of 25.0 cm³ of an acidified 0.025 moldm⁻³ $KMnO_4$ solution. What was the concentration of sodium nitrite solution in grams of anhydrous salt per dm³?

3.4 Electrochemical cells

A detailed treatment of electrochemical cells is beyond the scope of this book. Readers interested in these details can refer to any book of physical chemistry. However, the relevance of redox reactions to electrochemical cells is covered in this section.

In the previous section, we discovered that in a redox reaction electrons lost by the reducing agent are gained by the oxidising agent. Flow of electrons generates current thus; if two half cells are connected, a cell that generates current is produced. Such a cell is called an **electrochemical cell**. Each of the two half cells is called an **electrode**.

The following half equation shows potassium iodide acting as a reducing agent.

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

Iron(III) chloride can act as an oxidising agent by accepting electron, as shown by the following equation:

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

The two half cells above can be used to construct an electrochemical cell as follows;

- Two beakers are half filled, one with potassium iodide solution and the other with iron(III) chloride solution.
- A salt bridge, which prevents excessive mixing of the two solutions, is used to connect the two solutions. The salt bridge usually contains potassium chloride.
- A platinum electrode is dipped in each solution and they are joined together through a sensitive galvanometer (*fig. 3.1*)

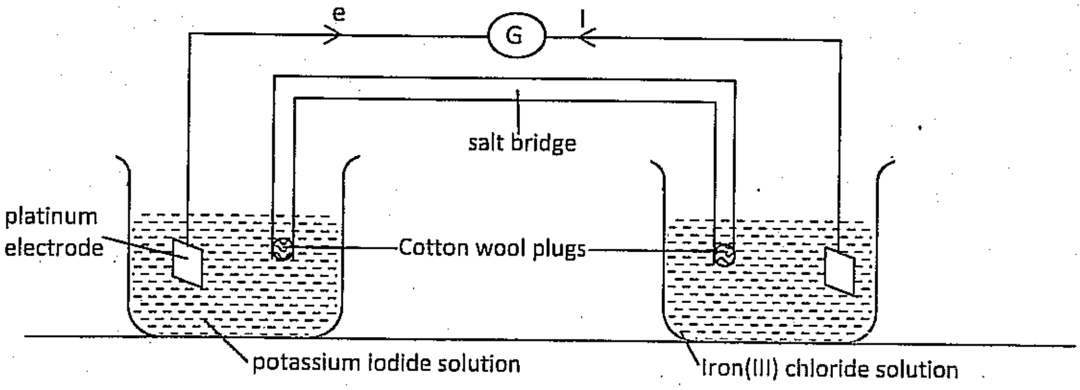
Observations

- The galvanometer will show a deflection indicating the follow of current. A bulb in place of the galvanometer may give out light.
- A brown colour (*initially appears yellow*) will be observed at the electrode dipping in potassium iodide due to liberation of iodine.
- Electrons will flow from the potassium iodide electrode to the iron(III) chloride electrode while current will take the opposite direction.
- The brown colour of iron(III) chloride solution fades and may turn to green due to reduction of iron(III) to iron(II).

The overall reaction taking place is;

$$2Fe^{3+}(aq) + 2I^{-}(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$$

Figure 3.1 Reaction between potassium iodide and iron(III) chloride to produce electric



3.5 Electrode potential

When a metal dips in a solution of its ions (*e.g. zinc in zinc sulphate solution*), there is a tendency for the metal ions to leave the metal lattice and go into solution thus leaving an excess of electrons and hence a negative charge on the metal. There is also a reverse tendency for metal ions from solution to deposit on the metal leading to a positive charge on the metal. In practice, one effect is greater than the other, so a potential difference is set between the metal and the solution.

The value of the potential difference for a particular metal depends on the concentration of the metal ions, temperature and, probably, the stability difference between the metal ions and the metal atoms. When concentration is 1 M and temperature 298 K, the potential difference set up in this case is called **standard electrode potential.**

Depending on the metal, it could be a negative potential with respect to the solution or a positive potential e.g. zinc has a negative standard electrode potential while copper has a positive one.

However, it is not possible to measure standard electrode potentials absolutely since the very act of carrying out the measurement would introduce another metal into solution which would set up its own electrode potential. Consequently, standard electrode potentials are measured against some reference electrode and the **Standard Hydrogen Electrode** (SHE) is adopted for this purpose.

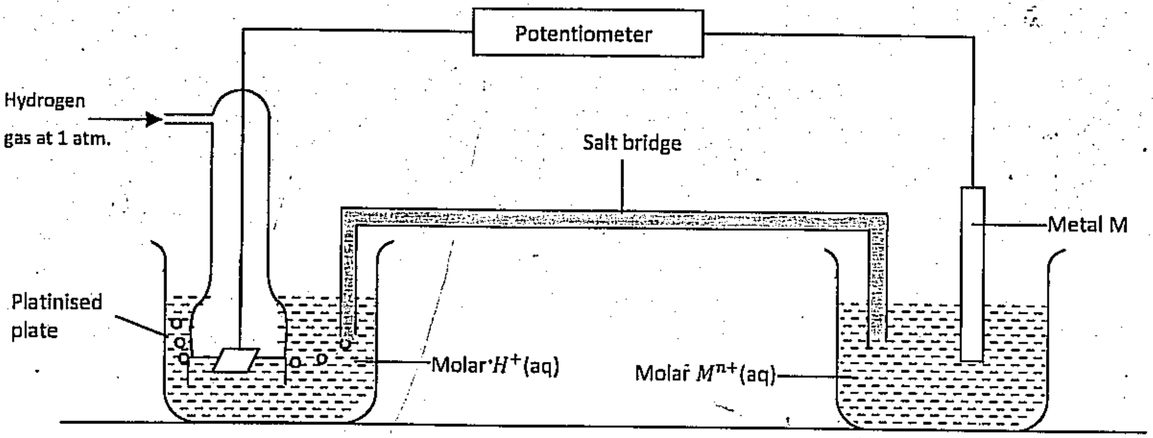
The SHE consists of hydrogen gas at 1 atmosphere in contact with a 1M solution of hydrogen ions at 298K; a platinum electrode, coated with platinum black, is incorporated into the set up (*fig.* 3.2). The SHE is connected, via a potassium chloride salt bridge, to the system $\boldsymbol{M^{n+}(aq)/M(s)}$ whose electrode potential is to be determined. The SHE is arbitrarily assigned a value of 0.0V. The potential difference measured by means of a high resistance voltmeter connected between the two electrodes is the standard electrode potential of $M^{n+}(aq)/M(s)$.

By convention, the SHE is the electron donor and constitutes the Left Hand Electrode (LHE). The second electrode is the electron acceptor. The reactions taking place in cell the shown in figure 3.2 are;

$$H_2(\text{g}) \longrightarrow 2H^+(\text{aq}) + 2\text{e}\,; \qquad M^{n+}(\text{aq}) + ne \longrightarrow M(\text{s})$$

M can be any metal such as $Zn, Cu,$ etc.

Figure 3.2 Measurement of electrode potential for the system M^{n+}/M



Standard electrode potential is thus defined as the reduction electrode potential of an electrode which is the e.m.f of the cell reaction with respect to the standard hydrogen electrode under standard conditions.

Since reduction is the gaining of electrons, all electrode potential measured are **reduction potentials.** This is because the second electrode is being reduced by gaining electrons from SHE.

The standard electrode potential for Zn^{2+}(aq)/Zn(s) is -0.76V and that for Cu^{2+}(aq)/Cu(s) is +0.34V.

A high positive electrode potential implies a strong oxidising agent while a high negative electrode potential value implies a strong reducing agent.

Table 3.3 shows some electrode potentials electrode potentials at 298K. A metal with a more negative electrode potential is a better reducing agent than one with a less negative one, thus such a metal can displace those below it from solution e.g.

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Factors that affect values of standard electrode potential (E^{θ}):

Standard electrode potentials are reduction potentials represented by the general half cell reaction below.

$$M^{n+}(aq) + ne \longrightarrow M(s)$$

To investigate the factors affecting values of electrode potentials of metals, we consider the formation of the hydrated metal ions M^{n+};

Table 3.2 Standard electrode (redox) potentials of common species

Increasing oxidising power ↓

Increasing reducing power ↑

Reaction	E^θ/ V
$Li^+(aq) + e \longrightarrow Li(s)$	-3.04
$K^+(aq) + e \longrightarrow K(s)$	-2.92
$Ba^{2+}(aq) + 2e \longrightarrow Ba(s)$	-2.90
$Ca^{2+}(aq) + 2e \longrightarrow Ca(s)$	-2.87
$Na^+(aq) + e \longrightarrow Na(s)$	-2.71
$Mg^{2+}(aq) + 2e \longrightarrow Mg(s)$	-2.37
$Al^{3+}(aq) + 3e \longrightarrow Al(s)$	-1.66
$Mn^{2+}(aq) + 2e \longrightarrow Mn(s)$	-1.18
$Zn^{2+}(aq) + 2e \longrightarrow Zn(s)$	-0.76
$Cr^{3+}(aq) + 3e \longrightarrow Cr(s)$	-0.74
$Fe^{2+}(aq) + 2e \longrightarrow Fe(s)$	-0.44
$Co^{2+}(aq) + 2e \longrightarrow Co(s)$	-0.28
$Ni^{2+}(aq) + 2e \longrightarrow Ni(s)$	-0.25
$Sn^{2+}(aq) + 2e \longrightarrow Sn(s)$	-0.14
$Pb^{2+}(aq) + 2e \longrightarrow Pb(s)$	-0.13
$H^+(aq) + e \longrightarrow \frac{1}{2}H_2(g)$	0.00
$Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$	+0.34
$Fe^{3+}(aq) + e \longrightarrow Fe^{2+}(aq)$	+0.76
$Ag^+(aq) + e \longrightarrow Ag(s)$	+0.80
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$Au^{3+}(aq) + 3e \longrightarrow Au(s)$	+1.50
$MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.52

Atomisation energy / sublimation energy

$M(s) \longrightarrow M(g) \qquad \Delta H$ = atomisation energy of M

Sublimation energy is the energy required to convert 1 mole of a solid substance into gaseous atoms. It is an endothermic process whose enthalpy change is positive. Therefore electrode potentials become more positive with increase in atomisation energy of the metal.

Ionisation energy of M

$M(g) \longrightarrow M^{n+}(g) + ne$

This is the energy required to remove an electron from a gaseous atom to form gaseous atom to form a gaseous cation. It is an endothermic process whose enthalpy change is positive. Therefore electrode potentials become more positive with increase in ionisation energy of the metal.

Hydration energy of M

$M^{n+}(g) + aq \longrightarrow M^{n+}(aq)$

This is the amount of energy given out when 1 mole of gaseous ions is surrounded completely by water molecules to form an infinitely dilute solution with no change in pH. This is an exothermic process (*enthalpy change is negative*). Therefore electrode potentials become more negative with increase in hydration energy.

Thus electrode potentials of metals depend on sublimation energy, ionisation energy and hydration energy.

For non-metals, electrode potentials become more;

- positive with increase in atomisation energy.
- negative with increase in electron affinity.
- negative with increase in hydration energy.

Alkali metals have the highest negative electrode potentials due to their low ionisation energies and enthalpies of sublimation. These cause the electrode potentials to be highly negative despite their low enthalpies of hydration.

In group I, lithium has an abnormally high negative electrode potential because hydration energy of its ions is much higher than that of other ions of group I elements owing to its very small atomic size.

Group II elements e.g. calcium, strontium, and barium have high negative electrode potentials (*even higher than that of sodium!*) because although their ionisation energies are higher than those of group I elements, their enthalpies of atomisation are fairly small and their hydration energies are very large (*due to their high charge*). The exceptionally high ionisation energy of beryllium makes its electrode potential less than those for other group II elements, despite its high hydration energy.

3.6 Analysis of oxidising agents

When oxidising agents are heated strongly, a gas that relights a glowing splint (oxygen) is given off; on warming oxidising agents with concentrated hydrochloric acid, chlorine gas is evolved. However, oxidising agents are usually tested by treating their solutions with reducing agents.

3.6.1 Using hydrogen sulphide

When treated with an oxidising agent, hydrogen sulphide gives a yellow precipitate (of sulphur). The half reaction below shows hydrogen sulphide acting as a reducing agent.

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

3.6.2 Using acidified potassium iodide solution

Acidified potassium iodide solution turns from colourless to brown when treated with an oxidising agent. This is because iodide ions are oxidised to iodine solution.

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

3.6.3 Using freshly prepared solution of iron(II) sulphate acidified with dilute sulphuric acid

An acidified solution of iron(II) sulphate turns from faint green to brown when treated with an oxidising agent. This is because iron(II) ions are oxidised to iron(III) ions; the iron(III) ions formed can further be detected by using potassium thiocyanate solution which turns to deep red.

3.7 Analysis of reducing agents

When a solid reducing agent is heated with a few drops of concentrated nitric acid, brown fumes of nitrogen dioxide are evolved. Reducing agents are usually tested by treating their aqueous solutions with oxidising agents.

3.7.1 Using potassium manganate (VII) solution acidified with dilute sulphuric acid

Reducing agents will turn acidified potassium manganate(VII) solution from purple to colourless.

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

3.7.2 Using acidified potassium dichromate solution

Reducing agents turn acidified potassium dichromate solution from orange to green.

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

3.7.3 Using iron(III) chloride solution

This solution will turn from brown to green due to reduction of iron(III) to iron(II)

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

Formation of the iron(II) ions can further be detected by addition of hexacyanoferrate(III) solution which turns to deep blue.

3.8 Summary

Oxidation numbers provide an easy way of writing and balancing redox reactions. Oxidising agents and reducing agents are frequently used in volumetric analysis and you will find knowledge gained in this chapter handy when performing calculations in volumetric analysis.

3.9 Suggested further reading on chapter 3

G. F. Liptrot, *Mordern Inorganic Chemistry*, Scotprint Ltd, Fourth Edition, 1983, Chapter 10

E. N. Ramsden, *Calculations for A-level Chemistry*, Nelson Thornes, Fourth Edition 2001

M. Ntanda, *Concise Solutions to U.A.C.E Chemistry paper one and two;*

Questions

P1 2011 Q9, P1 2011 Q6, P1 2010 Q7, P1 2009 Q9, P1 2007 Q12, P2 2006 Q1, P1 1999 Q1, P1 1999 Q6, P1 1998 Q10, P1 1994 Q17, P1 1993 Q14, P1 1990 Q5, P1 1988 Q9, P1 1988 Q16

3.10 Questions on chapter 3

1 (a) In acidified aqueous solution, iron (ii) ions, Fe^{2+} are oxidised at room temperature by

manganate (VII) ions. Above 60°C ethanedioate ions, $C_2O_4^{2-}$ are also oxidised by manganate (vii) ions. Write appropriate ion / electron half equations for:

- (i) the reduction of the oxidising agent
- (ii) oxidation of the reducing agent, Fe^{2+}
- (iii) oxidation of the reducing agent, $C_2O_4^{2-}$

(b) (i) By combining equations in (i), (ii), and (iii) above, write a balanced equation for the redox reaction which occurs between MnO_4^- and iron (II) ethanedioate, FeC_2O_4 (Fe^{2+} and $C_2O_4^{2-}$ ions) above 60°C in acid solution.

(ii) Use the equation above to calculate the concentration of manganate (vii) solution if 41.7 cm^3 of the solution required 0.2g of iron (II) ethanedioate for complete reaction. (Fe=55.85, 0=16, C=12.01)

2 (a) Determine the oxidation state of iodine in IO_3^- ion.

(b) Write down half cell reactions for the iodate ion and iodide ion (I^-) and hence write the overall reaction between the two ions.

(c) An unknown mass of KIO_3 was treated in aqueous solution with excess iodide ions and acidified. The resulting solution on titration required 53.70cm^3 of 0.20M sodium thiosulphate solution for complete reaction. Find the mass of KIO_3 used. (K=39.10, I=126.90, O=16.0)

3. Brass is a mixture of copper and zinc. It dissolves in nitric acid to give a mixture of zinc and copper ions e.g

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

The copper ions may be analysed by means of iodide ions and sodium thiosulphate solution. Zinc ions do not react during this analysis.

1.0g of brass was dissolved in nitric acid and after boiling off the oxides of nitrogen and neutralization, excess potassium iodide was added. The liberated iodine reacted completely with 10cm^3 of 1M sodium thiosulphate solution. Copper (II) ions react with iodide ions according to the equation:

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

(a) Write an equation between liberated iodine and sodium thiosulphate solution

(b) Calculate the percentage of copper in Brass

4. 25.0cm^3 of an aqueous solution containing 0.05 $moldm^{-3}$ of an ion M^{3+} was reduced using excess zinc and the un-reacted zinc removed. The resulting solution required 5.0cm^3 of 0.05M potassium manganate (VII) to restore M to its original +3 oxidation state. To what oxidation state was M^{3+} reduced by zinc?

5. (a) (i) Write an equation for the reaction between acidified potassium dichromate(vi) and iron (ii) ions.

(ii) Give the formula and colour of the chromium ion formed in the redox reaction.

(b) A sample of steel weighing 0.20g is dissolved in aqueous sulphuric acid. The resulting solution requires $34.0cm^3$ of 0.02M $KMnO_4$ for complete reaction. Steel contains iron which reacts with an acid as below.

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

(i) Explain why no indicator is used in this titration.

(ii) Calculate the percentage of iron in steel

6. Sodium sulphite (Na_2SO_3) is normally used in the preservation of beef. It was required to find the concentration of the preservative in beef. In this experiment, 1Kg of meat was boiled with excess dilute hydrochloric acid. The sulphur dioxide gas released was completely absorbed in excess dilute sodium hydroxide. The resultant solution was acidified with dilute sulphuric acid and titrated with 0.02M $KMnO_4$ solution. $30cm^3$ of $KMnO_4$ were required for the titration. The following equations are for the reactions that took place.

Step 1: Na_2SO_3(aq) + 2HCl (aq) $\longrightarrow$ 2NaCl(aq) + SO_2 (g) + H_2O(l)

Step 2: SO_2(g) + $2\bar{O}H$(aq) $\longrightarrow$ H_2O (l) + SO_3^{2-} (aq)

Step 3: SO_3^{2-}(aq)+ MnO_4^-(aq) $\longrightarrow$ --

(a) (i) How many moles of Na_2SO_3 are equivalent to 1 mole of MnO_4^-?

(ii) How many moles of MnO_4^- were used in the titration ?

(iii) How many moles of Na_2SO_3 were present in 1 Kg of meat?

(b) (i) In step 1, why is it necessary to use an excess of hydrochloric acid and to boil the solution ?

(ii) In step 3, why is it essential not to use hydrochloric acid to acidify the solution ?

(iii) What colour change would you observe in step 3.

✓7. (a) Work out the oxidation states of oxygen in the following compounds.

$HOCl$, $HClO_2$, $HClO_3$

(b) $S_2O_8^{2-}$ can be converted to SO_4^{2-} by Sn^{2+} ions. Sn^{2+} ions are converted to Sn^{4+} in the process.

(i) Determine the oxidation state of sulphur in $S_2O_8^{2-}$ and SO_4^{2-}

(ii) State with reasons, whether sulphur is oxidised or reduced in the conversion of $S_2O_8^{2-}$ to SO_4^{2-}

(c) (i) Write the half equations for the two conversions in (b) above.

(ii) Using the half equations, write an overall reaction for the reaction of Sn^{2+} and $S_2O_8^{2-}$

(d) State the conditions and write equations for the reaction between hydrogen peroxide and
   (i) iron II ions
   (ii) iron III ions
   (iii) iodide ions.

8. 0.877g of impure copper were allowed to react with dilute nitric acid. To the copper(ii)nitrate solution formed was added excess potassium iodide solution. The resulting solution was titrated with 0.48M thiosulphate solution and $23.70cm^3$ of the solution were required for complete reaction. Determine the percentage of copper in the impure sample. (Cu=63.5)

✓9. 8.492g of ammonium iron sulphate, $(NH_4)_2SO_4.FeSO_4.nH_2O$ were dissolved in water to make $250cm^3$ of solution. $25cm^3$ of this solution required $22.50cm^3$ of 0.015M potassium permanganate in presence of an acid for complete reaction.
   (a) Write an equation for the reaction of iron(II) ions in ammonium iron(II) sulphate and potassium permanganate.
   (b) Determine the value of n in the salt. (Fe=56, S=32, N=14, O=16, H=1)

✓ 10. Explain the following observations.
   (a) Potassium permanganate is not a primary standard
   (b) Sodium thiosulphate solutions should not be acidified.
   (c) Hydrochloric acid is not used to acidify potassium permanganate.
   (d) When sodium hydroxide is added to an orange solution of potassium dichromate, it immediately changes to yellow.

✓ 11. (a) Define the terms oxidation and reduction in terms of electron transfer.
   (b) For each of the following pairs of reagents, identify the oxidising agent and the reducing agent. In each case, write the have cell reactions and overall reaction that take place when the pair is mixed and also state what is observed.
      (i) hydrogen peroxide and potassium iodide.
      (ii) hydrogen peroxide and acidified potassium permanganate.
      (iii) hydrogen sulphide and moist sulphur dioxide.
      (iv) acidified potassium dichromate and sodium oxalate solution.

(v) Copper(II) sulphate solution and potassium iodide solution.

✓12. (a) Define the term standard electrode potential.

(b) Explain the factors that affect the standard electrode potential of a metal.

(c) Describe, with aid of a labeled diagram, how you would measure the standard electrode potential of silver and write equations representing the cell reaction.

(d) Explain the anomalous large negative electrode potential of lithium compared to group(I) elements.

CHAPTER 4

PERIODICITY

Learning Objectives

After reading this chapter and completing the exercises, you should be able to:

- Explain the variation of melting point, boiling point, electrical conductivity, atomic and ionic radius, ionisation energy, and electron affinity along elements of the 3rd short period.
- Discuss reactions of elements of the 3rd short period with water, sodium hydroxide and hydrochloric acid
- Discuss the physical properties of the oxides, chlorides, and hydrides of elements of the 3rd short period
- Describe the preparation of oxides, chlorides, and hydrides of elements of the third short period.
- Discussion the reactions of oxides, chlorides, and hydrides of elements of the 3rd short period with water, alkalis, and dilute acids
- Discuss the diagonal relationship between lithium and magnesium, beryllium and aluminium, boron and silicon

4.1 Introduction

Elements in the Periodic Table are arranged in order of their atomic numbers in such a way as to demonstrate the periodic law. **The periodic law** states that the properties of the elements are a periodic function of their atomic numbers.

In this chapter, we shall explore the variation of several properties across periods of the periodic table. The long form periodic table consists of 7 horizontal periods and 8 vertical groups. Groups I to VII are subdivided into A and B thus we can talk of group IVA and group IVB. Group VIII has three columns which include the iron group, nickel group and cobalt group. The noble gases belong to group 0. The long form of the Periodic Table is shown in table 1 at the end of this book. It should be noted that there is no special resemblance between the chemistry of the sub groups e.g. group IVA elements are not related to group IVB elements except perhaps their valences. The division into sub groups is merely a method used by Mendeleev in his original Periodic Table. For simplicity of this book, we shall just be merely referring to the groups as I, II, III, etc.

On critical analysis of the periodic table, it is observed that elements within the same group have the same outer electronic configuration and similar chemical properties. However, no element is exactly the same as another.

Elements within the same group show;

- similar properties owing to their similar outer electronic configuration.
- a gradation of properties down the group owing to a gradual change in electronegativity down the group.

However, the first member in any group usually shows anomalous behaviour due to high electronegativity, small size and restriction to an octet of valence electrons.

Elements usually exhibit a valency corresponding to their group number e.g. group IA elements have a valency of 1. In some cases, elements can also exhibit a valence of eight minus the group number e.g. phosphorous uses a valency of 3 and 5 (8-3), sulphur exhibits a valency of 6 and 2 (8-6) etc.

There is a gradual change of properties across periods. In this book, emphasis will be laid to period three. However similar trends of the properties occur in other periods such as the second period.

The third short period consists of the following elements;

Table 4.1 Elements of the 3rd short period

Group	I	II	III	IV	V	VI	VII	VIII
Element	Sodium	Magnesium	Aluminium	Silicon	Phosphorous	Sulphur	Chlorine	Argon
Symbol	*Na*	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*	*Ar*

4.2 Variation of physical properties along the 3rd short period

4.2.1 Metallic character

There is a gradual change from metallic character to non-metallic character on passing from left to the right of the Periodic Table. The oxides of sodium and magnesium are thus basic, aluminium oxide is amphoteric while oxides of the other elements of period three are acidic.

However, metallic character increases down the group.

4.2.2 Melting point

Melting point is the constant temperature at which a pure substance turns from solid state to liquid state at a given pressure when the two states are at equilibrium.

Melting temperature depends upon the magnitude of forces holding the particles of a solid together; the greater the magnitude, the higher is the melting temperature. Melting points also depends on the structure of the solid.

For metallic structures, melting point depends on;

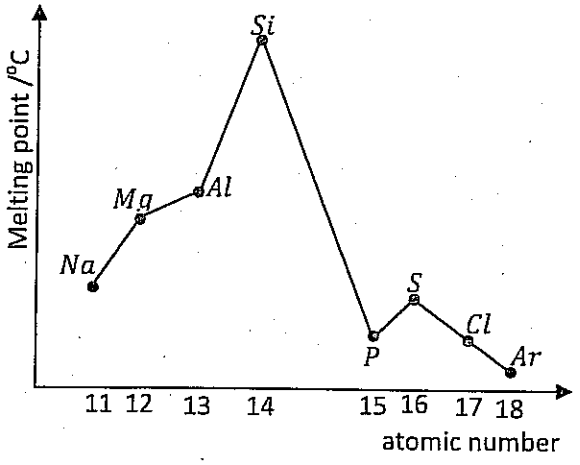
- The number of valency electrons each metal atom contributes towards metallic bond formation; the higher the number, the stronger the bond and the higher is the melting point.
- Metallic radius; the smaller the metallic radius, the shorter the bond and the stronger it is. Therefore melting point reduces with increase in metallic radius.

For non-metals, melting point depends on the type of structure formed. Giant molecular (*or atomic*) structures e.g. silicon and diamond have very high melting points due to a large number of covalent bonds that have to be broken before melting occurs. Simple molecular solids e.g. iodine have very low melting points since their molecules are held by weak Van der Waals forces.

Due to sudden structural changes across periods, variation of melting point across periods is not gradual e.g. the abrupt change of structure from silicon (*giant atomic structure*) to phosphorous (*simple molecular structure*) causes a sharp change in melting point.

Figure 4.1 shows a sketch (*not to scale*) of variation of melting point with atomic number across the 3rd short period.

Figure 4.1 Variation of melting point with atomic number of period 3 elements



Trend

There is a general increase in melting point from sodium to silicon and later on a general decrease in melting point up to argon.

Explanation

Melting point increases with increase in magnitude of the forces binding the particles of the solid.

From sodium to aluminium, the elements are metals whose atoms are held by **strong metallic bonds**. Strength of the metallic bond increases with increase in the number of valence electrons each metal contributes towards metallic bond formation. Sodium has 1 valence electron while magnesium and aluminium have 2 and 3 respectively. In addition, metallic radius decreases from sodium to aluminium which causes an increase in strength of the metallic bond from sodium to aluminium.

The increase from magnesium to aluminium is less sharp than the increase from sodium to magnesium because for aluminium, only two of its three valency electrons are always available for bonding.

Silicon forms a **giant atomic structure** with very many covalent bonds that have to be broken before melting occurs. This explains its abnormally high melting point.

From phosphorous to argon, the elements are **simple molecular** held by weak Van der Waals forces. Magnitude of Van der Waals forces increase with increasing molecular mass. Sulphur forms S_8 rings, phosphorus forms P_4 rings, chlorine is diatomic (Cl_2) while argon is mono-atomic. Molecular mass decreases in the order $S_8 > P_4 > Cl_2 > Ar$ hence melting point reduces in the same order.

4.2.3 Boiling point

Boiling point is the constant temperature at which the liquid's vapour pressure balances with external pressure.

Like melting point, boiling point also depends on the forces binding the molecules. Therefore boiling point shows a similar trend to melting point across the period.

4.2.4 Density

Density is mass per unit volume. There is an increase in density across period three reaching a maximum at the group(IV) element. This is due to increasing atomic mass with reducing atomic radius.

4.2.5 Atomic radius and ionic radius

Atomic radius is half the inter-nuclear distance between two covalently bonded atoms. Atomic radius and ionic radius largely depend on two factors;

Nuclear charge

If all other factors are constant, atomic radius reduces with increase in nuclear charge. This is because increase in nuclear charge causes an increase in attraction of the outermost electrons by the nucleus thus reducing atomic radius or ionic radius. However, because of influence from other factors, it is not un-common to find an atom with high nuclear charge having a larger atomic radius than an atom of lower nuclear charge e.g. the atomic radius of sodium (*atomic number 11*) is larger than that of magnesium (atomic number 12). Note that a high atomic number (*and therefore high number of protons*) implies a high nuclear charge.

Screen effect (or shielding effect)

Keeping other factors constant, increase in screening effect increases atomic radius. A very high screening effect on the outer electrons by inner electrons implies that the outermost electrons are effectively shielded from the nuclear charge. Consequently, the outermost electrons will receive less nuclear attraction causing an increase in atomic radius.

Variation of atomic radius across the 3rd short period

The table below shows atomic radii of elements of the 3rd short period

Table 4.2 Atomic radii of elements of the 3rd short period

Group	I	II	III	IV	V	VI	VII
element	*Na*	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*
Atomic radius (nm)	0.156	0.136	0.125	0.117	0.110	0.104	0.009

Trend

Atomic radius reduces across the period from left to right as atomic number increases.

Explanation

Across the period from one element to another, an electron is added to the outermost shell. This causes an increase in both nuclear charge and screening effect. However, since the electrons are added to the same main energy level, they shield each poorly from the increase nuclear charge such that the increase in nuclear charge outweighs the increase in screening effect. Consequently, effective nuclear charge increase across the period causing an increase in attraction of the outermost electrons. This reduces atomic radius.

Ionic radius shows a similar trend across the period and a similar explanation can be given.

4.2.6 Ionisation energy

In sub-section 1.8.5, we discussed the factors that affect ionisation energy. This sub section assumes that you have thorough knowledge of these factors or else, you may find it useful to read section 1.8.5 before reading this section.

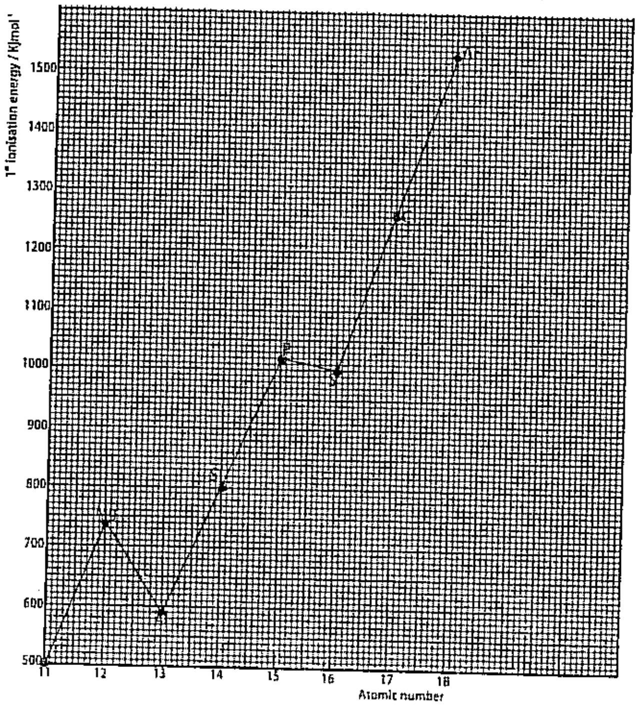
Across the period from left to right, both the nuclear charge and ionisation energy increase. Since electrons are being added to the same main energy level across the period, they shield each other poorly from the increasing nuclear charge such that increase in nuclear charge outweighs increase in screening effect. This increases effective nuclear charge across the period and thus increases ionisation energy.

Table 4.3 shows the first ionisation energies of elements of period three while figure 4.2 is graph of first ionisation energy against atomic number of elements of period three.

Table 4.3 Variation of first ionisation energies across the third short period

Element	*Na*	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*	*Ar*
First I.E (KJ/mol)	502	745	587	791	1020	1000	1260	1530
At.No	11	12	13	14	15	16	17	18

Figure 4.2 Graph of first ionisation energy against atomic number of period three elements



Explanation of the shape of the graph

There is a general increase in first ionisation energy from sodium to argon as atomic number increases. Across the period, electrons are added to the same main energy level as nuclear charge increases. These electrons shield each other poorly from the increasing nuclear charge. Therefore there is an increase in effective nuclear charge from sodium to argon and atomic radius reduces. Therefore first ionisation energy increases along the series.

Aluminium and sulphur show anomalous first ionisation energy because of their electronic structure, (Al: $1s^2 2s^2 2p^6 3s^2 3p^1$; S: $1s^2 2s^2 2p^6 3s^2 3p^4$). First ionisation energy involves leaving fully filled $3s^2$ sub-energy (for aluminium) and half-filled $3p^3$ sub-energy level (for sulphur) both of which configurations are very stable and relatively good shields.

4.2.7 Electron affinity

Electron affinity is the enthalpy change that occurs when one mole of electrons combine with one mole of gaseous atoms to form one mole of gaseous anions.

e.g. $Cl(g) + e \longrightarrow Cl^-(g)$ $\Delta H =$ first electron affinity of chlorine

On the other hand, **first electron affinity** is the energy given out when one mole of electrons combines with one mole of gaseous atoms to form one mole uni-negatively charged gaseous ions. First electron affinity is always an exothermic (ΔH is negative) process because the electron being added is attracted by the nucleus thus heat is given out. However, after the first electron is added, the gaseous atom acquires a negative charge thus becoming an ion. Subsequent electron affinities (2nd, 3rd, etc) are consequently endothermic processes because the electron being added is repelled by the negatively charged ion thus energy is required to add it.

The same factors that affect ionisation energy also affect electron affinity but their effect is different (*see section 1.8.5*). These include;

(a) The net charge on the atom or ion.
(b) The screening effect of inner electrons.
(c) Nuclear charge.
(d) The penetrating power of the valence electrons.
(e) Electronic configuration of the atom or ion

Net charge on the atom or ion

For gaseous atoms, the process of electron affinity is exothermic. However, for negatively charged ions, the process of electron affinity is endothermic (ΔH is positive). In addition, the magnitude of electron affinity increases with increase in negative charge on the ion. This is because the higher the negative charge on the ion, the stronger is the repulsion on the incoming electron and the higher is the amount of energy required to add the electron. Consequently, magnitude of electron affinity increases in the order 2nd < 3rd < 4th < 5th etc

The screening effect of the inner electrons

Shielding (*or screening*) of outer electrons by inner electrons reduces the attraction of outer electrons by the nucleus. Therefore increase in screening effect causes a decrease in effective nuclear charge and thus a decrease in ionisation energy.
Within a given shell, the screening efficiency of the inner electrons decreases in the order s > p > d > f. Therefore s-electrons are more screening than p-electrons and so on.

Nuclear charge

Increase in nuclear charge causes an increase in attraction of outer electrons by the nucleus. Therefore keeping other factors constant, increase in nuclear charge causes an increase in ionisation energy.

Penetrating power of valence electrons

In a given shell, the penetrating power of electrons towards the nucleus decreases in the order s > p > d > f; therefore the s-electrons are more penetrating and more firmly held than p-electrons and so on. Consequently in a given shell, ionisation energies increase in the order s > p > d > f.

Electronic configuration of the atom or ion:

Electronic configurations with half-filled sub-energy levels or fully-filled sub energy levels are relatively stable. For example, first ionisation energy of nitrogen ($1s^2 2s^2 2p^3$) is higher than that of oxygen ($1s^2 2s^2 2p^4$) although oxygen has a higher nuclear charge than nitrogen. This is because nitrogen has a half filled 2p sub-energy level which is more stable than the partially filled 2p sub-energy level of oxygen. Similarly, the first ionisation energy of helium (with fully filled 2s sub-energy level) is higher than that of lithium.

The concept of ionisation energy is very essential in understanding the chemistry of elements. Section 4.2.6 gives a detailed discussion of how the above factors affect ionisation energy down groups and across periods. It also explains how ionisation energies affect the chemistry of the groups and periods.

Unlike ionisation energies, reliable data for electron affinities is not readily available. However, some undependable available data reveals that electron affinity generally increases across the period. The table below shows variation of first electron affinity, in $Kjmol^{-1}$, across period 3.

Table 4.4 Variation of first electron affinity across the third short period

Element	Na	Mg	Al	Si	P	S	Cl
First E.A (KJ/mol)	-21	0	-26	-135	-60	-196	-348
Atomic number	11	12	13	14	15	16	17

It is worth noting that when we talk of an increase in electron affinity, we are strictly referring to the magnitude thus the magnitude of -348 is greater than magnitude of -196.

4.2.8 Electronegativity

Atomic radius

Electronegativity increases with a decrease in atomic radius.

For a small atomic radius, the bonding electrons are nearer to the nucleus thus they experience a greater attraction.

For a large atomic radius, the bonding electrons are far away from the nucleus thus they experience less attraction.

Nuclear charge

Electronegativity value increases with increase in nuclear charge.

For a low nuclear charge, the bonding electrons experience a low nuclear attraction leading to a low electronegativity value.

For a high nuclear charge, the bonding electrons experience a high nuclear attraction leading to a high electronegativity value.

Screening effect

Electronegativity increases with a decrease in screening effect.

A low screening effect implies that bonding electrons are less effectively shielded from the nuclear charge thus they experience a higher attraction.

A high screening effect implies that bonding electrons are effectively shielded from the nuclear charge thus they experience a less attraction leading to a low electronegativity value.

4.3 Diagonal relationship

Down any group of the Periodic Table, **charge density** and **electronegativity** reduce; this causes a reduction in polarising power.

On traversing across the period of the Periodic Table, **electronegativity** increases and so does **charge density**; thus polarising power increases across the period.

An increase in polarising power and electronegativity across the period is offset by a decrease in both polarising power and electronegativity down the group. Therefore elements diagonally opposite each other in consecutive groups of the Periodic Table have similar charge density, polarising power and electronegativity. Such elements therefore have similar chemistry.

Examples

$$\begin{tikzcd}
\textbf{Group} & \text{I} & \text{II} & \text{III} & \text{IV} \\
\textbf{Period 2} & \text{Li} \arrow[dr] & \text{Be} \arrow[dr] & \text{B} \arrow[dr] & \text{C} \\
\textbf{Period 3} & \text{Na} & \text{Mg} & \text{Al} & \text{Si}
\end{tikzcd}$$

From above, lithium which is in group I has similar polarising power and electronegativity to magnesium which is in group II. The two elements will have similar chemical properties and are said to possess a diagonal relationship.

Diagonal relationship is defined as the similarity in chemical properties between elements in period two to their diagonal neighbours in period three and adjacent groups.

Because of the diagonal relationship, the chemistry of **magnesium** and **lithium** is similar in the following ways.

- Both lithium and magnesium combine directly with nitrogen forming nitrides. Other alkali metals do not react with nitrogen.

- Both lithium and magnesium form normal oxides only; $Li_2O\ and\ MgO$. Other alkali metals form normal oxides, peroxides and even super oxides e.g. Na_2O_2.
- Carbonates and hydroxides of magnesium and lithium are sparingly soluble in water and decompose on heating. Carbonates and hydroxides of other alkali metals are soluble and not decomposed by heat.
- Nitrates of lithium and magnesium decompose on heating to form an oxide, nitrogen dioxide and oxygen. Nitrates of other alkali metals form nitrites and oxygen when heated.
- Hydroxides of both metals are not deliquescent.
- Hydrogen carbonates of both metals only exist in solution.
- Fluorides of both metals are soluble in organic solvents.
- Both metals form carbides when heated in carbon.

Likewise, the chemistry of **beryllium** and **aluminium** is similar in the following ways;

- Both metals are rendered passive by concentrated nitric acid.
- Both metals react with concentrated alkalis to give off hydrogen gas.
  - $Be(s) + 2\bar{O}H(aq) + 2H_2O(l) \longrightarrow Be(OH)_4^{2-}(aq) + H_2(g)$
  - $2Al(s) + 2\bar{O}H(\mathrm{aq}) + 6H_2O(\mathrm{l}) \longrightarrow Al(OH)_4^{-}(aq) + 3H_2(\mathrm{g})$
- Oxides and hydroxides of both metals are amphoteric.
- Carbides of both metals yield methane on hydrolysis.
  - $Be_2C(s) + 4H_2O(\mathrm{l}) \longrightarrow 2Be(OH)_2(s) + CH_4(g)$
  - $Al_4C_3(s) + 12H_2O(\mathrm{l}) \longrightarrow 4Al(OH)_3(\mathrm{s}) + 3CH_4(\mathrm{g})$
- Chlorides of both metals are covalent and polymeric solids when anhydrous e.g Al_2Cl_6 and Be_2Cl_4.

Likewise, the chemistry of **silicon** and **boron** is similar in the following ways;

- Both their oxides are acidic.
- Their hydrides are simple molecular.
- Both form only covalent compounds.
- Both exist in amorphous and crystalline state and exhibit allotropy.
- Their chlorides are liquids, fume in most air and are readily hydrolysed by water.

  $SiCl_4(\mathrm{l}) + H_2O(\mathrm{l}) \longrightarrow Si(OH)_4(\mathrm{aq}) + 4\mathrm{HCl(aq)}$

  $BCl_3(\mathrm{l}) + 3H_2O(\mathrm{l}) \longrightarrow B(OH)_3 + 3\mathrm{HCl(aq)}$

- Both form weak acids like H_3BO_3 and H_2SiO_3
- Both form binary compounds with several metals to give borides and silicide. These borides and silicide react with H_3PO_4 to give mixture of boranes and silanes.
- The carbides of both Boron and silicon (B_4C and SiC) are very hard and used as abrasives.
- Both the metals and their oxides are readily soluble in alkalis.
- Acids of both these elements form volatile esters on heating with alcohol in presence of concentrated sulphuric acid.

4.4 Chemical properties of elements of the 3rd short period

4.4.1 Introduction

In the third short period, metals tend to react as reducing agents by donating electrons

$$Ca(\text{s}) \longrightarrow Ca^{2+}(\text{aq}) + 2\text{e}$$

Relative reactivity of the metals can be measured in terms of ionisation energy, electropositivity or electrode potential. The lower the ionisation energy, the more reactive is the metal; the more negative the electrode potential, the more reactive is the metal. Since ionisation energy increases across the period, reactivity of the metals reduces across the period.

On the other hand, non-metals in this period react as oxidising agents by accepting electron

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

The relative tendency of non-metals to gain electrons (and thus reactivity) can be measured in terms of electron affinity and electronegativity; the higher the electron affinity and electronegatity, the more reactive is the non-metal. Since electron affinity increases across the period (*section 4.2.7*) reactivity of the non-metals also increases across the period.

4.4.2 Reaction with water

Sodium reacts vigorously with cold water to form sodium hydroxide and hydrogen gas.

$$2Na(\text{s}) + 2H_2O(\text{l}) \longrightarrow 2NaOH(\text{aq}) + H_2(\text{g})$$

Magnesium hardly reacts with cold water but burns brilliantly in steam to form magnesium oxide and hydrogen gas.

$$Mg(s) + H_2O(g) \longrightarrow MgO(s) + H_2(g)$$

Despite its high negative electrode potential, aluminium is not very reactive owing to a thin oxide layer on its surface. When this layer is removed by rubbing with mercury, aluminium reacts with water to form aluminium hydroxide and hydrogen gas.
Silicon does not react with cold water but attacks steam when heated strongly to form silicon (IV) oxide and hydrogen gas.

$$Si(s) + 2H_2O(l) \longrightarrow SiO_2(s) + 2H_2(g)$$

Red phosphorous is insoluble in water while white phosphorous is soluble but does not react with water. Similarly, sulphur does not react with water.
Chlorine reacts with cold water to form chloric (I) acid and hydrochloric acid.

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

4.4.3 Reaction with alkalis

Sodium and magnesium do not react with alkalis.
Aluminium is amphoteric and reacts with sodium hydroxide to form sodium tetrahydroxo aluminate (III) and hydrogen gas.

$$2Al(s) + 2\bar{O}H(aq) + 6H_2O(l) \longrightarrow 2Al(OH)_4^-(aq) + 3H_2(g)$$

Silicon reacts with hot concentrated sodium hydroxide to form sodium silicate and hydrogen gas.

$$Si(s) + 2\bar{O}H(aq) + H_2O(l) \longrightarrow SiO_3^{2-}(aq) + 2H_2(g)$$

Sulphur reacts slowly with hot concentrated sodium hydroxide to form sodium sulphite, sodium sulphide and water.

$$3S(s) + 6\bar{O}H(aq) \longrightarrow SO_3^{2-}(aq) + 2S^{2-}(aq) + 3H_2O(l)$$

However, with excess sulphur, sodium thiosulphate is formed instead of sodium sulphite.

$$4S(s) + 6\bar{O}H(aq) \longrightarrow S_2O_3^{2-}(aq) + 2S^{2-}(aq) + 3H_2O(l)$$

The sodium sulphide formed from the above two reactions reacts with more sulphur to form sodium pentasulphide.

$$S^{2-}(aq) + 4S(s) \longrightarrow S_5^{2-}(aq)$$

Chlorine reacts with cold dilute sodium hydroxide to form sodium chloride, sodium chlorate (I) and water.

$$Cl_2(g) + 2\bar{O}H(aq) \longrightarrow Cl^-(aq) + \bar{O}Cl(aq) + H_2O(l)$$

However, with hot concentrated sodium hydroxide, sodium chloride, sodium chlorate (V) and water are formed.

$$3Cl_2(g) + 6\bar{O}H(aq) \longrightarrow ClO_3^-(aq) + 5Cl^-(aq) + 3H_2O(l)$$

4.4.4 Reaction with acids

With dilute non-oxidising acids

Magnesium and aluminium react with dilute non oxidising acids such as hydrochloric acid and sulphuric acid to form hydrogen gas and corresponding salts.
However, dilute sulphuric acid does not attack aluminium perhaps because of insolubility of the oxide layer in the acid.
Silicon is resistant to attack by most acids; it is only attacked by hydrofluoric acid.

$$Si(s) + 6HF(l) \longrightarrow H_2SiF_6(l) + 2H_2(g)$$

With oxidising acids

Nitric acid

With exception of magnesium, dilute nitric acid does not react with metals; it reacts with magnesium to form magnesium nitrate and hydrogen gas.

$$Mg(s) + 2HNO_3(aq) \longrightarrow Mg(NO_3)_2(aq) + H_2(g)$$

Hot concentrated nitric acid oxidises metals to nitrates while it is its self reduced to nitrogen monoxide (or to nitrogen dioxide if the acid is very highly concentrated).

$$3Mg(s) + 8HNO_3(aq) \longrightarrow 3Mg(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

However, aluminium is rendered passive (does not react) by concentrated nitric acid due to formation of an impenetrable layer of oxide on its surface.
Similarly, hot concentrated nitric acid oxides not metals. It oxidises to phosphoric(V) acid while it is reduced to nitrogen dioxide. It also oxidises sulphur to sulphuric acid.

$$P(s) + 5HNO_3(aq) \longrightarrow H_3PO_4(aq) + 5NO_2(g) + H_2O(l)$$

OR: $P_4(s) + 20HNO_3(aq) \longrightarrow 4H_3PO_4(aq) + 4H_2O(l) + 20NO_2(g)$

$S(s) + 6HNO_3(aq) \longrightarrow H_2SO_4(aq) + 2H_2O(l) + 6NO_2(g)$

Concentrated sulphuric acid

Concentrated sulphuric acid is a less effective reducing agent than concentrated nitric acid.

Hot concentrated sulphuric acid oxidises magnesium to magnesium sulphate while it gets reduced to sulphur dioxide. It also oxidises aluminium to aluminium sulphate.

$$Mg(s) + 2H_2SO_4(l) \longrightarrow MgSO_4(aq) + 2H_2O(l) + SO_2(g)$$

$$2Al(s) + 6H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 6H_2O(l) + 3SO_2(g)$$

The acid has no reaction with silicon and phosphorous but oxidises sulphur to sulphur dioxide.

$$S(s) + 2H_2SO_4(l) \longrightarrow 2H_2O(l) + 3SO_2(g)$$

4.5 Compounds of elements of the 3rd short period

4.5.1 Introduction

Periodic three elements form several compounds including oxides, chlorides, hydroxides, hydrides etc. Properties of these compounds can be used to classify the elements into metals and non-metals. In this section, we look at properties of a few selected compounds including hydroxides, oxides, chlorides, and hydrides. Where appropriate, for all the compounds, we shall explore methods of preparation, type of bonding, reaction with water, alkalis and acids.

4.5.2 Hydroxides of the 3rd short period

Basing on the normal valency of the elements, we would expect the following hydroxides;

Element	Na	Mg	Al	Si	P	S	Cl
Valency	1	2	3	4	5	6	7
Expected hydroxide	$NaOH$	$Mg(OH)_2$	$Al(OH)_3$	$Si(OH)_4$	$P(OH)_5$	$S(OH)_6$	$Cl(OH)_7$
Hydroxide formed	$NaOH$	$Mg(OH)_2$	$Al(OH)_3$	H_2SiO_3	H_3PO_4	H_2SO_4	$HClO_4$

However, hydroxides of non-metals split off (lose) water molecules thus forming hydroxides shown below. The hydroxides of these non-metals are acidic.

Expected hydroxide	Water molecule(s) lost	Hydroxide formed
$Si(OH)_4$	$-H_2O$	H_2SiO_3
$P(OH)_5$	$-H_2O$	H_3PO_4
$S(OH)_6$	$-2H_2O$	H_2SO_4
$Cl(OH)_7$	$-3H_2O$	$HClO_4$

Acid-base character of the hydroxides

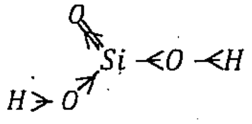
The hydroxides become more acidic across the period from left to right.

Hydroxide	$NaOH$	$Mg(OH)_2$	$Al(OH)_3$	H_2SiO_3	H_3PO_4	H_2SO_4	$HClO_4$
Character	Strong base	Weak base	Amphoteric	Weak acid	Weak acid	Strong acid	Strong acid

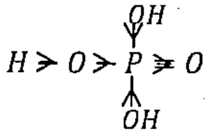
For metallic hydroxides, basic strength increases with increase in ease of loss of the hydroxyl group in form of $\bar{O}H$ ions. The less electronegative the metal, the weaker is the $M-OH$ bond and consequently the stronger is the base. Electronegativity of the metal atoms increases in the order Na < Mg < Al thus basic strength reduces in the order $NaOH > Mg(OH)_2 > Al(OH)_3$.

The non-metallic hydroxides (known as oxy-acids) are acidic. Their acidic strength increases with increase in the ease of loss of a proton. The acidic strength increases in the order $H_2SiO_3 < H_3PO_4 < H_2SO_4 < HClO_4$. This trend can be explained by considering the structures of the acids (*not drawn to scale*) below.

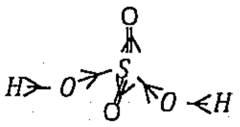
H_2SiO_3



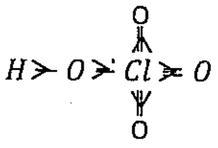
H_3PO_4



H_2SO_4



$HClO_4$



Oxygen atoms attached to the central atom withdraw electrons from the central atom which in turn withdraws electrons from hydroxyl groups bonded to it; this increases the partial positive charge on the hydrogen atom making it more easily lost. The greater the effect of withdrawing electrons, the stronger the acid. This effect increases with increase in number of oxygen atoms attached to the central atom and also with increase in electronegativity of the central atom. Electronegativity of the central atom increases in the order $Si < P < S < Cl$ thus acidic strength also increases in the same order.

4.5.3 Oxides of the 3rd short period

These include;

Element	Na	Mg	Al	Si	P	S	Cl
Oxide	Na_2O, Na_2O_2	MgO	Al_2O_3	SiO_2	P_2O_3, P_2O_5	SO_2, SO_3	Cl_2O_7, Cl_2O

Preparation

Sodium monoxide is formed by heating sodium in a limited supply of air. Sodium peroxide is a pale yellow solid manufactured by heating sodium metal in excess air at about 600K

$$4Na(s) + O_2(g) \longrightarrow 2Na_2O(s)\,; \qquad 2Na(s) + O_2(g) \longrightarrow Na_2O_2(s)$$

Magnesium oxide is a white solid prepared by heating a nitrate, carbonate or hydroxide of magnesium strongly.

$$MgCO_3(s) \xrightarrow{heat} MgO(s) + CO_2(g)$$

Acid-base character

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_3, P_2O_5	SO_2, SO_3	Cl_2O_7, Cl_2O
Character	Basic	Basic	Amphoteric	Acidic	Acidic	Acidic	Acidic

Structure and bonding

Sodium, magnesium and aluminum oxides form giant ionic structures; ionic character of these oxides decreases with increasing charge density of the cation. Silicon(IV) oxide forms a giant covalent structure. The rest of the oxides form simple molecular structures.

Melting point of the oxides

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_3	SO_3	Cl_2O_7
Melting point /°C	1193	3075	2300	1728	563	30	-91

The melting point increases from sodium oxide to magnesium oxide then reduces up to dichlorine heptoxide.

Sodium oxide, magnesium oxide and aluminium oxide have giant ionic structures. The ions are held together by strong ionic bonds. The melting point increases from sodium oxide to magnesium oxide due to increase in charge density of the cation; from magnesium oxide to aluminium oxide it decreases due to very high charge density of aluminium ion which makes aluminium oxide partly covalent (less ionic). Silicon dioxide has a giant covalent structure. Its atoms are held by strong covalent bonds, the rest of the oxides have simple molecular structures. Molecules are held by weak van der waals forces whose strength decreases with decrease in polarity of the molecules as a result of decrease in difference of electronegativity of bonding atoms.

Reaction with water

Sodium oxide reacts violently with water to form sodium hydroxide solution.

$$Na_2O(\text{s}) + H_2O(\text{l}) \longrightarrow 2NaOH(\text{aq})$$

Magnesium oxide reacts with water to form magnesium hydroxide.

$$MgO(\text{s}) + H_2O(\text{l}) \longrightarrow Mg(OH)_2(\text{s})$$

Aluminium oxide does not dissolve in water and has no reaction with water. Silicon(IV) oxide has no reaction with water up to its boiling point. It slightly reacts with water, when heated under pressure, to form silicic acid.

$$SiO_2(\text{s}) + H_2O(\text{l}) \longrightarrow H_2SO_3(\text{aq})$$

The rest of the oxides dissolve in water to form acidic solutions.

$$P_2O_5(\text{s}) + 3H_2O(\text{l}) \rightleftharpoons 2H_3PO_4(\text{aq})$$
$$P_4O_6(\text{s}) + 6H_2O(\text{l}) \longrightarrow 4H_3PO_3(\text{aq})$$
$$SO_3(\text{g}) + H_2O(\text{l}) \rightleftharpoons H_2SO_4(\text{aq})$$
$$SO_2(\text{g}) + H_2O(\text{l}) \rightleftharpoons H_2SO_3(\text{aq})$$
$$Cl_2O_7(\text{l}) + H_2O(\text{l}) \longrightarrow 2HClO_4(\text{aq})$$
$$Cl_2O(\text{g}) + H_2O(\text{l}) \longrightarrow 2HOCl(\text{aq})$$

Reaction with alkalis

Sodium and magnesium oxides are basic and therefore do not react with alkalis. Aluminium oxide is amphoteric and therefore reacts with concentrated alkalis to form complex salts.

$$Al_2O_3(\text{s}) + 2\bar{O}H(\text{aq}) + 3H_2O(\text{l}) \longrightarrow 2Al(OH)_4^-(\text{aq})$$

Silicon(IV) oxide reacts with concentrated alkalis to form silicates.

$$SiO_2(\text{s}) + 2\bar{O}H(\text{aq}) \longrightarrow SiO_3^{2-}(\text{aq}) + H_2O(\text{l})$$

The rest of the oxides are acidic and therefore react with alkalis to form salts and water.

$$P_2O_5(s) + 4NaOH(aq) \longrightarrow 2Na_2HPO_4(aq) + H_2O(l)$$

$$P_4O_6(s) + 8NaOH(aq) \longrightarrow 4Na_2HPO_3(aq) + 2H_2O(l)$$
$$SO_3(g) + 2NaOH(aq) \longrightarrow Na_2SO_4(aq) + H_2O(l)$$
$$Cl_2O_7(l) + 2NaOH(aq) \longrightarrow 2NaClO_4(aq) + H_2O(l)$$

Reaction with acids

Sodium, magnesium and aluminum oxides readily react with dilute mineral acids to form salts and water.

$$MgO(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2O(l)$$

$$Al_2O_3(s) + 6H^+(aq) \longrightarrow 2Al^{3+}(aq) + 3H_2O(l)$$

Silicon(IV) oxide has no reaction with mineral acids except hydrofluoric acid.

$$SiO_2(s) + 4HF(l) \longrightarrow SiF_4(g) + 2H_2O(l)$$

The rest of the oxides are acidic and therefore do not react with acids.

4.5.4 Chlorides of the 3rd short period

The table below shows chlorides formed by period 3 elements

Element	Na	Mg	Al	Si	P	S
Chloride	$NaCl$	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3, PCl_5	S_2Cl_2, SCl_2

Preparation

Sodium chloride is prepared by neutralization method involving sodium hydroxide and hydrochloric acid; magnesium chloride is prepared by reacting its carbonate, oxide, or hydroxide with dilute hydrochloric acid.

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

$$MgO(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l)$$

However, anhydrous magnesium chloride is prepared by direct synthesis since any attempt to obtain it from the hydrated magnesium chloride or by evaporation of its aqueous solution yields a basic chloride due to hydrolysis.

$$Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$$
$$MgCl_2.6H_2O(s) \xrightarrow{heat} MgCl(OH)(s) + 5H_2O(g) + HCl(g)$$

Aluminium chloride is a white solid prepared by passing dry chlorine (or dry hydrogen chloride) over the heated aluminium. It sublimes at 456K and at a temperature a little above 456K it exists as Al_2Cl_6.

$$2Al(s) + 3Cl_2(g) \longrightarrow Al_2Cl_6(s)$$

Silicon(IV) chloride may also be prepared by heating it with dry chlorine but a more convenient method is by heating a mixture of silcon(IV) oxide and carbon in a dry current of chlorine.

$$Si(s) + 2Cl_2(g) \longrightarrow SiCl_4(s)$$

$$SiO_2(s) + 2C(s) + 2Cl_2(g) \longrightarrow SiCl_4(g) + 2CO(g)$$

Phosphorous trichloride is a colourless liquid prepared by passing dry chlorine over heated white phosphorous.

$$P_4(s) + 6Cl_2(g) \longrightarrow 4PCl_3(l)$$

Phosphorous pentachloride is prepared by passing dry chlorine over heated phosphorous trichloride.

$$PCl_3(l) + Cl_2(g) \longrightarrow PCl_5(s)$$

Sulphur dichloride is a red liquid prepared by reacting chlorine with disulphur dichloride at 0°C.

$$S_2Cl_2(l) + Cl_2(g) \rightleftharpoons 2SCl_2(l)$$

Disulphur dichloride is a red liquid prepared by passing dry chlorine over molten sulphur.

$$2S(s) + Cl_2(g) \longrightarrow S_2Cl_2(l)$$

Bond type and structure

Electropositive metals form mainly ionic compounds but the degree of ionic character reduces as electropositivity decreases across the period. Magnesium and aluminium chlorides are ionic with some considerable degree of covalent character. The rest of the chlorides on the right are covalent though the bonds possess some polarity. Bond type and structure have a very big consequence on melting point of the chlorides (see below)

Chapter 4 Periodicity

Chloride	$NaCl$	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	PCl_5	S_2Cl_2	SCl_2
Bond type	ionic	Partly ionic	covalent	Covalent	Covalent	Covalent	Covalent	covalent
Structure	Giant ionic	Giant ionic	Layered molecular	Layered molecular	Simple molecular	Simple molecular	Simple molecular	Simple molecular

Melting point of the chlorides

Chloride	$NaCl$	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	PCl_5	S_2Cl_2	SCl_2
Melting point /°C	808	714	192	-68	-92	160	-76	-80
Physical state	Solid	Solid	Solid	Liquid	Liquid	Solid	Liquid	Liquid

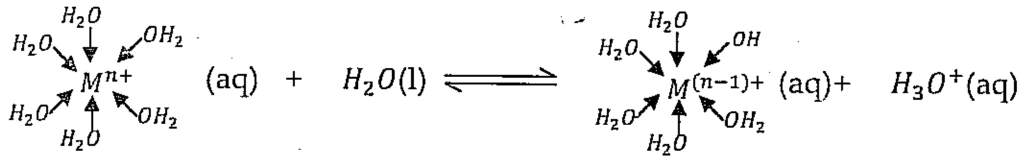
Melting point of the chlorides generally decreases as the period is traversed from left to right.

Sodium and magnesium chlorides form giant ionic lattices though the degree of ionic character decreases with increase in charge density in the same direction. Therefore magnesium chloride has a lower melting point than sodium chloride. Aluminium ions have a very high charge density which induces a very high covalent character in aluminium chloride thus a low melting point. Silicon tetrachloride is covalent consisting of molecules held by weak van der waals forces this a very low melting point. Phosphorous trichloride is also simple molecular thus the low melting point. Phosphorous pentachloride has an abnormally high melting point because at ordinary temperature it is known to consist of PCl_4^+ and PCl_6^- ions though in vapour state it consists of PCl_5 molecules. It is this ionic character that is responsible for its abnormally high melting point. The chlorides of sulphur are simple molecular held by weak van der waals forces. Magnitude of the van der waals forces decrease with decreasing molecular mass.

Reaction with water (hydrolysis)

Hydrolysis refers to chemical reactions of double decomposition brought about by water to form ions.

Cations of high charge density attract water molecules towards themselves. This attraction weakens the $O-H$ bond in the attracted water molecule making it to lose a proton. Consequently, solutions of such cations are acidic.



$$Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$$

Purely ionic chlorides do not hydrolyse in water thus sodium chloride does not undergo hydrolysis but dissolves in water to form sodium and chloride ions. Magnesium chloride undergoes partial hydrolysis in cold water to form a basic chloride.

$$MgCl_2(s) + H_2O(l) \longrightarrow MgCl(OH)(s) + HCl(g)$$

However, if heated, hydrolysis may go as far as magnesium oxide.

$$MgCl_2(s) + H_2O(l) \longrightarrow MgO(s) + 2HCl(g)$$

Aluminium chloride fumes in moist air by hydrolysis liberating hydrogen chloride gas. This explains why its solution is acidic.

$$AlCl_3(s) + 3H_2O(l) \longrightarrow Al(OH)_3(s) + 3HCl(g)$$

Silicon tetrachloride rapidly hydrolyses in cold water to form misty fumes of hydrogen chloride and silicic acid.

$$SiCl_4(l) + 3H_2O(l) \longrightarrow H_2SiO_3(s) + 4HCl(g)$$

It is not uncommon for this hydrolysis to proceed as far as silicon(IV) oxide.

$$SiCl_4(l) + 2H_2O(l) \longrightarrow SiO_2(s) + 4HCl(g)$$

Both phosphorous trichloride and phosphorous pentachloride hydrolyse in water to form phosphonic acid and tetraoxophosphoric(V) acid respectively, in addition to misty fumes of hydrogen chloride gas.

$$PCl_3(l) + 3H_2O(l) \longrightarrow H_3PO_3(s) + 3HCl(g)$$

$$PCl_5(s) + 4H_2O(l) \longrightarrow H_3PO_4\,(aq) + 5HCl(g)$$

Disulphur dichloride hydrolyses in water forming sulphurous acid, sulphur and hydrogen chloride gas.

$$2S_2Cl_2(l) + 3H_2O(l) \longrightarrow 4HCl(g) + H_2SO_3(aq) + 3S(s)$$

Reaction with acids

Sodium chloride reacts with concentrated sulphuric acid to yield hydrogen chloride gas.

$$NaCl(s) + H_2SO_4(l) \longrightarrow NaHSO_4(s) + HCl(g)$$

Chlorides of phosphorous react with carboxylic acids to yield corresponding acyl chlorides.

$$CH_3COOH(l) + PCl_5(s) \longrightarrow CH_3COCl(l) + POCl_3(l) + HCl(g)$$

$$3CH_3COOH(l) + PCl_3(l) \longrightarrow 3CH_3COCl(l) + H_3PO_3(s)$$

4.5.5 Hydrides of the 3rd short period

The table below shows hydrides formed by period 3 elements

Element	Na	Mg	Al	Si	P	S	Cl
Hydride	NaH	MgH_2	AlH_3	SiH_4	PH_3	H_2S	HCl

Preparation

Sodium hydride is a white crystalline solid prepared by heating sodium in a stream of dry hydrogen gas.

$$2Na(s) + H_2(g) \longrightarrow 2NaH(s)$$

Aluminium hydride is a white solid precipitated when lithium hydride is treated with excess aluminium chloride in a solution of ether.

$$3LiH(s) + AlCl_3(s) \longrightarrow AlH_3(s) + 3LiCl(s)$$

Silane is obtained by fractional distillation from a mixture of silicon hydrides formed when magnesium silicide is treated with 20 per cent hydrochloric acid.

$$Mg_2Si(s) + 4HCl(aq) \longrightarrow 2MgCl_2(aq) + SiH_4(g)$$

However, a more convenient way of preparing silane is by reduction of silicon tetrachloride with lithium aluminium hydride.

$$SiCl_4(l) + LiAlH_4(s) \longrightarrow SiH_4(g) + LiCl(s) + AlCl_3(s)$$

Phosphorous trihydride (phosphine) is prepared by heating concentrated sodium hydroxide solution with white phosphorous:

$$P_4(s) + 3\bar{O}H(aq) + 3H_2O(l) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq)$$

Hydrogen sulphide is prepared by action of dilute hydrochloric acid on iron(II) sulphide.

$$FeS(s) + 2HCl(aq) \longrightarrow FeCl_2(aq) + H_2S(g)$$

Hydrogen chloride is prepared by action of concentrated sulphuric acid on sodium chloride.

$$NaCl(s) + H_2SO_4(l) \longrightarrow NaHSO_4(s) + HCl(g)$$

Structure and bonding

Sodium is highly electropositive sodium hydride is ionic (Na^+H^-). Sodium hydride has a sodium chloride-like crystal lattice.

Hydrides of magnesium and aluminium are predominantly covalent and polymeric. The covalent character can be attributed to the small ionic radius and high charge (charge density) of the cations.

The rest of the hydrides in this period are covalent and simple molecular held by weak van der waals forces.

Acidity of the hydrides increases across the period from left to right

Reaction with water

Sodium hydride reacts with cold water to form hydrogen gas and sodium hydroxide.

$$NaH(s) + H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$$

Silane is hydrolysed by water but the hydrolysis is more rapid in presence of an alkali (see below).

Hydrogen sulphide does not hydrolyse in water but ionises to form an acidic solution.

$$H_2O(l) + H_2S(g) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$$

Hydrogen chloride does not react with water but ionises to form hydrogen ions.

$$HCl(g) + aq \longrightarrow H^+(aq) + Cl^-(aq)$$

Reaction with alkalis

Silane is hydrolysed by water in presence of an alkali to form sodium silicate and hydrogen gas.

$$SiH_4(g) + 2\bar{O}H(aq) + H_2O(l) \longrightarrow SiO_3^{2-}(aq) + 4H_2(g)$$

Hydrogen sulphide reacts with sodium hydroxide to form sodium hydrogen sulphide.

$$H_2S(g) + NaOH(aq) \rightleftharpoons NaHS(aq) + H_2O(l)$$

Aqueous hydrogen chloride reacts with sodium hydroxide to form sodium chloride and water.

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

Reaction with acids

Hydrogen sulphide reduces concentrated sulphuric acid to sulphurdioxide.

$$H_2SO_4(\text{l}) + H_2S(\text{g}) \longrightarrow SO_2(\text{g}) + 2H_2O(\text{l}) + S(\text{s})$$

It also reduces concentrated nitric acid to nitrogen monoxide.

$$2HNO_3(\text{aq}) + 3H_2S(\text{g}) \longrightarrow 4H_2O(\text{l}) + 2NO(\text{g}) + 3S(\text{s})$$

4.6 Summary

Across the period from left to right, elements gradually change from purely metallic to non-metallic. There is also a gradual change in bond type, acidity of the compounds and many other properties.

4.7 Suggested further reading on chapter 4

G. F. Liptrot, *Mordern Inorganic Chemistry*, Scotprint Ltd, Fourth Edition, 1983.
A. Holderness, Advanced Level Inorganic Chemistry, Thomson Press, Third Edition, 1979
H. L. Heys, Physical Chemistry, Chapter 8.
W. R. Kneen, *Chemistry, Facts, Patterns and Principles*, Addison-Wesley Pub (Sd), 1972

4.8 Questions on chapter 4

1. (a) Draw a graph of first ionisation energies of period 3 elements against atomic number.
   (See table 4.3 for the values of the ionisation energies)
   (b) Explain the general shape of the graph in (a) above.
   (c) Explain any abnormalities in the graph in (a) above.
2. Arrange the following elements/compounds in order of increasing melting point and explain your answer in each case.
   (a) Sodium, aluminium, magnesium.
   (b) sodium oxide, magnesium oxide, aluminium oxide
3. Discuss the trend in atomic radii of period 3 elements across the Periodic Table.
4. (a) Complete the following table about oxides of elements of the 3rd short period.

Element	*Na*	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*
Formula of oxide							
Nature of bonding							

(b) Describe the variation of the structures of the oxides across the period.

(c) From the table above, select one oxide which is basic, one which is amphoteric and one which is acid, then write equations for reactions to illustrate each property.

(d) Give and explain the shapes of the molecules formed by;

(i) Silane (ii) aluminium chloride (iii) hydrogen sulphide

(e) Write an equation for the reaction between sodium hydroxide and;

(a) sodium hydride (ii) silane

5. (a) Write equations to show how you would prepare the following chlorides;

(i) Magnesium chloride (ii) silicon tetrachloride (iii) hydrogen chloride

(b) Give the type of bonding in each of the chlorides in (a) above and state the structure formed.

(c) Write an equation (if any) for the chlorides above with water.

CHAPTER

5

GROUP TWO ELEMENTS

Learning Objectives

After reading this chapter and completing the exercises you should be able to:

- Explain the variation of melting point, atomic and ionic radius and ionisation energy down group(II) elements
- Discuss reactions of group(II) with water, sodium hydroxide and hydrochloric acid
- Discuss the physical properties of the oxides, chlorides, and hydrides of group(II) elements
- Describe the preparation of oxides, chlorides, and hydrides of group(II) elements
- Discussion the reactions of oxides, chlorides, and hydrides of elements of group(II) with water, alkalis, and dilute acids
- Discuss the solubility of sulphates and hydroxides of elements of group(II)

5.1 Introduction

Group two elements are often referred to as alkaline earth metals. They include beryllium, magnesium, calcium, strontium, barium, and radium. They are fairly electropositive metallic elements. Electropositivity increases down the group.

Table 5.1 Electronic configurations of group(II) elements

Element	Symbol	Atomic number	Electronic configuration
Beryllium	*Be*	4	$1s^22s^2$
Magnesium	*Mg*	12	$1s^22s^22p^63s^2$
Calcium	*Ca*	20	$1s^22s^22p^63s^23p^64s^2$
Strontium	*Sr*	38	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^2$
Barium	*Ba*	56	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^2$

Their general outer most shell configuration is ns^2
In most of their compounds, the elements show an oxidation state of +2 due to their low first and second ionisation energies.
Reactivity of the elements increases down the group due to decrease in ionisation energy in the same direction.
Beryllium significantly differs from the rest of the members of the group and its anhydrous compounds are covalent in character. This is because beryllium has a very small atomic radius and forms small

cations with high charge density and polarizing power compared to the other elements in the group.

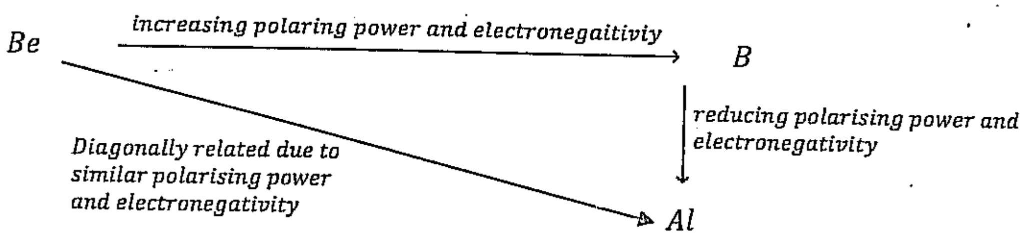
Magnesium too forms compounds which show some appreciable covalent character. Compounds of other elements in the group are essentially ionic. Radium is radioactive and is formed during decay of uranium compounds. All the members are highly reactive and are thus never found in free state in nature.

5.1.1 Diagonal relationship between beryllium and aluminium

Beryllium has a small atomic radius compared to other members of the group thus its chemistry differs significantly from the rest of the members.

Most beryllium compounds, when anhydrous, show considerable covalent character. Magnesium compounds show some covalent character while the rest of the elements form essentially ionic compounds.

From beryllium to boron, polarising power and electronegativity increase. From boron to aluminium polarising power and electronegativity reduce. The increase in polarising power and electronegativity from beryllium to boron is offset by a decrease from boron to aluminium, thus beryllium and aluminium have similar polarising power and electronegativity.



Due to similarity in polarising power and electronegativity, the chemistry of beryllium and aluminum is similar. They are said to have a diagonal relationship (*also see section 4.3*).

The chemistry of beryllium and aluminium is similar in the following ways

- Both react with concentrated sodium hydroxide solution to form complex salts.

$$Be(s) + 2\bar{O}H(aq) + 2H_2O(l) \longrightarrow Be(OH)_4^{2-}(aq) + H_2(g)$$

$$2Al(s) + 2\bar{O}H(aq) + 6H_2O(l) \longrightarrow 2Al(OH)_4^{-}(aq) + 3H_2(g)$$

- Both are rendered passive by concentrated nitric acid.
- Both their oxides and hydroxides are amphoteric.

$$BeO(s) + 2H^+(aq) \longrightarrow Be^{2+}(aq) + H_2O(l)$$

$$BeO(s) + 2OH^-(aq) + H_2O(l) \longrightarrow Be(OH)_4^{2-}(aq)$$

$$Al_2O_3(s) + 6H^+(aq) \longrightarrow 2Al^{3+}(aq) + 3H_2O(l)$$

$$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \longrightarrow 2[Al(OH)_4]^-(aq)$$

- Both their carbides yield methane on hydrolysis.

$$Be_2C(s) + 4H_2O(l) \longrightarrow 2Be(OH)_2(s) + CH_4(g)$$

$$Al_4C_3(s) + 12H_2O(l) \longrightarrow 4Al(OH)_3(s) + 3CH_4(g)$$

- Chlorides and bromides of both metals are covalent and polymeric solids (Al_2Cl_6 *and* Be_2Cl_4) when anhydrous and are hydrolysed by water.
- Both have a tendency to form complexes.

5.2 Physical properties of alkaline earth metals

Apart from barium, the alkaline earth metals have close packed structures at room temperature. Beryllium and magnesium have hexagonal close packed structures – *section 2.3.1*

All the elements have two valency electrons and strength of the metallic bond decrease down the group due to increase in metallic radius.

5.2.1 Atomic radius

Table 5.2 Atomic radii of group(II) elements

Element	Be	Mg	Ca	Sr	Ba	Ra
Atomic radius/picometers	96	141	176	195	215	221

Atomic radii of the elements increase down the group. Down the group, both the nuclear charge and screening effect increase. However, since an extra shell of electrons is added down the group, increase in screening outweighs increase in nuclear charge; effective nuclear charge thus decreases down the group. This increases atomic radius down the group since outer electrons become less strongly attracted.

5.2.2 Melting point

[illegible] Melting points of group(II) elements

Element	*Be*	*Mg*	*Ca*	*Sr*	*Ba*	*Ra*
melting point /°C	1280	651	845	789	725	700

Melting point generally reduces down the group. This is due to increase in metallic radius down the group, which results in decrease in metallic bond strength. However, magnesium has an abnormally lower melting point than calcium, because magnesium has a hexagonal close packed structure as compared to calcium with cubic close packed structure.

Note

Alkaline earth metals have high melting and boiling points than alkali metals. This is because alkaline earths use two electrons per atom in forming metallic bonds while alkali metals use only one electron. Therefore, there is stronger metallic bond in alkaline earths than in alkali metals.

5.2.3 Ionisation energy

Table 5.4 First ionisation energies of group(II) elements

Element	*Be*	*Mg*	*Ca*	*Sr*	*Ba*
First ionisation energy / KJmol^{-1}	900	738	590	549	502

Ionisation energy reduces down the group. Down the group, nuclear charge increases as well as screening effect. The increase in screening effect outweighs the increase in nuclear charge due to an extra shell of electrons added down the group. Effective nuclear charge therefore decreases down the group leading to decrease in ionisation energy.

5.2.4 Enthalpy of sublimation / atomisation

This reduces down the group due to decrease in metallic bond strength.

5.2.5 Enthalpy of hydration

Table 5.5 Enthalpies of hydration of group(II) cations

Cation	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Enthalpy of hydration / KJmol^{-1}	-2455	-1900	-1565	-1415	-1275

Enthalpy of hydration reduces down the group. This is due to increase in ionic radius of the cation down the group which causes a decrease in charge density. The lower the charge density, the lower the hydration energy.

5.2.6 Standard electrode potentials

Table 5.6 Standard Electrode potentials of group(II) elements

Element	*Be*	*Mg*	*Ca*	*Sr*	*Ba*
Electrode potential / V	-1.85	-2.37	-2.87	-2.89	-2.91

Electrode potentials, for metals, depend on sublimation energy, ionisation energy and hydration energy (*Section 3.5*)

Generally, standard electrode potentials increase down the group. This is because down the group, enthalpy of sublimation, hydration energy, and ionisation energy decrease. The decrease in enthalpy of sublimation and ionisation energy is more rapid than decrease in hydration energy. Electrode potentials thus become more negative down the group.

Note

Beryllium has a very small ionic radius, high sublimation energy, and high ionisation energy. Its high ionisation energy and sublimation energy almost offset its high hydration energy. This makes its electrode potential the least negative.

The alkali metals (group I) have higher negative electrode potentials than alkaline earth metals. This is because alkali metals have relatively lower heats of sublimation and ionisation energy compared to alkaline earth metals. This makes the electrode potentials of group I elements large and negative, despite their low enthalpies of hydration.

Barium, strontium, and calcium are in group II but have higher electrode potentials than sodium. This is because the ionisation energies of barium, strontium, and calcium are higher than that of sodium. Although their ionisation energies are higher, their hydration energies are higher than that of sodium due to their higher charge density compared to that of sodium. The sublimation energies of barium, strontium, and calcium are fairly small.

5.3 Chemical properties of alkaline earth metals

5.3.1 Introduction

The metals are very reactive but less so than alkali metals. Reactivity increases with increasing atomic number (down the group) due to decrease in ionisation energy and increase in electrode potential.

Due to decrease in electrode potentials down the group, elements become stronger reducing agents in aqueous solutions, as the group is descended.

5.3.2 With water

Beryllium does not react with water, even when heated.

Magnesium burns brilliantly when heated in steam to give its oxide and hydrogen gas.

$$Mg(\mathrm{s}) + H_2O(\mathrm{g}) \longrightarrow MgO(\mathrm{s}) + H_2(\mathrm{g})$$

Some literatures suggest a slow reaction between magnesium and cold water forming a hydroxide and hydrogen gas.

Calcium, strontium, and barium react with cold water to liberate hydrogen gas and a corresponding hydroxide.

$$Ca(\mathrm{s}) + 2H_2O(\mathrm{l}) \longrightarrow Ca(OH)_2(\mathrm{aq}) + H_2(\mathrm{g})$$

5.3.3 With air

All group II elements tarnish in damp air due to formation of a layer of an oxide that later forms a hydroxide and a carbonate; for example in the case of calcium below.

$$2Ca(s) + O_2(g) \longrightarrow 2CaO(s)$$

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$$

$$Ca(OH)_2(aq) + CO_2(g) \longrightarrow CaCO_3(aq) + H_2O(l)$$

All the metals react with air on heating to form an oxide, alongside some nitride.

$$2Mg(\mathrm{s}) + O_2(\mathrm{g}) \longrightarrow 2MgO(\mathrm{s})$$

$$3Mg(\mathrm{s}) + N_2(\mathrm{g}) \longrightarrow Mg_3N_2(\mathrm{s})$$

If the product is damped and warmed, ammonia is evolved.

$$Mg_3N_2(\mathrm{s}) + 6H_2O(\mathrm{l}) \longrightarrow 3Mg(OH)_2(\mathrm{s}) + 2NH_3(\mathrm{g})$$

On prolonged heating in oxygen under pressure, barium and strontium form peroxides of the type MO_2.

5.3.4 With acids

Dilute non oxidising acids, e.g. dilute hydrochloric acid and dilute sulphuric acid, react with the metals to form salts and hydrogen gas.

$$Mg(\text{s}) + H_2SO_4(\text{aq}) \longrightarrow MgSO_4(\text{aq}) + H_2(\text{g})$$

$$Ca(\text{s}) + 2HCl(\text{aq}) \longrightarrow CaCl_2(\text{aq}) + H_2(\text{g})$$

With beryllium, the reaction takes place on warming.

Hot concentrated sulphuric acid oxidises the metals to metal sulphates while it is its self reduced to sulphur dioxide and water.

$$Mg(\text{s}) + 2H_2SO_4(\text{l}) \longrightarrow MgSO_4(\text{aq}) + 2H_2O(\text{l}) + SO_2(\text{g})$$

Very dilute nitric acid does not react with the metals apart from magnesium. Magnesium reacts slowly to form hydrogen gas and magnesium nitrate.

$$Mg(\text{s}) + 2HNO_3(\text{aq}) \longrightarrow Mg(NO_3)_2(\text{aq}) + H_2(\text{g})$$

Hot moderately concentrated nitric acid **oxidises** the metals to nitrates while it is its self reduced to nitrogen monoxide (or nitrogen dioxide if the concentration of the acid is fairly high)

e.g. $3Ca(\text{s}) + 8HNO_3(\text{aq}) \longrightarrow 3Ca(NO_3)_2(\text{aq}) + 2NO(\text{g}) + 4H_2O(\text{l})$

$3Ba(\text{s}) + 8HNO_3(\text{aq}) \longrightarrow 3Ba(NO_3)_2(\text{aq}) + 2NO(\text{g}) + 4H_2O(\text{l})$

5.3.5 With alkalis

With exception of beryllium, the elements do not react with alkalis. Beryllium reacts with concentrated alkalis to form complex salts.

$$Be(\text{s}) + 2\bar{O}H(\text{aq}) + 2H_2O(\text{l}) \longrightarrow Be(OH)_4^{2-}(\text{aq}) + H_2(\text{g})$$

5.3.6 With chlorine

The elements react with chlorine on heating to form corresponding chlorides.

$$Mg(\text{s}) + Cl_2(\text{g}) \longrightarrow MgCl_2(\text{s})$$

5.3.7 With hydrogen

With exception of beryllium, the metals react with hydrogen to form corresponding hydrides e.g.

$$Ca(\text{s}) + H_2(\text{g}) \longrightarrow CaH_2(\text{s})$$

5.4 Compounds of group (II) elements

5.4.1 Introduction

They form white compounds in solid state which are largely ionic. They show an oxidation state of +2. Beryllium compounds are largely covalent due to a very high charge density (polarising power) of its ions. Magnesium compounds show appreciable covalent character too. Beryllium has a diagonal relationship with aluminium and thus their chemistry is similar. The chemistry of magnesium is slightly different from that of the rest of the elements.

5.4.2 Chlorides of group(II) elements

The chlorides include beryllium chloride ($BeCl_2$), magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), strontium chloride ($SrCl_2$), and barium chloride ($BaCl_2$).

5.4.2.1 Preparation

Anhydrous magnesium chloride is best prepared by heating magnesium in a current of dry chlorine gas or hydrogen chloride.

$$Mg(\mathrm{s}) + Cl_2(\mathrm{g}) \longrightarrow MgCl_2(\mathrm{s})$$

$$Mg(\mathrm{s}) + 2HCl(\mathrm{g}) \longrightarrow MgCl_2(\mathrm{s}) + H_2(\mathrm{g})$$

Hydrated magnesium chloride ($MgCl_2.6H_2O$) is prepared by crystallisation from its solution in water. Excess magnesium, its oxide, hydroxide, or carbonate is reacted with dilute hydrochloric acid to give a solution. The mixture is filtered, evaporated and cooled to crystallize hydrated magnesium chloride. The other chlorides are prepared similarly.

The chlorides are very deliquescent. Calcium chloride is very cheap and thus the anhydrous salt is used to dry gases and organic liquids. It can, however, not be used to dry ammonia and ethanol since it reacts with them to form complexes.

When heated, hydrated magnesium chloride is hydrolysed by its water of crystallisation to magnesium oxide (*see section 5.4.2.3 below*). For this reason, anhydrous magnesium chloride cannot be prepared by evaporation of an aqueous solution of magnesium chloride.

5.4.2.2 Melting points

Table 5.7 Melting points of chlorides of group(II) elements

Chloride	$BeCl_2$	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$
melting point/°C	405	714	782	875	962

Melting points generally increase down the group. This is because down the group, ionic radius of the cation increases with constant charge. This reduces charge density of the cation down the group hence polarising power reduces. This increases the ionic character of the chlorides down the group thus an increase in melting point.

5.4.2.3 Hydrolysis of the chlorides

Beryllium chloride is hydrolysed by water to form beryllium hydroxide and hydrogen chloride gas.

$$BeCl_2(s) + 2H_2O(l) \rightleftharpoons Be(OH)_2(s) + 2HCl(g)$$

Magnesium chloride only undergoes partial hydrolysis.

$$MgCl_2(s) + H_2O(l) \rightleftharpoons Mg(OH)Cl(s) + HCl(g)$$

When heated, hydrated magnesium chloride is hydrolysed by its water of crystallisation. It is therefore not possible to obtain the anhydrous chloride by evaporation of its aqueous solution.

$$MgCl_2(s) + H_2O(l) \longrightarrow MgO(s) + 2HCl(g)$$

Calcium chloride is only hydrolysed to a small extent to form calcium oxide or calcium hydroxide. Strontium chloride and barium chloride are not hydrolysed.

5.4.3 Oxides of group(II) elements

5.4.3.1 Preparation

Normal oxides are formed when the metals are heated in oxygen. Strontium and barium also form peroxides (BaO_2 and SrO_2) on prolonged heating.

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

Oxides are also prepared by heating carbonates or nitrates of the metals e.g.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

$$2Mg(NO_3)_2(s) \longrightarrow 2MgO(s) + 4NO_2(g) + O_2(g)$$

5.4.3.2 Reaction with water

Beryllium oxide is covalent and therefore does not react with water. The other oxides are largely ionic and sparingly dissolve in water forming corresponding hydroxides e.g.

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$$

5.4.3.3 With alkalis

Apart from beryllium oxide, which is amphoteric, all the other oxides are basic. Therefore only beryllium oxide reacts with alkalis to form complex salts.

$$BeO(s) + 2\bar{O}H(aq) + H_2O(l) \longrightarrow Be(OH)_4^{2-}(aq)$$

5.4.3.4 With acids

All the oxides react with dilute acids to form salts and water only e.g.

$$MgO(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l)$$

5.4.4 Hydroxides of group(II) elements

5.4.4.1 Preparation

They are white solids prepared by addition of sodium hydroxide to a solution containing the metal ions. Beryllium hydroxide cannot be prepared this way because it is amphoteric and therefore dissolves in excess sodium hydroxide.

$$Mg^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Mg(OH)_2(s)$$

$$Ca^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Ca(OH)_2(s)$$

They can also be prepared by dissolving the oxide of the metal in water e.g.

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$$

5.4.4.2 Solubility of the hydroxides

Solubility depends on lattice energy and hydration energy; it increases with increase in hydration energy and decreases with increase in lattice energy. However, for very small anions of high charge density, the changes in lattice energy decide the trend in solubility.

Solubility of the hydroxides increases down the group.

Down the group, both lattice energy and hydration energy decrease. Since the hydroxide ion is small, solubility will largely depend on lattice energy which decreases down the group. As a result of decrease in lattice energy down the group, solubility will also ~~decrease~~ Increases in the same direction. Solubility of other compounds of group(II) elements with small anions, for example chlorides, also follows the same trend. However, solubility of compounds with large anions takes the reverse trends – *section 5.4.5.2.*

5.4.4.3 Reaction of the hydroxides with alkalis

Apart from beryllium hydroxide, which is amphoteric, hydroxides of group(II) do not react with alkalis.

$$Be(OH)_2(s) + 2\bar{O}H(aq) \longrightarrow Be(OH)_4^{2-}(aq)$$

5.4.5 Sulphates of group(II) elements

5.4.5.1 Preparation

These are prepared by adding sulphate ions (e.g. from sodium sulphate) to a solution containing the metal ion.

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$$

$$Ca^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow CaSO_4(s)$$

Beryllium sulphate and magnesium sulphate are very soluble in water, therefore they are prepared by reacting their oxides or hydroxides with dilute sulphuric acid for example:

$$BeO(s) + H_2SO_4(aq) \rightarrow BeSO_4(aq) + H_2O(l)$$

5.4.5.2 Solubility of the sulphates

Table 5.8 Solubility of sulphates of group(II) elements

sulphate	$BeSO_4$	$MgSO_4$	$CaSO_4$	$SrSO_4$	$BaSO_4$
solubility (g/100g of water at 25°C)	43.00	35.50	0.18	0.01	0.0024

Solubility of the sulphates reduces down the group. Down the group, both hydration energy and lattice energy decrease. However, for large anions, changes in enthalpies of hydration of the cation decide the trend of solubility. Since the sulphate ion is large and hydration energy of the cations reduce down the group, solubility will also reduce down the group (*Compare with solubility of the hydroxides - section 5.4.4.2*). Solubility of carbonates and chromates takes similar trend because these anions are also large.

5.4.6 Carbonates of group(II) elements

5.4.6.1 Preparation

These are precipitated as white solids on addition of carbonate ions to a solution containing the metal ions e.g.

$$Ca^{2+}(\text{aq}) + CO_3^{2-}(\text{aq}) \longrightarrow CaCO_3(\text{s})$$

However, magnesium carbonate is obtained by using sodium hydrogen carbonate, since using sodium carbonate precipitates a basic carbonate of the formula $MgCO_3.Mg(OH)_2.4H_2O$

$$Mg^{2+}(\text{aq}) + 2HCO_3^-(\text{aq}) \longrightarrow MgCO_3(\text{s}) + H_2O(\text{l}) + CO_2(\text{g})$$

5.4.6.2 Thermal stability of the carbonates

Table 5.9 Dissociation temperatures of group(II) carbonates

carbonate	$BeCO_3$	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
dissociation temperature /°C	25	540	900	1290	1360

Temperature at which the carbonates decompose increase down the group thus thermal stability increases down the group due to increase in electropositivity of the metal down the group.

Beryllium ion has a very small radius and high charge (high charge density). Beryllium carbonate therefore has a very high covalent character thus an abnormally low decomposition temperature. Ionic radius increases down the group thus a decrease in charge density and increase in ionic character.

5.4.7 Phosphates of group(II)

Phosphates are salts derived from phosphoric(V) acid, H_3PO_4. The acid is tri-basic thus can be neutralised by sodium hydroxide in stages, forming sodium dihydrogen phosphate(V) (NaH_2PO_4) in the first stage and disodium hydrogen phosphate (Na_2HPO_4) in the second stage.

$$NaOH(\text{aq}) + H_3PO_4(\text{aq}) \longrightarrow NaH_2PO_4(\text{aq}) + H_2O(\text{l})$$

$$NaH_2PO_4\ (\text{aq}) + NaOH(\text{aq}) \longrightarrow Na_2HPO_4(\text{aq}) + H_2O(\text{l})$$

The third stage, leading to formation of trisodium phosphate(V), cannot be realised practically since the salt is highly hydrolysed in aqueous solution.

$$Na_3PO_4(\text{aq}) + H_2O(\text{l}) \rightleftharpoons NaOH(\text{aq}) + Na_2HPO_4(\text{aq})$$

Most phosphates of group(II) elements are insoluble in water but usually dissolve in presence of strong acids like hydrochloric acid.

Magnesium ammonium phosphate is formed as a white precipitate when disodium hydrogen phosphate or sodium phosphate is added to a solution containing magnesium ions in presence ammonium chloride and ammonia.

$$Mg^{2+}(aq) + NH_4^+(aq) + PO_4^{3-}(aq) + 6H_2O(l) \longrightarrow MgNH_4PO_4.6H_2O(s)$$

A white precipitate of calcium phosphate is also formed when disodium hydrogen phosphate is added to a solution containing calcium ions.

$$3Ca^{2+}(aq) + 2HPO_4^{2-}(aq) + 2\bar{O}H(aq) \longrightarrow Ca_3(PO_4)_2(s) + 2H_2O(l)$$

Calcium phosphate can be converted to super phosphate by treatment with 70% sulphuric acid solution.

$$Ca_3(PO_4)_2(s) + 2H_2SO_4(aq) \longrightarrow Ca(H_2PO_4)_2(s) + 2CaSO_4(s)$$

5.4.8 Carbides

5.4.8.1 Preparation

Beryllium carbide is prepared by heating the elements beryllium and carbon at temperatures above 900°C. It also may be prepared by reduction of beryllium oxide with carbon at a temperature above 1500°C.

$$2BeO(s) + 3C(s) \longrightarrow Be_2C(s) + 2CO(g)$$

Calcium carbide is produced by heating a mixture of lime and coke at 2000 °C in an electric furnace from.

$$CaO(s)\ +\ 3C(s) \longrightarrow CaC_2(s)\ +\ CO(s)$$

Calcium carbide is used in the manufacture of acetylene (ethyne) - *see its reaction with water below.*

5.4.8.2 Reaction with water

Beryllium carbide decomposes very slowly in water.

$$Be_2C(s) + 2H_2O(l) \longrightarrow 2BeO(s) + CH_4(g)$$

The rate of decomposition is faster in mineral acids with evolution of methane.

$$Be_2C(s) + 4\ H^+(aq) \longrightarrow 2Be^{2+}(aq) + CH_4(g)$$

However, in hot concentrated alkali the reaction is very rapid, forming alkali metal beryllates and methane:

$$Be_2C(s) + 4\bar{O}H(aq) \longrightarrow 2BeO_2^{2-}(aq) + CH_4(g)$$

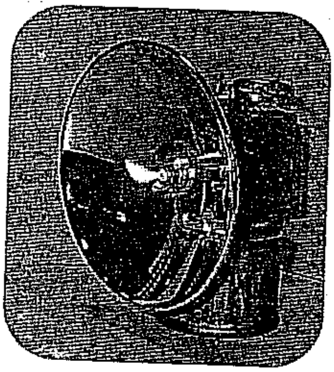
The reaction of calcium carbide with water was discovered by Friedrich Wöhler in 1862. It reacts with water to form acetylene (ethyne) and calcium hydroxide.

$$CaC_2(s) + 2H_2O(l) \longrightarrow C_2H_2(g) + Ca(OH)_2(aq)$$

This reaction is the basis of the industrial manufacture of acetylene, and is the major industrial use of calcium carbide.

Calcium carbide is used:

- in the desulfurisation of iron.
- as a fuel in steelmaking and carbide lamps
- as a powerful deoxidizer at ladle treatment facilities.



A carbide lamp

Carbide lamps were usable but dangerously in coal mines, where the presence of the flammable gas methane made them a serious hazard. However, carbide lamps were used extensively in slate, copper and tin mines, but most have now been replaced by electric lamps. Carbide lamps are still used for mining in some less wealthy countries. They are also still used by some cavers exploring caves and other underground areas though they are increasingly being replaced in this use by LED lights. They were also used extensively as headlights in early automobiles, motorcycles and bicycles, although in this application they are also obsolete, having been replaced entirely by electric lamps.

5.4.9 Complex formation

A complex ion is an ion that contains a central ion or atom linked to other atoms, ions or molecules via coordinate bonds.

Tendency of group II elements to form complexes decreases down the group due to decreasing charge density of the cation.

Beryllium forms several complexes including tetrafluoro beryllate(II) ions (BeF_4^{2-}), tetrahydroxo beryllate(II) ions ($Be(OH)_4^{2-}$), and tetra aqua beryllium(II) ions ($Be(H_2O)_4^{2+}$) among others.

Magnesium complexes with chlorophyll and EDTA. Calcium complexes with ethanol, $Ca(CH_3CH_2OH)_4^{2+}$.

5.5 Analysis of magnesium, calcium, and barium ions

Tests for the cations are mainly based on their reactions with alkalis that result into formation of precipitates.

5.5.1 Using sodium hydroxide solution

To the solution suspected to contain any of the cations, sodium hydroxide is added dropwise until in excess.

Formation of a white precipitate insoluble in excess shows presence of Mg^{2+}, Ca^{2+}, or Ba^{2+}.

$$Mg^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Mg(OH)_2(s)$$
$$Ca^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Ca(OH)_2(s)$$
$$Ba^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Ba(OH)_2(s)$$

5.5.2 Using aqueous ammonia

To the solution suspected to contain any of the cations, ammonia solution is added dropwise until in excess.

Formation of a white precipitate insoluble in excess shows presence of Mg^{2+} or Ba^{2+}.

$$Mg^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Mg(OH)_2(s)$$
$$Ba^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Ba(OH)_2(s)$$

Note:

Ammonium hydroxide does not precipitate calcium hydroxide. Not only is the concentration of hydroxyl ions from weakly basic ammonia too low to exceed the solubility product of calcium hydroxide, but there is also an ammine formation. Ammonium hydroxide in presence of ammonium chloride will not precipitate magnesium hydroxide. This is because presence of ammonium chloride provides a high concentration of ammonium ions which suppress ionisation of aqueous ammonia by reversing its equilibrium. There are therefore insufficient hydroxyl ions to exceed the solubility product of magnesium hydroxide.

$$NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$
$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$$

5.5.3 Using ammonium carbonate solution

Aqueous solutions containing Mg^{2+}, Ca^{2+}, and Ba^{2+} ions form white precipitates when ammonium carbonate solution is added. This is due to precipitation of corresponding carbonates.

However, in presence of ammonium chloride, magnesium ions will not form a precipitate when ammonium carbonate is added. This is because presence of ammonium chloride reduces the concentration of carbonate ions below that necessary to exceed the solubility product of magnesium carbonate.

$$NH_4^+(aq) + CO_3^{2-}(aq) \longrightarrow NH_3(aq) + HCO_3^-(aq)$$

5.5.4 Using sodium dihydrogen phosphate

To the solution of the unknown, add aqueous ammonia and ammonium chloride followed by sodium dihydrogen phosphate.

A white precipitate, of $MgNH_4PO_4$, shows presence of magnesium ions. Calcium ions and barium ions also give a similar observation – *Section 5.4.7.*

Note that disodium hydrogen phosphate may be used instead of sodium dihydrogen phosphate.

5.5.5 Using dilute sulphuric acid

Dilute sulphuric acid form a white precipitate when added to a solution containing calcium or barium ions.

$$Ca^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow CaSO_4(s)$$

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$$

However, calcium sulphate is soluble in excess acid due to complex formation.

$$CaSO_4(s) + SO_4^{2-}(aq) \longrightarrow Ca(SO_4)_2^{2-}(aq)$$

Note

Sulphuric acid does not precipitate magnesium sulphate thus this test can be used to distinguish Mg^{2+} from Ca^{2+} and Ba^{2+} ions.

5.5.6 Using ammonium oxalate and ethanoic acid

Ammonium oxalate forms a white precipitate with a solution containing calcium ions or barium ions.

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \longrightarrow CaC_2O_4(s)$$

$Ba^{2+}(aq) + C_2O_4^{2-}(aq) \longrightarrow BaC_2O_4(s)$

Calcium oxalate is insoluble in ethanoic acid but barium oxalate is soluble thus the white precipitate dissolves in ethanoic acid in case of barium ions.

5.5.7 Using potassium chromate(VI) and ethanoic acid

Potassium chromate(VI) forms a yellow precipitate when added to a solution containing calcium or barium ions.

$Ca^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow CaCrO_4(s)$

$Ba^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow BaCrO_4(s)$

Calcium chromate (yellow precipitate) is soluble in ethanoic acid but barium chromate is insoluble.

5.5.8 Using potassium chromate(VI) and sodium hydroxide

Potassium chromate(VI) forms a yellow precipitate when added to a solution containing calcium or barium ions.
Calcium chromate (yellow precipitate) is soluble in sodium hydroxide but barium chromate is not.

5.6 Summary

Group(II) elements are quite reactive but less so than group(I) elements. In this chapter we have discussed the reactions of group(II) elements and their compounds with water, acids, and alkalis.

5.7 Suggested further reading on chapter 5

G. F. Liptrot, *Mordern Inorganic Chemistry*, Scotprint Ltd, Fourth Edition, 1983.
A. Holderness, Advanced Level Inorganic Chemistry, Thomson Press, Third Edition, 1979
W. R. Kneen, *Chemistry, Facts, Patterns and Principles*, Addison-Wesley Pub (Sd), 1972

5.6 Questions on chapter 5

1. (a) Starting from calcium carbonate, outline, using equations only one method of preparing each of the following.
    (i) Calcium hydroxide.
    (ii) Calcium carbide.

(b) Using suitable examples to illustrate your answer, explain the following:
  (i) anhydrous calcium chloride is commonly contaminated with calcium oxide.
  (ii) Calcium carbonate is added to the furnace when smelting metal ores

2. Explain the following observations
  (a) Solubility of group(II) hydroxides increases down the group while the solubility of group(II) sulphates reduces down the group.
  (b) When aqueous ammonia is added to a solution of magnesium nitrate, a white precipitate is formed. However, in the presence of ammonium chloride, no precipitate is formed.
  (c) Aqueous ammonia forms a precipitate with barium ions but not with calcium ions.
  (d) Anhydrous magnesium chloride cannot be prepared from dilute hydrochloric acid and magnesium oxide.

3. (a) Draw a graph of melting points of group (II) elements and explain the shape.
  (b) Compare the trend in the solubilities of hydroxides and melting points of chlorides of group(II) elements and explain each trend.
  (c) Explain why salts of group(II) metals are generally less soluble than those of corresponding group(I) metals.

4. The table below shows the atomic and ionic radii of alkaline earth metals.

Element	Atomic radius /nm	Ionic radius /nm
Beryllium	0.112	0.030
Magnesium	0.160	0.065
Calcium	0.197	0.094
Strontium	0.215	0.110
Barium	0.221	0.134

  (a) Explain what is meant by;
    (i) atomic radius
    (ii) ionic radius
  (b) The ionic radius in each case is smaller than atomic radius. Explain.
  (c) Explain why the atomic radius increases from beryllium to barium.
  (d) The ions K^+ and Ca^{2+} have identical electronic configurations, yet K^+ is larger than Ca^{2+}. Explain this.

5. Discuss the reaction of beryllium, magnesium, calcium, and barium with;
   (a) water
   (b) acids
   (c) alkalis.

6. (a) Describe the general method of preparing chlorides of group(II) elements.
   (b) Discuss the reactivity of group(IV) chlorides with water.

7. Name one reagent that can be used to distinguish between the following pairs of ions. In each case, state what will be observed when each member of the pair is treated with the reagent you have named.
   (a) Mg^{2+}(aq) and Ca^{2+}(aq)
   (b) Mg^{2+}(aq) and Ba^{2+}(aq)
   (c) Ba^{2+}(aq) and Ca^{2+}(aq)

CHAPTER

6

GROUP IV ELEMENTS

Learning Objectives

After reading this chapter and completing the exercises you should be able to:

- Explain the variation of melting point, atomic and ionic radius, and ionisation energy down group(IV) elements
- Discuss reactions of group(IV) elements with water, sodium hydroxide and hydrochloric acid
- Discuss the physical properties of the oxides, chlorides and hydrides of group(IV) elements
- Describe the preparation of oxides, chlorides, and hydrides of group(IV) elements
- Discussion the reactions of oxides, chlorides, and hydrides of elements of group(IV) with water, alkalis, and dilute acids
- Explain the cause of the inert pair effect
- Appreciate the gradual change from non-metallic to metallic character down group(IV)

6.1 Introduction

The group consists of carbon, silicon, germanium, tin and lead. Carbon and silicon differ from each other and from the rest of group(IV) elements. The chemistry of germanium, tin and lead is generally similar. There is a strong diagonal relationship between silicon and boron which is in group(III) - *Section 2.1.2.*

Table 6.1 shows electronic configurations of group(IV) elements.

Table 6.1 Electronic configuration of group(IV) elements

Element	**Symbol**	**Atomic number**	**Configuration**
Carbon	C	6	$1s^2 2s^2 2p^2$
Silicon	Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Germanium	Ge	32	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
Tin	Sn	50	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2 4d^{10} 5p^2$
Lead	Pb	82	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^2$

6.2 Physical properties of group(IV) elements

6.2.1 Metallic character

Carbon and silicon are non-metals. Germanium has both metallic and non-metallic properties. Tin and lead are predominantly metallic.

6.2.2 Bonding and structure

Carbon consists of two main allotropes; graphite and diamond. Graphite is so contrast to diamond which is very hard.

Graphite

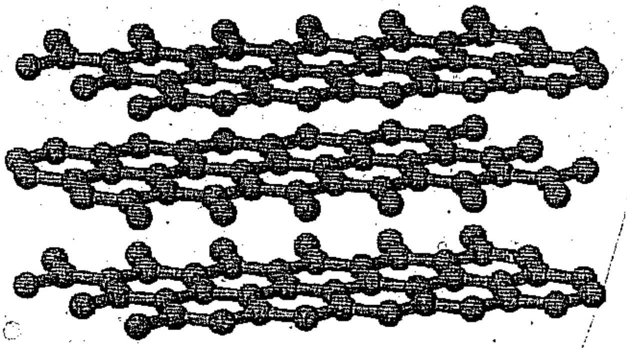


Figure 6.1 Graphite layers

In graphite, each carbon atom is b three others by covalent bonds fo hexagonal layers. The fourth vale electron is delocalised and is free along the layers. Therefore graphite c electricity along its layers. The la held by weak Van der Waals forc can slide over each other. Theref graphite is soft.

Diamond

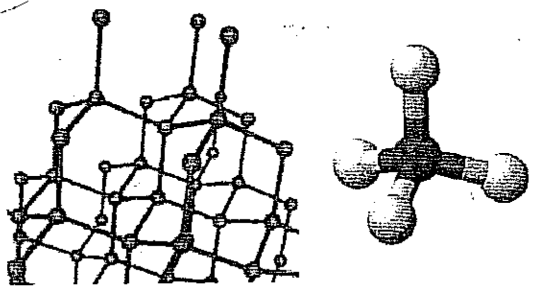


Figure 6.2 Diamond structure

In diamond, each carbon atom uses a valency electrons to form covalent bo four other carbon atoms. This results three dimensional giant atomic struct very high melting point. The structur tetrahedral shape. Since carbon uses valency electrons, diamond does not electricity. Silicon, germanium and ti diamond-like structures. Lead has a metallic structure.

6.2.3 Melting point

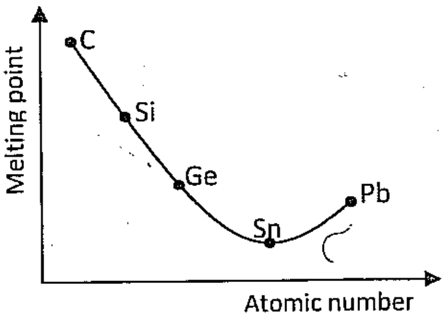


Figure 6.3 Variation of melting point d

Figure 6.3 shows a sketch for variatio melting points of group(IV) elements move down the group.

Melting points generally decrease do group from carbon to tin with an inc tin to lead.

Carbon forms a giant atomic structure with very many strong covalent bonds. This makes its melting point very high. From silicon to tin, the elements have diamond-like structures.

Down the group, there is an increase in atomic radius thus element-element bond length become longer and weaker. This explains the decrease in melting point. Lead has a metallic structure thus a higher melting point than tin.

6.3 Chemical properties of group(IV) elements

6.3.1 Introduction

The chemistry of carbon is significantly unique from the rest of the members of the group. Some of the unique features of carbon include;-

- **Catenation:** This is the direct bonding between atoms of the same element. Carbon has a small atomic radius thus is able to form strong carbon-carbon bonds.
- **Multiple bonding**: Carbon is able to form double and triple bonds with its self and with atoms of other elements such as oxygen and nitrogen.
- Formation of gaseous oxides.
- Formation of compounds that are relatively inert such as carbon tetrachloride does not hydrolyse while other tetrachlorides of group(IV) elements hydrolyse –*Section 6.4.3.2.*
- Carbon almost shows no inert pair effect.

The chemistry of silicon is also different from that of the rest of group(IV) elements but similar to that of boron, which belongs to group(III), due to diagonal relationship. The similarities between boron and silicon include;

- Both elements form acidic oxides.
- Their oxides react with metal oxides to form borates and silicates.
- Both their chlorides undergo hydrolysis to yield hydrogen chloride.
- Their hydrides are volatile and reactive.
- Both form a complex series of hydrides.
- Both form similar glassy materials.

6.3.2 Reaction with air

With exception of lead, group(IV) elements react with air on **heating** to form dioxides.

$$C(s) + O_2(g) \longrightarrow CO_2(g)\ ; \qquad Si(s) + O_2(g) \longrightarrow SiO_2(s)$$

$$Ge(s) + O_2(g) \longrightarrow GeO_2(s)\ ; \qquad Sn(s) + O_2(g) \longrightarrow SnO_2(s)$$

In insufficient oxygen, carbon forms poisonous carbon monoxide gas.

Lead quickly tarnishes in air by acquiring a thin layer of a hydroxide or carbonate. This protects it from further attack. When heated above its melting point, lead oxidises to a yellow lead(II) oxide. At high temperatures red lead oxide (*trilead tetraoxide*) is produced.

$$2Pb(l) + O_2(g) \longrightarrow 2PbO\ (s)$$

$$6PbO\ (s) + O_2(g) \longrightarrow 2Pb_3O_4(s)$$

6.3.3 Reaction with water

Carbon and silicon are not affected by cold water but, when **heated**, they react with **steam** to form oxides and hydrogen gas.

$$C(s) + H_2O(g) \longrightarrow CO(g) + 2H_2(g)$$

$$Si(s) + 2H_2O(g) \longrightarrow SiO_2(s) + 2H_2(g)$$

Germanium has no reaction with cold water or steam.
Tin has no reaction with cold water but displaces hydrogen from it at high temperatures.

$$Sn(s) + 2H_2O(l) \longrightarrow SnO_2(s) + 2H_2(g)$$

Pure soft water free from air does not attack lead. Presence of air, however, produces sparingly soluble lead(II) hydroxide.

$$2Pb(s) + 2H_2O(l) + O_2(g) \longrightarrow 2Pb(OH)_2(s)$$

6.3.4 With acids

6.3.4.1 Non-oxidising acids

Carbon, silicon and germanium do not react with dilute acids.
Silicon only reacts with hydrofluoric acid, owing to the stability of hexafluoro silicate(IV) complex, SiF_6^{2-}, formed.

$$Si(s) + 6HF(aq) \longrightarrow H_2SiF_6(aq) + 2H_2(g)$$

Tin reacts slowly with hot dilute acids to form hydrogen gas and a salt.

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

Hot concentrated hydrochloric acid attacks lead forming lead(II) chloride and hydrogen gas.

$$Pb(s) + 2HCl(aq) \longrightarrow PbCl_2(s) + H_2(g)$$

Lead reacts with ethanoic acid in presence of air to form lead(II) ethanoate.

$$Pb(s) + 3CH_3COOH(l) + O_2(g) \longrightarrow (CH_3COO)_2Pb(s) + H_2O(l)$$

6.3.4.2 Oxidising acids

With concentrated sulphuric acid

Concentrated sulphuric acid oxidises carbon, on heating, to carbon dioxide gas. Sulphur dioxide and water are also formed.

$$C(s) + 2H_2SO_4(l) \longrightarrow CO_2(g) + 2SO_2(g) + 2H_2O(l)$$

Silicon does not react with concentrated sulphuric acid.
Tin is oxidised by hot concentrated sulphuric acid to tin(IV) sulphate. Sulphur dioxide and water are also formed.

$$Sn(s) + 4H_2SO_4(l) \longrightarrow Sn(SO_4)_2(s) + 2SO_2(g) + 4H_2O(l)$$

Germanium undergoes a similar reaction to tin with the acid.
Hot concentrated sulphuric acid attacks lead to form lead(II) sulphate, sulphurdioxide and water.

$$Pb(s) + 2H_2SO_4(l) \longrightarrow PbSO_4(s) + SO_2(g) + 2H_2O(l)$$

With concentrated nitric acid

Warm concentrated nitric acid oxidises carbon to carbon dioxide while the acid is reduced to nitrogen dioxide and water.

$$C(s) + 4HNO_3(aq) \longrightarrow CO_2(g) + 4NO_2(g) + 2H_2O(l)$$

Silicon does not react with concentrated nitric acid.
Germanium forms germanium(IV) oxide, nitrogen monoxide and water.

$$3Ge(s) + 4HNO_3(aq) \longrightarrow 3GeO_2(s) + 4NO(g) + 2H_2O(l)$$

Tin forms tin(IV) oxide, nitrogen dioxide and water.

$$Sn(s) + 4HNO_3(aq) \longrightarrow SnO_2(g) + 4NO_2(g) + 2H_2O(l)$$

Very pure nitric acid (almost water free) is said not to attack lead. Any other concentration of the acid attacks lead to form lead(II) nitrate, water, and oxides of nitrogen.

$$3Pb(s) + 8HNO_3(aq) \longrightarrow 3Pb(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

Summary of the reactions

Acid	Reaction	Comments
Hot concentrated hydrochloric acid	$M(s) + 2H^+(aq) \longrightarrow M^{2+}(aq) + H_2(g)$	Only tin and lead undergo this reaction
Hot concentrated sulphuric acid	$C(s) + 2H_2SO_4(l) \longrightarrow CO_2(g) + 2SO_2(g) + 2H_2O(l)$ $M(s) + 4H_2SO_4(l) \longrightarrow M(SO_4)_2(s) + 2SO_2(g) + 4H_2O(l)$ $Pb(s) + 2H_2SO_4(l) \longrightarrow PbSO_4(s) + SO_2(g) + 2H_2O(l)$	$M = Sn$ or Ge
Warm concentrated nitric acid	$M(s) + 4HNO_3(aq) \longrightarrow MO_2(g) + 4NO_2(g) + 2H_2O(l)$ $3Ge(s) + 4HNO_3(aq) \longrightarrow 3GeO_2(s) + 4NO(g) + 2H_2O(l)$ $3Pb(s) + 8HNO_3(aq) \longrightarrow 3Pb(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$	$M = C$ or Sn
Hydrofluoric acid	$Si(s) + 6HF(aq) \longrightarrow H_2SiF_6(aq) + 2H_2(g)$	No reaction with other metals

6.3.5 With alkalis

Carbon does not react with alkalis.

Silicon reacts with alkalis to liberate hydrogen gas and silicates.

$$Si(s) + 2\bar{O}H(aq) + H_2O(l) \longrightarrow SiO_3^{2-}(aq) + 2H_2(g)$$

Germanium and tin undergo a similar reaction to silicon to form germanate(IV) ions and stannate(IV) ions respectively.

$$Ge(s) + 2\bar{O}H(aq) + H_2O(l) \longrightarrow GeO_3^{2-}(aq) + 2H_2(g)$$

$$Sn(s) + 2\bar{O}H(aq) + H_2O(l) \longrightarrow SnO_3^{2-}(aq) + 2H_2(g)$$

Lead is attacked by hot concentrated alkali to give plumbate(II) ions and hydrogen gas.

$$Pb(s) + 2\bar{O}H(aq) \longrightarrow PbO_2^{2-}(aq) + H_2(g)$$

Note

GeO_3^{2-}, SnO_3^{2-}, and PbO_2^{2-} are often written in hydrated form as $Ge(OH)_6^{2-}$, $Sn(OH)_6^{2-}$ and $Pb(OH)_6^{4-}$ respectively. It is therefore not un-common to find the above equations written as;

$$Ge(s) + 2\bar{O}H(aq) + 4H_2O(l) \longrightarrow Ge(OH)_6^{2-}(aq) + 2H_2(g)$$

$$Sn(s) + 2\bar{O}H(aq) + 4H_2O(l) \longrightarrow Sn(OH)_6^{2-}(aq) + 2H_2(g)$$

$$Pb(s) + 4\bar{O}H(aq) + 2H_2O(l) \longrightarrow Pb(OH)_6^{4-}(aq) + H_2(g)$$

6.3.6 With chlorine

With exception of lead, all the elements combine with chlorine to form tetrachlorides. Lead forms lead(II) chloride.

$$Ge(s) + 2Cl_2(g) \longrightarrow GeCl_4(s)$$

$$Pb(s) + Cl_2(g) \longrightarrow PbCl_2(s)$$

6.3.7 With sulphur

They all react with to form disulphides except lead which forms lead(II) sulphide.

$$C(s) + 2S(s) \longrightarrow CS_2(l)$$

$$Pb(s) + S(s) \longrightarrow PbS(s)$$

6.4 Compounds of group(IV) elements

6.4.1 Introduction

Group(IV) elements form compounds in two oxidation states; +2 and +4. The stability of +2 oxidation state increases down the group while stability of +4 oxidation state reduces down the group due to inert pair effect.

Inert pair effect

This is the inability of the s-electrons of the outer quantum shell to take part in chemical bonding.

Consider the electronic configurations below;

Carbon	$1s^2 2s^2 2p^2$
Silicon	$1s^2 2s^2 2p^6 3s^2 3p^2$
Germanium	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
Tin	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$
Lead	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^2$

For carbon and silicon, the outer s-electrons are shielded by **1s** and **2p** sub-energy levels respectively. For germanium, tin and lead, the outer s-electrons are shielded by **3d, 4d** and **5d** sub-energy levels respectively. Screening efficiency increases in the order **d<p<s.** Therefore in case of germanium, tin and lead (as you move down the group), the **d**-electrons poorly shield the outer s-electrons thus the nucleus strongly attracts the outer s-electrons causing their failure to un-pair. This causes the inert pair effect. Carbon and silicon hardly suffer any inert pair effect because the s and p electrons effectively shield the nuclear attraction of the outer p electrons.

Chapter 6 Group IV Elements

Carbon and silicon form no stable compounds in +2 oxidation state e.g. carbon monoxide is unstable and is a reducing agent while silicon monoxide is not known. Germanium(IV) compounds are more stable than germanium(II) compounds. Consequently, germanium(II) compounds are reducing agents.

Tin(IV) compounds are slightly more stable than tin(II) compounds. Consequently, tin(II) compounds are weak reducing agents. Tin(II) compounds are predominantly ionic.

Lead forms compounds in both +2 and +4 oxidation state, the +2 oxidation state being more stable. Therefore lead(IV) compounds tend to revert to lead(II) compounds by accepting electrons. Consequently, lead(IV) compounds are oxidising agents. Lead(II) compounds are mainly ionic while lead(IV) compounds are mainly covalent.

Due to the inert pair effect;

- Carbon monoxide is unstable and can easily be oxidised to carbon dioxide by air.

  $$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$

- Silicon monoxide is unstable and only exists in vapour state at 23000°C while silicon dioxide is widely distributed.
- Germanium forms oxides in both +2 and +4 oxidation states but germanium(IV) oxide is more stable than germanium(II) oxide.
- Tin(II) compounds are reducing agents.

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

- Lead(IV) oxide easily decomposes to lead(II) oxide on heating.

  $$2PbO_2(s) \xrightarrow{heat} 2PbO\ (s) + O_2(g)$$

$$CO_3^{2-}(aq) + 2H^+(aq) \longrightarrow CO_2(g) + H_2O(l)$$

Germanium(II) oxide is prepared by reducing germanium(IV) oxide with germanium.

$$GeO_2(s) + Ge(s) \longrightarrow 2GeO(s)$$

Tin(II) oxide and lead(II) oxide are prepared by action of heat on their hydroxides, nitrates or oxalates e.g.

$$Sn(OH)_2\ (s) \longrightarrow SnO(s) + H_2O(l)$$

$$SnC_2O_4(s) \longrightarrow SnO(s) + CO_2(g) + CO(g)$$

Silicon(IV) oxide, germanium(IV) oxide and tin(IV) oxide are prepared by heating the elements in oxygen e.g.

$$Ge(s) + O_2(g) \longrightarrow GeO_2(s)$$

Lead(IV) oxide is prepared by treating trilead tetraoxide with dilute nitric acid. It can also be obtained by oxidising a lead(II) salt using warm sodium chlorate(I).

$$Pb_3O_4(s) + 4HNO_3(aq) \longrightarrow 2Pb(NO_3)_2(aq) + PbO_2(s) + 2H_2O(l)$$

$$Pb^{2+}(aq) + ClO^-(aq) + H_2O(l) \longrightarrow PbO_2(s) + Cl^-(aq) + 2H^+(aq)$$

6.4.2.3 Melting point

Table 6.2 Melting points of dioxides of group(IV)

Oxide	CO_2	SiO_2	GeO_2	SnO_2	PbO_2
Melting point/°C	-56.5	1700	1116	1827	752 (*decomposes*)

Carbon dioxide is simple molecular thus a low melting point. Silicon dioxide forms a giant molecular structure with many covalent bonds that have to be broken before melting occurs. This explains its high melting point. The rest of the oxides adopt intermediate molecular and ionic structures.

6.4.2.4 Basicity of the oxides

Element	**Monoxide**	**Nature**	**Dioxide**	**Nature**
Carbon	CO	Weakly acidic	CO_2	Acidic
Silicon	-	-	SiO_2	Acidic
Germanium	GeO	Amphoteric	GeO_2	Amphoteric
Tin	SnO	Amphoteric	SnO_2	Amphoteric
Lead	PbO	Amphoteric	PbO_2	Amphoteric

Basic character increases down the group. For an individual element, basic character increases with decreasing oxidation number e.g. CO is weakly acidic but CO_2 is acidic. Carbon monoxide is slightly acidic and reacts with a hot solution of sodium hydroxide to form sodium methanoate

$$CO(\mathrm{g}) + NaOH(\mathrm{aq}) \xrightarrow{heat} HCOONa\ (\mathrm{s})$$

GeO, SnO and PbO are amphoteric though predominantly basic. They form salts with acids and also react with alkalis to form complex salts – *Section 6.4.2.5.*

Carbondioxide and silicon(IV) oxide are acidic and react with concentrated alkali solutions to form carbonates and silicates respectively.

GeO_2 SnO_2 and PbO_2 are amphoteric though acidic character predominates. They react with alkalis to form complex salts that have the general formula $M(OH)_6^{2-}$.

Basic character also increases on decreasing the oxidation number of the element for example lead(II) oxide is more basic than lead(IV) oxide.

6.4.2.5 Reaction with alkalis

All the dioxides react with hot concentrated alkalis to give solutions containing complex salts of the general formula $M(OH)_6^{2-}$ (*often written in dehydrated form as* MO_3^{2-}).

Carbon dioxide is more acidic than other dioxides thus it can react with dilute alkalis.

Carbondioxide reacts with dilute sodium hydroxide to form sodium carbonate.

Silicon dioxide reacts with hot concentrated sodium hydroxide solution to form sodium silicate and water.

Germanium dioxide reacts with hot concentrated alkalis to form hexahydroxo germanate (IV) ions.

Tin(IV) oxide and lead(IV) oxide undergo a similar reaction to germanium(IV) oxide.

The equations for the reactions are summarized below;

$$CO_2(\mathrm{g}) + 2\bar{O}H(\mathrm{aq}) \longrightarrow CO_3^{2-}(\mathrm{aq}) + H_2O(\mathrm{l})$$

$$SiO_2(\mathrm{s}) + 2\bar{O}H\ (\mathrm{aq}) \longrightarrow SiO_3^{2-}(\mathrm{s}) + H_2O(\mathrm{l})$$

$$GeO_2(\mathrm{s}) + 2\bar{O}H(\mathrm{aq}) + 2H_2O(\mathrm{l}) \longrightarrow Ge(OH)_6^{2-}(\mathrm{aq})$$

$$SnO_2(\mathrm{s}) + 2\bar{O}H(\mathrm{aq}) + 2H_2O(\mathrm{l}) \longrightarrow Sn(OH)_6^{2-}(\mathrm{aq})$$

$$PbO_2(\mathrm{s}) + 2\bar{O}H(\mathrm{aq}) + 2H_2O(\mathrm{l}) \longrightarrow Pb(OH)_6^{2-}(\mathrm{aq})$$

Or written in dehydrated form as;

$CO_2(\text{g}) + 2\bar{O}H(\text{aq}) \longrightarrow CO_3^{2-}(\text{aq}) + H_2O(\text{l})$

$SiO_2(\text{s}) + 2\bar{O}H\ (\text{aq}) \longrightarrow SiO_3^{2-}(\text{s}) + H_2O(\text{l})$

$GeO_2\ (\text{s}) + 2\bar{O}H(\text{aq}) \longrightarrow GeO_3^{2-}(\text{aq}) + H_2O(\text{l})$

$SnO_2(\text{s}) + 2\bar{O}H(\text{aq}) \longrightarrow SnO_3^{2-}(\text{s}) + H_2O(\text{l})$

$PbO_2(\text{s}) + 2\bar{O}H(\text{aq}) \longrightarrow PbO_3^{2-}(\text{s}) + H_2O(\text{l})$

However, when excess carbondioxide is passed through sodium hydroxide solution, sodium hydrogen carbonate is formed.

$CO_2(\text{g}) + 2NaOH(\text{aq}) \longrightarrow Na_2CO_3(\text{aq}) + H_2O(\text{l})$

$Na_2CO_3(\text{aq}) + H_2O(\text{l}) + CO_2(\text{g}) \longrightarrow 2NaHCO_3(\text{s})$

Carbonmonoxide reacts with sodium hydroxide, on heating, to form sodium methanoate

$$CO(\text{g}) + NaOH(\text{aq}) \xrightarrow{heat} HCOONa\ (\text{s})$$

The rest of the monoxides react with concentrated alkalis to form solutions containing complex salts of the general formula $M(OH)_6^{4-}$ (often written in dehydrated form as MO_2^{2-})

Germanium monoxide reacts with concentrated sodium hydroxide solution to form hexahydroxo germanate(II) complex ions. Tin(II) oxide and lead(II) oxide undergo a similar reaction. The reactions are summarized by equations below.

$$GeO(\text{s}) + 4\bar{O}H(\text{aq}) + H_2O(\text{l}) \longrightarrow Ge(OH)_6^{4-}(\text{aq})$$
$$SnO(\text{s}) + 2\bar{O}H(\text{aq}) + H_2O(\text{l}) \longrightarrow Sn(OH)_4^{2-}(\text{aq})$$
$$PbO(\text{s}) + 2\bar{O}H(\text{aq}) + H_2O(\text{l}) \longrightarrow Pb(OH)_4^{2-}\ (\text{aq})$$

Or written in dehydrated form as;

$$SnO(\text{s}) + 2\bar{O}H(\text{aq}) \longrightarrow SnO_2^{2-}(\text{aq}) + H_2O(\text{l})$$

and so on.

Summary of the reactions

Type of oxide	**Reaction**	**Comments**
Dioxides	$MO_2(\text{s or g}) + 2\bar{O}H\ (\text{aq}) \longrightarrow MO_3^{2-}(\text{s}) + H_2O(\text{l})$	$M = C, Si, Ge, Sn,$ *or* Pb
Monoxides	$CO(\text{g}) + NaOH(\text{aq}) \xrightarrow{heat} HCOONa\ (\text{aq})$ $MO(\text{s}) + 2\bar{O}H(\text{aq}) \longrightarrow MO_2^{2-}(\text{aq}) + H_2O(\text{l})$	$M = Sn, Ge$ *or* Pb

6.4.2.6 Reactions of the oxides with acids

Red lead usually reacts as if it was composed of lead(II) oxide and lead(IV) oxide. Consequently, it resembles lead(IV) oxide in its reactions as confirmed below.

With non-oxidising acids such as hydrochloric acid and dilute sulphuric acid

Dioxides

Carbondioxide and silicon dioxide are acidic and therefore do not react with dilute non-oxidising acids.

Silicon dioxide only reacts with dilute hydrofluoric acid to form silicon tetrafluoride.

$$SiO_2(\mathrm{s}) + 4HF(\mathrm{aq}) \longrightarrow SiF_4(\mathrm{g}) + 2H_2O(\mathrm{l})$$

Germanium(IV) oxide is amphoteric though the acidic character predominates. It therefore does not react with dilute acids.

Tin(IV) oxide is amphoteric and reacts with dilute acids to form tin(IV) salts and water.

Lead(IV) oxide is amphoteric and reacts with ice-cold concentrated hydrochloric acid to give lead(IV) chloride and water. The lead(IV) chloride formed readily decomposes to lead(II) chloride and water at normal temperatures.

$$PbO_2(\mathrm{s}) + 4HCl(\mathrm{aq}) \longrightarrow PbCl_4(\mathrm{l}) + 2H_2O(\mathrm{l})$$

With excess concentrated hydrochloric acid, a complex – *hexachloroplumbate(IV) ion* – is formed.

$$PbCl_4(\mathrm{l}) + 2Cl^-(\mathrm{aq}) \longrightarrow PbCl_6^{2-}(\mathrm{aq})$$

The above two reactions may be occur in one step as

$$PbO_2(\mathrm{s}) + 6HCl(\mathrm{aq}) \longrightarrow H_2PbCl_6(\mathrm{aq}) + 2H_2O(\mathrm{l})$$

Monoxides:

Carbon monoxide is slightly acidic and therefore does not react with dilute acids.

Germanium(II) oxide, tin(II) oxide and lead(II) oxide are amphoteric and react with dilute acids to give germanium(II), tin(II) and lead(II) salts respectively.

$$GeO(\mathrm{s}) + 2H^+(\mathrm{aq}) \longrightarrow Ge^{2+}(\mathrm{aq}) + H_2O(\mathrm{l})$$

$$SnO\ (\mathrm{s}) + 2H^+(\mathrm{aq}) \longrightarrow Sn^{2+}(\mathrm{aq}) + H_2O(\mathrm{l})$$

$$PbO\ (\mathrm{s}) + 2H^+(\mathrm{aq}) \longrightarrow Pb^{2+}(\mathrm{aq}) + H_2O(\mathrm{l})$$

However, the reaction of lead(II) oxide with dilute hydrochloric acid and dilute sulphuric acid gives insoluble lead(II) chloride and lead(II) sulphate respectively which retard the reaction.

With hot concentrated hydrochloric acid

Lead(IV) oxide oxidises warm concentrated hydrochloric acid to chlorine gas.

$$PbO_2(s) + 4HCl(aq) \longrightarrow PbCl_2(s) + 2H_2O(l) + Cl_2(g)$$

Red lead, Pb_3O_4, behaves as a mixture of lead(II) oxide and lead(IV) oxide. Like lead(IV) oxide, red lead oxidises hot concentrated hydrochloric acid to chlorine gas.

$$Pb_3O_4(s) + 8HCl(aq) \longrightarrow 3PbCl_2(s) + Cl_2(g) + 4H_2O(l)$$

With concentrated sulphuric acid

Tin(IV) oxide reacts with concentrated sulphuric acid to give tin(IV) sulphate.

$$SnO_2(s) + 2H_2SO_4(l) \longrightarrow Sn(SO_4)_2(s) + 2H_2O(l)$$

Lead(IV) oxide reacts with hot concentrated sulphuric acid to give a white precipitate of lead(II) sulphate, water and oxygen gas.

$$2PbO_2(s) + 2H_2SO_4(l) \longrightarrow 2PbSO_4(s) + 2H_2O(l) + O_2(g)$$

Red lead oxide has a similar reaction to lead(IV) oxide.

$$2Pb_3O_4(s) + 6H_2SO_4(l) \longrightarrow 6PbSO_4(s) + 6H_2O(l) + O_2(g)$$

With nitric acid:

Red lead reacts with hot dilute nitric acid to form lead(IV) oxide, lead(II) nitrate and water.

$$Pb_3O_4(s) + 4HNO_3(aq) \longrightarrow PbO_2(s) + 2Pb(NO_3)_2(aq) + 2H_2O(l)$$

6.4.2.7 Action of heat on oxides

Lead (IV) oxide is decomposed to lead (II) oxide by heat. Lead(II) oxide is brown when hot and yellow on cooling.

$$2PbO_2(s) \longrightarrow 2PbO(s) + O_2(g)$$

Red lead behaves similarly

$$2Pb_3O_4(s) \longrightarrow 6PbO(s) + O_2(g)$$

6.4.2.8 Other reactions

Silicon(IV) oxide reacts with magnesium to form magnesium oxide and silicon.

$$2Mg(s) + SiO_2(s) \longrightarrow 2MgO(s) + Si(s)$$

Carbondioxide has a similar reaction.

$$2Mg(s) + CO_2(g) \longrightarrow 2MgO(s) + C(s)$$

6.4.3 Chlorides of group(IV) elements

6.4.3.1 Introduction

They generally form two chlorides: MCl_2 and MCl_4. However, carbon and silicon do not form chlorides in the +2 oxidation state.

Element	Dichloride	Nature	Tetrachloride	Nature
Carbon	-	-	CCl_4	Colourless covalent liquid
Silicon	-	-	$SiCl_4$	Colourless covalent liquid
Germanium	$GeCl_2$	Pale yellow ionic solid	$GeCl_4$	Colourless fuming liquid
Tin	$SnCl_2$	White solid	$SnCl_4$	Colourless liquid
Lead	$PbCl_2$	White ionic solid	$PbCl_4$	Yellow covalent liquid

The dichlorides are solids while the tetrachlorides are volatile covalent liquids. Lead(IV) chloride exists but lead(IV) bromide and lead(IV) iodide do not exist. This is because bromine and iodine are not sufficiently strong oxidising agents to convert Pb^{2+} to Pb^{4+}.

6.4.3.2 Preparation

Tetrachlorides

Carbon tetrachloride is prepared by action of chlorine on carbon disulphide.

$$CS_2(l) + 3Cl_2(g) \longrightarrow CCl_4(l) + S_2Cl_2(l)$$

Silicon tetrachloride, germanium(IV) chloride and tin(IV) chloride are prepared by direct synthesis;

$$Si(s) + 2Cl_2(g) \longrightarrow SiCl_4(l)$$

Lead (IV) chloride is obtained as a yellow liquid when cold concentrated hydrochloric acid is added to lead (IV) oxide

$$PbO_2(s) + 4HCl(aq) \longrightarrow PbCl_4(l) + H_2O(l)$$

Dichlorides

Germanium(II) chloride is a pale yellow solid made by passing a vapour of germanium(IV) chloride over hot germanium.

$$GeCl_4(g) + Ge(s) \rightleftharpoons 2GeCl_2(s)$$

Tin(II) chloride is a white crystalline solid prepared by action of hydrochloric acid on tin.

$$Sn(s) + 2HCl(aq) \longrightarrow SnCl_2(s) + H_2(g)$$

Lead (II) chloride is obtained as a white precipitate by action of dilute hydrochloric acid on lead (II) nitrate

$$Pb^{2+}(aq) + 2Cl^-(aq) \longrightarrow PbCl_2\ (s)$$

Lead (II) chloride is insoluble in cold water but soluble in hot water. It also dissolves in concentrated hydrochloric acid due to formation of a soluble complex.

$$PbCl_2(s) + 2Cl^-(aq) \rightleftharpoons PbCl_4^{2-}(aq)$$

6.4.3.3 Reaction with water (hydrolysis)

Tetrachlorides

Carbon tetrachloride is not hydrolysed by water since it lacks d-orbitals to accept electrons.

In other chlorides, the central atoms have empty d-orbitals. The central atom is able to accept lone pairs of electrons from water molecules thus, besides lead(II) chloride which is insoluble, all the other chlorides undergo hydrolysis.

In general, the tetra chlorides undergo hydrolysis in water to form hydrated oxides of the general formula, $XO_2.2H_2O$, and misty fumes of hydrogen chloride gas;

$$SiCl_4(l) + 4H_2O(l) \longrightarrow SiO_2.2H_2O(s) + 4HCl(aq)$$

$$GeCl_4(l) + 2H_2O(l) \longrightarrow GeO_2(s) + 4HCl(aq)$$

$$SnCl_4(l) + 4H_2O(l) \longrightarrow SnO_2.2H_2O(s) + 4HCl(aq)$$

$$PbCl_4(l) + 4H_2O(l) \longrightarrow PbO_2.2H_2O(s) + 4HCl(aq)$$

Note

The above oxides may be written in various dehydrated forms. It is therefore common to find some of the above equations written as;

$$SiCl_4(l) + 3H_2O(l) \longrightarrow H_2SiO_3(s) + 4HCl(aq)$$

$$SiCl_4(l) + 4H_2O(l) \longrightarrow Si(OH)_4(s) + 4HCl(aq)$$

$$PbCl_4(l) + 2H_2O(l) \longrightarrow PbO_2(s) + 4HCl(aq)$$

Dichlorides

Generally, the dichlorides hydrolyse to give monoxides (*or hydroxides*) and hydrogen chloride gas.

Germanium(II) chloride hydrolyses to form germanium(II) oxide and hydrochloric acid.

$$GeCl_2(\mathrm{s}) + H_2O(\mathrm{l}) \longrightarrow GeO(\mathrm{s}) + 2HCl(\mathrm{aq})$$

In cold water, tin(II) chloride only undergoes partial hydrolysis to form a white basic hydroxide and hydrochloric acid.

$$SnCl_2(\mathrm{s}) + H_2O(\mathrm{l}) \rightleftharpoons Sn(OH)Cl(\mathrm{s}) + HCl(\mathrm{aq})$$

However, tin(II) chloride undergoes complete hydrolysis in hot and excess water to form tin(II) hydroxide and hydrochloric acid.

$$SnCl_2(\mathrm{s}) + 2H_2O(\mathrm{l}) \longrightarrow Sn(OH)_2(\mathrm{s}) + 2HCl(\mathrm{aq})$$

Because of this hydrolysis, it is always better to dissolve tin(II) chloride in moderately concentrated hydrochloric acid with heating. Consequently, laboratory bottles of tin(II) chloride contain fairly concentrated hydrochloric acid. Metallic tin is added to maintain the stability of tin(II) chloride.

Lead(II) chloride does not hydrolyse in water since it is insoluble.

6.4.4 Hydrides of group(IV)

6.4.4.1 Introduction

Carbon forms the largest number of hydrides followed by silicon. The striking stability of hydrides of carbon compared with hydrides of other group(IV) elements is attributed to the relatively high $C - C$ bond energy, high $C - H$ bond energy and the fact that carbon does not have easily accessible d orbitals. Most common group(IV) hydrides include methane, silane, germanane, stannane, and plumbane.

Element	**Name**	**Formula**
Carbon	Methane	CH_4
Silicon	Silane	SiH_4
Germanium	Germanane	GeH_4
Tin	Stannane	SnH_4
Lead	Plumbane	PbH_4

6.4.4.2 Preparation

Apart from methane, other hydrides are made by reduction of the corresponding tetrachloride using lithium aluminium tetrahydride. Methane is made by decarboxylation of sodium ethanoate.

$$CH_3COONa(s) \xrightarrow{Ca(OH)_2\,/\,NaOH(s)} CH_4(g) + Na_2CO_3(s)$$

$$SiCl_4(l) + LiAlH_4(l) \xrightarrow{ether} SiH_4(g) + AlCl_3(s) + LiCl\,(s)$$

6.4.4.3 Boiling point and melting point

Boiling points (*and also melting point*) of the hydrides increase down the group. This is because molecules of the hydrides are held by weak Van der Waals forces. Magnitude of the Van der Waals forces increase down the group with increasing molecular mass.

6.4.4.4 Reaction with water

Methane does not hydrolyse in water since carbon lacks empty d-orbitals to accommodate lone pairs of electrons. Other hydrides hydrolyse in water due to presence of vacant d-orbitals into which water donates electrons to initiate hydrolysis. Silane is hydrolysed by water, but more so in presence of an alkali, to form silicon hydroxide.

$$SiH_4(g) + 4H_2O(l) \longrightarrow Si(OH)_4(s) + 4H_2(g)$$

6.4.4.5 Reaction with dilute hydrochloric acid

Methane does not react with dilute hydrochloric acid. Other hydrides react to form tetrachlorides and hydrogen gas e.g.

$$SiH_4(g) + 4HCl(g) \longrightarrow SiCl_4(l) + 4H_2(g)$$

$$PbH_4(g) + 4HCl(g) \longrightarrow PbCl_4(l) + 4H_2(g)$$

6.4.4.6 Reaction with sodium hydroxide

With exception of silane, the hydrides do not react with sodium hydroxide.

$$SiH_4(g) + 2NaOH(aq) + H_2O(l) \longrightarrow Na_2SiO_3(aq) + 4H_2(g)$$

6.4.4.7 With oxygen

They burn in oxygen to produce dioxides and water.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$SiH_4(g) + 2O_2(g) \longrightarrow SiO_2(s) + 2H_2O(l)$$

6.4.5 Sulphides of group(IV) elements

The disulphides all exist except lead disulphide. They are all covalent compounds. Carbon disulphide is a pale yellow liquid.

Tin(II) sulphide is a yellow solid while others are white solids with giant covalent structures. They are all insoluble in water.

Lead(II) sulphide (galena) is a black solid while tin(II) sulphide is a dark brown solid.

6.4.6 Oxalates of group(IV) elements

Oxalates are salts of oxalic acid ($H_2C_2O_4$) e.g. sodium oxalate, and ammonium oxalate. All oxalates are insoluble except those of group(I) elements, iron(II) oxalate and ammonium oxalate. Lithium oxalate is also insoluble.

All oxalates are soluble in solutions of strong acids e.g.

$$BaC_2O_4(\text{s}) + 2H^+(\text{aq}) \longrightarrow Ba^{2+}(\text{aq}) + H_2C_2O_4(\text{aq})$$

Analysis of oxalate ions ($C_2O_4^{2-}$)

They react with barium chloride (*or barium nitrate*) solution to give a white precipitate of barium oxalate which is soluble in strong acids but insoluble in ethanoic acid and oxalic acid.

$$Ba^{2+}(\text{aq}) + C_2O_4^{2-}(\text{aq}) \longrightarrow BaC_2O_4(\text{s})$$

They react with silver nitrate solution to give a white precipitate of silver oxalate which is soluble in dilute nitric acid and ammonia. (Note that also chloride ions give a white precipitate with silver nitrate solution. However, this precipitate is insoluble in nitric acid but soluble in ammonia).

$$2Ag^+(\text{aq}) + C_2O_4^{2-}(\text{aq}) \longrightarrow Ag_2C_2O_4(\text{s})$$

They turn acidified potassium permanganate solution from purple to colourless with evolution of a colourless gas that turns limewater milky. This test distinguishes oxalates from carbonates.

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

All oxalates (like carbonates) decompose on heating to yield carbondioxide gas and sometimes carbonmonoxide gas.

$$Ag_2C_2O_4(\text{s}) \longrightarrow 2Ag(\text{s}) + 2CO_2(\text{g})$$

$$SnC_2O_4(\text{s}) \longrightarrow SnO(\text{s}) + CO(\text{g}) + CO_2(\text{g})$$

6.4.7 Carbonates and hydrogen carbonates

Carbonates and hydrogen carbonates are salts of carbonic acid (H_2CO_3). The carbonate ion is trigonal planar in shape.

All carbonates are insoluble in water except those of group(I) metals and ammonium carbonate. However, like group(II) carbonates, lithium carbonate is also insoluble.

All carbonates except those of group(I) metals decompose on heating to give an oxide and carbondioxide gas. However, lithium carbonate has resemblance to group(II) carbonates and thus also decomposes on heating.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

All carbonates and hydrogen carbonates liberate carbondioxide gas on treatment with dilute acids. This can be used to test for carbonates.

$$CO_3^{2-}(aq) + 2H^+(aq) \longrightarrow CO_2(g) + H_2O(l)$$

Only hydrogen carbonates of group(I), except lithium carbonate, exist in solid state. The rest of the hydrogen carbonates only exist in solution.

All hydrogen carbonates decompose on heating to yield carbonates, carbondioxide and water e.g.

$$2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$$

Distinguishing a carbonate from a hydrogen carbonate

To the solution of the unknown, magnesium sulphate solution is added.

Formation of a white precipitate shows presence of carbonate ions.

$$Mg^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow MgCO_3(s)$$

In case of a hydrogen carbonate, there is no observable change but a white precipitate is formed on boiling.

$$Mg^{2+}(aq) + 2HCO_3^-(aq) \xrightarrow{heat} MgCO_3(s) + H_2O(l) + CO_2(g)$$

6.4.8 Analysis of lead(II), tin(II), and tin(IV) ions

With sodium hydroxide solution

To the solution of the unknown, sodium hydroxide solution is added dropwise until in excess. Formation of a white precipitate soluble in excess to give colourless solution shows presence of Pb^{2+}, Sn^{2+} or Sn^{4+} ions.

$Pb^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Pb(OH)_2(s)$
$Pb(OH)_2(s) + 2\bar{O}H(aq) \longrightarrow Pb(OH)_4^{2-}(aq)$

$Sn^{2+}aq) + 2\bar{O}H(aq) \longrightarrow Sn(OH)_2(s)$
$Sn(OH)_2(s) + 2\bar{O}H(aq) \longrightarrow Sn(OH)_4^{2-}(aq)$

$Sn^{4+}aq) + 4\bar{O}H(aq) \longrightarrow Sn(OH)_4(s)$
$Sn(OH)_4(s) + 2\bar{O}H(aq) \longrightarrow Sn(OH)_6^{2-}(aq)$

With aqueous ammonia

Aqueous ammonia is added to the solution of the unknown dropwise until in excess. Formation of a white precipitate insoluble in excess shows presence of Pb^{2+}, Sn^{2+} or Sn^{4+}ions.

$Pb^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Pb(OH)_2(s)$

$Sn^{2+}aq) + 2\bar{O}H(aq) \longrightarrow Sn(OH)_2(s)$

$Sn^{4+}aq) + 4\bar{O}H(aq) \longrightarrow Sn(OH)_4(s)$

Note that ammonia is a weaker base than sodium hydroxide. Ammonia therefore does not produce enough hydroxyl ions to enable complex formation as in the case of sodium hydroxide.

With dilute hydrochloric acid

To the solution of the unknown, add a few drops of dilute hydrochloric acid. Formation of a white precipitate that dissolves on warming shows presence of Pb^{2+}.

$Pb^{2+}(aq) + 2Cl^-(aq) \longrightarrow PbCl_2(s)$

Sn^{2+} and Sn^{4+} show no observable change.

With dilute sulphuric acid

A small amount of dilute sulphuric acid is added to the solution of the unknown. Formation of a white precipitate may show presence of Pb^{2+}.

$Pb^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s)$

Sn^{2+} and Sn^{4+} show no observable change.

With potassium chromate solution

To the solution of the unknown, potassium chromate solution is added.

Formation of a yellow precipitate may show presence of Pb^{2+}. Note that Ba^{2+} ions give a similar observation – *Sections 5.5.8 and 5.5.9.*

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow PbCrO_4(s)$$

With potassium iodide solution

To the solution of the unknown, add a few drops of potassium iodide solution. Formation of a yellow precipitate shows presence of Pb^{2+}. This distinguishes Pb^{2+} from Ba^{2+}.

$$Pb^{2+}(aq) + 2I^-(aq) \longrightarrow PbI_2(s)$$

With mercury(II) chloride solution

To the solution of the unknown, add mercury(II) chloride solution.
Formation of a white precipitate that slowly turns gray shows presence of Sn^{2+} owing to reduction of mercury(II) chloride to mercury(I) chloride by tin(II) ions.

$$Sn^{2+}(aq) + 2HgCl_2(aq) \longrightarrow Hg_2Cl_2(s) + Sn^{4+}(aq) + 2Cl^-(aq)$$

Sn^{4+} shows no observable change.

With acidified potassium permanganate solution

To the solution of the unknown, add acidified potassium permanganate solution. Changing of potassium permanganate solution from purple to colourless shows presence of Sn^{2+}. This is a redox reaction and distinguishes Sn^{2+} from Sn^{4+}.

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

Note that Sn^{2+} is a strong reducing agent, thus it reduces MnO_4^- (purple) to Mn^{2+}(colourless).
Sn^{2+} can also reduce Fe^{3+} to Fe^{2+} thus turning the solution from brown to green.

6.5 Summary

Group(IV) elements exhibit two oxidation states, +2 and +4; this makes the chemistry of the group wide as compared to group(II) and group(VII). Stability of the +2 oxidation state increases down the group due to inert pair effect while that of +4 oxidation state reduces down the group. As we move down the group, the dioxides become strong oxidising agents owing to the instability of the +4 oxidation state. Conversely, the monoxide of carbon is a reducing agent owing to instability of the +2 oxidation state in the first members of the group.

6.6 Suggested further reading on chapter 6

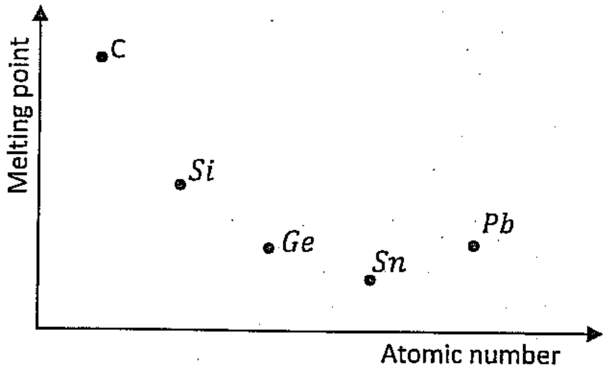
G. F. Liptrot, *Mordern Inorganic Chemistry*, Scotprint Ltd, Fourth Edition, 1983.

A. Holderness, Advanced Level Inorganic Chemistry, Thomson Press, Third Edition, 1979

W. R. Kneen, *Chemistry, Facts, Patterns and Principles*, Addison-Wesley Pub (Sd), 1972

6.7 Questions on chapter 6

1. The elements of group(IV) of the periodic table are in increasing order of atomic number C, Si, Ge, Sn, Pb
   (a) Write down the general electronic configuration of the elements.
   (b) Tin and to a greater extent, lead, are said to show the inert pair effect.
      (i) What is meant by inert pair effect?
      (ii) Give a reason for the existence of the inert pair effect.
      (iii) Give an evidence for the existence of the inert pair effect.
   (c) The diagram below shows a plot of melting point against atomic number for the elements in group(IV).



      (i) Why is the melting point of carbon so much higher than that of the others?
      (ii) Suggest a reason for the steady fall in melting point from silicon to tin.
   (d) (i) Write the formula of the typical hydrides of silicon, tin and lead.
      (ii) Write equations for the hydrolysis of the above hydrides in water.
2. Compare the properties of the following compounds:
   (a) Carbon dioxide and silicon(IV) oxide.
   (b) Carbon tetrachloride and silicon(IV) chloride.
   (iv) Lead(II) oxide and lead(IV) oxide.

3. The melting points of group(IV) oxides (in °C) are CO_2 , -57; SiO_2, 1720; GeO_2, 1120; SnO_2, 1130. Account for this trend.

4. (a) The tendency to form concatenate compounds in group(IV) decreases as atomic number increases. Explain.
   (b) Discuss the trend of acid/base character of oxides of group(IV) elements.
   (c) Discuss the reactivity of tetrachlorides of group(IV) elements with water.

5. (a) Give one method in each case for the preparation of the monoxides and dioxides of
   lead and carbon.
   (b) Explain why:
      (i) silicon tetrachloride is readily hydrolysed by water while carbon tetrachloride is not.
      (ii) lead forms Pb^{2+} ion but carbon does not form C^{2+} ion.
   (c) Compare the reactions of:
      (i) tin and lead with chlorine.
      (ii) carbon and lead with nitric acid.

6. (a) Give a comparative account for the properties of the hydrides of carbon, silicon, tin and lead.
   (b) How and under what conditions does carbonmonoxide react with:
      (i) chlorine
      (ii) hydrogen
      (iii) sodium hydroxide

CHAPTER

7

GROUP VIIB ELEMENTS

Learning Objectives

After reading this chapter and completing the exercises, you should be able to:

- Explain the variation of melting point, atomic and ionic radius, and ionisation energy down group(VII) elements.
- Discuss reactions of group(VII) elements with water, sodium hydroxide, and acids.
- Discuss the physical properties of the oxides, and hydrides of group(VII) elements.
- Describe the preparation of oxides, and hydrides of group(VII) elements.
- Discussion the reactions of oxides, and hydrides of elements of group(VII) with water, alkalis, and dilute acids.

7.1 Introduction

Elements of group(VII) are known as the Halogens. They include Fluorine (F), Chlorine (Cl), Bromine(Br), Iodine (I), and Astatine (At) which is generally radioactive.

All the halogens exist as non-polar diatomic molecules. They are coloured, highly electronegative and very reactive.

Table 7.1 Electronic configuration of group(VII) elements

Halogen	Atomic number	Outer electronic configuration	Colour and physical state
F	9	$2s^22p^5$	Pale yellow gas
Cl	17	$3s^23p^5$	Greenish yellow gas
Br	35	$4s^24p^5$	Red-brown liquid
I	53	$5s^25p^5$	Black solid

7.2 Preparation of halogens

Fluorine is prepared by electrolysis of hydrogen fluoride, to which some potassium fluoride has been added to increase electrical conductivity. Carbon is used as the anode and a steel vessel serves as the cathode.

At the anode, fluorine gas is discharged.

$$2F^-(\mathrm{l}) \longrightarrow F_2(\mathrm{g}) + 2\mathrm{e}$$

At the cathode, hydrogen gas is liberated.

$$2H^+(\mathrm{l}) + 2\mathrm{e} \longrightarrow H_2(\mathrm{g})$$

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Chlorine, bromine and iodine are generally prepared by heating a chloride, bromide or iodide respectively with concentrated sulphuric acid and manganese(IV) oxide.

$$2Cl^-(aq) + 4H^+(aq) + MnO_2(s) \longrightarrow Cl_2(g) + Mn^{2+}(aq) + 2H_2O(l)$$
$$2Br^-(aq) + 4H^+(aq) + MnO_2(s) \longrightarrow Br_2(aq) + Mn^{2+}(aq) + 2H_2O(l)$$
$$2I^-(aq) + 4H^+(aq) + MnO_2(s) \longrightarrow I_2(aq) + Mn^{2+}(aq) + 2H_2O(l)$$

Solid potassium manganate(VII) can be used in place of manganese(IV) oxide but in this case, no heating is required.

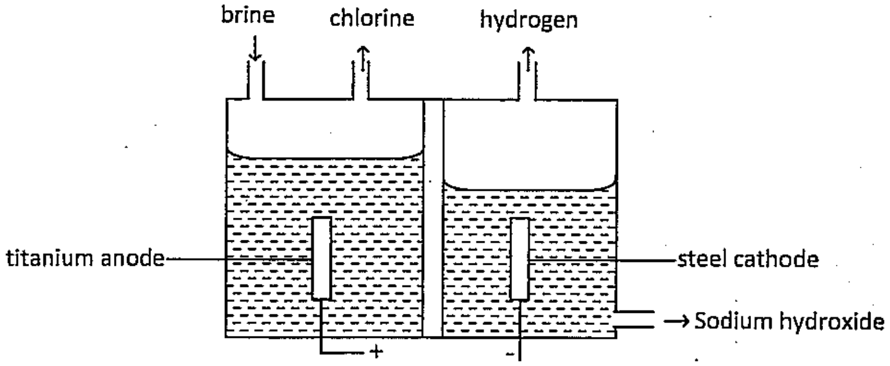
$$MnO_4^-(aq) + 16H^+(aq) + 10Cl^-(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Cl_2(g)$$

Manufacture of chlorine

Chlorine, and sodium hydroxide, is manufactured by electrolysis of concentrated sodium chloride solution (brine).

Traditionally, this electrolysis has been carried out by the mercury amalgam or diaphragm cell (shown below) processes but the ion exchange membrane cell is taking a growing share on environmental and economic grounds.

Figure 7.1 The diaphragm cell for manufacture of chlorine



Sodium ions are discharged at the cathode to form sodium which reacts with water to form sodium hydroxide and hydrogen gas.

Chloride ions area discharged at the anode to form chlorine gas.

Chlorine is also produced in a number of other ways, for example, by electrolysis of potassium chloride with co-production of potassium hydroxide; by electrolysis of molten sodium chloride or magnesium chloride to make elemental sodium or magnesium metal; by electrolysis of hydrochloric acid; and by non-electrolytic processes.

7.3 Physical properties of halogens

7.3.1 Boiling point

Table 7.2 Boling points of group(VII) elements

Halogen	F_2	Cl_2	Br_2	I_2
Boiling point/°C	-188	-34.5	59	183

Boiling points (*and also melting points*) of the halogens increase with increasing molecular mass down the group.
This is because the molecules are held by weak Van der Waals forces. As molecular mass increases, magnitude of the Van der Waals forces also increase consequently increasing boiling point.
Fluorine and chlorine are gases at room temperature. Bromine is a liquid while the Van der Waals forces in iodine are strong enough to hold its molecules in solid state.

7.3.2 Atomic radius

Atomic radius increases down the group. Down the group, an extra shell of electrons is added. The increase in screening effect outweighs the increase in nuclear charge down the group. The atom therefore becomes bigger.

7.3.3 Electronegativity

Table 7.3 Electronegativity of group(VII) elements

Element	F	Cl	Br	I
Electronegativity	4.10	2.85	2.75	2.20

This is the tendency of an atom to become negatively charged in a covalent bond. Electronegativity decreases down the group. This is due to increase in atomic radius and screening effect down the group.

7.3.4 Electron affinity

Table 7.4 Electron affinities of group(VII) elements

Element	F	Cl	Br	I
Electron affinity /KJmol^{-1}	-333	-348	-340	-297

Electron affinity generally decreases down the group. This is because down the group, increase in screening effect outweighs increase in nuclear charge, owing to an extra shell of electrons added. The attraction for the incoming electron consequently reduces down the group thus reducing electron affinity. Fluorine has an abnormally lower electron affinity than chlorine because of its small size.

7.3.5 Bond dissociation enthalpy (bond energy)

Table 7.5 Bond energies of group(VII) elements

Molecule	F_2	Cl_2	Br_2	I_2
Bond energy /KJmol^{-1}	79.1	122.0	111.0	106.0

Bond energy is the amount of energy required to break one mole of a covalent bond into its constituent gaseous atoms.

$X_2(g) \longrightarrow 2X(g)$ $\Delta H=$ Bond energy of $X-X$ bond.

Bond energy usually decreases with increase in bond length.

Bond energy generally decreases down the group. This is because down the group, atomic radius increases causing an increase in $X-X$ bond length. The longer the bond, the weaker it is. Fluorine has an abnormally low bond enthalpy because of its very small atomic radius. Due to the small atomic radius of fluorine, the non-bonding electron pairs on the fluorine atoms are very close to each other causing a strong repulsion. This weakens the $F-F$ bond.

7.3.6 Electrode potential

The values of electrode potentials depend on electron affinity, bond energy, and hydration energy.

Electrode potentials become negative with increase in electron affinity and increase in hydration energy. They become more positive with increase in bond energy.

Table 7.6 shows electrode potentials of the halogens

Table 7.6 Electrode potentials of group(VII) elements

Element	F_2	Cl_2	Br_2	I_2
Electrode potential /V $^1/_2 X_2(g) + e \longrightarrow X^-(aq)$	+2.87	+1.36	+1.07	+0.54

Electrode potentials decrease (become less positive) down the group. Down the group, there is a decrease in bond dissociation energy and electron affinity. Both these factors favour electrode potential to become less positive.

However, although fluorine has a lower electron affinity than chlorine, its low bond dissociation enthalpy enables it to have a higher electrode potential than chlorine. Electrode potentials give a measure of oxidising power – the higher (more positive) the electrode potential, the stronger is the oxidising power. Therefore oxidising power of the halogens decreases down the group.

7.4 Chemical properties of the halogens

7.4.1 Introduction

Due to the small size of fluorine, its chemistry differs significantly from the chemistry of the rest of the halogens. Fluorine is the most reactive halogen due to its very low bond dissociation energy. Generally, fluorine differs from the rest of the halogens in the following ways;

- Lithium fluoride, calcium fluoride and magnesium fluoride are insoluble in water while the corresponding chlorides, bromides, and iodides are soluble.
- Silver fluoride is soluble in water while silver chloride, silver bromide, and silver iodide are insoluble.
- Hydrogen fluoride is a polymeric and exists as a liquid at room temperature while hydrogen chloride, hydrogen bromide, and hydrogen iodide are not polymeric and are gases at room temperature.
- Fluorine reacts with cold dilute sodium hydroxide to give oxygen difluoride, sodium fluoride and water. Other halogens yield corresponding halates(I), halides and water as shown below – *Section 7.4.3.*
  $2F_2(g) + 2\bar{O}H(aq) \longrightarrow OF_2(g) + 2F^-(aq) + H_2O(l)$
  $Cl_2(g) + 2\bar{O}H \longrightarrow OCl^-(aq) + Cl^-(aq) + H_2O(l)$
  $Br_2(l) + 2\bar{O}H(aq) \longrightarrow \bar{O}Br(aq) + Br^-(aq) + H_2O(l)$
- Reaction of fluorine with hot concentrated sodium hydroxide yields different products from other halogens as shown by the reactions below – *Section 7.4.4.*
  $2F_2(g) + 4\bar{O}H(aq) \longrightarrow 4F^-(aq) + 2H_2O(l) + O_2(g)$
  $3X^- + 6\bar{O}H(aq) \longrightarrow XO_3^-(aq) + 5X^-(aq) + 3H_2O(l)$
  $X = Cl, Br, or\ I$
- Oxides of fluorine are not acidic while those of other halogens are acidic.

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Ionic bond formation

Halogens form ionic compounds with other elements. Ease of ionic bond formation increases with;

- decrease in bond dissociation energy,
- increase in electron affinity,
- increase in lattice energy of the halide formed.

Due to its low bond dissociation energy, high electron affinity and high negative lattice energy of its halides, fluorine forms more ionic compounds than other elements. Order of reactivity towards ionic bond formation is $F_2 > Cl_2 > Br_2 > I_2$

Covalent bond formation

Halogens form covalent bonds in their diatomic molecules e.g. in chlorine (Cl_2) and in compounds such as HCl, CCl_4, $SiCl_4$, Cl_2O_7 etc.

Fluorine has one oxidation state of -1. However, other halogens can have oxidation states of +1, -1, -3, -5, and -7 due to availability of empty d-orbitals.

When fluorine combines with other elements, the elements employ their highest oxidation states.

Oxidising reactions

Oxidising power of halogens decreases down the group due to decrease in their electrode potentials – *Section 7.3.6*. Therefore a higher halogen can displace a lower halogen from a solution containing its ions by oxidising it. E.g.

$$Cl_2(g) + 2Br^-(aq) \longrightarrow Br_2(aq) + 2Cl^-(aq)$$

Due to their oxidising power, halogens can oxidise;

- sulphites to sulphates,

  $$SO_3^{2-}(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e$$

- hydrogen sulphide to sulphur

Iodine oxidises the thiosulphate ion to tetrathionate ion.

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

Chlorine and bromine, being stronger oxidising agents than iodine, oxidise the thiosulphate ion to sulphate ions.

$$S_2O_3^{2-}(aq) + 4Cl_2(g) + 5H_2O(l) \longrightarrow 2SO_4^{2-}(aq) + 10H^+(aq) + 8Cl^-(aq)$$

7.4.2 Reactions of the halogens with water

Fluorine fumes in moist air. It reacts vigorously with water to form oxygen and hydrofluoric acid.

$$2F_2(\text{g}) + 2H_2O(\text{l}) \longrightarrow 4HF(\text{aq}) + O_2(\text{g})$$

Chlorine and bromine react with water to give hydrochloric acid and hydrobromic respectively acid as well as chloric(I) acid and bromic(I) acid respectively.

$$Cl_2(\text{g}) + H_2O(\text{l}) \longrightarrow HOCl(\text{aq}) + HCl(\text{aq})$$

$$Br_2(\text{l}) + H_2O(\text{l}) \longrightarrow HOBr(\text{aq}) + HBr(\text{aq})$$

If chlorine water is exposed to sunlight, chloric(I) acid decomposes to form hydrochloric acid and oxygen gas.

$$2HOCl(\text{aq}) \xrightarrow{u.v} 2HCl(\text{aq}) + O_2(\text{g})$$

Iodine is sparing soluble in water and there is hardly any reaction.

7.4.3 Reaction with cold dilute alkalis

Fluorine reacts with cold dilute sodium hydroxide to form oxygen difluoride, sodium fluoride and water.

$$2F_2(\text{g}) + 2\bar{O}H(\text{aq}) \longrightarrow OF_2(\text{g}) + 2F^-(\text{aq}) + H_2O(\text{l})$$

Chlorine produces a pale yellow solution of sodium chlorate(I), sodium chloride and water. Bromine produces a pale yellow solution of sodium bromate(I), sodium bromide and water.

$$Cl_2(\text{g}) + 2\bar{O}H(\text{aq}) \longrightarrow \bar{O}Cl(\text{aq}) + Cl^-(\text{aq}) + H_2O(\text{l})$$

$$Br_2(\text{l}) + 2\bar{O}H(\text{aq}) \longrightarrow \bar{O}Br(\text{aq}) + Br^-(\text{aq}) + H_2O(\text{l})$$

Note

The sodium chlorate(I) and sodium bromate(I) formed above disproportionate at temperatures above 70°C. i.e.

$$3\bar{O}Cl(\text{aq}) \longrightarrow 2Cl^-(\text{aq}) + ClO_3^-(\text{aq})$$

$$3\ \bar{O}Br(\text{aq}) \longrightarrow 2Br^-(\text{aq}) + BrO_3^-(\text{aq})$$

This is known as a disproportionation reaction – a reaction in which the same species undergoes simultaneous oxidation and reduction.
Notice that the $\bar{O}Cl$ (*oxidation state of Cl is +1*) ion has been oxidised to ClO_3^- (*oxidation state of Cl is +5*) and also reduced to Cl^- (*oxidation state of Cl is -1*)
Consequently, reaction of halogens with warm alkalis yield different products from reaction with cold alkalis as shown in the following section.

7.4.4 With hot concentrated alkalis

Fluorine reacts with hot concentrated sodium hydroxide to produce sodium fluoride, water and oxygen.

$$2F_2(g) + 4\bar{O}H(aq) \longrightarrow 4F^-(aq) + 2H_2O(l) + O_2(g)$$

Chlorine, bromine, and iodine produce corresponding halates(V), halides and water.

$$3Cl_2(g) + 6\bar{O}H(aq) \longrightarrow ClO_3^-(aq) + 5Cl^-(aq) + 3H_2O(l)$$
$$3Br_2(l) + 6\bar{O}H(aq) \longrightarrow BrO_3^-(aq) + 5Br^-(aq) + 3H_2O(l)$$
$$3I_2(s) + 6\bar{O}H(aq) \longrightarrow IO_3^-(aq) + 5I^-(aq) + 3H_2O(l)$$

Note

- These reactions are used as a basis for preparation of potassium chlorate(V) ($KClO_3$), sodium chlorate(V), potassium iodate(V) (KIO_3) etc.

  To prepare potassium chlorate(V), chlorine is passed through a hot concentrated solution of potassium hydroxide. The resulting solution is saturated by evaporation. The saturated solution is cooled to obtain crystals of potassium chlorate(V). The crystals are filtered off, washed and dried to remove potassium chloride.

  $$Cl_2(g) + 6KOH(aq) \longrightarrow KClO_3(aq) + 5KCl(aq) + 3H_2O(l)$$

- Chlorine is more soluble in sodium hydroxide solution than in water. This is because chlorine is non-polar and sparingly dissolves in water to give the equilibrium below

  $$Cl_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + Cl^-(aq) + HOCl(aq)$$

  In sodium hydroxide, the hydroxyl ions from sodium hydroxide react with the hydrogen ions. More chlorine dissolves to replace the hydrogen ions thus shifting the equilibrium from left to right.

  $$H^+(aq) + \bar{O}H(aq) \longrightarrow H_2O(l)$$

7.4.5 With sodium thiosulphate

Iodine oxidises the thiosulphate ion to tetrathionate ion.

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

Chlorine and bromine, being stronger oxidising agents than iodine, oxidise the thiosulphate ion to sulphate ion.

$$4Cl_2(g) + S_2O_3^{2-}(aq) + 5H_2O(l) \longrightarrow 8Cl^-(aq) + 2SO_4^{2-}(aq) + 10H^+(aq)$$

$$4Br_2(l) + S_2O_3^{2-}(aq) + 5H_2O(l) \longrightarrow 8Br^-(aq) + 2SO_4^{2-}(aq) + 10H^+(aq)$$

7.4.6 With sulphite ions (saturated solution of sulphurdioxide)

All halogens oxidise sulphite ions to sulphate ions e.g.

$$SO_3^{2-}(aq) + Cl_2(g) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2Cl^-(aq)$$

$$SO_3^{2-}(aq) + Br_2(l) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2Br^-(aq)$$

7.4.7 With metals

Fluorine combines readily and directly with metals. With chlorine, the metal has to be heated in the dry gas. Iodine reacts slowly with metals at high temperature. In all cases, the corresponding metal halide is formed e.g.

$$Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$$

$$2Fe(s) + 3Cl_2(g) \longrightarrow 2FeCl_3(s)$$

If the metal has variable oxidation states, it employs the highest oxidation state since halogens are oxidising agents. If a lower metal halide is required, then a hydrogen halide is used e.g.

$$Fe(s) + 2(g) \longrightarrow {}_2(s) + {}_2(g)$$

7.4.8 With hydrogen sulphide

They all oxidise hydrogen sulphide to sulphur e.g.

$$Cl_2(g) + H_2S(g) \longrightarrow 2HCl(g) + S(s)$$

7.4.9 With hydrogen

Fluorine explodes in hydrogen to form hydrogen fluoride.

$$F_2(g) + H_2(g) \longrightarrow 2HF(g)$$

Reaction with chlorine is slow in diffuse light but explosive in sunlight or ultra violet light.

$$Cl_2(g) + H_2(g) \longrightarrow 2HCl(g)$$

Bromine and iodine only react in presence of a catalyst at high temperature.

$$H_2(g) + Br_2(l) \xrightarrow[200^\circ C]{Pt} 2HBr(g)$$

$$H_2(g) + I_2(g) \xrightarrow[400^\circ C]{Pt} 2HI(g)$$

7.4.10 With sulphur

Chlorine reacts with molten sulphur to give disulphur dichloride, which is a yellow liquid.

$$Cl_2(g) + 2S(l) \longrightarrow S_2Cl_2(l)$$

Bromine reacts similarly to give a yellow liquid of disulphur dibromide while iodine does not react.

7.4.11 With phosphorous

Heated phosphorous reacts with dry chlorine to form phosphorous trichloride.

$$P_4(s) + 6Cl_2(g) \longrightarrow 4PCl_3(l)$$

If more chlorine is passed through phosphorous trichloride, phosphorous pentachloride is formed

$$PCl_3(l) + Cl_2(g) \longrightarrow PCl_5(s)$$

Bromine reacts similarly but the reaction takes place in carbon disulphide.
Iodine forms only phosphorous triiodide.

7.4.12 Bleaching reactions

Bleaching action of chlorine is brought about by the chlorate(I) ion, which is an oxidising agent. Chlorine bleaches by oxidising the dye. Therefore dry chlorine does not bleach.

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

$$HOCl(aq) + \underset{\text{coloured}}{\text{dye}} \longrightarrow HCl(aq) + \underset{\text{colourless}}{\text{oxidised dye}}$$

The oxidised dye is colourless. Loss of colour is caused by structural changes in the organic molecule. Bromine has a similar action but much less vigorous. Iodine does not react with water and therefore does not bleach.

7.5 Compounds of halogens

7.5.1 Hydrides

They are colourless gases. They fume in moist air and are very soluble in water. They include HF, HCl, HBr, HI etc.

Preparation

Hydrogen fluoride and hydrogen chloride are prepared by heating concentrated sulphuric acid with a corresponding halide.

Hydrogen fluoride is prepared by heating concentrated sulphuric acid with calcium fluoride.

$$CaF_2(\mathrm{s}) + H_2SO_4(\mathrm{l}) \longrightarrow CaSO_4(\mathrm{s}) + 2HF(\mathrm{g})$$

Hydrogen chloride is prepared by heating concentrated sulphuric acid with sodium chloride.

$$2NaCl(\mathrm{s}) + H_2SO_4(\mathrm{l}) \longrightarrow Na_2SO_4(\mathrm{aq}) + 2HCl(\mathrm{g})$$

Hydrogen bromide and hydrogen iodide cannot be prepared by a similar method using concentrated sulphuric acid because hydrogen bromide and hydrogen iodide are strong reducing agents which can be oxidised by concentrated sulphuric acid to bromine and iodine respectively.

Hydrogen bromide and hydrogen iodide are prepared by hydrolysis of phosphorous tribromide and phosphorous triiodide respectively.

$$PBr_3(\mathrm{l}) + 3H_2O(\mathrm{l}) \longrightarrow H_3PO_3(\mathrm{aq}) + 3HBr(\mathrm{g})$$

$$PI_3(\mathrm{s}) + 3H_2O(\mathrm{l}) \longrightarrow H_3PO_3(\mathrm{aq}) + 3HI(\mathrm{g})$$

Bond dissociation energy

Table 7.7 Bond energies of hydrides of group(VII) elements

HX	HF	HCl	HBr	HI
Bond energy /KJmol^{-1}	+560	+430	+370	+300

Bond energy decreases down the group. This is due to increase in atomic radius of the halogen down the group. Increase in atomic radius causes an increase in $H - X$ bond length. The longer the bond, the weaker it is.

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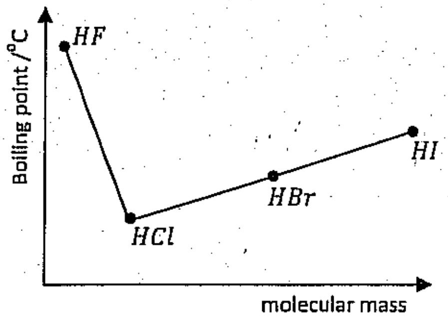
Boiling point

Figure 7.2 Graph of boiling points of halogen hydrides against molecular mass



Generally, boiling point increases down the group with hydrogen fluoride having an abnormally high boiling point. This is because molecules of the hydrides are held by weak Van der Waals forces whose magnitude increase with increasing molecular mass. Fluorine is highly electronegative thus hydrogen fluoride molecules associate through strong hydrogen bonds. This gives hydrogen fluoride an abnormally high boiling point.

Acidic strength

Halogen hydrides dissolve in water to form acidic solutions. The pK_a values of the acids can be used as a measure of acidic strength – the lower the value, the stronger is the acid. The table below shows the pK_a values of the halogen halides.

Table 7.8 pKa values of hydrides of group(VII) elements

HX	HF	HCl	HBr	HI
pK_a	3.25	-7.4	-9.5	-10

Acidic strength of the hydrides increases down the group. This is because atomic radius increases down the group in the order $F < Cl < Br < I$. Consequently the $H - X$ bond length increases down the group. The longer the bond, the weaker it is. The weaker the bond, the stronger is the acid.

Note

Hydrofluoric acid is a weak acid which is slightly ionised in aqueous solution.

$$HF(\text{aq}) + H_2O(\text{l}) \rightleftharpoons H_3O^+(\text{aq}) + F^-(\text{aq})$$

Moist hydrogen fluoride and aqueous solution of the acid attack silica and glass, so the solution is stored in polythene containers.

$$SiO_2(\text{s}) + 4HF(\text{aq}) \longrightarrow SiF_4(\text{g}) + 2H_2O(\text{l})$$

Reducing action

The power of halides to act as reducing agents increase down the group
i.e. $HF < HCl < HBr < HI$
Thus hydrogen fluoride almost does not undergo any reducing reaction. Hydrogen chloride will only react with very strong oxidising agents such as permanganates, chromates, lead(IV) oxide etc; hydrogen bromide reacts with moderately strong oxidising agents like concentrated sulphuric acid, chloride and hydrogen peroxide; hydrogen iodide reacts with even mild (weak) oxidising agents like aqueous iron(III) salts, dilute nitric acid etc.

Consequently, hydrogen fluoride and hydrogen chloride do not react with concentrated sulphuric acid. Hydrogen bromide is oxidised by concentrated sulphuric acid, on heating, to bromine.

$$2HBr(\text{g}) + 2H_2SO_4(\text{l}) \longrightarrow Br_2(\text{l}) + SO_2(\text{g}) + 2H_2O(\text{l})$$

Concentrated sulphuric acid oxidises hydrogen iodide to iodine. Sulphuric in turn gets reduces mainly to hydrogen sulphide since hydrogen iodide is a stronger reducing agent than hydrogen bromide.

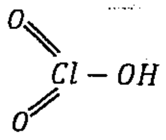
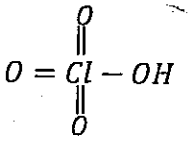
$$8HI(\text{g}) + H_2SO_4(\text{l}) \longrightarrow H_2S(\text{g}) + 4H_2O(\text{l}) + I_2(\text{s})$$

7.5.2 Oxides of the halogens

Chlorine forms six oxides some of which include chlorine monoxide (Cl_2O), chlorine dioxide (ClO_2), and dichlorine heptoxide (Cl_2O_7). The oxides are acidic. Oxides of bromine have not been extensively studied since they are unstable. The best known oxide of iodine is iodine pentoxide (I_2O_5).

7.5.3 Oxy acids of chlorine

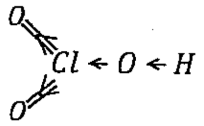
Chlorine forms several oxy acids which include;

Oxy acid	**formula**	**structure (*not accurate*)**
Chloric(I) acid	$HClO$	$Cl-O-H$
Chloric(III) acid	$HClO_2$	$O=Cl-OH$
Chloric(V) acid	$HClO_3$	
Chloric(VII) acid	$HClO_4$	 $O=\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cl}}-OH$

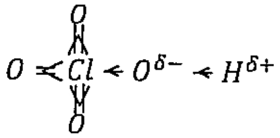
Acidic strength

Acidic strength of the acids decreases in the order $HClO_4 > HClO_3 > HClO_2 > HClO$. Acidic strength increases with increase in number of oxygen atoms attached to the chlorine atom. Oxygen is more electronegative than chlorine. The oxygen atoms withdrawal electrons from the $O-H$ bond through the chlorine atom. This increases the partial positive charge on the hydrogen atom hence weakening the $O-H$ bond. The weaker the $O-H$ bond, the stronger is the acid.

$Cl-O^{\delta-} \leftarrow H^{\delta+}$



$O \Leftarrow Cl \leftarrow O^{\delta+} \leftarrow H^{\delta+}$



$O \Leftarrow \overset{\overset{O}{\Downarrow}}{\underset{\underset{O}{\Uparrow}}{Cl}} \leftarrow O^{\delta-} \leftarrow H^{\delta+}$

Increase in number of oxygen atoms causes an increase in partial positive charge on the hydrogen atom thus weakening the $O-H$ bond. This increases the ease with which a proton is lost.

Preparation

Chloric(I) acid

This is prepared by passing chlorine through a suspension of freshly prepared mercury (II) oxide in water.

$$HgO(s) + 2Cl_2(g) + H_2O(l) \longrightarrow HgCl_2(s) + 2HClO(aq)$$

Both the acid and its salts are powerful oxidising agents and are used as bleaching agents. The active oxidising agent in the acid is the chlorate(I) ion, ClO^-. The half cell reaction for the chlorate(I) ion acting as an oxidising agent is shown below.

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

By accepting electrons, the chlorate ion can oxidise;

- Iron(II) ions to iron(III) ions.

  $Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e$
- Iodide ions to iodine.

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

The chlorate(I) ion is the active bleaching agent in commercial bleaching agents like JIK. Chloric(I) acid and sodium chlorate(I) disproportionate to chloride ions and chlorate(V) ions when heated.

$3ClO^-(aq) \longrightarrow 2Cl^-(aq) + ClO_3^-(aq)$

Chloric(III) acid, $HClO_2$

This is only known in solution and is of little importance. It is used industrially as a textile bleaching agent.

Chloric(V) acid, $HClO_3$

This is prepared by action of barium chlorate(V) on equimolar quantities of sulphuric acid in dilute solution.

$Ba(ClO_3)_2(aq) + H_2SO_4(aq) \longrightarrow 2HClO_3(aq) + BaSO_4(s)$

Chloric(V) acid and its salts like sodium chlorate(V) are powerful oxidising agents in solution.

$ClO_3^-(aq) + 6H^+(aq) + 6e \longrightarrow Cl^-(aq) + 3H_2O(l)$

Similarly, bromates(V) and iodates(V) are powerful oxidising agents.

$BrO_3^-(aq) + 6H^+(aq) + 6e \longrightarrow Br^-(aq) + 3H_2O(l)$

$IO_3^-(aq) + 6H^+(aq) + 6e \longrightarrow I^-(aq) + 3H_2O(l)$ (1)

The iodate(V) ion oxidises iodide ions to iodine.

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

The overall reaction between iodate(V) ions and iodide ions is

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

This is obtained by multiplying equation (2) by 3 and then combining it with equation (1). This is done to balance the number of electrons in either equation.

Potassium iodate(V), KIO_3, can be obtained in a high degree of purity and is stable in aqueous solution. It can therefore be used as a primary standard in volumetric analysis. In acidic solution, it reacts with excess potassium iodide to give a quantitative yield of iodine as shown in equation (3) above. The liberated iodine can be titrated with sodium thiosulphate solution. This reaction can be used as a basis to standardise sodium thiosulphate which is not a primary standard.

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

Chloric(VII) acid, $HClO_4$

This is prepared by vacuum distillation of a mixture of potassium chlorate(VII) with concentrated sulphuric acid. Chlorates(VII) are also powerful oxidising agents.

7.5.4 Poly-iodides

Iodine is almost insoluble in water. However, it readily dissolves in a concentrated solution of potassium iodide. This occurs because iodine combines with iodide ions to form a soluble complex of triiodide ions, I_3^-

$$I_2(\text{s}) + I^-(\text{aq}) \rightleftharpoons I_3^-(\text{aq})$$

The complex can readily release iodine for titration with sodium thiosulphate in volumetric analysis.

7.6 Analysis of chloride, bromide, and iodide ions

7.6.1 Using concentrated sulphuric acid

To the unknown solid substance, add a little concentrated sulphuric acid and warm;

- Evolution of a colourless gas, with a sharp smell, which forms dense white fumes with ammonia shows presence of chloride ions. Note that sulphuric acid displaces hydrogen chloride gas (*the colourless gas*) from chlorides.
- Evolution of a brown gas (bromine) shows presence of a bromide.
- Formation of a purple vapour (iodine vapour) shows presence of an iodide.

7.6.2 Using dilute nitric acid and silver nitrate

To the solution of the unknown, add dilute nitric acid followed by silver nitrate solution;

- Formation of a white precipitate shows presence of a chloride. The precipitate dissolves in excess ammonia due to complex formation.

$$Ag^+(\text{aq}) + Cl^-(\text{aq}) \longrightarrow AgCl(\text{s})$$

$$AgCl(s) + 2NH_3(aq) \longrightarrow Ag(NH_3)_2^+(aq) + Cl^-(aq)$$

- Formation of a cream precipitate (or pale yellow) shows presence of bromide ions.

$$Ag^+(aq) + Br^-(aq) \longrightarrow AgBr(s)$$

- Formation of a yellow precipitate shows presence of iodide ions.

$$Ag^+(aq) + I^-(aq) \longrightarrow AgI(s)$$

7.6.3 Using sulphuric acid and manganese(IV) oxide

To the unknown solid sample, add manganese(IV) oxide and a little concentrated sulphuric acid and then warm.

- Evolution of a greenish yellow gas that turns blue litmus red shows presence of chloride ions,

$$MnO_2(s) + 4H^+(aq) + 2Cl^-(aq) \longrightarrow Mn^{2+}(aq) + Cl_2(g) + 2H_2O(l)$$

- Evolution of brown fumes (reddish) shows presence of bromide ions,

$$MnO_2(s) + 4H^+(aq) + 2Br^-(aq) \longrightarrow Mn^{2+}(aq) + Br_2(g) + 2H_2O(l)$$

- Evolution of a purple vapour shows presence of iodide ions.

$$MnO_2(s) + 4H^+(aq) + 2I^-(aq) \longrightarrow Mn^{2+}(aq) + I_2(g) + 2H_2O(l)$$

Note that a mixture of manganese(IV) oxide and concentrated sulphuric acid is a powerful oxidising agent which oxidises chloride, bromide and iodide ions to chlorine, bromine and iodine respectively.

7.6.4 Using chlorine water (or slightly acidified sodium hypochlorite) and carbon tetrachloride

To the solution of the unknown, add 1 or 2 drops of chlorine water followed by 3 cm^3 of carbon tetrachloride. Shake well and allow to settle.

- A brown (or red) carbon tetrachloride layer shows presence of bromide ions. This is because the reagent oxidises bromide ions to bromine which is dissolves in carbon tetrachloride layer turning it to brown.
- A purple (or violet) carbon tetrachloride layer shows presence of iodide ions.

7.6.4 Using lead(II) ethanoate or lead(II) nitrate

To the solution of the unknown, add a few drops of lead(II) nitrate solution.

- Formation of a white precipitate that dissolves on warming shows presence of a chloride or a bromide.

$$Pb^{2+}(aq) + 2Cl^{-}(aq) \longrightarrow PbCl_2(s)$$

$$Pb^{2+}(aq) + 2Br^{-}(aq) \longrightarrow PbBr_2(s)$$

- Formation of a yellow precipitate soluble on heating shows presence of iodide ions.

$$Pb^{2+}(aq) + 2I^{-}(aq) \longrightarrow PbI_2(s)$$

Using other oxidising agents

Strong oxidising agents like acidified potassium iodate, acidified potassium dichromate, and acidified hydrogen peroxide oxidise chloride ions, bromide ions, and iodide ions to chlorine, bromine and iodine respectively.

7.7 Summary

Though not transition elements, the halogens are coloured. They are predominantly non-metals. Their physical state gradually changes from gaseous to solid as the group is descended. They are quite reactive and oxidising.

7.8 Suggested further reading on chapter 7

G. F. Liptrot, *Mordern Inorganic Chemistry*, Scotprint Ltd, Fourth Edition, 1983.
A. Holderness, Advanced Level Inorganic Chemistry, Thomson Press, Third Edition, 1979
W. R. Kneen, *Chemistry, Facts, Patterns and Principles,* Addison-Wesley Pub (Sd), 1972

7.9 Questions about chapter 7

1. Discuss the trends in reducing action, boiling points and acid strength of hydrogen halides.
2. (a) Draw the structures of the following acids and name the shapes attained. $HClO$, $HClO_2$, $HClO_3$, and $HClO_4$.

(b) Discuss the trend of acidic strength of the acids in (a) above.

3. Discuss the similarity in the chemistry of chlorine, bromine and iodine. Your discussion should include;
   (a) reactions of the elements with;
      (i) hydrogen
      (ii) sodium hydroxide
      (iii) silver nitrate
   (b) action of the elements as oxidising agents.

4. Explain the following observations
   (a) When solid iodine is added to water, most of it remains un-dissolved; addition of potassium iodide to the solution causes more iodine to dissolve.
   (b) When acidified bleaching powder is added to a starch-potassium iodide solution, an intense blue colouration occurs.
   (c) When hydrogen sulphide is bubbled through bromine water, a colourless solution containing a pale yellow precipitate is formed.
   (d) Addition of silver nitrate solution to sodium chloride solution produces a white precipitate. When excess ammonia is added, the white precipitate dissolves.
   (e) Hydrogen chloride may be prepared by action of concentrated sulphuric acid on potassium chloride but a corresponding method may not be used for hydrogen bromide.

5. Using equations only and stating conditions, outline the reactions which occur between iodine and;
   (a) sodium thiosulphate.
   (b) potassium hydroxide.
   (c) nitric acid.
   (d) potassium iodide.

8. (a) Outline the chemistry of an industrial process in which chlorine is one of the major products.
   (b) Discuss the reaction of the reagents below with the salts sodium chloride, sodium bromide and sodium iodide. In each case, state what is observed, and write equations for the reactions.
      (i) Concentrated sulphuric acid.

(ii) Aqueous silver nitrate added to aqueous solutions of the salts.

(iii) Chlorine water followed by tetrachloromethane added to aqueous solutions of the salts.

9. Compare and contrast the properties of elements chlorine and iodine by reference to their reactions with:
   - (a) Potassium iodide,
   - (b) Hydrogen,
   - (c) Sodium hydroxide,
   - (d) Sodium thiosulphate,
   - (e) Concentrated nitric acid.

10 (a) (i) Briefly describe the preparation of chlorine and iodine.

(ii) Why is the same method not used in the preparation of the halogens in (i) above.

(b) The following reaction takes place on warming:

$$3Br_2(l) + 6\bar{O}H(aq) \longrightarrow 5Br^-(aq) + BrO_3^-(aq) + 3H_2O(l)$$

(i) Determine the oxidation number of bromine in BrO_3^- and in Br^-

(ii) What name is given to this reaction?

(iii) Suggest the shape of BrO_3^- and explain your reasoning.

(c) On reacting chlorine with hot aqueous sodium hydroxide, disproportionation occurs.

(i) What is disproportionation?

(ii) Write equation for the reaction and give oxidation states of chlorine in the product.

CHAPTER

8

TRANSITION METAL CHEMISTRY

Learning Objectives

After reading this chapter and completing the exercises, you should be able to

- Explain the variation of melting point, atomic and ionic radius, and ionisation energy down across the transition series.
- Discuss reactions of transition elements with water, sodium hydroxide, oxidising acids, and hydrochloric acid.
- Discuss the physical properties of the oxides, and chlorides of transition elements.
- Describe the preparation of oxides, and hydrides of transition elements.
- Discussion the reactions of oxides, and chlorides of transition elements with water, alkalis, and dilute acids.
- Appreciate the use potassium manganate(VII) and potassium dichromate(VI) in volumetric analysis.

8.1 Introduction

A transition element is an element that forms at least one ion with partially filled d-subenergy level. Transition elements are d-block elements. A d-block element is one whose outermost electrons are in the d-subenergy level. Table 8.1 shows d-block elements in the first transition series.

Table 8.1 Electronic configurations of the first transition series

Element	Symbol	Atomic number	Electronic configuration
Scandium	Sc	21	$1s^22s^22p^63s^23p^64s^23d^1$
Titanium	Ti	22	$1s^22s^22p^63s^23p^64s^23d^2$
Vanadium	V	23	$1s^22s^22p^63s^23p^64s^23d^3$
Chromium	Cr	24	$1s^22s^22p^63s^23p^64s^13d^5$
Manganese	Mn	25	$1s^22s^22p^63s^23p^64s^23d^5$
Iron	Fe	26	$1s^22s^22p^63s^23p^64s^23d^6$
Cobalt	Co	27	$1s^22s^22p^63s^23p^64s^23d^7$
Nickel	Ni	28	$1s^22s^22p^63s^23p^64s^23d^8$
Copper	Cu	29	$1s^22s^22p^63s^23p^64s^13d^{10}$
Zinc	Zn	30	$1s^22s^22p^63s^23p^64s^23d^{10}$

General remarks

- Zinc forms ions only in +2 oxidation state (Zn^{2+}), which fully filled d-subenergy level. Similarly, scandium only forms ions in +3 oxidation state with fully filled d-subenergy level. For these reasons, zinc and scandium are not transition elements. Copper is also not a transition element but Cu^{2+} has transitional properties. Unlike compounds of transition elements, compounds of scandium and zinc are not coloured.

- The electronic configuration of chromium is $1s^22s^22p^63s^23p^6\mathbf{4s^13d^5}$ but not $1s^22s^22p^63s^23p^6\mathbf{4s^23d^4}$, as would be expected. This is because the half-filled 3d-subenergy level in $1s^22s^22p^63s^23p^6\mathbf{4s^13d^5}$ makes the configuration more stable than $1s^22s^22p^63s^23p^6\mathbf{4s^23d^4}$. Similarly, due to high stability of a fully filled 3d-subenergy level, the electronic configuration of copper is $1s^22s^22p^63s^23p^6\mathbf{4s^13d^{10}}$ but not $1s^22s^22p^63s^23p^6\mathbf{4s^23d^9}$ as would be expected.
- Iron forms ions in two oxidation states; Fe^{2+} ($1s^22s^22p^63s^23p^6\mathbf{4s^03d^6}$), and Fe^{3+} ($1s^22s^22p^63s^23p^6\mathbf{4s^03d^5}$). Note that a transition element ionizes by losing the 4s electrons first, followed by the 3d electrons. Because of the high stability associated with Fe^{3+}(half-filled 3d-subenergy level), Fe^{2+} is easily oxidized to Fe^{3+}.
- Cu^+ions ($1s^22s^22p^63s^23p^6\mathbf{3d^{10}}$) have no transitional properties because of the fully filled 3d-subenergy level in the electronic configuration of Cu^+. Consequently, copper(I) compounds are not coloured. However, Cu^{2+} ($1s^22s^22p^63s^23p^6\mathbf{3d^9}$) has transitional properties and thus copper(II) compounds are coloured.
- Copper, scandium, and zinc are included in the transition series on account of chemical resemblance of their compounds to transitional metal compounds.

8.2 Physical Properties of Transition elements

8.2.1 Physical state

They are hard, dense and good conductors of electricity and heat. Their melting points and boiling points are higher than those of s-block metals. This is because they use all their d-electrons and s-electrons in formation of the metallic bond, unlike s-block elements that use only s-electrons.

8.2.2 Ionisation energy

Table 8.2 shows the first ionisation energies of elements in the first transition series. It shows that there a general slight increase in ionisation energy across the transition series, from left to right.

Table 8.2 First ionisation energies of the first transition series

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
First ionisation energy /KJmol^{-1}	633	659	650	653	717	762	759	736	745	906

Explanation

Across the period, both nuclear charge and screening effect increase. Since electrons are added to the inner 3d-subenergy level, they screen the 4s electrons fairly high thus the increase in effective nuclear charge across the period is slight. Therefore the increase in ionisation energy across the transition series is not as sharp as that across the short 3rd period (*see section 4.2.6*).

8.2.3 Atomic radius

Table 8.3 shows atomic radii of elements in the first transition series.

Table 8.3 Atomic radii of first transition series

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic Radius/nm	0.144	0.132	0.122	0.117	0.117	0.116	0.116	0.115	0.117	0.125

Plotting atomic radius against the element yields the graph in figure 8.1.

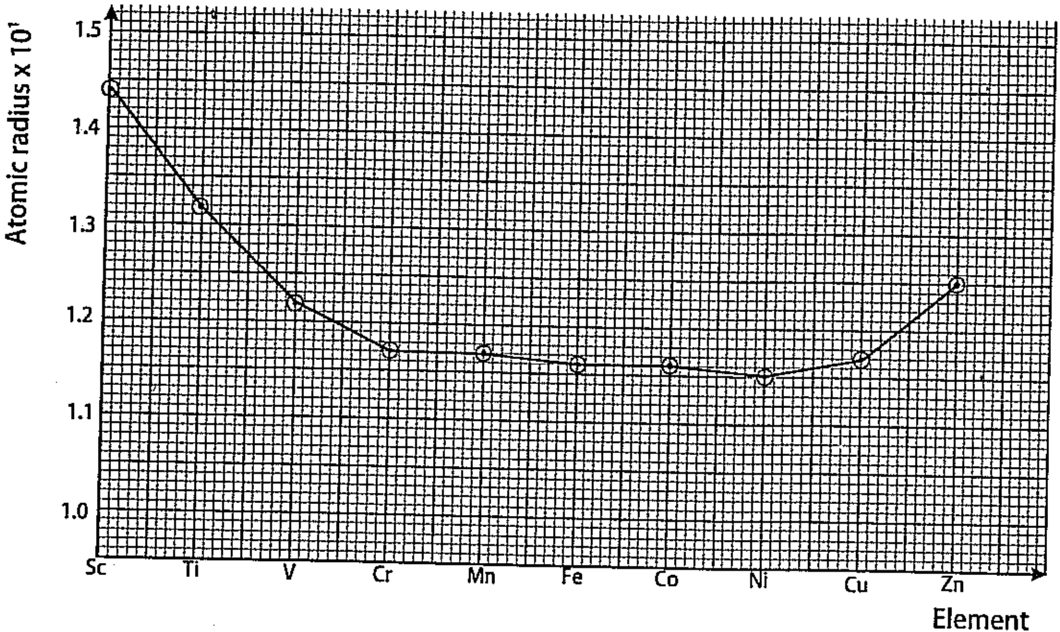


Figure 8.1 Graph of atomic number against element

The graph shows a general slight decrease in atomic radii as the atomic number increases. As the atomic number increases, the nuclear charge also increases. However, the electrons are being added to the inner 3d-subenergy level. These electrons are poorly shielded from the nuclear charge. The nuclear attraction for the outer electrons therefore increases leading to a slight decrease in atomic radii.

There is a slight increase in atomic radius from nickel to copper because the 3d-subenergy level in copper is fully filled with electrons. This increases the shielding of the outer electrons from the nuclear charge thus atomic radius increases.

8.3 Chemical Properties

Transition elements are typically characterized by the following chemical properties;

- Variable oxidation states
- Formation of coloured ions (compounds)
- Complex ion formation
- Paramagnetism
- Catalytic activity

8.3.1 Variable oxidation states

During ionisation, 4s electrons are removed first followed by 3d electrons. The energy difference between the 3d and 4s electrons is very small thus transition elements can easily lose both 3d and 4s electrons. Consequently, transition elements have variable oxidation states.

Table 8.4 shows oxidation states exhibited by elements in the first transition series. The **bolded** oxidation states are the most usual (stable) ones for the particular element. When a transition element forms a compound using an oxidation state higher than its most stable one, the compound formed is an oxidizing agent; the oxidation state of manganese in potassium permanganate is +7, which is higher +2 (the most stable oxidation state for manganese). Consequently, potassium permanganate is an oxidizing agent.

Table 8.4 Oxidation states of first transition series

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	**+4**	+5	+6	+7	+6	+4	+4	**+2**	**+2**
	+3	**+4**	**+3**	+6	**+3**	+3	**+2**	+1	
	+2	+3	+2	+4	+2	**+2**			
		+2		+3					
				+2					

Lower oxidation states are generally reducing e.g. Cu^+ and $Mn^{2+}$are reducing; higher oxidation states are oxidizing e.g. $MnO_4^-$and CrO_4^{2-}.

Lower oxidation states form mainly basic compounds while higher oxidation states are generally acidic.

Compounds in high oxidation states are mainly covalent e.g. $TiCl_4$, and Mn_2O_7. This is due to the high charge density of the cation which makes it highly polarizing.

8.3.2 Formation of coloured ions

Transition elements form coloured compounds due to possession of partially filled d-subenergy level. In a transition metal atom, the d-orbitals are degenerate; however, in a transition metal ion, the d-orbitals are non-degenerate. Therefore, with in a transition ion, electron transitions can occur within the non-degenerate d-orbitals. These transitions lead to absorption of energy. The frequency of light absorbed is in the visible region of the spectrum; thus transition ions are coloured.

The scandium ion (Sc^{3+}) has no d-electrons, and thus it is colourless; the copper(I) ion (Cu^+) and the zinc ion (Zn^{2+}) have fully filled d-orbitals and thus lack any possible d-d electron transitions. Consequently, copper(I) and zinc ions are colourless.

When a transition metal ion is surrounded by ligands (e.g. water), the energy of its d-orbitals is affected; different ligands affect this energy differently thus a transition metal ion may show different colours when surrounded by different ligands e.g.

- $[Cu(H_2O)_4]^{2+}$ is light blue while $[Cu(NH_3)_4]^{2+}$ is deep blue;
- $CuCl_4^{2-}$ is yellow while $CuCl_2$ is green.

In addition to nature of ligand, colour of a particular transition metal ion also depends on oxidation state thus;

- Fe^{2+} is green while Fe^{3+} is brown
- MnO_4^- is purple while MnO_4^{2-} is green

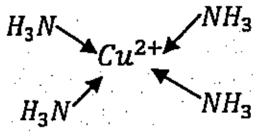
Table 8.5 shows colour of some few transition ions in aqueous solution.

Table 8.5 Colour of some aqueous transition ions

Ion	Sc^{3+}	V^{3+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Co^{3+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Colour	Colourless	Purple	Faint pink	Green	Pink	Blue	Green	Blue	colourless

8.3.3 Complex ion formation

A complex ion is an ion that contains a central ion or atom linked to other atoms, ions or molecules via coordinate bonds. E.g $Cu(NH_3)_4^{2+}$ shown below



Transition metals form complexes (*also known as coordination compounds*) with ligands. During complex formation, a lone pair of electrons is coordinated from the ligand (donor atom, ion or molecule) to the central atom or ion. The central atom or ion must possess empty or partially filled orbitals to accommodate the lone pair.

Transition elements are able to form complexes because they possess partially filled d-orbitals which can accommodate lone pairs of electrons from ligands.

A ligand is a neutral molecule or ion capable of coordinating a lone pair of electrons into empty orbitals of a central atom or ion. Examples of neutral ligands include ammonia (NH_3), water (H_2O), and carbonmonoxide (CO) among others. Examples of anionic ligands include a chloro (Cl^-), cyano (CN^-), and hydroxo ($\bar{O}H$) among others.

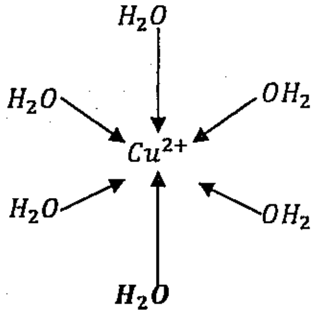
Coordination number

This is the number of coordinate bonds a central atom or ion is able to form with ligands.

Examples

Complex	**Coordination number.**
$Co(NH_3)_6^{3+}$	6
$CuCl_4^{2-}$	4
$[CrCl_2(H_2O)_4]^+$	6

The majority of transition metals form complexes with a coordination number of six (six *ligands surrounding the central atom or ion*). Such complexes adopt octahedral structure as the structure below illustrates (*see section 2.2.3 for a detailed discussion of shapes of molecules*)

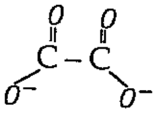


$Cu(H_2O)_6{}^{2+}$

In some cases, a coordination number of four is used and the complex formed adopts a tetrahedral structure or square planar. Coordination numbers may vary from element to element; an element may also use varying coordination numbers as in case of copper and iron.

Element	**Common coordination number used**
Cu	4 and 6
Fe	4 and 6
Cr	6
Co	6

A ligand must possess atleast a non-bonding pair of electrons. A ligand which forms only one coordinate bond with the central atom or ion is called **monodentate;** examples of such ligands include NH_3, CN^-, and H_2O among others.

A ligand which forms more than one coordinate bond with the central atom or ion is called **polydentate;** examples include oxalates () and ethane-1,2-diamine ($H_2\ddot{N}CH_2CH_2\ddot{N}H_2$) among others.

In case of monodentate ligands, coordination number corresponds to the number of ligands. However, for bidentate ligands, coordination number is twice the number of ligands; in the complex $[Cu(H_2NCH_2CH_2NH_2)_2]^{2+}$, coordination number is four. Both transition and non-transition metals, for example beryllium, form complexes but complex formation is more pronounced in transition elements due to presence of incompletely filled 3d-subenergy level.

8.3.3.1 Nomenclature of complexes

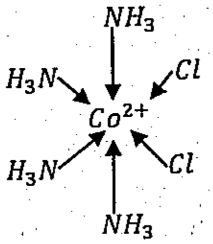
Within a formula of a complex, the central atom appears first, followed by anionic ligands and then neutral ligands, as in $CoCl_2(NH_3)_4^+$, $Fe(OH)_2(H_2O)_4^+$ and so on. The following rules are applied to name the complexes;

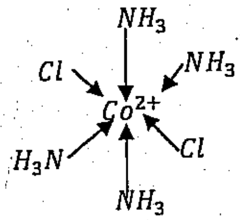
(a) Cations are named before anions.

(b) Names of ligands precede the name of the central atom or ion.

(c) Oxidation state of the central ion is shown in roman numerals after the name of the ion.

$[Co(NH_3)_4Cl_2]^+$





Ionisation isomerism

This is the type of isomerism where compounds having the same formula yield different ions in solution for example;

$[Co(NH_3)_5Br]^{2+}SO_4^{2-}$ and $[Co(NH_3)_5SO_4]^+Br^-$

Hydrate isomerism

These differ by the amount of water of crystallisation, for example

$[Cr(H_2O)_6]Cl_3$ Violet
$[Cr(H_2O)_5Cl]Cl_2.H_2O$ Green
$[Cr(H_2O)_4Cl_2]Cl.2H_2O$ Green

The above complexes precipitate different amounts of silver chloride when treated with silver nitrate solution. The amount of silver chloride precipitated is in the ratio 3:2:1 respectively. They also show different conductivity.

Optical isomerism

This usually occurs in complexes which contain bidentate ligands. By this isomerism, the isomers are not super-imposable on each other.

8.3.4 Paramagnetism

Substance which are weakly attracted by a strong magnetic field are said to be paramagnetic. Transition metals are paramagnetic due to possession of un-paired electrons. Un-paired electrons spin on their axes thus inducing magnetic moments. Paramagnetic strength increases with increase in the number of un-paired electrons.

8.3.5 Catalytic activity

Catalytic activity of transition metals and their compounds is associated with their variable oxidation states. Transition elements in the first transition series use both their 4s and 3d electrons for bonding. This enables the transition element to form temporary bonds with the reactant molecules. This increases the concentration of the reactants at the surface of the transition metal (catalyst) and weakens the bonds in the reacting molecules, thus lowering activation energy.

In homogeneous catalysis, the variable oxidation state of the transition element enables it to take part in a sequence of reaction stages and emerges unchanged at the end of the reaction.

Transition elements and their compounds are used to catalyse the following chemical reactions;

Platinum, nickel, and palladium are used in hydrogenation of alkenes and alkynes,

Finely divided iron is used in the Haber process to combine nitrogen and hydrogen,

Platinum is used in the oxidation of ammonia,

Vanadium(V) oxide in used in the Contact process for manufacture of sulphuric acid,

Haemoglobin, which contains iron(II), is the catalyst used in respiration.

8.4 Chemistry of Chromium

Chromium is a hard white metal which is resistant to chemical attack at room temperature. Its atomic number is 24 and electronic configuration is [Ar]$4s^1 3d^5$. Possible oxidation states of chromium are +2, +3, and +6. The +3 oxidation state is the most stable one. Compounds in +2 oxidation state are reducing agents while those in +6 oxidation state, for example potassium dichromate (VI), are oxidising agents.

When a solution of acidified potassium dichromate(VI) is reduced using zinc amalgam, its orange colour changes to green (+3 oxidation state) and finally to blue (+2 oxidation state).

8.4.1 Reactions of chromium

With air

It reacts with air on heating to form chromium(III) oxide.

$$4Cr(\mathrm{s}) + 3O_2(\mathrm{g}) \longrightarrow 2Cr_2O_3(\mathrm{s})$$

With chlorine

It reacts with chlorine, on heating, to form chromium(III) chloride.

$$2Cr(\mathrm{s}) + 3Cl_2(\mathrm{g}) \longrightarrow 2CrCl_3(\mathrm{s})$$

With dilute acids

It reacts with dilute hydrochloric acid and dilute sulphuric acid to form chromium(II) chloride and chromium(II) sulphate respectively, with liberation of hydrogen gas. The chromium(II) salts are readily oxidised to chromium(III) salts by air.

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

It is rendered passive by concentrated nitric acid.

With water

Chromium decomposes steam, at red heat, to form chromium(III) oxide and hydrogen gas.

$$2Cr(s) + 3H_2O(l) \longrightarrow Cr_2O_3(s) + 3H_2(g)$$

8.4.3 Uses of chromium

Used in production of steel alloys.

Used in plating steel articles.

8.4.3 Compounds of chromium

It forms compounds mainly in oxidation states of +3 and +6.

8.4.3.1 Chromium(VI) compounds

Chromium(VI) oxide, (CrO_3)

This is prepared by reacting concentrated sulphuric acid with a cold solution of concentrated potassium dichromate(VI). It exists as red crystals.

It is soluble in water form chromic(VI) acid. It's therefore an acidic oxide.

$$CrO_3(s) + H_2O(l) \longrightarrow H_2CrO_4(aq)$$

It is decomposed by heat to form chromium(III) oxide.

$$4CrO_3(s) \xrightarrow{heat} 2Cr_2O_3(s) + 3O_2(g)$$

It is a powerful oxidising agent.

Chromate(VI), CrO_4^{2-} and dichromate(VI), $Cr_2O_7^{2-}$

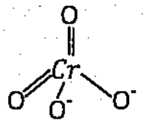
Chromates

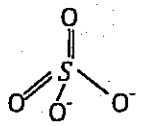
Chromates are yellow and stable only in alkaline solutions. Silver chromate is red. When acidified, the chromate ion is converted into a dichromate ion.

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

Chromates are also stable in aqueous solutions due to hydrolysis of the chromate ions to produce hydroxyl ions.

A chromate ion has a similar structure to a sulphate ion i.e. tetrahedral shape.





Chromates are prepared by oxidation of chromium(III) salts with sodium peroxide in aqueous solution.

$$2Cr^{3+}(aq) + 4\bar{O}H(aq) + 3O_2^{2-}(aq) \longrightarrow 2CrO_4^{2-}(aq) + 2H_2O(l)$$

Soluble chromates are used to test for silver ions, barium ions, and lead(II) ions.

$$2Ag^{+}(aq) + CrO_4^{2-}(aq) \longrightarrow Ag_2CrO_4(s)$$

red precipitate

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow PbCrO_4(s)$$

yellow precipitate

$$Ba^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow BaCrO_4(s)$$

yellow precipitate

Chromates are oxidising agents when acidified.

$$CrO_4^{2-}(aq) + 8H^{+}(aq) + 3e \longrightarrow Cr^{3+}(aq) + 4H_2O(l)$$

Dichromates

Dichromates are orange in colour. They are only stable in acidic solutions. In alkaline solutions, they are converted to chromates.

$$Cr_2O_7^{2-}(aq) + 2\bar{O}H(aq) \rightleftharpoons 2CrO_4^{2-}(aq) + H_2O(l)$$

Sodium dichromate is highly deliquescent; therefore it cannot be used as a primary standard. Potassium dichromate is, however, a primary standard since it is highly soluble and not deliquescent. It can also be easily obtained in pure state.
Dichromates are strong oxidising agents when acidified.

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

They can oxidise;

Sulphites to sulphates

$$SO_3^{2-}(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H^{+}(aq) + 2e$$

Hydrogen sulphide to sulphur

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

Iodide ions to iodine

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

Iron(II) ions to iron(III) ions

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

Oxalates to carbon dioxide

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

8.4.3.2 Chromium(III) compounds

Chromium(III) oxide, (Cr_2O_3)

This is obtained by heating chromium in oxygen or by heating ammonium dichromate(VI)

$$4Cr(s) + 3O_2(g) \longrightarrow 2Cr_2O_3(s)$$

$$(NH_4)_2Cr_2O_7(s) \longrightarrow Gr_2O_3(s) + 4H_2O(l) + N_2(g)$$

It is a dark green solid which is amphoteric.

$$Cr_2O_3(s) + 6H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3H_2O(l)$$

$$Cr_2O_3(s) + 6\bar{O}H(aq) + 3H_2O(l) \longrightarrow 2Cr(OH)_6^{3-}(aq)$$

Chromium(III) hydroxide, $Cr(OH)_3$

This is obtained as a green precipitate when an alkali is added to a solution containing chromium(III) ions.

$$Cr^{3+}(aq) + 3\bar{O}H(aq) \longrightarrow Cr(OH)_3(s)$$

$$2Cr^{3+}(a2) + 3CO_3^{2-}(aq) + 3H_2O(l) \longrightarrow 2Cr(OH)_3(s) + 3CO_2(g)$$

It is amphoteric hence the green precipitate dissolves in excess alkali. It also dissolves in acid.

$$Cr(OH)_3(s) + \bar{O}H(aq) \longrightarrow Cr(OH)_4^-(aq)$$

Or $Cr(OH)_3(s) + 3\,\bar{O}H(aq) \longrightarrow Cr(OH)_6^{3-}(aq)$

Therefore when dilute sodium hydroxide is added to a solution of a chromium(III) salt (e.g. chromium(III) chloride), a green precipitate that dissolves in excess to give a green solution is observed.

Solutions of chromium(III) salts are acidic due to hydrolysis of chromium(III) ions. The chromium(III) ion has a high charge density which weakens the O-H bond of the water molecule resulting into proton loss.

$$Cr(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons [Cr(OH)_5OH]^{2+}(s) + H_3O^+(aq)$$

Chromium(III) chloride, $CrCl_3$

This is a reddish-brown solid obtained by passing chlorine over heated chromium. The hydrated salt is dark green.

$$2Cr(s) + 3Cl_2(g) \longrightarrow 2CrCl_3(s)$$

Chromium(III) sulphate, $Cr_2(SO_4)_3.nH_2O$

This occurs with a range of amounts of water of crystallisation thus its colour ranges from violet to green.

8.4.4 Analysis of chromium(III) ions

Appearance

Chromium(III) compounds are either green or violet in solid state.

Using sodium hydroxide solution

To the solution of the unknown, add sodium hydroxide dropwise until in excess followed by hydrogen peroxide.

Formation of a green precipitate soluble in excess to form a green solution shows presence of chromium(III) ions. The solution turns yellow on addition of hydrogen peroxide due to formation of chromate ions. If lead(II) ethanoate (Pb^{2+} ions) is added to the above solution, a yellow precipitate is observed.

$$Cr^{3+}(aq) + 3\bar{O}H(aq) \longrightarrow Cr(OH)_3(s)$$

$$Cr(OH)_3(s) + \bar{O}H(aq) \longrightarrow Cr(OH)_4^-(aq)$$

$$2Cr^{3+}(aq) + 10\bar{O}H(aq) + 3H_2O_2(aq) \longrightarrow 2CrO_4^{2-}(aq) + 8H_2O(l)$$

$$Pb^{2+}(aq) + 2CrO_4^{2-}(aq) \longrightarrow PbCrO_4(s)$$

Using ammonia solution

To the solution of the unknown, add ammonia solution dropwise until in excess. Formation of a green precipitate soluble in excess to form a violet solution shows presence of chromium(III) ions.

$$Cr^{3+}(\text{aq}) + 3\bar{O}H(\text{aq}) \longrightarrow Cr(OH)_3(\text{s})$$

$$Cr(OH)_3(\text{s}) + 6NH_3(\text{aq}) \longrightarrow Cr(NH_3)_6^{3+}(\text{aq}) + 3\bar{O}H(\text{aq})$$

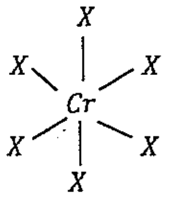
Using a solution of a carbonate

To the solution of the unknown, add sodium carbonate solution.
Formation of a green precipitate with bubbles of a colourless gas that turns lime water milky shows presence of Cr^{3+} ions.

$$2Cr^{3+}(\text{aq}) + 3CO_3^{2-}(\text{aq}) + 3H_2O(\text{l}) \longrightarrow 2Cr(OH)_3(\text{s}) + 3CO_2(\text{g})$$

8.4.5 Complex formation by chromium(III) ions

Chromium(III) ions form a great number of complexes in which chromium is octahedrally surrounded by six neutral ligands (e.g. NH_3 and H_2O) or charged ligands (e.g. Cl^- and $\bar{O}H$) or a mixture of both.



Where X is the ligand. The

Examples include $Cr(NH_3)_6^{3+}$, $Cr(OH)_6^{3-}$, and $[Cr(NH_3)_4Cl_2]^+$

8.5 Chemistry of Manganese

Manganese is a silvery metal. Its atomic number is 25 and electronic configuration is $1s^22s^22p^63s^23p^64s^23d^5$. Possible oxidation states of manganese include +2, +3, +4, +6 and +7.

8.5.1 Reactions of manganese

With air

It reacts with air, **on heating**, to form tri-manganate tetraoxide.

$$3Mn(\text{s}) + 2O_2(\text{g}) \longrightarrow Mn_3O_4(\text{s})$$

With chlorine

It burns in chlorine to form manganese(II) chloride.

$$Mn(\text{s}) + Cl_2(\text{g}) \longrightarrow MnCl_2(\text{s})$$

With dilute acids

It reacts with dilute acids to form manganese (II) salts and hydrogen gas.

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

With nitrogen

$$3Mn(\text{s}) + N_2(\text{g}) \longrightarrow Mn_3N_2(\text{s})$$

With sulphur:

$$Mn(\text{s}) + S(\text{s}) \longrightarrow Mns(\text{s})$$

8.5.2 Compounds of Manganese

It forms compounds in oxidation states of +2, +3, +4, +6 and +7. The +2 oxidation state ($1s^22s^22p^63s^23p^63d^5$) is the most stable one owing to the stability of the half-filled 3d-subenergy level. The +2 oxidation state can be oxidised to +7 oxidation state by powerful oxidising agents like lead(IV) oxide, and sodium bismuthate among others. The +7 oxidation state is a powerful oxidising agent.

8.5.2.1 Manganese(II) Compounds

Manganese(II) oxide

This is a grey-green solid obtained by heating manganese(II) carbonate or manganese(II) oxalate in absence of air.

$$MnCO_3(\text{s}) \xrightarrow{heat} MnO(\text{s}) + CO_2(\text{g})$$

$$MnC_2O_4(\text{s}) \xrightarrow{heat} MnO(\text{s}) + CO(\text{g}) + CO_2(\text{g})$$

Manganese(II) hydroxide, $Mn(OH)_2$

This is formed as a white precipitate when sodium hydroxide is added to a solution containing manganese(II) ions. The precipitate rapidly turns to brown due to oxidation to hydrated manganese(III) oxide (*or hydrated manganese(IV) oxide*) by air.

$$Mn^{2+}(\text{aq}) + 2\bar{O}H(\text{aq}) \longrightarrow 2Mn(OH)_2(\text{s})$$

then $2Mn(OH)_2(\text{s}) + \tfrac{1}{2}\,O_2(\text{g}) \longrightarrow Mn_2O_3.2H_2O(\text{s})$

or $2Mn(OH)_2(\text{s}) + O_2(\text{g}) \longrightarrow 2MnO_2.H_2O(\text{s})$

Manganese(II) carbonate, $MnCO_3$

This is precipitated as a white solid when manganese(II) ions combine carbonate ions.

$$Mn^{2+}(\text{aq}) + CO_3^{2-}(\text{aq}) \longrightarrow MnCO_3(\text{s})$$

Manganese(II) sulphide, MnS

This is a pale pink solid formed when hydrogen sulphide is passed through an aqueous solution of manganese(II) ions in presence of aqueous ammonia and ammonium chloride.

$$Mn^{2+}(\text{aq}) + S^{2-}(\text{aq}) \longrightarrow MnS(\text{s})$$

The hydrated manganese(II) ion, $Mn(H_2O)_6^{2+}$, is pale pink but solutions containing manganese(II) ions appear colourless when sufficiently dilute.

8.5.2.2 Manganese(III) Compounds

These are un-common and they tend to disproportionate to Mn^{2+} and Mn^{4+}in aqueous solution.

Manganese(III) oxide, Mn_2O_3

This is a brown solid made by heating manganese(IV) oxide to red hot in air. In aqueous solution, the Mn^{3+} ion is a strong oxidising agent.

8.5.2.3 Manganese(IV) Compounds

Manganese(IV) oxide is the only important manganese(IV) compound. It is a black solid, insoluble in water, made by heating manganese(II) nitrate.

$$Mn(NO_3)_2(\text{s}) \xrightarrow{heat} MnO_2(s) + 2NO_2(\text{g})$$

It is a powerful oxidising agent and readily oxidises concentrated hydrochloric acid to chlorine.

Half-equations

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

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

Overall reaction

$$MnO_2(\mathrm{s}) + 4H^+(\mathrm{aq}) + 2Cl^-(\mathrm{aq}) \longrightarrow Mn^{2+}(\mathrm{aq}) + 2H_2O(\mathrm{l}) + Cl_2(\mathrm{g})$$

It also oxidises oxalates to carbondioxide.

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

Overall reaction is

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

When heated, manganese(IV) oxide decomposes to oxygen and tri-manganese tetraoxide.

$$3MnO_2(\mathrm{s}) \xrightarrow{heat} Mn_3O_4(s) + O_2(\mathrm{g})$$

Manganese(IV) oxide is used as a catalyst in the decomposition of potassium chlorate and hydrogen peroxide to oxygen gas.

8.5.2.4 Manganese(VI) Compounds

Only potassium manganate(VI) and sodium manganate(VI) are the manganese(VI) compounds known to exist. They are dark green solids and powerful oxidising agents. The manganate(VI) ion readily disproportionates to manganate(VII) ion (MnO_4^-) and manganese(IV) oxide in neutral or acidic solution.

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

$$MnO_4^{2-}(\mathrm{aq}) + 4H^+(\mathrm{aq}) \rightleftharpoons 2MnO_4^-(\mathrm{aq}) + MnO_2(\mathrm{s}) + 2H_2O(\mathrm{l})$$

The manganate(VI) ion can be stabilized by addition of an alkali ($\bar{O}H$) which reverses the above equilbria.

8.5.2.5 Manganese(VII) Compounds

Manganese(VII) oxide

This is prepared by addition of potassium manganate(VII) to cold concentrated sulphuric acid. It is a dark covalent liquid which readily decomposes to manganese(IV) oxide and oxygen.

$$2Mn_2O_7(l) \longrightarrow 4MnO_2(s) + 3O_2(g)$$

Potassium manganate(VII), $KMnO_4$

This is prepared by fusing manganese(IV) oxide and potassium hydroxide in presence of an oxidising agent, e.g. potassium chlorate(V), to form potassium manganate(VI).

$$3MnO_2(s) + 6\bar{O}H(aq) + ClO_3^-(aq) \longrightarrow 3MnO_4^{2-}(aq) + 3H_2O(l) + Cl^-(aq)$$

The green potassium manganate(VI) obtained above is dissolved in water and the mixture is boiled to form potassium manganate(VII) and manganese(IV) oxide.

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

Carbondioxide is bubbled through the solution to remove the hydroxyl ions. This allows the reaction to go to completion.

$$CO_2(g) + 4\bar{O}H(aq) \longrightarrow 4HCO_3^-(aq)$$

Manganese(IV) oxide is removed by filtration. The remaining solution is heated until crystallisation of potassium manganate(VII) begins.

Potassium manganate(VII) is also prepared by reaction of potassium manganate(VI) with chlorine.

$$2MnO_4^{2-}(aq) + Cl_2(g) \longrightarrow 2MnO_4^-(aq) + 2Cl^-(aq)$$

Powerful oxidising agents, like sodium bismuthate in presence of nitric acid, oxidise manganese(II) ions to a pink solution of manganate(VII) ions. This is a confirmatory test for manganese(II) ions.

Potassium manganate(VII) is decomposed by heat to potassium manganate(VI), manganese(IV) oxide and oxygen.

$$2KMnO_4(s) \xrightarrow{heat} K_2MnO_4(s) + MnO_2(s) + O_2(g)$$

Potassium manganate(VII) is a powerful oxidising agent. The half-equation for the reaction is shown below.

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

It can oxidise chloride ions to chlorine gas, iodide ions to iodine, sulphites to sulphates, iron(II) to iron(III), oxalates to carbondioxide, and nitrites to nitrates, as shown by the half equations below.

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

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

$$SO_3^{2-}(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e$$

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

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

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

Uses of potassium manganate(VII)

It is used;

- in volumetric analysis as an oxidising agent,
- in qualitative analysis to identify Cl^-, $C_2O_4^{2-}$, and SO_3^{2-} ions,
- as an oxidising agent in organic synthesis.

Advantages of using potassium permanganate in volumetric analysis

- It does not require an indicator.
- It has a relatively high formula mass thus weighing errors can be minimized.
- It can oxidise a wide range of substances.
- It is fairly soluble in water.
- It is neither hygroscopic nor deliquescent.
- Its reactions are fast at room temperature.

However, potassium manganate(VII) is not a primary standard because;

- It cannot easily be obtained in pure state free from manganese(IV) oxide.
- It is a very powerful oxidising agent such that it can be easily reduced by weak reducing agents even in ordinarily distilled water.
- Its aqueous solutions are un-stable since it can easily be decomposed by light.

$$4MnO_4^-(aq) + 4H^+(aq) \xrightarrow{u.v} 4MnO_2(s) + 3O_2(g) + 2H_2O(l)$$

For this reason, it must be kept in dark bottles.

In neutral or alkaline conditions, potassium manganate(VII) is a weaker oxidising agent than under acidic condition thus;

Alkaline potassium manganate(VII) oxidises iodide ions to iodate (*instead of to I_2 as in case of acidic conditions*) and itself gets reduced to manganese(IV) oxide (*but not manganese(II) ions as in case of acidic conditions*).

Alkaline potassium permanganate is used in organic synthesis to oxidise alkenes to alcohols.

8.5.3 Analysis of manganese(II) ions

Using sodium hydroxide

To the solution of the unknown, add sodium hydroxide solution dropwise until in excess.

Formation of a white precipitate insoluble in excess, which rapidly turns to brown shows presence of manganese(II) ions.

$$Mn^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow 2Mn(OH)_2(s)$$

then $$2Mn(OH)_2(s) + \tfrac{1}{2}O_2(g) \longrightarrow Mn_2O_3.2H_2O(s)$$

Using aqueous ammonia

To the solution of the unknown, add ammonia solution dropwise until in excess.

Formation of a white precipitate insoluble in excess, which rapidly turns to brown shows presence of manganese(II) ions.

$$Mn^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow 2Mn(OH)_2(s)$$

then $$2Mn(OH)_2(s) + \tfrac{1}{2}O_2(g) \longrightarrow Mn_2O_3.2H_2O(s)$$

Using sodium carbonate solution

To the solution of the unknown, add sodium carbonate solution.

Formation of a white precipitate shows presence of manganese(II) ions.

$$Mn^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow MnCO_3(s)$$

Using sodium bismuthate or lead(IV) oxide

To the solution of the unknown, add a few drops of concentrated nitric acid followed by solid sodium bismuthate (*or solid lead(IV) oxide*). Boil the mixture.

Formation of a purple solution confirms presence of manganese(II) ions.

Lead(IV) oxide and sodium bismuthate are powerful oxidising agents in acid solutions. They oxidise Mn^{2+} ions to purple MnO_4^- ions.

$$2Mn^{2+}(aq) + 5PbO_2(s) + 4H^+(aq) \longrightarrow 5Pb^{2+}(aq) + 2MnO_4^-(aq) + 2H_2O(l)$$

8.6 Chemistry of Iron

The atomic number of iron is 26 and its electronic configuration is $1s^22s^22p^63s^23p^64s^23d^6$. When pure, iron is a silvery metal with a very high melting point. It naturally occurs in ores such as Haematite (Fe_2O_3), siderite ($FeCO_3$), and iron pyrites (FeS_2).

8.6.1 Reactions of iron

8.6.1.1 With non metals

With oxygen

It burns in oxygen with bright sparks to form iron(III) oxide.

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

With chlorine

It burns in chlorine to form iron(III) chloride.

$$2Fe(s) + 3Cl_2(g) \longrightarrow 2FeCl_3(s)$$

With sulphur

It reacts with sulphur when heated to form iron(II) sulphide.

$$Fe(s) + S(s) \longrightarrow FeS(s)$$

8.6.1.2 With water

Iron does not react with cold air-free water. It is attacked by steam when red hot to form triiron tetraoxide.

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

In presence of oxygen, iron reacts with cold water to form hydrated iron(III) oxide (*iron rust*)

8.6.1.3 With acids

It reacts with dilute non-oxidising acids (e.g. hydrochloric acid and sulphuric acid) to form iron(II) salts and hydrogen gas.

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

It is oxidised by hot dilute nitric acid to iron(III) salts.

It is rendered passive by concentrated nitric acid.

Formation of a green precipitate insoluble in excess which turns to brown on standing shows presence of iron(II) ions.

$$Fe^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Fe(OH)_2(s)$$

Using ammonia solution

To the solution of the unknown, add ammonia solution dropwise until in excess. Formation of a green precipitate insoluble in excess which turns to brown on standing shows presence of iron(II) ions.

$$Fe^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Fe(OH)_2(s)$$

Using potassium hexacyano ferrate(II) solution

To the solution of the unknown, add potassium hexacyano ferrate(II) solution. Formation of a white precipitate that rapidly turns blue shows presence of iron(II) ions.

Using potassium hexacyano ferrate(III) solution

To the solution of the unknown, add potassium hexacyano ferrate(III) solution. Formation of a dark blue precipitate shows presence of iron(II) ions.

Using potassium thiocyanate solution

To the solution of the unknown, add potassium thiocyanate solution. There will be no observable change. (*compare with iron(III) ions that form a blood red solution*)

8.6.2.2 Iron(III) Compounds

Iron(III) oxide, Fe_2O_3

This occurs naturally as haematite. It is prepared by heating iron(II) hydroxide or iron(II) sulphate.

$$2FeSO_4(s) \xrightarrow{heat} Fe_2O_3(s) + SO_2(g) + SO_3(g)$$

Iron(III) hydroxide, $Fe(OH)_3$

This is best represented as hydrated iron(III) oxide. It is precipitated as a brown solid when dilute sodium hydroxide is added to a solution containing iron(III) ions.

$$Fe^{3+}(aq) + 3\bar{O}H(aq) \longrightarrow Fe(OH)_3(s)$$

Triiron tetraoxide

This occurs naturally as magnetite, which is magnetic. It is a black solid formed when heated iron reacts with steam.

Iron(III) sulphate, $Fe_2(SO_4)_3$

This is prepared by heating an aqueous acidified solution of iron(II) sulphate with hydrogen peroxide (*an oxidising agent*).

$$2FeSO_4(\text{aq}) + H_2SO_4(\text{aq}) + H_2O_2(\text{aq}) \longrightarrow Fe_2(SO_4)_3(\text{aq}) + 2H_2O(\text{l})$$

Iron(III) chloride, $FeCl_3$

This is prepared by passing dry chlorine over heated iron. Iron(III) fluoride, and iron(III) bromide are prepared similarly.

8.6.4 Analysis of iron(III) ions

Using sodium hydroxide solution

To the solution of the unknown, add sodium hydroxide dropwise until in excess. Formation of a brown precipitate insoluble in excess shows presence of iron(III) ions.

$$Fe^{3+}(\text{aq}) + 3\bar{O}H(\text{aq}) \longrightarrow Fe(OH)_3(\text{s})$$

Using aqueous ammonia

To the solution of the unknown, add ammonia solution dropwise until in excess. Formation of a brown precipitate insoluble in excess shows presence of iron(III) ions.

$$Fe^{3+}(\text{aq}) + 3\bar{O}H(\text{aq}) \longrightarrow Fe(OH)_3(\text{s})$$

Using potassium hexacyano ferrate(II) solution

To the solution of the unknown, add potassium hexacyano ferrate(II) solution. Formation of a dark blue precipitate shows presence of iron(III) ions.

Using potassium hexacyano ferrate(III) solution

To the solution of the unknown, add potassium hexacyano ferrate(III) solution. Formation of a brown colouration shows presence of iron(III) ions.

Using potassium thiocyanate solution

To the solution of the unknown, add an equal volume potassium thiocyanate solution. Formation of a blood red solution shows presence of iron(III) ions.

Conversion of iron(III) ions to iron (II) ions

Iron(III) can easily be converted to iron(II) by;

adding dilute sulphuric acid to it followed zinc powder,

$$\text{Zn(s)} + 2\text{Fe}^{3+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq})$$

bubbling hydrogen sulphide gas through its solution.

$$2\text{Fe}^{3+}(\text{aq}) + \text{S}^{2-}(\text{aq}) \longrightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{S(s)}$$

8.7 Chemistry of Cobalt

Cobalt is a hard bluish-white metal which is fairly un-reactive at low temperature. Its atomic number is 27 and electronic configuration is $1s^22s^22p^63s^23p^6\mathbf{4s^23d^7}$. Possible oxidation states of cobalt are +2 and +3. The +2 oxidation state is the most stable one. Compounds in +3 oxidation state are oxidising agents.

8.7.1 Reactions of cobalt

8.7.1.1 With non-metals

With oxygen

It reacts with oxygen, **on heating**, to form cobalt(II) oxide.

$$2Co(\mathrm{s}) + O_2(\mathrm{g}) \longrightarrow 2CoO(\mathrm{s})$$

With sulphur

It combines with sulphur, **on heating**, to form cobalt(II) sulphide.

$$Co(s) + S(s) \longrightarrow CoS(s)$$

8.7.1.2 With acids

It reacts slowly with dilute sulphuric acid and hydrochloric acid to liberate hydrogen gas with formation of cobalt(II) salts.

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

Concentrated nitric acid renders the metal passive due to formation of a film of an oxide around the metal.

It reacts with dilute nitric acid to form cobalt(II) nitrate, nitrogen monoxide and water.

8.7.2 Compounds of Cobalt

8.7.2.1 Cobalt(II) Compounds

Cobalt(II) salts form pink solutions, the colour being due to presence of $Co(H_2O)_6^{2+}$ ions.

Cobalt(II) oxide, CoO

This is a green solid prepared by heating cobalt(II) carbonate or cobalt(II) nitrate.

$$CoCO_3(s) \xrightarrow{heat} CoO(s) + CO_2(\mathrm{g})$$

$$2Co(NO_3)_2(\mathrm{s}) \xrightarrow{heat} 2CoO(\mathrm{s}) + 4NO_2(\mathrm{g}) + O_2(\mathrm{g})$$

Cobalt(II) hydroxide, $Co(OH)_2$

This is precipitated as a blue solid when dilute sodium hydroxide is added to a solution containing Co^{2+} ions.

$$Co^{2+}(\text{aq}) + 2\bar{O}H(\text{aq}) \longrightarrow Co(OH)_2(\text{s})$$

Cobalt(II) hydroxide dissolves in dilute acids forming a pink solution of cobalt(II) ions.

Cobalt(II) sulphide, CoS

This is formed as a black solid when hydrogen sulphide is passed through a solution containing cobalt(II) ions in presence of aqueous ammonia and ammonium chloride.

$$Co^{2+}(\text{aq}) + S^{2-}(\text{aq}) \longrightarrow CoS(\text{s})$$

The solubility product of cobalt(II) sulphide is too high for it to precipitate in acidic solution. Therefore presence of ammonia and ammonium chloride is necessary. When a solution of a cobalt(II) salt is treated with concentrated hydrochloric acid, the pink colour of the solution deepens and eventually becomes deep blue. This is due to formation of a complex, $CoCl_4^{2-}$, which is blue.

$$Co(H_2O)_6^{2+}(\text{aq}) + 4Cl^-(\text{aq}) \rightleftharpoons CoCl_4^{2-}(\text{aq}) + 6H_2O(\text{l})$$

If the blue solution is diluted by adding water (*or cooled*), the above equilibrium is reversed and the pink colour is restored. Why does cooling reverse the above equilibrium?

$$CoCl_4^{2-}(\text{aq}) + 6H_2O(\text{l}) \rightleftharpoons Co(H_2O)_6^{2+}(\text{aq}) + 4Cl^-(\text{aq})$$

8.7.2.2 Cobalt(III) Compounds

The oxidation state of +3 for cobalt is unstable and some of the known compounds include cobalt(III) fluoride (CoF_3) and hydrated cobalt(III) sulphate, $Co_2(SO_4)_3.18H_2O$. Many cobalt(III) complexes exist and are octahedral in shape. Examples include $Co(NH_3)_6^{3+}$, $Co(CN)_6^{3-}$, *and* $Co(NO_2)_6^{3-}$ among others.
$Na_3Co(NO_2)_6$ is soluble while $K_3Co(NO_2)_6$ is insoluble. A solution of $Co(NO_2)_6^{3-}$ ions is therefore used to distinguish between K^+ and Na^+ ions.

8.7.3 Analysis of cobalt(II) ions

Using sodium hydroxide solution

To the solution of the unknown, add sodium hydroxide dropwise until in excess. Formation of a blue precipitate insoluble in excess, which turns to brown on standing shows presence of cobalt(II) ions.

Using aqueous ammonia

To the solution of the unknown, add ammonia solution dropwise until in excess.
Formation of a blue precipitate insoluble in excess, which turns to red on standing shows presence of cobalt(II) ions.

Using a sulphide

To the solution of the unknown, add ammonium sulphide solution (*or hydrogen sulphide*).
Formation of a black precipitate shows presence cobalt(II) ions.

Using potassium thiocyanate solution

To the solution of the unknown, add potassium thiocyanate solution,or ammonium thiocyanate (SCN^-)
Formation of a blue solution shows presence of cobalt(II) ions.

Using concentrated hydrochloric acid

To the solution of the unknown, add concentrated hydrochloric acid.
Formation of a blue solution shows presence of cobalt(II) ions.

8.8 Chemistry of Nickel

Atomic number of nickel is 28 and its electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$.

8.8.1 Reactions of nickel

With oxygen

It reacts with oxygen, on heating, to form nickel(II) oxide.

$$2Ni(\mathrm{s}) + O_2(\mathrm{g}) \longrightarrow 2NiO(\mathrm{s})$$

With acids

It reacts slowly with dilute acids to liberate hydrogen gas with formation of nickel(II) salts.

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

Concentrated nitric acid renders the metal passive due to formation of a film of an oxide around the metal.

8.8.2 Compounds of nickel

Possible oxidation states of nickel are +2, +3, and +4. +2 is the most important one. Most nickel(II) compounds are green and their solutions are green owing to presence of $Ni(H_2O)_6^{2+}$.

Nickel(II) oxide, NiO

This is a green solid prepared by heating nickel(II) carbonate or nickel(II) nitrate.

$$NiCO_3(s) \xrightarrow{heat} NiO(s) + CO_2(\mathrm{g})$$

$$2Ni(NO_3)_2(\mathrm{s}) \xrightarrow{heat} 2NiO(\mathrm{s}) + 4NO_2(\mathrm{g}) + O_2(\mathrm{g})$$

It is basic and dissolves in dilute acids to give green solutions.

Nickel(II) hydroxide, $Ni(OH)_2$

This is precipitated as a green solid when dilute sodium hydroxide is added to a solution containing nickel(II) ions.

$$Ni^{2+}(\mathrm{aq}) + 2\bar{O}H(\mathrm{aq}) \longrightarrow Ni(OH)_2(\mathrm{s})$$

It is basic and therefore does not dissolve in excess sodium hydroxide. However, it dissolves in excess ammonia to form a blue solution. This is due to formation of a soluble complex.

$$Ni(OH)_2(s) + 6NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{2+}(aq) + 2\bar{O}H(aq)$$

Other insoluble salts of nickel include nickel(II) carbonate, nickel(II) sulphide among others.

Complexes of nickel

Nickel forms a variety of complexes such as $Ni(H_2O)_6^{2+}$ (*green*), and $Ni(NH_3)_6^{2+}$ (*blue*), which are octahedral in shape. $[Ni(CN)_4]^{2-}$ is square planar.

Another important complex of nickel is ***nickel dimethylglyoximate*** which is formed as red precipitate when ***dimethylglyoxime*** is added to a solution containing nickel(II) ions, just made alkaline by addition of ammonia. This is used as a confirmatory test for nickel(II) ions.

8.8.3 Analysis of nickel(II) ions

Nickel(II) compounds form green solutions.

Using sodium hydroxide solution

To the solution of the unknown, add sodium hydroxide dropwise until in excess. Formation of a green precipitate insoluble in excess shows presence of Ni^{2+} ions.

$$Ni^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Ni(OH)_2(s)$$

Using aqueous ammonia

To the solution of the unknown, add ammonia solution dropwise until in excess. Formation of a green precipitate soluble in excess to give a blue solution shows presence of Ni^{2+} ions.

$$Ni^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Ni(OH)_2(s)$$

$$Ni(OH)_2(s) + 6NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{2+}(aq) + 2\bar{O}H(aq)$$

Using sodium carbonate

To the solution of the unknown, add sodium carbonate solution.

Formation of a green precipitate may show presence of nickel(II) ions.

$$Ni^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow NiCO_3(s)$$

Using ammonium sulphide

To the solution of the unknown, ammonium sulphide (*or hydrogen sulphide*).
Formation of a black precipitate may show presence of nickel(II) ions.

$$Ni^{2+}(aq) + S^{2-}(aq) \longrightarrow NiS(s)$$

Using dimethylglyoxime

To the solution of the unknown, add ammonia until just alkaline then followed by dimethylglyoxime.
Formation of a red precipitate confirms presence of nickel(II) ions.

8.9 Chemistry of Copper

Atomic number of copper is 29 and its electronic configuration is $1s^22s^22p^63s^23p^64s^13d^{10}$. Copper is a reddish brown metal of very high melting point.

8.9.1 Reactions of Copper

8.9.1.1 With non metals

With air

It reacts with oxygen on heating to form copper(II) oxide

$$2Cu(\mathrm{s}) + O_2(\mathrm{g}) \longrightarrow 2CuO(\mathrm{s})$$

With sulphur

It is attacked by sulphur vapour on heating to form copper(I) sulphide.

$$2Cu(s) + S(s) \longrightarrow Cu_2S(\mathrm{s})$$

With halogens

It is attacked by halogens when heated to form copper(II) halides, except iodine which forms copper(I) iodide. Why does iodine form copper(I) iodide instead of copper(II) iodide?

$$Cu(\mathrm{s}) + F_2(\mathrm{g}) \longrightarrow CuF_2(\mathrm{s}); \qquad Cu(\mathrm{s}) + Cl_2(\mathrm{g}) \longrightarrow CuCl_2(\mathrm{s})$$

$$Cu(\mathrm{s}) + Br_2(\mathrm{l}) \longrightarrow CuBr_2(\mathrm{s})\ ; \qquad Cu(\mathrm{s}) + I_2(\mathrm{s}) \longrightarrow 2CuI(\mathrm{s})$$

8.9.1.2 With water

It is not attacked by water or steam

8.9.1.3 With acids

It is not attacked by dilute non-oxidising acids since it is below hydrogen in the reactivity series.

It is oxidised to copper(II) sulphate by hot concentrated sulphuric acid.

$$Cu(\mathrm{s}) + 2H_2SO_4(\mathrm{l}) \longrightarrow CuSO_4(\mathrm{s}) + 2H_2O(\mathrm{l}) + SO_2(\mathrm{g})$$

It is oxidised by dilute nitric acid to copper(II) nitrate. Water and nitrogen monoxide are also formed.

$$3Cu(\mathrm{s}) + 8HNO_3(\mathrm{aq}) \longrightarrow 3Cu(NO_3)_2(\mathrm{aq}) + 4H_2O(\mathrm{l}) + 2NO(\mathrm{g})$$

It is oxidised by concentrated nitric to copper(II) nitrate; nitric acid is its self reduced to nitrogen dioxide and water.

$$Cu(s) + 4HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2H_2O(l) + 2NO_2(g)$$

8.9.2 Uses of copper

- Used for making winding of dynamos.
- Used for construction of condensers for chemical plants and car radiators due to its high thermal conductivity.
- Brass, which is an alloy of copper and zinc, is used for making working parts of watches and clocks.

8.9.3 Compounds of copper

Possible oxidation states of copper are +1 and +2. +2 is the most stable one. Most copper(II) compounds are green and some blue.

8.9.3.1 Copper(I) Compounds

Copper(I) oxide, Cu_2O

This is obtained as a red solid by reduction of an alkaline solution of copper(II) sulphate.

Copper(I) chloride, $CuCl$

This is a white solid obtained by boiling a solution of copper(II) chloride with excess copper turnings and concentrated hydrochloric acid.

Copper(I) sulphate, Cu_2SO_4

This is obtained as a white solid when copper(I) oxide is heated with anhydrous dimethyl sulphate.

8.9.3.2 Copper(II) Compounds

Copper(II) salts form blue or green solutions due to presence of $Cu(H_2O)_6^{2+}$ complex ions.

Copper(II) oxide

This is a black solid prepared by heating copper(II) carbonate or copper(II) nitrate.

$$CuCO_3(s) \xrightarrow{heat} CuO(s) + CO_2(g)$$

$$2Cu(NO_3)_2(s) \xrightarrow{heat} 2CuO(s) + 4NO_2(g) + O_2(g)$$

It is basic thus dissolves in dilute acids to give blue solutions.

Copper(II) hydroxide, $Cu(OH)_2$

This is precipitated as a blue solid when dilute sodium hydroxide is added to a solution containing copper(II) ions.

$$Cu^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Cu(OH)_2(s)$$

It is basic and therefore does not dissolve in excess sodium hydroxide. However, it dissolves in excess ammonia to form a deep blue solution. This is due to formation of a soluble complex.

$$Cu(OH)_2(s) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq) + 2\bar{O}H(aq)$$

Copper(II) sulphide

This is a black solid formed by passing hydrogen sulphide through an aqueous solution of copper(II) ions

$$Cu^{2+}(aq) + S^{2-}(s) \longrightarrow CuS(s)$$

Other insoluble compounds of copper include hydrated copper(II) sulphate $[CuSO_4.5H_2O]$, hydrated copper(II) nitrate $[Cu(NO_3)_2.3H_2O]$, and copper(II) carbonate $[CuCO_3]$.

8.9.4 Analysis of copper(II) ions

Using sodium hydroxide solution

To the solution of the unknown, add sodium hydroxide dropwise until in excess. Formation of a blue precipitate insoluble in excess shows presence of copper(II) ions.

$$Cu^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Cu(OH)_2(s)$$

Using aqueous ammonia

To the solution of the unknown, add ammonia solution dropwise until in excess. Formation of a blue precipitate soluble in excess to give a blue solution shows presence of copper(II) ions.

$$Cu^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Cu(OH)_2(s)$$

$$Cu(OH)_2(s) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq) + 2\bar{O}H(aq)$$

Using sodium carbonate solution

To the solution of the unknown, add sodium carbonate solution.

Formation of a green precipitate shows presence of copper(II) ions.

$$Cu^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CuCO_3(s)$$

Using ammonium sulphide

To the solution of the unknown, add ammonium sulphide (*or hydrogen sulphide*). Formation of a black precipitate may show presence of copper(II) ions.

$$Cu^{2+}(aq) + S^{2-}(aq) \longrightarrow CuS(s)$$

Using potassium iodide solution

To the solution of the unknown, add potassium iodide solution. Formation of a white precipitate in a brown solution shows presence of copper(II) ions.

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

If sodium thiosulphate is added to the above solution, the solution turns colourless and a white precipitate is left.

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

Using potassium hexacyanoferrate(II) solution

To the solution of the unknown, add potassium hexacyanoferrate(II) solution. Formation of a brown precipitate shows presence o f copper(II) ions.

8.10 Chemistry of Zinc

Atomic number of zinc is 30 and its electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$. Zinc is a white lustrous metal.

8.10.1 Reactions of zinc

With oxygen

It reacts with oxygen, on heating, to form zinc oxide.

$$2Zn(\text{s}) + O_2(\text{g}) \longrightarrow 2ZnO(\text{s})$$

With water

It does not react with cold water but reacts with steam, when heated, to form hydrogen gas and zinc oxide.

$$Zn(\text{s}) + H_2O(\text{g}) \longrightarrow ZnO(\text{s}) + H_2(\text{g})$$

With acids

It reacts with dilute, non-oxidising acids to form zinc salts and hydrogen gas.

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

It is oxidised to zinc sulphate by hot concentrated sulphuric acid.

$$Zn(\text{s}) + 2H_2SO_4(\text{l}) \longrightarrow ZnSO_4(\text{s}) + 2H_2O(\text{l}) + SO_2(\text{g})$$

It is oxidised by dilute nitric acid to zinc nitrate. Water and nitrogen monoxide are also formed.

$$3Zn(\text{s}) + 8HNO_3(\text{aq}) \longrightarrow 3Zn(NO_3)_2(\text{aq}) + 4H_2O(\text{l}) + 2NO(\text{g})$$

In very rare instances, very dilute nitric acid is reduced to dinitrogen oxide by zinc.

$$4Zn(\text{s}) + 10\ HNO_3(\text{aq}) \longrightarrow 4\ Zn(NO_3)_2(\text{aq}) + 5H_2O(\text{l}) + N_2O(\text{g})$$

It is oxidised by concentrated nitric to zinc nitrate while nitric acid is reduced to nitrogen dioxide and water.

$$Zn(\text{s}) + 4HNO_3(\text{aq}) \longrightarrow Zn(NO_3)_2(\text{aq}) + 2H_2O(\text{l}) + 2NO_2(\text{g})$$

With sodium hydroxide

It reacts with sodium hydroxide to liberate hydrogen gas.

$$Zn(\text{s}) + 2\bar{O}H(\text{aq}) + 2H_2O(\text{l}) \longrightarrow Zn(OH)_4^{2-}(\text{aq}) + H_2(\text{g})$$

With sulphur

It reacts with sulphur, on heating, to form zinc sulphide.

$$Zn(\text{s}) + S(\text{s}) \longrightarrow ZnS(\text{s})$$

With halogens

It reacts with halogens, on heating, to form zinc halides.

$$Zn(\text{s}) + Cl_2(\text{g}) \longrightarrow ZnCl_2(\text{s})$$

8.10.2 Uses of zinc

- Used to protect iron from rusting.
- Brass, which is an alloy of copper and zinc, is used for making working parts of watches and clocks.

8.10.3 Compounds of zinc

Most zinc compounds are white and their solutions are colourless. It has one oxidation state of +2.

Zinc oxide, ZnO

This is a white solid prepared by heating zinc carbonate or zinc nitrate. It is yellow when hot.

$$ZnCO_3(s) \xrightarrow{heat} ZnO(s) + CO_2(\text{g})$$

$$2Zn(NO_3)_2(\text{s}) \xrightarrow{heat} 2ZnO(\text{s}) + 4NO_2(\text{g}) + O_2(\text{g})$$

Zinc hydroxide, $Zn(OH)_2$

This is precipitated as a white solid when dilute sodium hydroxide is added to a solution containing zinc ions.

$$Zn^{2+}(\text{aq}) + 2\bar{O}H(\text{aq}) \longrightarrow Zn(OH)_2(\text{s})$$

It is amphoteric and therefore dissolves in excess sodium hydroxide.

$$Zn(OH)_2(\text{s}) + 2\bar{O}H(\text{aq}) \longrightarrow Zn(OH)_4^{2-}(\text{aq})$$

It dissolves in excess ammonia to form a colourless blue solution. This is due to formation of a soluble complex.

$$Zn(OH)_2(\text{s}) + 4NH_3(\text{aq}) \rightleftharpoons Zn(NH_3)_4^{2+}(\text{aq}) + 2\bar{O}H(\text{aq})$$

Other compounds of zinc include zinc chloride $[ZnCl_2]$, hydrated zinc nitrate $[Zn(NO_3)_2.7H_2O]$, and zinc carbonate $[ZnCO_3]$ among others.

Aqueous solutions of zinc are acidic due to hydrolysis.

$$Zn(H_2O)_4^{2+}(\mathrm{aq}) + H_2O(\mathrm{l}) \rightleftharpoons Zn(H_2O)_3(OH)^{+}(\mathrm{aq}) + H_3O^{+}(\mathrm{aq})$$

8.10.4 Analysis of zinc ions

Using sodium hydroxide solution

To the solution of the unknown, add sodium hydroxide dropwise until in excess. Formation of a white precipitate soluble in excess to form a colourless solution may show presence of Zn^{2+} ions.

$$Zn^{2+}(\mathrm{aq}) + 2\bar{O}H(\mathrm{aq}) \longrightarrow Zn(OH)_2(\mathrm{s})$$

$$Zn(OH)_2(\mathrm{s}) + 2\bar{O}H(\mathrm{aq}) \longrightarrow Zn(OH)_4^{2-}(\mathrm{aq})$$

Using aqueous ammonia

To the solution of the unknown, add ammonia solution dropwise until in excess. Formation of a white precipitate soluble in excess to form a colourless solution shows presence of zinc ions.

$$Zn^{2+}(\mathrm{aq}) + 2\bar{O}H(\mathrm{aq}) \longrightarrow Zn(OH)_2(\mathrm{s})$$

$$Zn(OH)_2(\mathrm{s}) + 4NH_3(\mathrm{aq}) \rightleftharpoons Zn(NH_3)_4^{2+}(\mathrm{aq}) + 2\bar{O}H(\mathrm{aq})$$

Using sodium carbonate solution

To the solution of the unknown, add sodium carbonate solution.
Formation of a white precipitate shows presence of zinc ions.

$$Zn^{2+}(\mathrm{aq}) + CO_3^{2-}(\mathrm{aq}) \longrightarrow ZnCO_3(\mathrm{s})$$

Using disodium hydrogen phosphate

To the solution of the unknown, add solid ammonium chloride followed by 2-3 drops of disodium hydrogen phosphate and then excess ammonia.
Formation of a white precipitate soluble in excess confirms presence of zinc ions.

$$Zn^{2+}(\mathrm{aq}) + NH_4^{+}(\mathrm{aq}) + HPO_4^{2-}(\mathrm{aq}) \longrightarrow ZnNH_4PO_4(\mathrm{s}) + H^{+}(\mathrm{aq})$$

8.11 Summary

Transition elements are characterised by formation of coloured compounds and ions, complex formation, paramagnetism, variable oxidation states, and catalytic activity. This chapter has looked at the chemistry of transition elements in period three.

8.11 Suggested further reading on chapter 8

G. F. Liptrot, *Mordern Inorganic Chemistry*, Scotprint Ltd, Fourth Edition, 1983, Chapter 10

W. R. Kneen, *Chemistry, Facts, Patterns and Principles*, Addison-Wesley Pub (Sd), 1972

M. Ntanda, *Concise Solutions to U.A.C.E Chemistry paper one and two;*

Questions

P1 2011 Q12, P2 2009 Q8, P1 2007 Q15, P1 2006 Q4, P1 2006 Q6, P2 2006 Q8, P1 2004 Q15, P2 2004 Q5(a), P1 2002 Q7, P2 2002 Q3, P2 2001 Q8, P1 1998 Q12, P2 1998 Q1, P2 1997 Q3, P2 1985 Q4

8.12 Questions on chapter 8

1. Cobalt, copper, iron and manganese are d-block elements.
   (a) What is meant by a 'd-block element'?
   (b) Write the electronic configuration of Cu, Fe^{2+}, and Mn^{2+}.
   (c) Explain why Fe^{2+} ions are readily oxidised to Fe^{2+} but Mn^{2+} not readily oxidised to Mn^{3+}.
   (d) Cobalt forms a complex compound of the formula $[Co(NH_3)_4Cl_2]^+Cl^-$.
      (i) Determine the oxidation state of cobalt in this complex.
      (ii) Name the complex ion contained in this compound.
      (iii) How many moles of silver chloride would be precipitated from one mole of this compound in aqueous solution by addition of an excess of silver nitrate?

2 (a) (i) Write the electronic configurations of Sc^{3+}, Mn^{3+}, and Zn^{2+}.
      (ii) Which of the ions in (i) above is/are coloureless?
      (iii) What feature of the electronic configuration is responsible for the lack of colour in some ions of d-block elements?
      (iv) What is the maximum possible oxidation state of vanadium (z=23)?
   (b) (i) How would you obtain an aqueous solution of the complex ion $[Cr(NH_3)_6]^{3+}$?
      (ii) What is the oxidation state of chromium in the ion in b(i) above?
      (iii) Name the complex ion $[Cr(NH_3)_4Cl_2]^+$.

3. Give an account of complex ions, paying particular attention to bonding, stability, and different ligand types.

4. Discuss the trend of the following properties across the first row of transition elements.
   - (a) atomic radii
   - (b) oxidation states
   - (c) catalytic behaviour

5. Discuss the reactions of copper with acids.

6. Compare and contrast the chemistry of chromium with;
   - (a) Zinc
   - (b) Aluminium

   Your answer should include reaction of the elements with;
   - (i) water
   - (ii) acids
   - (iii) alkalis

7. Explain the following observations
   - (a) When sodium hydroxide is added to a solution of chromium(III) chloride followed by excess hydrogen peroxide, a green precipitate is formed and later a yellow solution.
   - (b) Potassium manganate(VII) cannot be acidified using dilute hydrochloric acid.
   - (c) Solutions of potassium manganate(VII) should be kept in dark bottles.
   - (d) Rusting of iron is an electrochemical process.
   - (e) When concentrated hydrochloric acid is added to a solution of cobalt(II) sulphate, the solution becomes deep blue; when the deep blue solution is cooled, it turns to pink.

CHAPTER

9

APPLIED INORGANIC CHEMISTRY

Learning Objectives

After reading this chapter, you should be able to:

- Explain the general principles behind the extraction of elements.
- Describe the process of extraction of;
  - Sodium
  - Aluminum
  - Iron
  - Copper
  - zinc
- Describe the process for manufacture of;
  - Ammonia
  - Sulphuric acid
  - Nitric acid
  - Cement

9.1 Occurrence and extraction of metals

9.1.1 General principles of metallurgy

An important aspect of metallurgy is the extraction and refining of metals from their ores.

An **ore** is a naturally occurring rock which is rich in minerals such that certain elements can be extracted from it.

All metals occur naturally as compounds, most especially as oxides, sulphides, chlorides, or carbonates. These compounds are mixed with earthly materials (*gangue*).

Group 1 and group 2 metals are highly reactive and are generally extracted by electrolysis.

Other metals are generally extracted by reduction of their oxides using carbon, carbonmonoxide, or more reactive metals.

Extraction of a metal from its ore generally involves 3 major processes namely;

(a) Concentration (*or extraction*) of the ore.

(b) Reduction of the ore to the impure metal.

(c) Refining (*or purification*) of the impure metal.

9.1.1.1 Concentration of the ore

Ores normally occur mixed with earthly materials. Gangue is removed before extraction. The process of removing gangue is called **concentration of the ore.**

There are various methods of concentrating the ore; some physical while others are chemical.

Physical methods of concentrating the ore include:

(i) Froth flotation

By this method, the ore is powdered (pulverised), mixed with water and oil (frothing agent) and then air is blown through the mixture. A froth is formed. The oil wets the ore while water wets the gangue. The froth of the oil, which mainly contains the ore, floats and is skimmed off the surface. Gangue sinks. An acid is added to break up the froth; the concentrated ore is then filtered and dried.

This method works on the principle of different abilities of the minerals and gangue particles to be moistened by water. It is mostly used to concentrate metal sulphide ores like Galena (PbS), zinc blende (ZnS), copper pyrites ($CuFeS_2$) and iron pyrites (FeS_2).

(ii) Hand picking

By this method, the ore is separated into a fair degree of purity by hand picking and breaking away adherent gangue using a hammer.

(iii) Washing

The ore is usually denser than gangue. The gangue is flushed away by water leaving behind the enriched ore.

(iv) Magnetic separation

If the ore is magnetic, then a magnet is used. To separate magnetite (Fe_3O_4) from gangue, the ore is crushed and electromagnets are used to attract particles of magnetite which is ferromagnetic.

Chemical methods of concentrating the ore include;

(i) Leaching

By this method, the ore is treated with a suitable aqueous reagent that dissolves the ore leaving behind the impurities. For example pure aluminium oxide is obtained from bauxite using concentrated sodium hydroxide. Aluminium oxide dissolves (*since it is amphoteric*) together with silicon(IV) oxide but some impurities do not dissolve.

(ii) Roasting

By this method, the ore is heated in air. Roasting may cause oxidation or reduction and may be accompanied by **calcination**. Calcination is the heating of the ore to bring about decomposition with elimination of volatile products. The volatile products can be carbon dioxide, water or sulphur dioxide in case of sulphites

For example;

$$2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$$
$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

(iii) Smelting

This is the method of concentrating the ore by melting it. Two layers are formed, after melting, which include the molten metal layer and slag. Slag, being less dense, floats on the metal layer.

9.1.1.2 Reduction of the ore

By this process, the ore is reduced to impure metal. There are various methods of reduction but choice of the method depends on position of the metal in the reactivity series. Ores of most electropositive metals (most reactive) are the most difficult to reduce. Reductive methods include;

(i) Roasting in air

This is mostly used for metals below hydrogen in the reactivity series

For example;

$$2HgS(s) + 3O_2(g) \longrightarrow 2SO_2(g) + 2HgO(s)$$
$$2CuFeS_2(s) + 4O_2(g) \longrightarrow Cu_2S(s) + 2FeO(s) + 3SO_2(g)$$
$$2Cu_2S(s) + 3O_2(g) \longrightarrow 2Cu_2O(s) + 2SO_2(g)$$
$$Cu_2S(s) + 2Cu_2O(s) \longrightarrow 6Cu(s) + SO_2(g)$$

(ii) High temperature reduction using carbon or carbon monoxide

For example;

$$2Fe_2O_3(s) + 3C(s) \longrightarrow 4Fe(s) + 3CO_2(g)$$

(iii) Electrolysis

This is used for metals with high negative reduction potentials (*see table* 3.2) for which carbon reduction is not possible. These metals include the most electropositive metals like sodium, aluminium, magnesium, etc

(iv) Reduction by a more reactive metal

By this method, a more reactive metal is used to reduce the ore. However the method is very expensive since it involves the use of an already purified reactive metal.

9.1.1.3 Refining

Various methods are used to refine the impure metal. These include:

- Electrolysis for example in the case of copper.
- Distillation e.g in the case of zinc.
- Zone-refining. This method is used for elements required in a very high state of purity.

9.1.4 Extraction of aluminium

The main ore of aluminium is Bauxite, which is hydrated aluminium oxide ($Al_2O_3.2H_2O$). Other ores include aluminium oxide (Al_2O_3), diaspore ($Al_2O_3.H_2O$), and cryolite which is sodium hexafloro aluminate(III) (Na_3AlF_6). Aluminium is mainly extracted from bauxite, which is usually mixed with impurities such as silica (SiO_2), titanium(IV) oxide and oxides of iron.

The process of extraction

Bauxite is first heated at low temperature to convert iron to +3 oxidation state. The powdered product is heated with excess concentrated sodium hydroxide. The amphoteric aluminium oxide and acidic silicon dioxide dissolve in the alkali.

$$Al_2O_3(s) + 2\bar{O}H(aq) + 3H_2O(l) \longrightarrow 2\,Al(OH)_4^-(aq)$$

$$SiO_2\,(s) + 2\bar{O}H(aq) \longrightarrow SiO_3^{2-}\,(aq) + H_2O(l)$$

Basic iron(III) oxide and titanium(IV) oxide do not dissolve. The un dissolved impurities are filtered off.

The mixture is seeded using pure aluminium hydroxide or carbondioxide gas to precipitate aluminium hydroxide.

$$Al(OH)_4^-\,(aq) \longrightarrow Al(OH)_3(s) + \bar{O}H(aq)$$

$$\textbf{OR}\ 2Al(OH)_4^-\,(aq) + CO_2 \longrightarrow 2\,Al(OH)_3(s) + CO_3^{2-}(aq) + H_2O(l)$$

Aluminium hydroxide is filtered off and heated strongly to form anhydrous aluminium(III) oxide, alumina

$$2Al(OH)_3(s) \longrightarrow Al_2O_3(s) + 3H_2O(g)$$

The alumina is dissolved in molten cryolite and electrolysed between graphite electrodes at about 900°C, low voltage, and high current density. Aluminium is discharged at the cathode.

$$Al^{3+}\,(l) + 3e \longrightarrow Al\,(l)$$

Oxide ions are discharged at the anode liberating oxygen gas

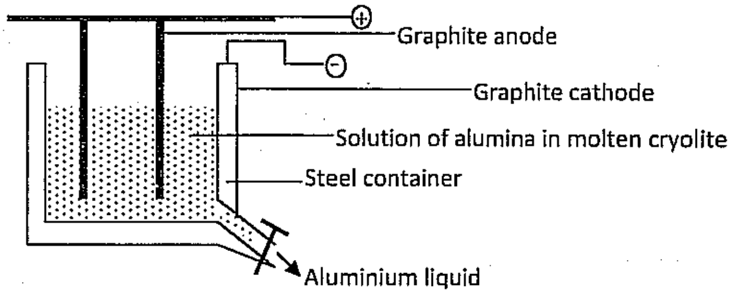


Figure 9.3 Electrolysis of aluminium oxide

Note

- A high voltage is used to avoid decomposition of the solvent, cryolite.
- The process required a large amount of energy, thus it is uneconomical.
- The anode burns in oxygen, thus it has to be replaced from time to time.
- The purpose of sodium hydroxide added is to remove aluminium oxide from impurities.

Uses of aluminium

- Since it is a good conductor of heat, it is used to make saucepans.
- Since it has ability to reflect heat and light, it is used for wrapping food.
- Since it is a good conductor of electricity and has low density, it is used for transmission of electricity.
- Because of its low density and strength, it is used for making bodies of aircrafts.

Reactions of aluminium with;

Air

It reacts with air on heating to form aluminium oxide and aluminium nitride.

$$4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3\,(s)$$

$$2Al(s) + N_2(g) \longrightarrow 2AlN(s)$$

Sodium hydroxide

It reacts with aqueous sodium hydroxide to form sodium aluminate(III).

$$2\,Al\,(s) + 2\bar{O}H(aq) + 6H_2O(l) \longrightarrow 2Al(OH)_4^-(aq) + 3H_2(g)$$

Because of the above reaction, aluminium utensils should not be washed using soap solutions; soap solution contains hydroxyl ions produced by hydrolysis.

$$RCOO^-(aq) + H_2O(l) \rightleftharpoons RCOOH(aq) + \bar{O}H(aq)$$

Hydrochloric acid

It reacts with hot dilute sodium hydroxide to form aluminium chloride.

$$2\,Al(s) + 6H^+(aq) \longrightarrow 2Al^{3+}(aq) + 3H_2(g)$$

9.1.5 Extraction of iron

Ores from which iron is extracted include haematite (Fe_2O_3), magnetite (Fe_3O_4), siderite ($FeCO_3$), and pyrites (FeS_2). The major ores used are haematite and magnetite.

The extraction is carried out in a blast furnace. Haematite, limestone, and coke are fed into the furnace from the top. Hot air at 600°C is fed from the bottom through pipes called tuyeres.

Coke reacts with oxygen to give carbon dioxide in a highly exothermic reaction. The energy given out keeps the process going once the reaction starts.

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

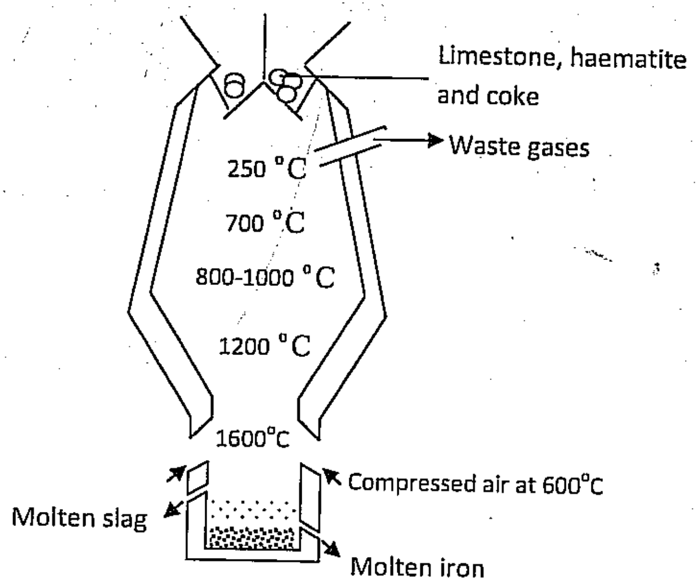


Figure 9.4 Extraction of iron in the blast furnace

Carbon dioxide is reduced to carbonmonoxide by coke thus producing the chief reducing agent.

$$CO_2(g) + C(s) \longrightarrow 2CO(g)$$

At 700°C, haematite is reduced by carbon monoxide to iron.

$$Fe_2O_3(s) + 3CO(g) \rightleftharpoons 2Fe(s) + 3CO_2(g)$$

At 800°C, limestone decomposes to calcium oxide which reacts with impurities (silica) to form a slag of calcium silicate.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

$$CaO(s) + SiO_2(g) \longrightarrow CaSiO_3(l)$$

Molten iron and slag trickle down the furnace. Slag, which has a lower density, floats on iron thus preventing iron from being oxidised by hot air. Iron is tapped off and taken for further treatment.

Waste gases are removed from the top of the furnace and used to produce hot air fed into the furnace. They include carbon monoxide, carbon dioxide, hydrogen, and nitrogen.

9.1.6 Extraction of zinc

Major ores of zinc include zinc blende (ZnS) and zinc carbonate ($ZnCO_3$). Impurities include lead(II) sulphide and silicon(IV) oxide.

The ore is concentrated by froth flotation. The ore is crushed and then mixed with water and a frothing agent. Air is blown through the mixture to form froth. Earthly materials are wetted by water and sink to the bottom. The ore is driven to the surface in froth. The ore is skimmed off.

The concentrated ore is roasted in air to convert it to zinc oxide.

$$2ZnS(\text{s}) + 3O_2(\text{g}) \longrightarrow 2ZnO(\text{s}) + 2SO_2(\text{g})$$

Zinc oxide, coke, and limestone are heated in a furnace. Zinc oxide is reduced to zinc by coke. Zinc boils off and is collected as vapour and then cooled with molten lead and slag.

$$ZnO(\text{s}) + C(\text{s}) \longrightarrow Zn(\text{s}) + CO(\text{g})$$

$$PbO\ (\text{s}) + C(\text{s}) \longrightarrow Pb(\text{s}) + CO(\text{g})$$

$$SiO_2(\text{s}) + CaO(\text{s}) \longrightarrow CaSiO_3(\text{l})$$

Zinc is purified by distillation because of its low boiling point.

9.1.7 Extraction of copper

Ore of copper include copper pyrites ($CuFeS_2$), malachite ($CuCO_3.Cu(OH)_2$), cuprite (CuO), melaconite (CuO). The major ore is copper pyrites.

The extraction process involves three major stages i.e.

- Concentration of the ore.
- Reduction of the ore.
- Purification / refining of copper.

Concentration of the ore:

This is done by froth flotation. The ore is crushed and then mixed with water and a frothing agent. Air is blown through the mixture to produce froth. Earthly materials are wetted by water and sink to bottom. The ore is driven to the surface in froth. The froth is skimmed off, an acid is added to break the ore from the froth, and the mixture is filtered.

Reduction of the ore:

The ore is roasted to convert it to copper(I) sulphide, sulphur dioxide and iron(II) oxide.

$$2CuFeS_2(\text{s}) + 4O_2(\text{g}) \longrightarrow Cu_2S(\text{s}) + 2FeO(\text{s}) + 3SO_2(\text{g})$$

Sand and limestone are added. The mixture is heated in a blast furnace, in absence of air, to convert iron(II)oxide into iron(II) silicate (slag).

$$FeO(\text{s}) + SiO_2(\text{s}) \longrightarrow FeSiO_3(\text{l})$$

The mixture is then heated in a controlled amount of air to produce impure copper (blister copper).

$$2Cu_2S(\text{s}) + 3O_2(\text{g}) \longrightarrow 2Cu_2O(\text{s}) + 2SO_2(\text{g})$$

$$Cu_2S(\text{s}) + 2Cu_2O(\text{s}) \longrightarrow 6Cu(\text{s}) + SO_2(\text{g})$$

Purification of blister copper

Blister copper is purified by electrolysis. Impure blister copper is made the anode while pure copper is made the cathode. The electrolyte is acidified copper(II) sulphate solution.

During electrolysis, the anode dissolves to form copper(II) ions which are deposited at the cathode as pure copper. Reactions taking place are;

At the anode

$$Cu(\text{s}) \longrightarrow Cu^{2+}(\text{aq}) + 2\text{e}$$

At the cathode

$$Cu^{2+}(\text{aq}) + 2\text{e} \longrightarrow Cu(\text{s})$$

Uses of copper

For making electric wires.

For making alloys e.g. bronze (copper and tin), brass (zinc and copper)

For making water pipes.

9.2 Ammonia

9.2.1 Manufacture of ammonia

Raw materials used are nitrogen (from fractional distillation of liquid air) and hydrogen (from natural gas).

$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3H_2(g)$

The gases are purified from carbonmonoxide, sulphur compounds and water vapour which would poison the catalyst. The gases are mixed in the ratio 1:3; nitrogen : hydrogen, compressed and passed over finely divided iron catalyst at a pressure of about 250-350atm and a temperature of between 450-500°C. The gases are cooled while still under pressure and liquid ammonia is removed. The un-reacted hydrogen and nitrogen are recycled for further conversion into ammonia.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Note

A detailed discussion of the reasons behind the choice of pressure, and temperature employed in the Haber process is beyond the scope of this book. This detailed discussion is covered in physical chemistry.

9.2.2 Uses of ammonia

- It is used in the manufacture of nitric acid
- It is used in the manufacture of fertilisers e.g. ammonium sulphate.
  $2NH_3(g) + H_2O(l) + CO_2 g) + CaSO_4(s) \longrightarrow CaCO_3(s) + (NH_4)_2SO_4(aq)$
- Liquid ammonia is used in refrigeration because of its volatility and high molar enthalpy of vaporisation.
- It is used in the manufacture of man-made fibre for textiles e.g nylon.

9.3 Nitric acid

9.3.1Manufacture of nitric acid

It is manufactured by catalytic oxidation of ammonia which involves 3 stages:

- A mixture of dry ammonia and air is passed over platinum catalyst at a temperature of 850°C. Nitrogen monoxide and steam are formed in a highly exothermic reaction.

  $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$ $\Delta H = -950KJ/mol$

- The mixture is cooled and nitrogen monoxide is allowed to react with more air to form nitrogen dioxide.

  $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

- Nitrogen dioxide is then allowed to react with water and more air to produce nitric acid.

  $4NO_2(g) + 2H_2O(l) + O_2(g) \longrightarrow 4HNO_3(aq)$

  Or

  $3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$

Note

The reaction between ammonia and oxygen, in stage 1, is reversible. Therefore, to obtain a better yield of nitric acid, the conditions of this reaction must be tailored appropriately in accordance to La-chateliers principle. A detailed discussion of choice of conditions for this reaction is covered in physical chemistry.

9.3.2 Uses of nitric acid

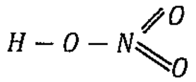
- It is used in the manufacture of nitrogenous fertilisers e.g. ammonium nitrate.
- It is used in the manufacture of explosives and dyes when it reacts with organic compounds.

9.3.3 Properties of nitric acid

Nitric acid is a colourless liquid. However, it readily decomposes photochemically to nitrogen dioxide and soon appears yellow.

$$4HNO_3(aq) \longrightarrow 4NO_2(g) + 2H_2O(l) + O_2(g)$$

Its boiling point is 86°C and its vapour consists of molecules which are planar



$$H-O-N\begin{matrix}\nearrow O\\ \searrow O\end{matrix}$$

Pure nitric acid has no acid properties but its aqueous solutions are acidic.

9.3.3.1 As an acid

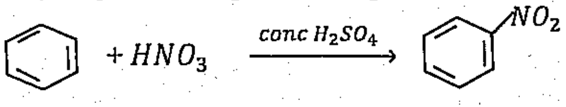
- Dilute nitric acid reacts with carbonates to form carbon dioxide gas.

  $$CO_3^{2-}(aq) + 2H^+(aq) \longrightarrow CO_2(g) + H_2O(l)$$

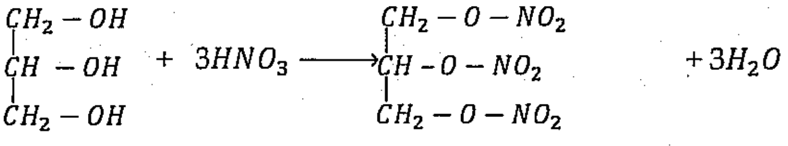
- It reacts with bases to form salts and water only.
- With exception of magnesium and perhaps manganese, metals DO NOT liberate hydrogen from dilute nitric acid. This is because nitric acid is an oxidising agent.

$$Mg(s) + 2HNO_3(aq) \longrightarrow Mg(NO_3)_2(aq) + H_2(g)$$

- In presence of concentrated sulphuric acid, concentrated nitric acid reacts with many organic compounds e.g



- Nitric acid reacts with propane 1,2,3-triol (glycerol) to give glycerol trinitrate which is an explosive.



$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + 3HNO_3 \longrightarrow \begin{array}{l} CH_2-O-NO_2 \\ | \\ CH-O-NO_2 \\ | \\ CH_2-O-NO_2 \end{array} + 3H_2O$$

Glycerol   Glycerol trinitrate

9.3.3.2 As an oxidising agent

Concentrated nitric acid passivates many metals such as beryllium, chromium, and iron by forming a thin impervious oxide film which stops further reaction.

The oxidation state of nitrogen in nitric acid is +5. When nitric acid acts as an oxidising agent, itself gets reduced to nitrogen dioxide (+4 oxidation state) or nitrogen monoxide (+2 oxidation state)

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

$$NO_3^-(aq) + 4H^+(aq) + 3e \longrightarrow NO(g) + 2H_2O(l)$$

It is rare for one of the above reaction to occur in total exclusion of the other. However, under some conditions, one of the above reactions may predominate. The first reaction usually predominates when the acid is highly concentrated while the second reaction predominates when the acid is fairly dilute.

Nitric acid therefore oxidises some metals and non metals. These are basically redox reactions (*see chapter 3 for a detailed discussion of redox reactions*).

Concentrated nitric acid oxidises metals like copper and zinc.

- Warm concentrated nitric acid oxidises copper to copper(II) nitrate while it is reduced to nitrogen dioxide.

$$Cu(s) + 4HNO_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + 2H_2O(l) + 2NO_2(g)$$

However, moderately dilute nitric acid (50% acid) is reduced by copper to nitrogen monoxide instead of nitrogen dioxide.

$$Cu(s) + 8HNO_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO_2(g)$$

- Zinc, being more reducing than copper, tends to further reduce the dilute acid to an ammonium salt.

  $$4Zn(s) + NO_3^-(aq) + 10H^+(aq) \longrightarrow 4Zn^{2+}(aq) + NH_4^+(aq) + 3H_2O(l)$$

- Concentrated nitric acid oxidises tin, on heating, to tin (IV) oxide. The acid is reduced to nitrogen dioxide.

  $$Sn(s) + 4HNO_3(aq) \longrightarrow SnO_2(s) + 4NO_2\,(aq) + 2H_2O(l)$$

- Gold, platinum and rhodium are not attached by acids.

The acid also oxidises some non-metals.

- The hot concentrated acid oxidises sulphur to sulphuric acid. The acid is reduced to brown fumes of nitrogen dioxide.

  $$S(s) + 6HNO_3(aq) \longrightarrow 2H_2O(l) + 6NO_2(g) + H_2SO_4(aq)$$

- The hot concentrated acid oxidises carbon to carbon dioxide.

  $$C(s) + 4HNO_3(aq) \longrightarrow CO_2(g) + 4NO_2(aq) + 2H_2O(l)$$

- The hot concentrated acid oxidises phosphorus to phosphoric(V) acid.

  $$P(s) + 5HNO_3(aq) \longrightarrow H_3PO_4\,(aq) + 5NO_2(aq) + H_2O(l)$$

- Similarly, the acid oxidises iodine to iodic(V) acid.

  $$I_2(s) + 10HNO_3(aq) \longrightarrow 4H_2O(l) + 10NO_2(g) + 2HIO_3(aq)$$

Nitric acid often oxidises compounds of metals that have variable oxidation states.

- The acid oxidises acidified solutions of iron(II) salts e.g. iron(II)sulphate to iron(III) sulphate.

  $$2Fe^{2+}(aq) + 4H^+(aq) + NO_3^-(aq) \longrightarrow 3Fe^{3+}(aq) + 2H_2O(l) + NO_2(g)$$

  The solution turns from pale green to brown.
  This forms a basis for brown ring test of nitrates since nitrogen monoxide formed by the reaction combines with concentrated sulphuric acid to form a brown complex, $Fe(NO)(H_2O)_5^{2+}$

- Concentrated nitric acid oxidises hydrogen sulphide to sulphur.

  $$3H_2S(g) + 2HNO_3(aq) \longrightarrow 2H_2O(l) + 2NO_2(g) + 3S(s)$$

  Or

  $$3H_2S(g) + 2HNO_3(aq) \longrightarrow 4H_2O(l) + 2NO(g) + 3S(s)$$

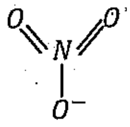
- The acid also oxidises hydrogen chloride gas and sulphites as shown by the equations below.

$$3HCl(g) + HNO_3(aq) \longrightarrow Cl_2(g) + NOCl(g) + 2H_2O(l)$$

$$SO_3^{2-}(aq) + 2H^+(aq) + 2NO_3^-(aq) \longrightarrow SO_4^{2-}(aq) + H_2O(l) + 2NO_2(g)$$

9.3.4 Analysis of nitrates

Nitrates are soluble compounds. The nitrate ion is trigonal planar



Presence of nitrates is usually detected by the brown ring test.

To the solution of the suspected compound, iron(II)sulphate solution is added followed by concentrated sulphuric acid down the sides of the tube.

Formation of a brown ring at the junction of the two liquids confirms presence of nitrate ions.

9.4 Sulphuric acid

9.4.1 Manufacture of sulphuric acid

Sulphuric acid is manufactured by the contact process. The raw materials are sulphurdioxide (obtained by burning sulphur in air) and oxygen.

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

The gases are purified to avoid poisoning of the catalyst by arsenic(III)oxide.

A mixture of sulphur dioxide and air is passed over vanadium(V) oxide catalyst at a temperature of about 430°C-450°C. An exothermic reaction occurs and temperature rises to about 600°C.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The mixture is cooled to 430°C. The mixture is passed through three more converters to bring about a 98% conversion of sulphur dioxide into sulphur trioxide.

Sulphur trioxide is absorbed into 98% sulphuric acid to form oleum.

$$SO_3(g) + H_2SO_4(l) \longrightarrow H_2S_2O_7(l)$$

Oleum is diluted with water to form concentrated sulphuric acid.

$$H_2S_2O_7(l) + H_2O(l) \longrightarrow 2H_2SO_4(l)$$

Note:

- For a high yield of sulphur trioxide, a low temperature is required. However, a low temperature is not used since the reaction would be very slow.
- A detailed discussion of optimum conditions for the reaction is covered in physical chemistry.
- Platinum catalyst would be more efficient than V_2O_5 but the former is readily poisoned by traces of sulphur.

9.4.2 Uses of sulphuric acid

- In manufacture of fertilisers e.g. ammonium sulphate
- In manufacture of paints and pigment.
- In manufacture of detergents.
- In manufacture of organic chemicals e.g. dye stuffs, explosives and drugs.

9.4.3 Properties of sulphuric acid

Pure sulphuric acid is a viscous liquid with a freezing point of 10.5°C. In absence of water, it has no acidic properties. It decomposes on boiling to form sulphur trioxide and steam and a constant boiling point mixture is formed containing 98.3% of the acid. Sulphuric acid can react as an acid, a dehydrating agent, or an oxidising agent.

9.4.3.1 As an acid

- Dilute sulphuric acid liberates carbondioxide from carbonates.
  $CO_3^{2-}(aq) + 2H^+(aq) \longrightarrow CO_2(g) + H_2O(l)$
- Dilute sulphuric reacts with bases to form salts and water.
- Dilute sulphuric reacts with reactive metals to form salts and hydrogen gas.

9.4.3.2 As a dehydrating agent

Sulphuric acid has a high affinity for water. It can remove water from compounds and mixtures with evolution of heat. Dilution of the acid is very exothermic, and the acid must always be added to water but not water to acid.

- The acid dehydrates methanoic acid to give carbonmonoxide.

$$HCOOH(l) \xrightarrow{H_2SO_4(l)} CO(g) + H_2O(l)$$

- It dehydrates oxalic acid to give carbon monoxide and cabondioxide.

$$H_2C_2O_4(s) \xrightarrow{H_2SO_4(l)} CO(g) + H_2O(l) + CO_2(g)$$

- It dehydrates sugar (sucrose) to leave a black mass of carbon.

$$C_{12}H_{22}O_{11}(s) \xrightarrow{H_2SO_4(l)} 12C(s) + 11H_2O\ (l)$$

9.4.3.3 As an oxidising agent

Concentrated sulphuric acid is an oxidising agent, though weaker than concentrated nitric acid. When it acts as an oxidising agent, the acid is usually reduced to sulphurdioxide and sometimes to sulphur or hydrogen sulphide.

- Non-metals, such as carbon and sulphur, reduce hot concentrated sulphuric acid to sulphurdioxide. They, themselves get oxidised to their dioxides.

$$C(s) + 2H_2SO_4(l) \longrightarrow 2H_2O(l) + CO_2(g) + 2SO_2(g)$$

$$S(s) + 2H_2SO_4(l) \longrightarrow 2H_2O(l) + 3SO_2(g)$$

- In general, metals with low electrode potentials reduce hot concentrated sulphuric acid to sulphurdioxide. However, the acid may be reduced to sulphurdioxide if the metal is highly reactive and concentration of the acid is relatively low e.g.

$$Cu(s) + 2H_2SO_4(l) \longrightarrow CuSO_4(aq) + 2H_2O(l) + 2SO_2(g)$$

$$2Al(s) + 6H_2SO_4(l) \longrightarrow Al_2(SO_4)_3(aq) + 6H_2O\ (l) + 3SO_2(g)$$

$$2Fe(s) + 6H_2SO_4(l) \longrightarrow Fe_2(SO_4)_3(aq) + 6H_2O(l) + 3SO_2(g)$$

$$\underset{(98\%\ acid)}{Zn(s) + 2H_2SO_4(l)} \longrightarrow ZnSO_4(aq) + 2H_2O(l) + 2SO_2(g)$$

However,

$$\underset{(90\%\ acid)}{Zn(s) + 5H_2SO_4(l)} \longrightarrow 4ZnSO_4(aq) + 4H_2O(l) + H_2S(g)$$

- Some compounds are oxidised by sulphuric acid, e.g;

$$2Fe^{2+}(aq) + 2H_2SO_4(l) \longrightarrow 2Fe^{3+}(aq) + 2H_2O(l) + SO_2(g) + SO_4^{2-}(aq)$$

$$2HBr(g) + H_2SO_4(l) \longrightarrow 2H_2O(l) + SO_2(g) + Br_2(l)$$

$$2HI(g) + H_2SO_4(l) \longrightarrow 4H_2O(l) + H_2S(g) + 4I_2(s)$$

9.4.3.3 Displacement reactions

Having a relatively high boiling point (i.e. low volatility), concentrated sulphuric acid displaces more volatile acids from their compounds. For this reason the acid is used to prepare volatile acids, e.g. hydrochloric acid and nitric acid, from their compounds.

$$NaCl(s) + H_2SO_4(l) \longrightarrow NaHSO_4(s) + HCl(g)$$

$$KNO_3(s) + H_2SO_4(l) \longrightarrow KHSO_4(s) + HNO_3(l)$$

However, this method cannot be used to prepare hydrogen bromide and hydrogen iodide. This is because hydrogen bromide and hydrogen iodide are stronger reducing agents than hydrogen chloride thus they reduce the concentrated acid to sulphur dioxide and hydrogen sulphide respectively.

$$2HBr(g) + H_2SO_4(l) \longrightarrow 2H_2O(l) + SO_2(g) + Br_2(l)$$

$$2HI(g) + H_2SO_4(l) \longrightarrow 4H_2O(l) + H_2S(g) + 4I_2(s)$$

9.4.4 Sulphates

Sulphates are salts of sulphuric acid. The sulphate ion has the formula SO_4^{2-} and has a tetrahedral structure.

With exception of barium sulphate and lead(II)sulphate, other sulphates are soluble in water. Calcium sulphate and silver sulphates are only sparingly soluble.

The sulphate ion is tested by adding nitric acid followed by barium nitrate (H^+/Ba^{2+}). Formation of a white precipitate shows presence of sulphate ions.

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$$

Sulphates also form a white precipitate with lead(II) nitrate solution or lead(II)ethanoate solution. However, this cannot be used to confirm a sulphate since chloride ions give a similar observation due to insolubility of lead(II)chloride.

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s)$$

$$Pb^{2+}(aq) + 2Cl^-(aq) \longrightarrow PbCl_2(s)$$

Hydrated sulphates are decomposed by strong heating yield sulphurdioxide gas.

9.4.5 Thiosulphates

Thiosulphates are salts of thiosulphuric acid ($H_2S_2O_3$). Like the sulphate ion, the thiosulphate ion has a tetrahedral shape.

The best known thiosulphate is sodium thiosulphate ($Na_2S_2O_3 .5H_2O$) which is used in photography for fixing the negative.

The thiosulphate ion is unstable in presence of an acid and breaks down to give a sulphite (which then reacts to give sulphur dioxide and water) and free sulphur.

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

For this reason, solutions of sodium thiosulphate should be prepared by using freshly distilled water. This water does not contain carbon dioxide which would make it acidic and consequently break down sodium thiosulphate.

The thiosulphate ion is a reducing agent thus reduces;

- Chlorine to chloride ions

$$S_2O_3^{2-}(aq) + 4Cl_2(g) + 5H_2O(l) \longrightarrow 2SO_4^{2-}(aq) + 10H^+(aq) + 8Cl^-(aq)$$

- Iodine to iodide ions

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

This reaction is used in volumetric analysis for estimating iodine liberated.

- Iron(III) to iron(II)

$$2Fe^{3+}(aq) + 2\,S_2O_3^{2-}(aq) \longrightarrow 2Fe^{2+}(aq) + S_4O_6^{2-}(aq)$$

9.5 Fertilisers

Fertilizers are compounds whose addition to soil increases plant nutrients thus increasing the productivity of land. There are two major types of fertilizers namely natural fertilizers and artificial fertilizers.

Natural fertilizers include animal waste, dead plants, and dead animals.

Artificial fertilizers mainly provide plants with nitrogen and some phosphorous and potassium. The NPK values of a fertilizer gives its composition with respect to nitrogen, phosphorous, and potassium. A good fertilizer should;

- Contain a high percentage of elements required by plants.
- Be cheap and highly soluble in water.

A disadvantage of highly soluble fertilizer is that they are easily washed away by rain. An advantage of less soluble fertilizers is that they stay in soil for a long time thus providing a constant supply of plant nutrients.

Disadvantages of fertilizers

- Extensive use of fertilizers leads to environmental degradation.
- Use of fertilizers leads to contamination of water bodies which may cause death to aquatic life.
- Phosphate fertilizers promote growth of algae which deprive aquatic life of oxygen.
- Examples of artificial fertilizers include ammonium sulphate, ammonium nitrate, calcium phosphate, etc.

Manufacture of fertilizers

Ammonium phosphate fertilizer is manufactured by passing carbon dioxide and ammonia gases through a heated suspension of calcium sulphate.

$$2NH_3(g) + H_2O(l) + CO_2(g) + CaSO_4(aq) \longrightarrow CaCO_3(s) + (NH_4)_2SO_4(aq)$$

Single super phosphate (SSP) is manufactured by grinding calcium phosphate and calcium fluoride. The mixture is put in a tank and stirred continuously to avoid setting. The resulting slurry is sieved to separate big particles from smaller ones. Lime is then removed and the resulting product is sent to a floatation tank where sodium olerate ($C_{17}H_{33}COONa$) is added as a collecting agent. Here sodium ions adhere to particles containing the calcium salts while the olerate ions to water. Air is blown forming froth where impurities like lime sink to the bottom while particles containing the calcium salts float are removed. They are treated with sulphuric acid forming calcium dihydrogen phosphate which is sold as SSP fertilizer.

$$3Ca_3(PO_4)_2(aq) + 7H_2SO_4(aq) \longrightarrow 3Ca(H_2PO_4)_2(aq) + 7CaSO_4(aq).$$

9.6 Cement

Portland cement is made by strong heating of limestone ($CaCO_3$) and clay. Limestone is ground and mixed with clay which has already been mixed with water. This mixture is allowed to flow down a sloping rotating cylinder. The cylinder is heated internally by a blast of burning coal- dust and air. The resulting clinker is allowed to cool down, and ground to a fine powder called **cement**. Gypsum ($CaSO_4$) is added so as to slow down the reaction between cement and water.

Reactions that take place during the process are:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

$$2CaO(s) + SiO_2(s) \longrightarrow (CaO)_2SiO_2(s)$$

$$2Al_2O_3(s) + CaO(s) \longrightarrow CaO(Al_2O_3)_2(s)$$

Cement is used in making concrete. Concrete is made by mixing cement, sand, and water with gravel. When fresh, it can be poured into moulds (usually wood) and sets into a very hard rock-like mass in a day. For additional strength, girdles (or iron rods) may put inside concreted and is then said to be reinforced concrete.

UNEB Chemistry Syllabus for Inorganic Properties

8. **Inorganic Properties**

8.1 Oxidation numbers should be used, where appropriate, in discussing the chemistry of the elements and their compounds. Some practice should be given in balancing equations using oxidation numbers. (Teachers should refer to the UNEB booklet on 'nomenclature' for guidance.)

8.2 A simple comparative study of the variation of physical properties of the elements within a period and a group of the Periodic Table. This is illustrate by reference to:

(a) The period: Na, Mg, Al, Si, P, S, Cl, Ar. Each element in the period should be considered in context of its group. Brief reference should be made to the second short period (lithium to neon) with particular reference to the anomalous behaviour of some elements in this period: e.g. Li, Be and B. Oxygen and nitrogen should be considered with sulphur and phosphorous. The second short period should not be considered in detail. The diagonal relationship can be mention when considering beryllium and aluminium. The detailed chemistry of the elements should include:

(i) Physical properties: melting point, boiling point, electrical conductivity, atomic radius, ionic radius (related to structure and bonding), electronic structure, and ionisation energy and electron affinity. The periodic variation of these properties should be brought out where appropriate.

(ii) Chemical properties: the reactions, where appropriate, with water, sodium hydroxide solution and hydrochloric acid.

(iii) The compounds: Oxides, chlorides, and hydrides.

General methods for formation, volatility (related to structure and bonding), reactions with water. The reactions of oxides with dilute acids and alkalis should be included. The general properties of the bonding in these compounds. The detailed chemistry of the oxo-acids of phosphorous and the oxides of chlorine is not required. The oxo-acids of sulphur and chlorine should be studied.

(b) Group II, IV, and VII

The knowledge of the chemistry of the elements of these groups, will be similar to that required for the elements in the third short period (above), with the following additional points:

(i) Group II. The solubility of the sulphates and hydroxides should be related to their lattice energies and hydration energies (see Section 4.2).

(ii) Group IV. There should be an emphasis on the ability of carbon to form long chains and rings (see Section 9.1). Stress should be laid on the changes of the properties on going down the group from carbon to lead.

(iii) Group VII. There should be relatively little emphasis on the oxides of the elements, apart from pointing out their acid nature. The hydrides should be studied with particular reference to hydrogen bonding (see section 4.3)

(c) The first series of d-block elements.

(i) The physical properties of the elements should be studied in comparative terms (as in (a) and (b) above.)

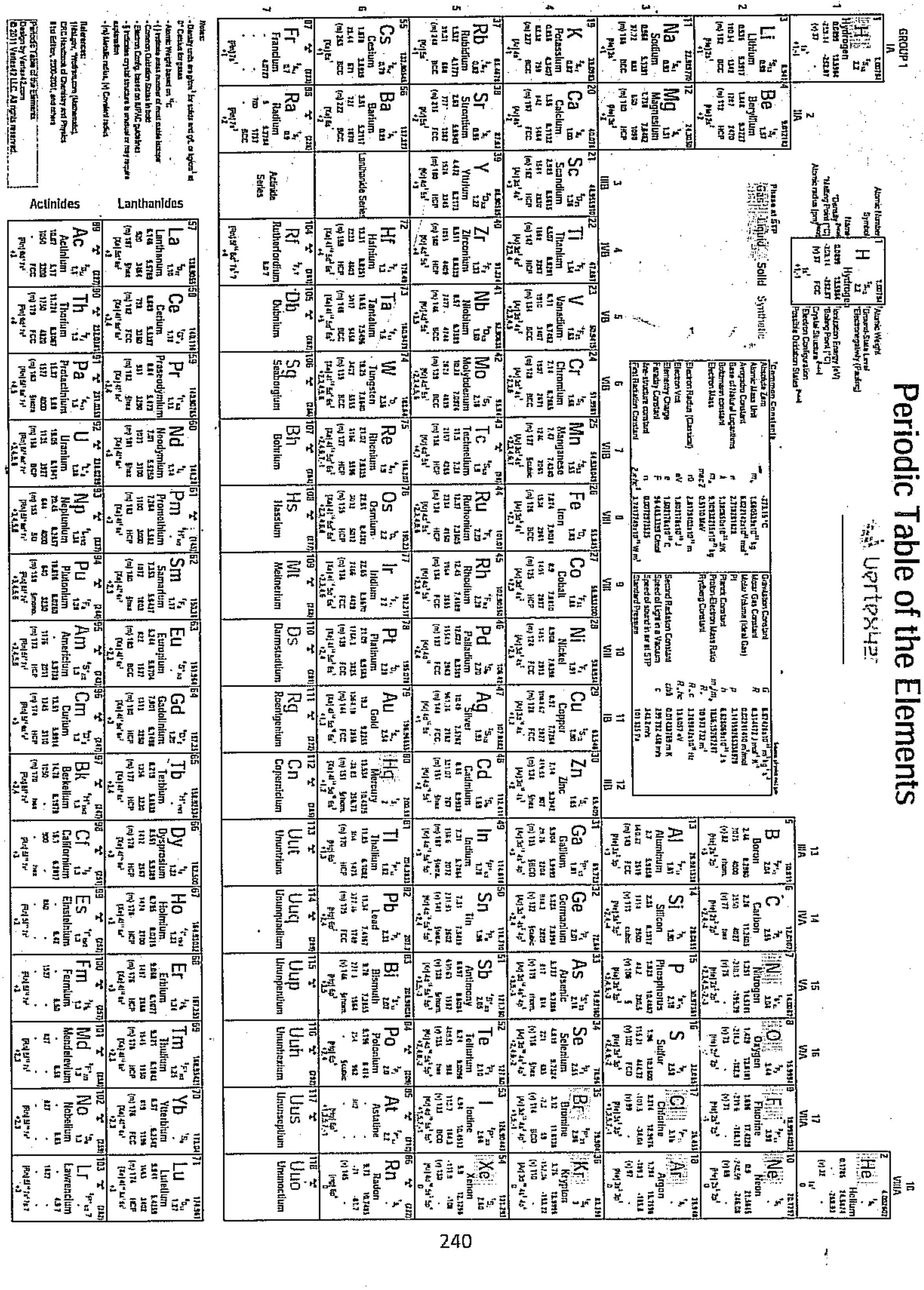
(ii) Chemical properties: reactions of the elements with water, hydrochloric acid and oxidising acids. Stress should be laid on ability of these elements to exist with different oxidation numbers (cf. colour)and to form complexes (only water, chlorine, and ammonia should be considered as ligands).

(iii) Compounds: a general study of the properties of oxides, hydroxides and oxo-anions. The amphoteric behaviour of a compound should be considered, where appropriate. The use of manganate(VII) and dichromate(VI) ions in volumetric analysis should be related to electrode potentials and redox systems (see section 6.4). In this section, the appropriate industrial processes can be introduced when discussing the appropriate elements and compounds:

Manufacture of NH_3, HNO_3, H_2SO_4, HCl, $NaOH$, fertilisers, extraction of metals (Al, Fe, Zn, Cu).

Appendences

Table 1: Long form of the periodic table



Periodic Table of the Elements

Period	GROUP 1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9 VIII	10 VIII	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 H Hydrogen																	2 He Helium
2	3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
3	11 Na Sodium	12 Mg Magnesium											13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
4	19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
5	37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
6	55 Cs Cesium	56 Ba Barium	Lanthanide Series	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
7	87 Fr Francium	88 Ra Radium	Actinide Series	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Uut Ununtrium	114 Uuq Ununquadium	115 Uup Ununpentium	116 Uuh Ununhexium	117 Uus Ununseptium	118 Uuo Ununoctium

Lanthanides	57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
Actinides	89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium

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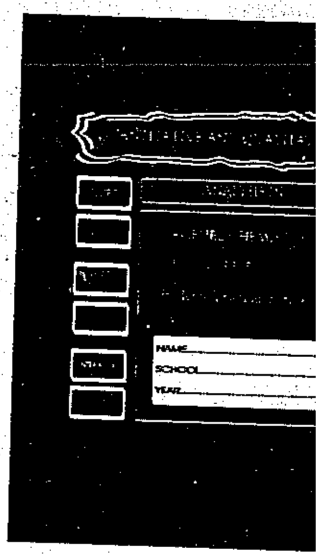

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