

A Unique Approach To Advanced Level Inorganic Chemistry

First edition 2012

Kidega Denis (Bsc Educ, chemistry major, Muk)

Namilyango College

Other books by the same author

- 1) A unique approach to advanced level physical chemistry
- 2) A unique approach to advanced level organic chemistry
- 3) A unique approach to advanced level chemistry practical
- 4) A unique approach to ordinary level chemistry

A unique approach to advanced level inorganic chemistry, first edition

Copyright © 2012 by Kidega Denis

All rights reserved. No part of this publication may be reproduced or distributed in any form or by any means, or stored in a data base or retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying or otherwise without prior written permission of the publisher.

Printed in 2012
Kampala,Uganda

Preface

A unique approach to advanced level inorganic chemistry, first edition has been written to match the latest requirements of Uganda national examination board.

This book is written in a point where all the information is set out clearly and concisely, making it easy for students to study. A large number of worked examples are included in the last chapter of this book. All worked examples have solutions ranging from a simple statement to a short explanation or step by step solution.

The well designed questions at the end of each chapter enhance comprehension and understanding.

Please do not hesitate to contact the author through the oriental academic publication, email kidegadenis@yahoo.com with any suggestions or comments that could improve the text.

Kidega Denis
Tel. +256783290117/+256715733133
Namilyango College
P.O.Box 7091, Kampala

Acknowledgements

I am much indebted to the staff of Namilyango College and in particular the head master Mr Muguluma Gerald for their valuable assistance and encouragement throughout the writing of this book. I wish also to express my thanks to chemistry students and chemistry teachers of Namilyango College like Mr Musinguzi Dick, Mr.Apuatum Geroge, Mr.Wathum Jimmy and numerous colleagues from other schools such as, Idha Ajax Filbert of Kings College Budo, Mr.Busulwa George of Kyambogo college whose comments, criticism, and advice helped me to solve many difficulties.

I am also grateful to father, Mr. Abwola Samuel Lewis and mother Mrs. Atto Filder for their helpful support and guidance and assistance rendered towards the production of this book without which this would have not been a success.

Table of Contents

Preface	ii
Acknowledgements	iii
CHAPTER ONE	1
1.00 INTRODUCTION	1
1.01 Periodicity	1
1.02 The modern periodic table	2
1.03 More about arrangement of elements in the periodic table	3
1.04 Terms used to explain trends in the periodic table	3
1.05 Trends in the periodic table	4
a) Metallic character of the elements	4
b) Atomic radius	4
c) Ionization energy (IE)	5
d) Electronegativity	8
e) Electron affinity	9
f) Melting and boiling point	11
g) Ionic radius	12
1.06 Charge density	13
1.07 Polarizing power	13
1.08 Solubility of ionic compounds	14
1.09 Sample Revision questions 1	15
CHAPTER TWO	21
2.00 GROUP (I) ELEMENTS	21
2.01 General properties	21
2.02 Chemical reactions of group (I) elements	21
2.03 Summarising the reason for the increase in the reactivity as you go down the Group	23
2.04 Compounds of group (I) elements	23
a) Carbonates	23
b) Hydrogen carbonates	24
c) Nitrates	24
d) Halides (chlorides, bromides, iodides)	24
2.05 Properties in which lithium behaves differently from the rest of group (I) elements	24
2.06 Group (I) chemistry sample questions	24
CHAPTER THREE	26
3.00 GROUP (II) ELEMENTS (THE ALKALINE EARTH METALS)	26
3.01 General properties	26

<u>3.02 Chemical reactions of group (II) elements</u>	26
<u>3.03 Compounds of group (II) elements</u>	28
a) <u>Metal hydroxides, M(OH)₂</u>	28
b) <u>Metal sulphates, MSO₄</u>	28
c) <u>Metal chlorides, MCl₂</u>	29
d) <u>Hydrides of group (II) elements</u>	31
e) <u>Metal oxides of group (II) elements</u>	31
f) <u>Carbonates and hydrogen carbonates</u>	32
<u>3.04 Diagonal relationship</u>	32
<u>3.05 Properties in which beryllium resembles aluminium</u>	33
<u>3.06 Complex formation by group (II) elements</u>	33
<u>3.07 Effect of ionic radius of group (II) ions on the properties of their compounds</u>	34
<u>3.08 Chemical test for group (II) cations</u>	34
<u>3.09 Group (II) chemistry sample questions</u>	36
<u>CHAPTER FOUR</u>	38
<u>4.00 GROUP (III) ELEMENTS</u>	38
<u>4.01 General properties</u>	38
<u>4.02 Chemical properties of group (III) elements</u>	38
<u>4.03 Primary standard</u>	38
<u>4.04 Aluminum</u>	39
a) <u>Extraction of aluminium</u>	39
b) <u>Uses of aluminium</u>	40
c) <u>Chemical properties of aluminium</u>	41
d) <u>Compounds of aluminium</u>	41
(i) <u>Aluminium chloride</u>	41
(ii) <u>Aluminium carbonate, Al₂(CO₃)₃</u>	42
<u>Behaviour of Al³⁺ ions in water</u>	42
<u>Bonding in aluminium halides</u>	42
<u>4.05 Identification of Al³⁺ ions</u>	42
<u>4.06 Group 3 chemistry sample questions</u>	43
<u>CHAPTER FIVE</u>	45
<u>5.00 GROUP (IV) ELEMENTS</u>	45
<u>5.01 General properties</u>	45
<u>5.02 Oxidation states</u>	45
<u>5.03 Trend in electropositivity</u>	46
<u>5.04 Chemical properties of group (IV) elements</u>	47
<u>5.05 Compounds of group (IV) elements</u>	48

a) <u>Oxides group(IV) elements</u>	48
b) <u>Chlorides of group (IV) elements</u>	51
c) <u>Hydrides of group (IV) elements</u>	55
<u>5.06 Testing for lead (II) ion,Pb^{2+}</u>	56
<u>5.07 Group 4 questions</u>	57
<u>CHAPTER SIX</u>	59
<u>6.00 GROUP (VII) ELEMENTS</u>	59
<u>6.01 Physical properties</u>	59
1) <u>Boiling points</u>	59
2) <u>Bond dissociation energy.</u>	60
3) <u>Electron affinity</u>	60
<u>6.02 Preparation of halogens</u>	61
<u>6.03 Industrial preparation of chlorine</u>	61
<u>6.04 Chemical reactions of the halogens</u>	62
<u>6.05 Compounds of group (VII) elements</u>	65
a) <u>Hydrogen halides (HX)</u>	65
b) <u>The oxy salts of chlorine</u>	67
<u>6.06 Estimation of percentage available of chlorine in bleaching powder (calcium hypochlorite)</u>	67
<u>6.07 Testing for chloride, bromide and iodide ions</u>	68
<u>6.08 Group (VII) questions</u>	69
<u>CHAPTER SEVEN</u>	71
<u>7.00 CHEMICAL PROPERTIES OF PERIOD 2 AND 3 ELEMENTS AND THEIR COMPOUNDS</u>	71
<u>7.01 Chemical properties of period two and three elements</u>	71
a) <u>Oxides</u>	73
i) <u>Structure and bonding of oxides of period and three elements</u>	74
ii) <u>Volatility of the oxides (melting and boiling point)</u>	74
iii) <u>Nature of the oxides of period 2 and 3</u>	74
iv) <u>Methods of preparation of the oxides</u>	75
v) <u>Reaction of the oxides of period 2 and 3</u>	75
b) <u>Chlorides of period 2 and 3</u>	76
<u>Conductivity of period 2 and 3 chlorides</u>	78
<u>Methods of preparation of the chlorides</u>	78
<u>Reactions of the chlorides of period 2 and 3</u>	79
c) <u>Hydrides of period 2 and 3 elements</u>	81
<u>Methods of preparation of hydrides of period 2 and 3 elements</u>	81
<u>7.03 Period 2 and 3 questions</u>	83

<u>CHAPTER EIGHT</u>	86
<u>8.00 CHEMICAL PROCESSES</u>	86
<u>8.01 Manufacture of sulphuric acid</u>	86
<u>8.02 Uses of sulphuric acid</u>	86
<u>8.03 Manufacture of ammonia</u>	87
<u>8.04 Uses of ammonia</u>	87
<u>8.05 Effects of temperature and pressure on the production of ammonia</u>	87
<u>8.06 The manufacture of nitric acid</u>	88
<u>8.07 Uses of nitric acid</u>	88
<u>8.08 Preparation of chlorine and sodium hydroxide</u>	88
<u>8.09 Uses of chlorine</u>	89
<u>8.10 Uses of sodium hydroxide</u>	89
<u>8.11 Manufacture of sodium carbonate</u>	89
<u>8.12 Uses of sodium carbonate (soda ash)</u>	90
<u>8.13 Cement</u>	90
<u>8.14 Uses of cement</u>	90
<u>8.15 Setting of cement</u>	90
<u>8.16 Concrete</u>	91
<u>8.17 Mortar</u>	91
<u>8.18 Fertilizers</u>	91
<u>CHAPTER NINE</u>	92
<u>9.00 TRANSITION ELEMENTS</u>	92
<u>9.01 Physical properties of transition elements</u>	92
a) <u>Atomic radius.</u>	92
b) <u>Ionization energy.</u>	92
c) <u>Melting and boiling points.</u>	93
<u>9.02 Characteristics of transition elements</u>	93
a) <u>Variable oxidation state.</u>	93
<u>Examples</u>	93
a) Fe..... <u>$3d^64s^2$</u>	94
b) Mn..... <u>$3d^54s^2$</u>	94
<u>NB//zinc and scandium are not regarded as typical transition elements because of the following reasons:</u>	95
<u>For scandium</u>	95
(i) <u>The Sc^{3+} has a $3d^0$ configuration hence it cannot form coloured compounds since it lacks electrons in the 3d sub shell.</u>	95
(ii) <u>It is limited to only one oxidation state of +3.</u>	95
<u>For zinc</u>	95

<u>(i) In Zn^{2+}, the $3d^{10}$ configuration is fully occupied by electrons therefore it cannot form coloured compounds.</u>	95
<u>(ii) It is also limited to a fixed oxidation state of +2.</u>	95
<u>However zinc resembles transition elements in that it is capable of forming complexes.</u>	
<u>E.g. $[Zn(NH_3)_4]^{2+}$</u>	95
<u>Most of the chemical properties of zinc are related to those of group (II) elements. The following are the properties in which zinc resembles group (II) elements;</u>	95
<u>a) They both form normal oxides.</u>	95
<u>b) They both have a fixed oxidation state of +2.</u>	95
<u>c) They do not form coloured compounds.</u>	95
<u>d) Zinc is capable of complex formation just like beryllium of group (II) elements.</u>	95
<u>e) Zinc can undergo hydrolysis like the beryllium and magnesium in group (II).</u>	95
<u>b) Formation of coloured ions or compounds.</u>	95
<u>The majority of transition metal ions are coloured and in aqueous state these ions are normally hydrated. E.g.</u>	95
<u>$[Cu(H_2O)_4]^{2+}$Blue</u>	95
<u>$[Co(H_2O)_6]^{3+}$Pink</u>	95
<u>$[Cr(H_2O)_6]^{3+}$Green</u>	95
<u>$[Fe(H_2O)_6]^{2+}$Pale green</u>	95
<u>c) Catalytic activity</u>	96
<u>d) Exhibition of Paramagnetism in many of their compounds.</u>	96
<u>e) Formation of many complex ions by the elements.</u>	96
<u>9.03 Chemistry of each of the elements</u>	100
<u>a) Titanium</u>	100
<u>Atomic number 22</u>	100
<u>b) Vanadium</u>	101
<u>c) Chromium</u>	102
<u>Atomic number 24</u>	102
<u>Cr^{2+}$1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^0$</u>	102
<u>Properties of chromium</u>	103
<u>Compounds of chromium</u>	103
<u>For complete hydrolysis</u>	104
<u>d) Manganese</u>	108
<u>Atomic number 25</u>	108
<u>e) Iron</u>	114
<u>Atomic number 26</u>	114
<u>f) Cobalt</u>	121
<u>Atomic number 27</u>	121

<u>g) Nickel</u>	124
<u>Atomic number 28</u>	124
<u>h) Copper</u>	126
<u>Atomic number 29</u>	126
<u>i) Zinc</u>	131
<u>Atomic number 30</u>	131
<u>9.04 Sample questions</u>	135
<u>CHAPTER ELEVEN</u>	162
<u>SAMPLE QUESTIONS AND ANSWERS</u>	162

CHAPTER ONE

1.00 INTRODUCTION

Inorganic chemistry deals with the study of all chemical substances other than compounds of carbon which are studied under organic chemistry. However, few elements of carbon such as carbondioxide, carbonmonoxide, carbonates, and hydrogencarbonates are studied under inorganic chemistry.

In the study of inorganic chemistry, the following areas are considered;

- ❖ The General properties of all the elements in the periodic table. This includes ionization energy, electron affinity, atomic radii, electronegativity, electropositivity, melting points, boiling points etc.
- ❖ Methods of preparation of inorganic substances.
- ❖ Physical and chemical properties of inorganic substances.
- ❖ Similariteies and differences in the chemical properties of the inorganic substances.

All the inorganic compounds are formed from about 100 elements in the periodic table and the properties of these elements are related to the following;

- ❖ Position in the periodic table i.e group, period, and block.
- ❖ The nature of the bonding between atoms.
- ❖ The size of the atom formed by the element

1.01 Periodicity

In chemistry, there are a number of scholars who tried to classify elements with similar properties together.

Lavoiscier(1987) classified elements into metals and non metals but these were big classes so other scholars followed with improved classification.eg

Dobereiner(1890) with the law of triads, Newland with the law of octaves

Mendeleef is credited for being the first chemist to arrange elements in a periodic table that is acceptable. He arranged them in order of their increasing atomic weight putting those with similar properties together leaving room for undiscovered elements and predicting some of the properties of undiscovered elements.

He even suggested that period 4, 5 6, 7 and 8 could have more than eight elements.

According to him, the elements were dependent on atomic weight.

Periodicity is the study of variation in the physical properties of elements in the periodic table.

The variations in these properties are orderly and graded. In the study of these properties, two aspects are considered;

- i) Variation of properties down the group.
- ii) Variation of properties across the period in the periodic table.

The physical properties are given below;

- a) Atomic radius (ionic radius, covalent radius)
- b) Ionization energy
- c) Electron affinity
- d) Electronegativty
- e) Electropositivity

- f) Melting and boiling points
- g) Solubility (lattice and hydration energy)
- h) Electrical conductivity

1.02 The modern periodic table

In the modern periodic table, the elements are arranged in order of increasing atomic number in horizontal rows. The elements with similar properties occur at regular intervals. So the horizontal arrangements of elements are called **periods**. With the exception of the first period, each period begins with an alkali metal and ends with a noble gas e.g

- Period 2 begins with lithium and ends with neon.
- Period 3 begins with sodium and ends with argon.

The vertical arrangement of elements in a periodic table is called **group**. Here the elements with similar properties are placed in a vertical column.e.g

- Group (I) elements are lithium, sodium, potassium e.t.c

The periodic law

It states that, "*the properties of elements vary in relation to their atomic numbers*".

Therefore the properties of elements are a periodic function of their atomic number.

Note//. Atomic number = number of electrons in a neutral atom.

The properties of elements depend on the electronic arrangement of atom which in turn depends on atomic number.

The modern periodic table is divided into blocks of elements depending on which sub energy level is filling.

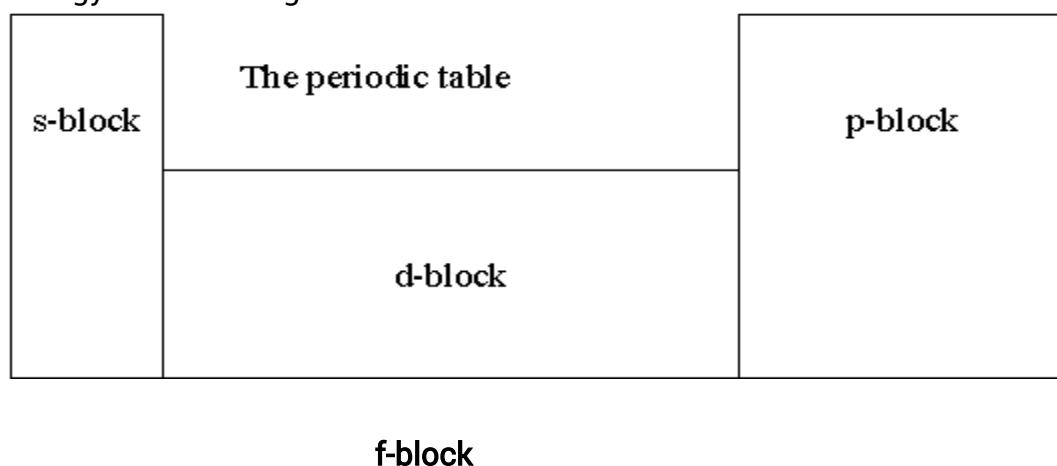


Table 1

- For the s-block elements, the filling electrons ends at ns , where s = sub energy level and n = principal quantum number.
- For the p-block elements, the filling electrons end at np . Where n = principal quantum number and p = sub energy level.
- The d-block elements where the filling electrons end at nd . These are usually called the transition elements. If they were to be left out, periods would be of equal length each

having 8 elements.

- The f- block elements where electrons are filled in the f- sub energy level.

1.03 More about arrangement of elements in the periodic table

The groups

The elements which are placed in the same group have similar properties. This is because the properties of elements depend on the electron arrangement.

All the elements in the same group have similar outer electron arrangement. E.g.

- Li: $1s^2 2s^1$
- K: $1s^2 2s^2 2p^6 3s^2 3p^6 3s^1$

All have one electron in the outer most shell and are found in group (I) (alkali metals).

Hydrogen does not exactly fit in the above group because it is a gas and also forms negative ions (H⁻) with metals.

Helium is placed in group (VIII) together with neon, argon etc

The periods

The elements which are placed in the same period have the same number of shells i.e have the same type of shell filling e.g.

- Li $1s^2 2s^1$
- B $1s^2 2s^2 2p^1$
- C $1s^2 2s^2 2p^2$

In the above case they all have the second shell filling.

The period in which the element belongs is given by the number of shells that have electrons e.g.

- Boron ($1s^2 2s^2 2p^1$) has two shells and therefore it belongs to period 2.
- Potassium ($1s^2 2s^2 2p^6 3s^2 3p^6 3s^1 4s^1$). The principal quantum number of the outer most shell is 4 therefore it is in period 4.

1.04 Terms used to explain trends in the periodic table

1) Nuclear charge. This is the total charge carried by all the protons in the nucleus of an atom. It is this charge which attracts the negatively charged electrons.

2) Screening effect or shielding effect. This is the effect of electron repulsion within the same orbitals as well as between inner and outer electrons. However the inner electron shields the outer electrons more effectively than electrons of the same subshell. The more symmetrically arranged the electrons are around the nucleus, the greater is the shielding. Therefore half filled and filled subenergy levels have the greatest shielding effect. There are two types of screening effect;

a) **Primary screening effect.** This is the repulsion between electrons in the inner orbitals and the electrons in the outer orbitals. This is greatest and most significant. There is a great increase in screening effect whenever a new shell is added to the existing shells.

b) **Secondary screening effect.** This is as a result of repulsion between electrons in the same energy level. The change in the screening effect whenever electrons are added to the same energy level is very small and can be neglected.

The order of the screening effect of electrons in the different subenergy levels of the same shell is s > p > d > f

3) Effective nuclear charge. This is the net positive charge that an electron experiences from the nucleus, equal to the nuclear charge but reduced by any shielding or screening from any intervening electron distribution.

Effective nuclear charge = actual nuclear charge (proton number)-shielding constant (number of electrons in the inner shells)

For example, lithium has an effective nuclear charge = $3 - 2 = +1$

For aluminium, effective nuclear charge = $13 - 10 = +3$

1.05 Trends in the periodic table

a) Metallic character of the elements.

- ❖ Metallic character refers to the ability to conduct electricity or heat and high melting/boiling point.
- ❖ The metallic character generally decreases across a period from left to right for example for period 3 elements. Na, Mg and Al are metals, Si is a metalloid and the rest (P, S and Cl) are non-metals,
- ❖ Metallic behavior increases when descending down a group e.g. in group (IV) of the periodic table. C is a non-metal, Si is semi-metal (metalloid), Ge, Sn, and Pb are metals. This can be explained in terms of shielding. The further down a group an element finds itself, the more protons it has in its nucleus but the more electrons there are surrounding the nucleus thus the outer electrons become progressively easier to remove. In other words the tendency to make positive ions (cations) and to behave as reducing agents increases. This is also attributed to decreasing ionization energy.

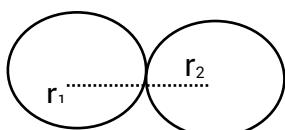
b) Atomic radius.

This is the measure of the size of an atom. Theoretically, it would be the distance from the centre of the nucleus to the end of the atom. Since it is difficult to determine precisely the radius of an atom because there is no clear boundary, therefore atomic radius is defined as half the internuclei distance between two identical atoms in a given bonding situation i.e. it is the distance of the closest approach of one atom to another nucleus of identical atom in a given bonding situation . At this distance, the repulsive and attractive force between the atoms balances.

The type of bonding affects the atomic radii, so when talking about atomic radius we could mean;

(i) Covalent atomic radius.

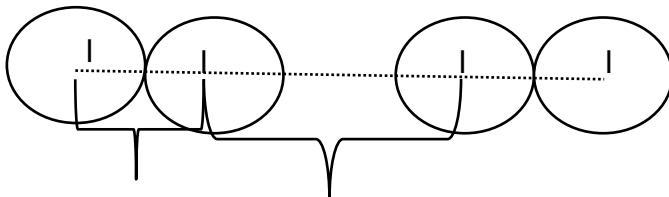
This is half the distance between the nuclei of two covalently bonded identical atoms.



$$\text{Covalent atomic radius} = \frac{r_1 + r_2}{2}$$

(ii) Vanderwaals radius.

This is half the internuclei distance between two identical atoms in a crystal lattice which are not chemically bonded.



Covalent radius vanderwaals radius

Note//. The vander waals radius is much bigger than the covalent radius.

(iii) Metallic radius.

This is half the distance between the nuclei of two adjacent atoms in a metallic crystal lattice.

ATOMIC RADII OF PERIOD 2 AND 3

NB//. In chemistry, the atomic radius usually quoted is covalent atomic radius.

Period 2 atoms	Li	Be	B	C	N	O	F
Radius/n m	0.123	0.089	0.082	0.077	0.070	0.066	0.064
Period 3 atoms	Na	Mg	A/	Si	P	S	C/
Radius/n m	0.156	0.136	0.125	0.117	0.110	0.104	0.899

Table 2

The trend in atomic radius

- Generally atomic radii decrease across the period from **left to right** of the periodic table. The major factor responsible for this is the nuclear charge. The greater the nuclear charge, the more strongly the electrons in the outer most shell are attracted towards the nucleus hence the smaller the radius.
- **Down the group**, atomic radius increases. The important factor here is the screening effect. The greater the increase in the screening effect the weakly the electrons are attracted to the nucleus thus the bigger the radius.

Explanation

- **Across the period**, both the nuclear charge and screening effect are increasing. The screening effect increases by a small margin because electrons are being added to the same energy level but the nuclear charge increases by big margin since a proton is progressively added from element to the next. As a result of this, the increase in nuclear charge outweighs the increase in nuclear charge therefore causing an increase in

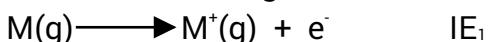
effective nuclear charge across the period. This makes the electrons to experience greater attractions towards the nucleus hence causing the atoms to reduce in size.

• **Down the group**, both the nuclear charge and screening effect are increasing but the increase in screening outweighs the increment in the nuclear charge effect. This is because an extra shell occupied by electrons is progressively added from one element to the next. Consequently, the effective nuclear charge decreases resulting into weaker attraction of the electrons towards the nucleus hence causing the increase in the atomic radius.

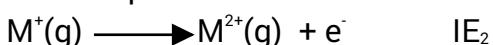
c) Ionization energy (IE)

This is defined as the least or minimum amount of energy required to completely remove one mole of electrons from one mole of gaseous atoms.

The first ionization energy is the minimum energy needed to remove one mole of electrons from one mole of gaseous atoms to form one mole of gaseous, unipositive cations.



The second ionization energy is the amount of energy needed to remove one mole of electrons from 1 mole of unipositive gaseous cations to form one mole of gaseous, divalent positive ions.



Ionization energy is measured in kilojoules per mole and is determined from spectra.

The magnitude of ionization energy correlates with the strength of the attractive force between the nucleus and the outermost electron.

The lower the ionization energy, the easier it is to form a cation.

Factors affecting ionization energy

The factors affecting ionization energy are;

i) Nuclear charge (number of protons in the nucleus).

The bigger the nuclear charge, the more strongly the electrons are attracted towards the nucleus and the higher is the ionization energy.

ii) Screening or shielding effect.

The greater it is, the less attracted are the electrons towards the nucleus. So ionization energy decreases with increase in the number of shells occupied by electrons. The screening efficiency of the inner electrons decreases in the order s > p > d > f.

iii) Net charge on the ion/atom

The greater the net positive charge (the fewer the number of electrons being attracted by unchanging nuclear charge), the greater the effective nuclear charge, the higher the ionization energy for example in a given element, the successive ionization energy increase in the order 1st < 2nd < 3rd < 4th and so on.

iv) Penetrating power of the valence electrons

In any given shell, the penetrating power decreases in the order s > p > d > f. The s-electrons are more firmly attracted to the nucleus than the p-electrons and so on.

Therefore the ionization energy increases in the order s < p < d < f

v) Distance of electrons from the nucleus (atomic radius/size)

The more closely the electrons are (the smaller the atomic radius/size) to the nucleus, the greater is the ionization energy and vice versa.

Note//

- The second ionization energy is greater than the first ionization energy because after the removal of the first electron, the proton to electron ratio increases so that the nuclear attraction for the remaining few electrons increases. Since the remaining electrons are now strongly attracted, the removal of the next electron requires more energy.
- The energy required to remove the second electron is about twice for the removal of the first electron.

Trend in Ionization energy for period 2 and 3 elements

Period 2 elements	Li	Be	B	C	N	O	F	Ne
IE/KJmol ⁻¹	520	899	801	1086	1400	1314	1680	2080
Period 3 Elements	Na	Mg	Al	Si	P	S	C/	Ar
IE/KJmol ⁻¹	495.	738.	577.	786.	1012	999.	1251	1521
	9	1	9	3		5		

Table 3

Generally, the first ionization energy increases across the period from left to right of both period 2 and period 3.

Explanation

Both the nuclear charge and screening effect increase across the period, but the increase in the nuclear charge outweighs the increase in screening effect because electrons are being added to the same energy level.

As a result of effective nuclear charge increase from sodium to argon, electrons progressively get more and more attracted towards the nucleus as you move across the period hence the general increase in the first ionization energy.

Note// filled and half filled subenergy level have the greatest energetic stability and greatest shielding effect. The **observed anomalies** in the values of ionization energy are explained as follow;

In period 2, there is a slight decrease in first ionization energy between

a) Beryllium (Be) and boron (B)

b) Nitrogen (N) and oxygen (O)

- This is mainly due to their electronic configurations. Both Be and N have abnormally stable electronic configurations.

Element	Electron	Electronic configuration
Z		
Be	4	1s ² 2s ²
B	5	1s ² 2s ² 2p ¹
N	7	1s ² 2s ² 2p ³
O	8	1s ² 2s ² 2p ⁴

Table 4

- On average, an s-electron is attracted to the nucleus more than a p-electron in the same principle shell. This means that an s-electron is harder to remove from an atom than a

p-electron in the same shell.

- The electron removed during ionization of Be is an s-electron, whereas electron removed during the ionization of B is a p-electron. This results in smaller first ionization energy for B, even though its nuclear charge is greater by one unit.
- The first ionization energy for O is slightly less than that of N because of the repulsion between the two electrons occupying the same 2p-orbital in the oxygen atom. These two electrons occupy the same region of space. As such, their repulsion overcomes the additional nuclear charge of the O nucleus. N has higher ionization energy because of its half-filled p-orbitals and hence exhibits extra stability.

In period 3;

- For Mg ($1s^2 2s^2 2p^6 3s^2$), the 3-s subenergy level is completely full and therefore stable and requires a lot of energy to remove the electron.
- For Al ($1s^2 2s^2 2p^6 3s^2 3p^1$), the 3s subenergy level which is completely full completely screens (shields) the 3-p electron from the nuclear attraction therefore making it easy to be removed.
- For P ($1s^2 2s^2 2p^6 3s^2 3p^3$), the 3-p subenergy level is half-full and therefore stable. It requires a lot of energy to remove the electron.
- For S ($1s^2 2s^2 2p^6 3s^2 3p^4$), the 3-s subenergy level has one more electron than the stable half-filled configuration. Therefore it requires relatively low energy to remove the electron.

Variation of ionization energy down a group

For group (I) elements;

Element	1 st ionization energy
Li	520
Na	500
K	420
Rb	400
Cs	380

Table 5

Ionisation energy **decreases** down group. Increasing atomic radius and shielding effect are the most important factors leading to a decrease in the first ionization energy.

Explanation

This is because the distance between the outermost orbitals and the nucleus increases on the basis that the increase in the nuclear charge is outweighed by increase in the screening effect due to the increase in the number of shells of electrons as you move down the group.

This causes a decrease in attractive forces and less energy is needed to remove their first electron i.e. the electrons get loosely held as one moves down the group.

Importance of ionisation energy

- (i) Ionisation energy provides information about atomic number. For example, given that

sodium has 11 successive ionisation energies implies that its atomic number is 11.

(ii) The arrangement of electrons and distribution of energy level can be seen from plots of successive ionisations against the number of electrons to be removed. For example potassium.

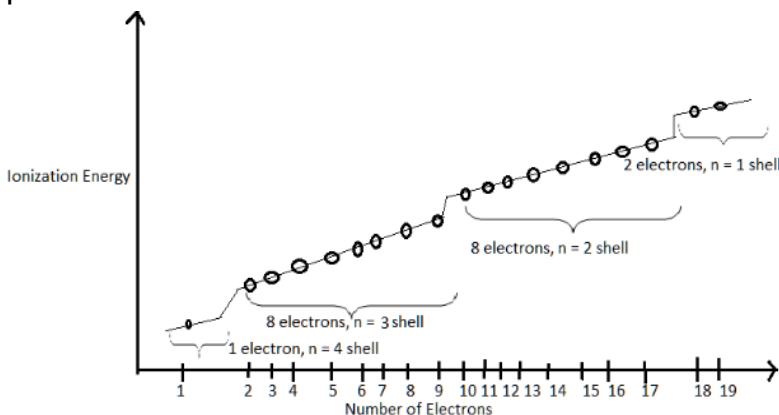


Figure 1

- Potassium has 19 electrons.
- from the figure above, there are big increase between $\rightarrow IE_1 \rightarrow IE_2, \rightarrow IE_9 \rightarrow IE_{10}$ and $\rightarrow IE_{17} \rightarrow IE_{18}$
- We can predict that there is one electron in $n = 4$ shell, 8 electrons in $n = 3$ shell, 8 electrons in $n = 2$ shell and 2 electrons in $n = 1$ shell.
- therefore, electronic configuration of K can be stated as $1s^2 2s^2 2p^6 3s^2 3p^6 3s^1$

(iii) Ionisation energy can be used to determine the metallic and non-metallic nature of elements. The first ionisation energies of metals are all nearly below 800KJmol^{-1} while those of non-metals are above 800KJmol^{-1} .

d) Electronegativity.

This is the measure of the tendency an atom in a molecule to attract shared or bonded electrons towards itself in a covalent bond.

Electronegativity increases from left to right across the period, but decreases when descending the group. It depends on;

i) **Effective nuclear charge.** The greater the effective nuclear charge the greater the tendency of an atom to pull electrons towards itself.

ii) **Atomic radius.** Electronegativity decreases as the atomic radius increases.

Electronegativity values for some elements

Element	Li	Be	B	C	N	O	F
Electronegativity	1.0	1.5	2.0	2.5	3.0	3.5	4.0

y

Element	Na	Mg	Al	Si	P	S	Cl
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	

y

Element	K
Electronegativity	0.8

y

Table 6

Electronegativity is calculated from the formula;

$$\frac{\text{ionisation energy} + \text{electron affinity}}{544}$$

Where both ionization energy and electron affinity are in kilojoules per mole

Explanation of trends

Across the period, there is increase in electronegativity because of the increase in effective nuclear charge associated with continuous decrease in atomic radius from one element to the next i.e. the atoms have an increasing electron attracting power.

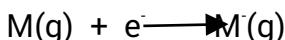
Down the group, the electronegativity decreases because of the effective nuclear charge decrease as the atomic radius increases. more shells are added as you move from one element to the next therefore the electrons get far away from the nucleus thus making it difficult for the atom attract electrons in a covalent bond to itself.

NB//.

- The greater the electronegativity difference the bonded atoms, the more ionic character is the compound.
- Electronegativity is not considered as physical properties of elements because it cannot be measured directly i.e. there are no machines that can measure electronegativity.

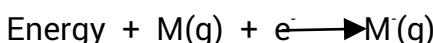
e) Electron affinity

This is the energy change when one mole of electrons is added to one mole of gaseous atoms or ions.



EA is usually quoted in kilojoules per mole so it is better defined as the enthalpy change when one mole of an atom/ion of gaseous atom or ions gain one mole of electrons to gain a net negative charge.

Electron affinity is negative if energy is released when an electron is accepted by an atom. A positive value for electron affinity indicates that energy must be supplied to the system to force the electron onto the atom, as represented in the equation:



Below are some of the EA values of period 2 and period 3 elements.

Period 2 elements	Li	Be	B	C	N	O	F	Ne
Electron affinity/ KJmol ⁻¹	-60	+18	-27	-122	+7	-141	-328	+29
Period 3 Elements	Na	Mg	Al	Si	P	S	Cl	Ar
Electron affinity/ KJmol ⁻¹	-20	+67	-30	-135	-60	-200	-364	+35

Table 7

Generally, EA becomes more exothermic as you move from **left to right** of any period but less exothermic on descending any **group**.

Electron affinity is an indication of how easily the added electron is absorbed into the existing electron cloud. It depends on;

- Effective nuclear charge.** As it increases electron affinity also increases.
- Atomic radius.** Electron affinity decreases with increasing atomic radius.
- Charge on the ions.** The greater the charge on the ion, the more endothermic is the electron affinity.

Explanation of the trends

a) Variation of electron affinity across a period

Across the period, the EA increases because as the atomic radius decreases, effective nuclear charge increases therefore the nuclear attraction for the incoming electrons increases i.e. the attraction between the nucleus and the electron becomes stronger. However, **anomalies** are found among the elements of group 2, 5 and group 8. This is because these groups have fully filled subshells or half-filled subshells which represent relatively stable electronic configurations.

- In Mg ($1s^22s^22p^63s^2$), the electron is being added to a full 3-s subshell which is thermodynamically stable and resists the addition and hence energy should be put in to effect it.
- Similarly the electron affinity of P is less negative than expected because in P ($1s^22s^22p^63s^23p^3$), the electron is being added to a half full 3-p subshell which is also stable and resists addition hence less energy is released.
- For argon ($1s^22s^22p^63s^23p^6$), the value is positive because electron is being added to $3p^6$ fully filled shell which is energetically very stable hence a lot of energy must be supplied to overcome the repulsion between the $3p^6$ electrons and the incoming electron.

b) Variation of electron affinity down a group

For group (VII) elements

Element	Electron affinity/ KJmol ⁻¹
F	-328
Cl	-349
Br	-325
I	-295
At	-270

Table 8

The magnitude of electron affinity decreases down the group because an extra shell of electrons is progressively added thus the increase in the screening effect outweighs that of nuclear charge and the effective nuclear charge decreases. There is therefore decreasing ability to attract electrons hence decrease in the electron affinity.

However, fluorine has unexpectedly low electron affinity than chlorine. This is because of the abnormally small size of fluorine atoms that creates a strong repulsive field around the fluorine atom hence the incoming electron will be strongly repelled by the lone pair of electrons of the fluorine atom which are concentrated in a small area thus some energy which would have been released is used to overcome this repulsive forces.

f) Melting and boiling point.

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

Boiling point is the constant temperature at which the vapour pressure above liquid is equal to the atmospheric pressure.

Generally, the trends in melting points and boiling points do not follow a clear pattern as

seen in other properties. This is because the melting point and boiling point of a substance is determined by more than one factor.

The following factors determine melting point;

- i) The number of electrons each atom contributes to the metallic bond.
- ii) The type of crystal structure in the compound.
- iii) The molecular mass or size of molecules for non-metals.
- iv) The shape of molecules or surface area.
- v) The way molecules are packed in a solid.

Explanation of the trends

Down the group, e.g for group 2 elements

Generally the melting point of group (II) elements decreases with increasing atomic number. As atomic number increases, the charge density decreases and the force of attraction between the bonding electrons and the positive ions decreases. Therefore this leads to a decrease in the strength of the metallic bonding consequently melting point will decrease.

Considering group (VII) elements

The melting point of non-metals is determined by the strength of the vanderwalls forces which is inturn is determined by the molecular mass of the element. The bigger the molecular mass the stronger the vanderwalls forces hence the higher the melting point and viceversa.

For group (VII) elements, they form discrete diatomic molecules and the molecular mass increase down the group. The molecules are held together by the vanderwalls forces whose strength increases with increase in molecular mass, hence increase in melting point from fluorine to iodine.

Transition metals generally have higher melting points than non-transition elements. This is because the transition elements use more electrons from both s and d subenergy levels while non-transition elements use only electrons from one subenergy level. Further more the atomic radius decreases from non-transition elements to transition elements hence this leads to stronger bonding in transition elements than non-transition elements.

Across the period.

Consider period 3 elements.

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Melting point/°C	98	660	680	1410	44	119	-101	-189

Table 9

Generally the melting point increases progressively from Na to Si and begins to decrease from S to Ar.

This period is made up of metals, metalloids, and non-metals. For metals, melting point is determined by the number of electrons each atom in the metallic lattice has contributed in

the formation of the bond. The greater the number of electrons contributed, the stronger the metallic bond and the higher the melting point and also viceversa.

Considering Na, Mg, and Al. Al has the highest melting point because each aluminium atom contributes 3 electrons during the formation of a metallic bond while Mg and Na each of their atoms contribute 2 and 1 electrons respectively. This results in the metallic bond being stronger in Al than in Mg and Na hence Al has the highest melting point while Na has the lowest melting point amongst the metals.

Si has the highest melting point among the non-metals because Si forms a giant atomic structure with very many strong covalent bonds which are very hard to break just like the one of diamond.

The melting point drops suddenly through the non-metals. This is because melting point in non-metals is determined by the van der waals forces of attraction between their molecules. These forces are weak and easier to break leading to low melting point of non-metals compared to metals and metalloids.

g) Ionic radius. This is the space occupied by an ion in any direction of the lattice of an ionic lattice. I.e it can also be defined as half the internuclear distance of the two adjacent ions in an ionic crystal. There are two types of ions, namely;

- i) Positively charged ions (cations)
- ii) Negatively charged ions (anions)

Positive ions are formed by loss of electrons and they are smaller than the neutral atoms from which they are formed. Eg



Explanation

As the atom loses electrons, the nuclear charge remains constant and the number of electrons to be attracted decreases. This result into decrease in the screening effect, thus the effective nuclear charge increases because the nuclear charge outweighs the screening effect. Hence the nuclear attraction for the remaining few electrons increases dramatically resulting into the decrease in the size of the cation.

Negative ions are formed by addition of one or more electrons to the neutral atom.

Negative ions are larger than the corresponding neutral atom from which they are formed.

Explanation

As the electrons are added, the nuclear charge remains constant and the added electrons result into increase in the screening effect which outweighs the nuclear charge leading to a decrease in the effective nuclear charge thus the nuclear attraction on the outer electrons decreases, leading to the increase in the size of the ion.

Variation of ionic radius across the period

Ions	Na^+	Mg^{2+}	Al^{3+}	Si^{4+}	P^{3-}	S^{2-}	Cl^-
Ionic radii/nm	0.950	0.650	0.050	0.041	0.212	0.184	0.181

Table 10

Generally, ionic radius decreases from Na^+ to Si^{4+} , sharply rises from Si^{4+} to P^{3-} and it eventually decreases from P^{3-} to Cl^- .

Explanation

From Na^+ to Si^{4+} , the ions have the same number of electrons (i.e they are isoelctronic) but the nuclear charge increases from one ion to the next. This results into high effective nuclear charge since the screening effect is constant, therefore the progressive decrease in the ionic radii from Na^+ to Si^{4+} .

From Si^{4+} to P^{3-} , ionic radii increases because of the successive addition of more electrons from one ion to the next, hence, the increase in the screening effect outweighs the increasing nuclear charge thus reducing the effective nuclear charge.

From P^{3-} to Cl^- , ionic radii decreases because the number of electrons added during the formation of the ions decreases from ion to the next hence the nuclear charge also increases because the screening effect will slightly decrease resulting into a slight increase in the effective nuclear charge causing a progressive decrease in the ionic radii. On this basis P^{3-} has the biggest ionic radius compared to Cl^- since three electrons are added to the phosphorous atom while only one electron is added to the chlorine atom.

Variation of ionic radius down the group

Down the group, the ionic radius increases because the screening effect of progressive addition of an extra shell of electrons outweighs the increasing nuclear charge thus the decrease in the effective nuclear charge.

1.06 Charge density

This refers to the ratio of charge to radius of a particular ion.

$$\text{Charge density} = \frac{\text{charge of the ion}}{\text{ionic radius}}$$

Consider the group (II) ions

Ion	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Ionic radii	0.03	0.06	0.09	0.11	0.13
	1	5		3	5
Charge density	64.5	30.8	20.2	17.7	14.8

Table 11

Cations with high charge density e.g. Li^+ , Be^{2+} , Al^{3+} , Fe^{3+} , Cr^{3+} have a high polarising power while cations with low charge density have a very low polarizing power.

1.07 Polarizing power

This is the ability of an ion with a high charge density to distort the electron cloud of a neighbouring ion with a low charge density. This process is called polarization.

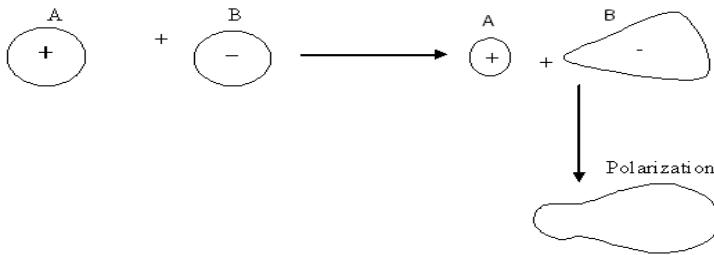


Figure 2

A cation with a high charge density will form compounds which have a high degree of covalent character. Most of these compounds will not be very soluble in water. Solutions of these compounds are acidic.

These compounds are formed between cations of high charge density with anions which are very large having a big electron cloud e.g. sulphate, carbonate, phosphate, and nitrate. And anions resist polarization because their electron clouds are small and effectively attracted by the nucleus e.g. OH^- , Br^- , Cl^- , I^- , F^- .

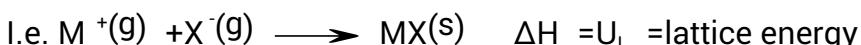
1.08 Solubility of ionic compounds

For ionic compound dissolved in water, two energy terms must be overcome. They are;

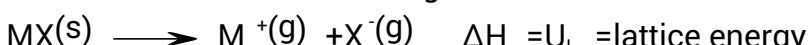
- a) Lattice energy
- b) Hydration energy

Lattice energy:

This is the enthalpy change that occurs when one mole of a crystal lattice is formed from its constituent gaseous ions.



It can also be defined as the enthalpy change that occurs when one mole of an ionic solid is broken into its constituent gaseous ions.



Factors affecting lattice energy

(i) Charge on the ions

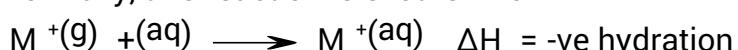
The higher the charges on the opposite ions, the stronger the electrostatic force of attraction between the oppositely charged ions and the smaller the charges on the ions the weaker the electrostatic force of attraction between the oppositely charged ions and the lower the lattice energy e.g. the lattice energy of magnesium chloride is greater than that of sodium chloride.

(ii) Size of the ions

The smaller the ions, the closer the inter-nuclear distance between the oppositely charged ions and the stronger the lattice energy and vice versa.

Hydration energy

This is the enthalpy change that occurs when one mole of a gaseous ion is completely dissolved in water. Normally, this reaction is exothermic.

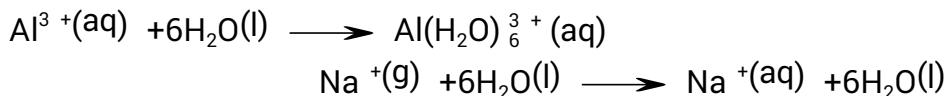


Factors affecting hydration energy

(i) Charge density on the ion

An ion with a high charge density becomes readily hydrated with water molecules leading to evolution of energy and an ion with low charge density is less readily hydrated and very small amount of energy is released.

Consider;

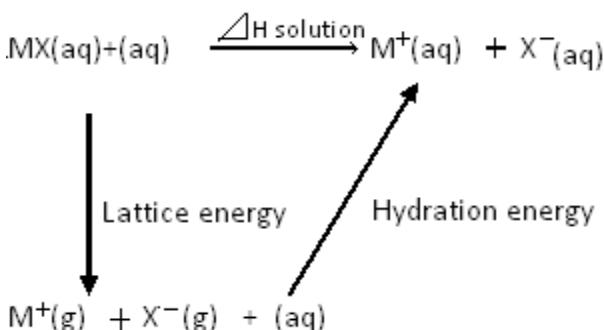


(ii) Size of the ion

An ion with a small size has high hydration energy and those with big size have low hydration energy.

Hydration energy and lattice energy are related by the expression given below;

$$\Delta H_{\text{solution}} = \text{lattice energy} + \text{hydration energy}$$



Ionic compounds with negative values of the enthalpy of solution are very soluble in water. For this value to be negative, the enthalpy of hydration must be more negative than the lattice energy while for ionic compounds which have a positive value for heat of solution means that their lattice energy must be greater than their hydration energy.

1.09 Sample Revision questions 1

- 1) The following table gives the first four ionisation energies in KJmol^{-1} of the elements boron, carbon, nitrogen and oxygen.

Ionisation energy (KJmol^{-1})	1 st	2 nd	3 rd	4 th
B	800	2400	3700	25000
C	1090	2400	4600	6200
N	1400	2900	4600	7500
O	1310	3400	5300	7500

- (i) Give the equation for the process for which the ionisation energy is 3700 KJmol^{-1} .
- (ii) Explain why the ionisation energies for each element increase in the order 1st, 2nd, 3rd and 4th.
- (iii) In general first ionisation energies increase with atomic number. Why does oxygen have a lower first ionisation energy than nitrogen?
- (iv) Why is the 4th ionisation energy of boron higher than any other values in the table?

(v) From the table above, predict the first ionisation energy of fluorine, giving a reason for your choice.

(vi) Write an equation for the first electron affinity of oxygen.

(vii) The first electron affinity of oxygen is negative (heat given out) and the second electron affinity is positive (heat is taken in). Explain the difference in sign.

(viii) Explain how the size of the atoms changes from boron to oxygen.

2) (a) The table below shows the first ionisation energy of the elements from sodium to argon.

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic number	11	12	13	14	15	16	17	18
First ionisation energy(KJmol ⁻¹)	495	738	577	787	1060	1000	1255	1520

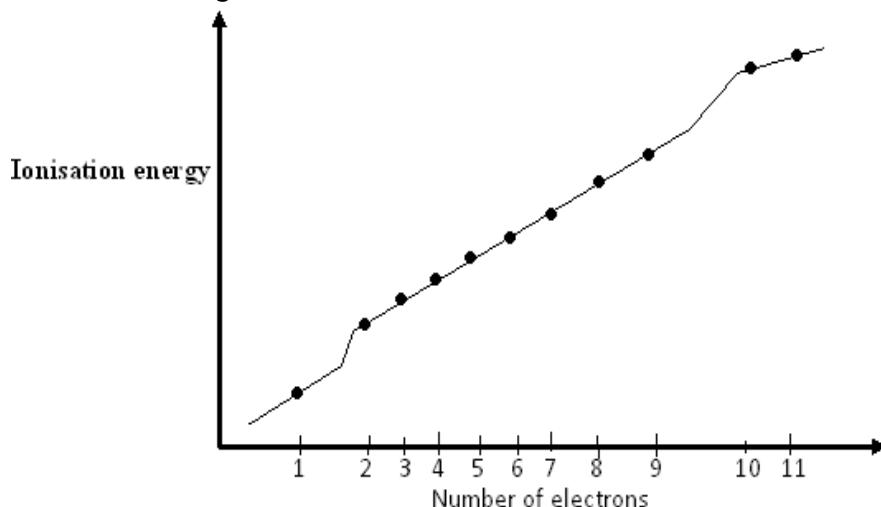
(i) What is meant by 'first ionisation energy'?

(ii) Write an equation for the process involving first ionisation.

(iii) Plot a graph of first ionisation against atomic number for the elements given in the table above.

(iv) Explain the shape of the graph in terms of the electronic structure of these elements.

(b) The graph below shows a plot of successive ionisation energies of sodium against electrons being removed from the atom.



(i) What information can be obtained from this graph about the sodium atom?

(ii) Explain the trend in the ionisation energies of sodium.

(c) Sodium and solid argon both have close-packed structures. Sodium is a good electrical conductor but solid argon is an insulator. Explain all these observations and describe the bonding in sodium and solid argon.

3) (a) Explain what is meant by atomic radius.

(b) Describe and discuss the changes in radius in the following series:

(i) Na, Mg, Al, Si, P, S and Cl

(ii) F, Cl, Br and I

(iii) Ti, V, Cr, Mn, Fe, Co

4) (a) The first eight ionisation energies of an element B are shown below:

Ionisation energies (KJmol ⁻¹)							
1 st	2 nd	3 rd	4 th	5 th	6 th	7 th	8 th
786	1580	3230	4360	160000	20000	23600	29100

(i) Explain what is meant by the term first ionisation energy.

(ii) State the factors that determine the value of the first ionisation energy.

(iii) To which group in the periodic table does element B belong? Explain.

(b) Explain what is meant by the term electronegativity.

(c) Explain how the following factors affect the value of electronegativity of an element:

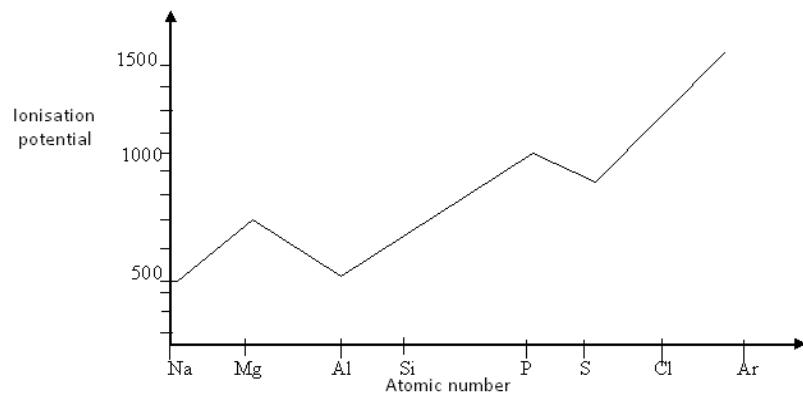
(i) Atomic radius

(ii) Nuclear charge

(iii) The screening effect of the inner electrons

(d) Explain the difference between electronegativity and electron affinity.

5) The graph below shows the variation of the first ionisation potential with atomic number for the elements from sodium to argon.



(a) Explain why;

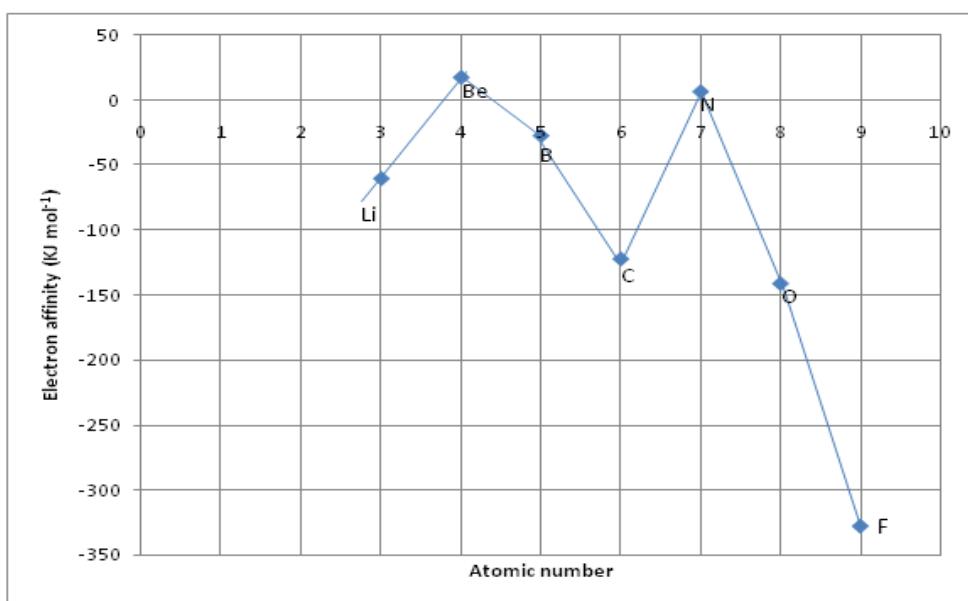
(i) The first ionisation potential of argon is much greater than that of sodium.

(ii) The first ionisation potential of aluminium and sulphur are lower than might be expected.

(b) What is the importance of ionisation potential in determining the chemistry of an element. Illustrate briefly by referring to the chemistry of sodium, chlorine and

argon.

- (c) How would the first ionisation potential change in going from magnesium to barium down group (II)?
- 6) (a) The graph below shows the first electron affinities for the elements of the second period of the periodic table, plotted against atomic number. Use the graph to answer the questions below:



- (i) Explain what is meant by the term electron affinity of an element.
- (ii) Explain the difference in the first electron affinity between;
- Li and Be
 - C and N
 - O and F
- (iii) What value of the first electron affinity would you predict for neon? Give a reason for the answer (atomic number: Ne = 10).
- (b) Explain the following statements:
- (i) The first ionisation energy of sodium is lower than that of aluminum but higher than that of potassium (atomic number: Al = 13, Na = 11, K = 19)
 - (ii) Sulphur hexafluoride is a stable molecule whereas sulphur hexaiodide does not exist.
 - (iii) Silicon dioxide is a high melting point solid whereas carbon dioxide is a gas at room temperature.
 - (iv) Silicon tetrabromide is hydrolysed by water while carbon tetrabromide is not.

(v) The H-O-H bond angle in water is experimentally found to be 104.5° .

7) The first three ionisation energies in KJmol^{-1} of seven successive elements in the periodic table are given below;

	A	B	C	D	E	F	G
1 st	897	799	1088	1399	1310	1675	2080
2 nd	1752	2417	2349	2850	3380	3369	3948
3 rd	4811	3650	4612	4564	5287	6028	6115

(i) Give equations for each of the ionisation energies for element D.

(ii) Which element would belong to the halogen group? Give reasons for your choice.

(iii) Explain why the first ionisation energies decrease in going from

(a) A to B

(b) D to E

8) The table below gives some data on substances A to D

Substance	A	B	C	D
Melting point ($^{\circ}\text{C}$)	1610	-183	2015	98
Conduction of electricity in molten state	Does not	Does not	Does	Does

(i) Classify the solid formed by each substance according to its structure.

(ii) What type of bonding exists in each substance?

9) The first ionisation energies of some group (II) metals of the periodic table and the melting points of their chlorides are given in the table below:

Metal	Mg	Ca	Sr	Ba
First ionisation energy(KJmol^{-1})	738	590	549	505
Melting point of chlorides ($^{\circ}\text{C}$)	708	772	873	967

Explain:

(i) Why ionisation energy decreases with increasing atomic number

(ii) Why the melting points of the chlorides of these metals increase with increase in atomic number.

10) The data given below are for the elements A, B, C and D which belong to the same group in the periodic table.

Element	A	B	C	D
First ionisation energy(KJmol^{-1})	495	580	790	1255
Melting point of oxide ($^{\circ}\text{C}$)	920	2300	1610	-20

(a) Which one of the elements A, B, C and D is a metal? Explain your answer.

(b) State the type of bonding and structure of the oxides of elements A and D.

(c) The second, third and fourth ionisation energies of element B are 1500, 7700, and 10500 KJmol^{-1} respectively. To which group in the periodic table does B belong?

Give reasons for your answer.

- 11) The table below shows the first three ionisation energies in KJmol^{-1} of the elements A, B, C and D.

Element	Ionisation energies		
	1^{st}	2^{nd}	3^{rd}
A	730	1500	7730
B	500	4560	6900
C	580	1815	2740
D	1310	3460	5300

- (i) Which one of the elements belongs to group (I) of the periodic table? Give a reason for your answer.
- (ii) Which one of the elements forms a cation with three positive charges?
- (iii) Write the formula of the compound formed by the elements A and D.

- 12) Explain the following observations:

- (a) There is general increase in first ionisation energy from lithium to neon.
- (b) The first ionisation energy of beryllium is higher than that of boron.
- (c) The first ionisation energy of oxygen is lower than that of nitrogen.

- 13) The first ionisation energies and the first electron affinities of the group (VII) elements are given in the table:

Element	First ionisation energy (KJmol^{-1})	First electron affinity (KJmol^{-1})
Fluorine	1681	-328
Chlorine	1250	-349
Bromine	1139	-325
Iodine	1007	-295

- (a) State how the first electron affinities of the elements generally vary with their first ionisation energies.
- (b) Explain why the first electron affinities of these elements have negative signs.
- (c) Give reasons for the abnormally low value of electron affinity of fluorine.
- (d) State the trend in the first ionisation energies of the elements and give a reason for your answer.

- 14)(a) The first five successive ionisation energies of elements X and Y are given in the table below:

Element	Ionisation energies (KJmol^{-1})				
	1^{st}	2^{nd}	3^{rd}	4^{th}	5^{th}
X	1310	3390	5320	7460	11000
Y	1410	2860	4710	7470	9450

- (i) State the group in the periodic table to which each of the elements belongs.
- (ii) Explain your answer in (i).
- (b) Elements A and B both have high ionisation energies and high electron affinities. State the type of bond that exists in the compound formed by A and B.

- 15)(a) What is meant by the term electron affinity?

- (b) Explain the factors that determine the value of electron affinity of an element.
- (c) The first electron affinity of oxygen atom is -141 KJmol^{-1} while the second electron affinity is $+798 \text{ KJmol}^{-1}$.
 - (i) Write the equation for the second electron affinity of oxygen atom.
 - (ii) Suggest reasons for the observed difference in the sign of the 1^{st} and 2^{nd}

electron affinity of oxygen.

16)(a) Define the term melting point.

(b) State and explain the factors which affect the melting point of:

- (i) Metals
- (ii) Non-metals

(c) The table below shows the melting points of period three elements.

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Melting point/K	371	923	933	1680	317	392	172	84

Explain the following:

- (i) Magnesium has a higher melting point than sodium.
- (ii) Silicon has a very high melting point.
- (iii) Sulphur has a higher melting point than phosphorous.
- (iv) Argon has the lowest melting point.

17)(a) Explain the difference between ionic radius and atomic radius.

(b) Describe how the following ions are formed;

- (i) Positive ions
- (ii) Negative ions

(c) The table shows the ionic radius of period three ions.

Ions	Na ⁺	Mg ²⁺	Al ³⁺	Si ⁴⁺	P ³⁻	S ²⁻	Cl ⁻
Ionic radii (nm)	0.55	0.65	0.05	0.041	0.212	0.184	0.181

Explain the variation in the ionic radius from sodium ion to chloride ion.

18)The table below shows the atomic and ionic radius of group (II) metals.

Element	Atomic radius (nm)	Ionic radius (nm)
Be	0.112	0.030
Mg	0.160	0.065
Ca	0.197	0.094
Sr	0.215	0.110
Ba	0.221	0.134

(a) Explain why the atomic radius increase from Be to Ba.

(b) Explain why the atomic radius is larger than the ionic radius in each case.

(c) The ions K⁺ and Ca²⁺ have identical electronic configurations (iso-electronic), yet ionic radius of K⁺ ion is larger than that of Ca²⁺.

- (i) Write the electronic arrangement for the two ions.
- (ii) Explain the difference in ionic radius of the two ions.

CHAPTER TWO

2.00 GROUP (I) ELEMENTS

The elements of this group are;

Elements	Symbol
Lithium	Li
Sodium	Na
Potassium	K
Rubidium	Rb
Caesium	Cs
Francium	Fr

Table 12

2.01 General properties

- The general outer electronic configuration of

these elements is ns^1 where n is the principal quantum number.

- They have a fixed oxidation state of +1 due to the low 1st ionisation energy.
- All the elements are strongly electropositive that is they easily loose their outer electrons from their outer shells due to the low ionization energy. This makes them to be chemically reactive.
- They have a fixed valency of one i.e. oxidation state of one thus they can not exhibit oxidation state of +2 because of the very high second ionization which makes it not possible for them to loose the 2nd electron hence this limits them to a fixed oxidation state of +1.
- Of the group (I) members, lithium has abnormally high negative electrode potential. This is because the lithium ion is very small in size therefore it is strongly hydrated in aqueous solution. For this reason lithium is a better reducing agent in solution but poorer reducing agent since solvation cannot take place.
- They are soft metals with low densities and low melting points.
- Their oxides and hydroxides are strongly basic, dissolving in water to form colourless alkaline solutions.
- Their compounds are nearly all soluble in water forming colourless solutions which are neutral to litmus paper except carbonates.
- Their compounds have high melting and boiling points and are non-volatile.
- Their salts with weak acids are extremely hydrolysed, giving alkaline solutions e.g sodium carbonate, sodium ethanoate etc.

NB//. Lithium as one of the members of this group has some abnormal behaviours from the rest of the members. This is because of the small size of its atom and ion making lithium to have a high charge density consequently high polarizing power than the rest of the elements. This results in the tendency of Li to form covalent bond instead of ionic bond hence majority of its compounds are covalent in character and tends to behave like

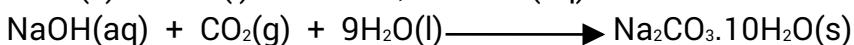
group (II) compounds.

2.02 Chemical reactions of group (I) elements

1) Reaction with air

a) oxygen

All group (I) elements react when exposed to moist air to form oxides. For this reason, they are kept under oil to protect them from reacting with air e.g. when sodium is exposed to moist air, it reacts to form sodium monoxide which is deliquescent and therefore absorbs water vapour from the atmosphere to form sodium hydroxide solution. The sodium hydroxide then absorbs carbondioxide to form sodium carbonate.



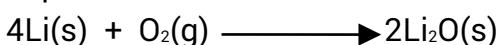
The sodium carbonate when exposed to air loses all the water of crystallization to form white powder of anhydrous sodium carbonate.

However, when group (I) elements (alkali metals) are burnt in air, they react with oxygen to form oxides and the type of oxides formed depend on the size of the metal.

There are three types of oxides;

- Monoxides, (M_2O)
- Peroxides, (M_2O_2)
- Superoxides, (MO_2)

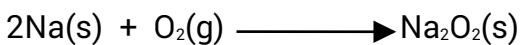
Metals with small size mainly form monoxides and those with big size form only peroxides and super oxides therefore Lithium forms only lithium monoxide. Lithium, by the virtue of its small size is not able to surround itself by the peroxide ion to give a stable crystal lattice and consequently, it forms only monoxide. The ions of K, Rb, and Cs get progressively larger down the group and are able to form stable structures with superoxide ion.



Sodium forms monoxide in limited supply of oxygen but if oxygen gas is in excess, it forms sodium peroxide which is a yellow solid.

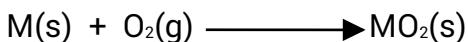


In excess oxygen



It does not form super oxide

Potassium, rubidium, and caesium form super oxides.

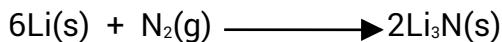


($\text{M} = \text{K, Rb, Cs}$)

b) Reaction with nitrogen

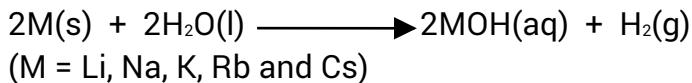
All the metals do not react with nitrogen except lithium which forms lithium nitride.

This is because lithium has anomalous behaviour from the rest of other group (I) elements. In this respect lithium behaves like group (II) elements and the resulting nitride formed has a compact structure with very high lattice energy.



2) Reaction with water.

All the elements react readily and vigorously with cold water to form metal hydroxides with evolution of a colourless gas that explodes with a pop sound on exposure to burning splint, but the vigor of reactivity increases down the group because electropositivity increases in that order.



3) Reaction with halogens

They readily combine with

2.03 Summarising the reason for the increase in the reactivity as you go down the Group

The reactions become easier as the energy needed to form positive ions falls. This is in part due to a decrease in ionisation energy as you go down the Group, and in part to a fall in atomisation energy reflecting weaker metallic bonds as you go from lithium to caesium. This leads to lower activation energies, and therefore faster reactions.

2.04 Compounds of group (I) elements

They have the following characteristics;

- (i) They are white crystalline solids except when the anion is coloured e.g potassium permanganate.
- (ii) They are soluble in water except lithium compounds due to their covalent nature because of;
 - Abnormally small size of lithium
 - High charge to radius ratio (charge density)
 - High polarizing power of lithium
- (iii) They freely ionize in aqueous solution and most of their solutions are neutral except their salts of weak acids from alkaline solution for example sodium carbonate, sodium ethanoate etc.

The compounds include the following;

a) Carbonates

Group (I) carbonates are very stable to heat i.e. they do not decompose on heating except lithium carbonate which easily decomposes on heating because of its covalent character which gives it low lattice energy.

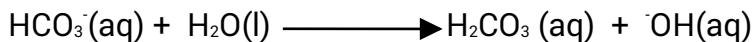


The rest of group (I) carbonates are ionic and have very high lattice energy and therefore resistant to decomposition.

The covalent character of lithium compounds is due to small size of lithium ion, Li^+ making it to have high charge density leading to high polarizing power hence it greatly polarizes the carbonate ion leading to formation of covalent bond instead of ionic bond.

Other group (I) elements do form mainly ionic carbonates because of their low polarizing power due to small charge density and big size.

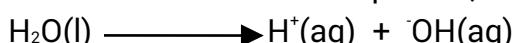
Aqueous solutions of group (I) carbonates are alkaline due to hydrolysis of the carbonate ion.



Hydrolysis is the reaction between water molecules and highly charged metal ion or salt ion which disturbs the water equilibrium producing more hydrogen ions or hydroxyl ions resulting into the solution of pH greater or less than 7

Carbonate ions are highly negatively charged, they withdraw protons from water molecules and releasing a high concentration of hydroxyl ions in to the solution hence the concentration of hydroxyl ions outweighs the effect of carbonic acid formed because the carbonic acid is weak and poorly dissociated.

NB. Water dissociation equation;



$[\text{OH}] = [\text{H}^+]$ neutral solution

$[\text{H}^+] > [\text{OH}]$ acidic solution

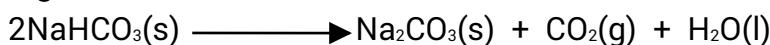
$[\text{OH}] > [\text{H}^+]$ basic solution

b) Hydrogen carbonates.

The hydrogen carbonates of group (I) elements exist as solids except lithium hydrogen carbonate which exists only in solution.

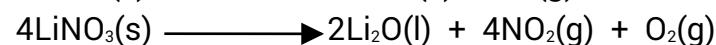
The hydrogen carbonates when heated decompose to form carbonate, carbondioxide, and water.

E.g.



c) Nitrates

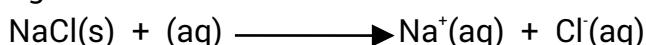
When heated, they decompose to form nitrite and oxygen except lithium nitrate which decomposes completely to give lithium oxide, nitrogen dioxide and oxygen. But, as you go down the Group, the decomposition gets more difficult, and higher temperatures have to be used.



d) Halides (chlorides, bromides, iodides)

They form ionic halides except lithium which forms covalent halides which are soluble in organic solvents while the rest of group (I) halides are soluble in water and their aqueous solutions are neutral to litmus paper.

Eg



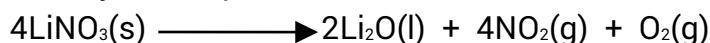
2.05 Properties in which lithium behaves differently from the rest of group (I) elements

- (i) It forms normal oxide only when burnt in air but the rest of group (I) elements form peroxides and super oxides.
- (ii) The hydroxide of lithium is not deliquescent and less soluble in water while hydroxides of the rest of group (I) metals are deliquescent and very soluble in water.
- (iii) Lithium forms nitride when heated in air while the rest of the alkali metals do not form

nitride when burnt in air.



- (iv) The oxy salts of lithium e.g. carbonate, nitrate, etc are easily decomposed when heated to form a metal oxide while the oxy salts of other group (I) elements do not easily decompose when heated.



- (v) The hydrogen carbonates of lithium only exist in solution while the hydrogen carbonates of other group (I) elements exist in solid form.

- (vi) The fluorides, phosphates, and carbonates of lithium are sparingly soluble in water while corresponding salts of other group (I) elements are soluble in water.

2.06 Group (I) chemistry sample questions

- 1) (a) Write the general outer electronic configuration of group (IA) elements.

- (b) State five general properties of group (IA) elements.

- 2) (a) State how the melting point and boiling point of group (IA) elements differs from those of groups (IIA) elements.

- (b) Give reason(s) for your answer in 2 (a)

- (c) Explain why group (IA) elements cannot form compounds in +2 oxidation state but only forms in +1 oxidation state.

- 3) (a) State reasons why lithium differs from the rest of the elements of group (IA) elements in the periodic table.

- (b) State six properties in which lithium resembles magnesium in group (IIA) but differs from the rest of group (IA) elements.

- 4) (a) Explain why lithium has abnormally high negative electrode potential.

- (b) The conductivity of caesium ion is higher than that of lithium ion yet lithium ion is smaller than caesium ion. Explain.

- 5) Explain each of the following observations.

- (a) The solubility of lithium halides in water is in the order; $\text{LiF} > \text{LiCl} > \text{LiBr} > \text{LiI}$

- (b) The reduction potential of lithium is much the same as that of caesium despite the fact that the ionization energy of lithium is much greater than that of caesium. Explain.

- (c) (i) What is meant by the term "metallic bonding"?

- (ii) Why is the melting point of sodium higher than that of potassium?

CHAPTER THREE

3.00 GROUP (II) ELEMENTS (THE ALKALINE EARTH METALS)

These elements include;

Element	Symbol
Berryllium	Be
Magnesium	Mg
Calcium	Ca
Strontium	Sr
Barium	Ba
Radium	Ra

3.01 General properties

- The general electronic configuration of group (II) elements is ns^2 where n is the principal quantum number.
- These elements have a fixed oxidation state of +2
- The melting and boiling points of group (II) elements are higher than those of group (I) elements. This is because the number of electrons contributed for bonding is proportional to both melting and boiling points and since group (II) metals donates two electrons for metallic bond formation they have higher boiling point and melting points than the group (I) metals.

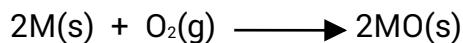
In comparison to group (I) elements, both group (I) and group (II) are reducing agents. This is reflected by the ease with which they reduce water to hydrogen gas i.e. they are all electropositive metals.

3.02 Chemical reactions of group (II) elements

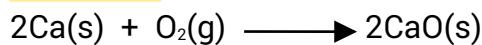
1) Reaction with air.

a) With oxygen

All the metals when burnt in air forms monoxide (normal oxide). In this reaction, group (II) elements resemble lithium in group (I).



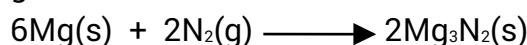
But when just exposed to moist air, they react slowly forming a film of the oxide deposited on their surface and this oxide absorbs carbon dioxide from air to form a carbonate.



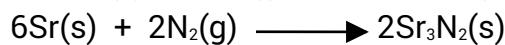
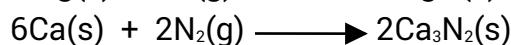
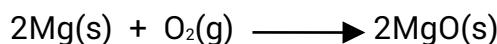
b) Reaction with nitrogen.

Only magnesium, calcium and strontium react with nitrogen when heated to form a metal nitride. However when heated in air they form a mixture of oxide and the nitride.

The nitrides are soluble in water to give a basic solution with evolution of ammonia gas.

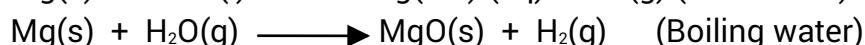


But when heated in air,

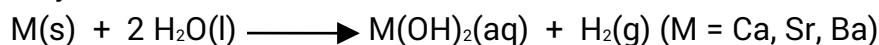


2) Reaction with water.

They react less vigorously as compared to group (I) elements because they are less electropositive. Nevertheless, the vigor of the reaction with water increases down the group because of the increasing electropositivity. However, beryllium does not react with water under any condition. Magnesium reacts very slowly with cold water to form magnesium hydroxide and hydrogen gas but when heated, it burns to form white powder of magnesium oxide with evolution of a hydrogen gas that explodes with a pop sound on exposure to a burning splint.



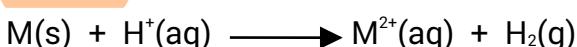
Calcium, strontium and barium react more vigorously with cold water to form the corresponding metal hydroxide and hydrogen gas. This is because their hydroxides are very soluble.



3) Reaction with acids.

(a) With dilute acids.

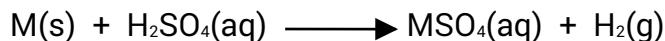
All the metals liberate the hydrogen gas from dilute acids and the corresponding salt is formed.



With dilute sulphuric acid, Be reacts only on warming the acid and it does not react with cold dilute acid.

Other group (II) metals react vigorously with dilute sulphuric acid both when cold and

warm. However with calcium the reaction is retarded due to the formation of an insoluble calcium sulphate which is deposited on the surface of the metal.



(M = Be, Mg, Ca, Sr, Ba)

(b) With concentrated acid.

All the metals do not react with cold concentrated sulphuric acid but reacts when the acid is hot. In this reaction the acid is reduced to water and sulphur dioxide and the metal is oxidized to water and a sulphate. eg

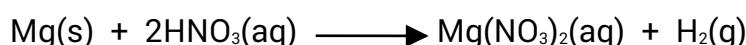


- Concentrated hydrochloric acid does not react with the group (II) elements because it is non-oxidizing acid but the metals react with dilute hydrochloric acid to form hydrogen gas and the corresponding salt.

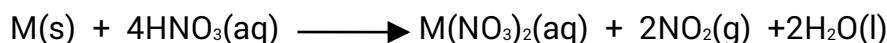


(M = Be, Mg, Ca, Sr, Ba)

- With dilute nitric acid. All the metals except magnesium do not liberate hydrogen gas from dilute nitric acid.

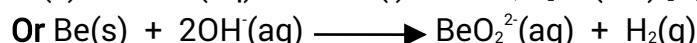


- With concentrated nitric acid. The concentrated acid oxidizes the metals resulting in to the formation of nitrogen dioxide, water and a metal nitrate. However, beryllium does not react with concentrated nitric acid and instead rendered passive by the acid due the formation of the oxide layer on the metal. Other metals rendered passive by concentrated nitric acid include aluminium, chromium and iron,



4) Reaction with alkalis.

All the metals except beryllium do not react with aqueous alkalis. This is because beryllium is amphoteric while the rest of the metals are basic.

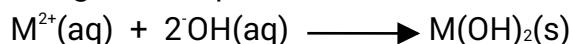


3.03 Compounds of group (II) elements

a) Metal hydroxides, $M(OH)_2$

They are prepared by adding aqueous alkalis to a solution containing group (II) cations.

The general equation for the reaction is given as;



Where (M = Be, Mg, Ca, Ba, Sr)

Solubility of the hydroxides $KJmol^{-1}$

Metal Hydroxide	solubility at 25°C/mole per 100g of H_2O	Lattice energy/ $KJmol^{-1}$	Hydration energy/ $KJmol^{-1}$	ΔH solution
$Be(OH)_2$	Insoluble			
$Mg(OH)_2$	2.0×10^{-5}	2842.8	-2840	+2.8

$\text{Ca}(\text{OH})_2$	1.5×10^{-3}	2553.8	-2570	-16.2
$\text{Sr}(\text{OH})_2$	3.4×10^{-3}	2354	-2400	-46
$\text{Ba}(\text{OH})_2$	1.5×10^{-2}	2218	-2280	-51.8

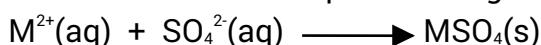
The solubility of the group (II) metal hydroxides increases down the group i.e. from $\text{Be}(\text{OH})_2$ to $\text{Ba}(\text{OH})_2$.

The solubility of any ionic salt is determined by both the lattice energy and hydration energy. As you move down the group, both the lattice energy and hydration energy decreases as the cationic size increases but the lattice energy decreases more rapidly than the magnitude of the hydration energy thus favouring increase in solubility down the group.

However, $\text{Be}(\text{OH})_2$ is insoluble in water because it is predominantly covalent in nature. This arises due to its small size and high charge density hence it greatly polarizes the -OH ion leading to the formation of a covalent bond hence making it insoluble in water.

b) Metal sulphates, MSO_4

They can be prepared by adding dilute sulphuric acid to a solution containing group (II) metal cations. The sulphates are generally sparingly soluble in water.



Solubility of sulphates

Metal Sulphate solubility at
 25°C/mole per 100g
 of H_2O

BeSO_4	3.7×10^{-1}
MgSO_4	1.8×10^{-1}
CaSO_4	4.66×10^{-3}
SrSO_4	7.11×10^{-5}
BaSO_4	9.4×10^{-7}

The solubility of sulphates decreases down the group from BeSO_4 to BaSO_4 .

This is because both the lattice energy and hydration energy decreases down the group but the decrease in hydration energy is much more rapid than the decrease in lattice energy thus, the decrease in solubility down the group.

c) Metal chlorides, MCl_2

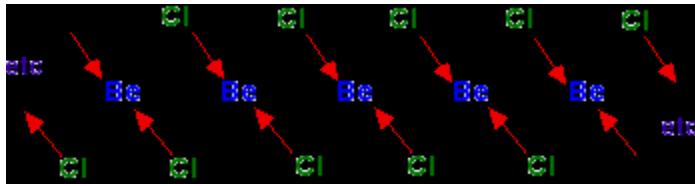
All the chlorides are electrovalent and soluble in water except BeCl_2 which is covalent and soluble in non polar solvents such as ethanol. The covalent nature of BeCl_2 is because of its small size and high charge density making it a highly polarizing cation.

Anhydrous BeCl_2 in vapour state is dimerised i.e. two molecules of BeCl_2 are joined to form one molecule i.e.

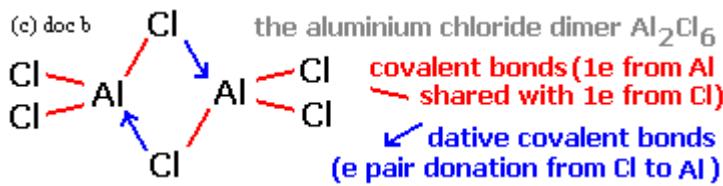


In this state, Be resembles Al

Structure of BeCl_2 in the vapour state



Structure of AlCl₃ in the vapour state

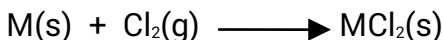


When BeCl₂ is dissolved in water, it undergoes hydrolysis and the resulting solution is acidic with a pH of less than 7. Chlorides of other group (II) elements do not undergo hydrolysis except MgCl₂

NB// solubility of chlorides, sulphates and carbonates decrease down the group while that of hydroxide increases down the group.

Preparation of group (II) metal chlorides

They are prepared by heating the element in dry chlorine.



(M = Be, Mg, Ca, Sr, Ba)

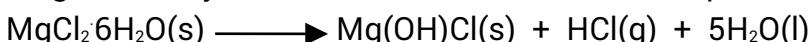
They are also prepared by neutralization of the metal carbonate with dilute hydrochloric acid. Here excess metal carbonate is added to the dilute hydrochloric acid to ensure that all the acid is reacted. The excess solid is filtered off and the salt is crystallized from excess water.



(M = Be, Mg, Ca, Sr, Ba)

NB//

(i) Anhydrous magnesium chloride cannot be prepared by crystallization of hydrated magnesium chloride because the hydroxide readily undergoes hydrolysis to form basic magnesium hydroxide with one of the OH not replaced.



On further heating magnesium oxide and hydrogen chloride gas are formed.



(ii) The chlorides of group (I) can be prepared by either of the two methods. The chlorides of group (I) elements do not undergo hydrolysis because their cations have a low charge density.

Nature of the chlorides

The chlorides are generally ionic with relatively high melting point. Their melting points are higher than that of the corresponding group (I) chlorides in the same period.

This is because group (II) ions have high charge so their lattice energy is greater than that of group (I) chlorides. Therefore, more energy is required to overcome the electrostatic

force of attraction between the metal and the halogen of group (II) metal chlorides. BeCl_2 has a lower melting point. This is because Be cation has a high charge density thus high polarizing power so in its chloride there is a greater degree of covalent character and this suggests that there are weak forces of attraction between its molecules which requires little energy to break or overcome.

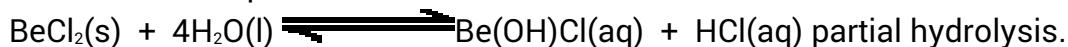
Chemical properties of group (II) chlorides

1) Reaction with water.

All the chlorides are soluble in water.



BeCl_2 in solution is acidic because it undergoes hydrolysis reaction to produce white fumes of hydrogenchloride gas. This arises from the small size of Be ion which makes it able to extract a proton from water.



In solution Be ion exists as $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ as given by reaction equation below



The hydrolysis equation is given as;

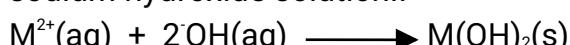


MgCl_2 is also slightly acidic since it undergoes hydrolysis reaction.



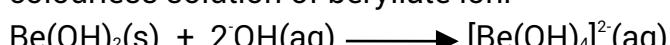
2) Reaction with alkalis.

Be, Mg, Ba, Sr and Ca chlorides solution forms white precipitates when reacted with sodium hydroxide solution..



M = (Be, Mg, Ba, Sr and Ca)

However, beryllium hydroxide dissolves in the excess sodium hydroxide to form a colourless solution of beryllate ion.



NB//

To precipitate any metal hydroxide, the concentration of the alkali should be high to provide enough OH^- to reach and exceed the solubility product of the metal hydroxide.

d) Hydrides of group (II) elements

They are made by direct combination of the metal with hydrogen except BeH_2 which is made by reaction of its chloride with lithium aluminium hydride.



M = Mg, Ba, Sr and Ca

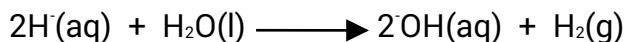


The hydrides are ionic though BeH_2 has a high degree of covalent character.

Reaction of the hydrides

1) Reaction with water.

The hydride ion, H^- is a strong base (proton acceptor) so it can easily extract a proton from water resulting into the formation of an alkaline solution with evolution of hydrogen gas.



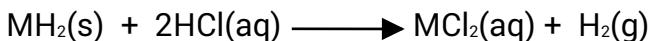
General equation for the reaction is;



M = (Be, Mg, Ba, Sr and Ca)

2) Reaction with acids

They react with acids to form salts and hydrogen gas.



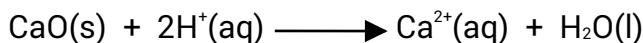
M = (Be, Mg, Ba, Sr and Ca)

e) Metal oxides of group (II) elements

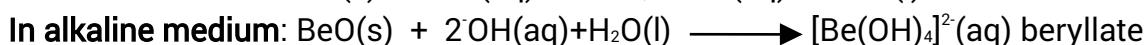
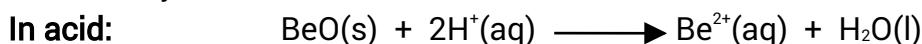
They are prepared by heating group (II) carbonates or nitrates.eg



The group (II) metal oxides are basic except BeO which is amphoteric ie dissolves in both acids and bases.ie

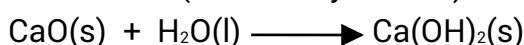


But for beryllium oxide,



Another name for calcium oxide is quick lime. This is prepared by strongly heating calcium carbonate. Since calcium oxide has a high affinity for water, it is used as a drying agent.

NB// when cold water is added to CaO, it swells with a hissing sound liberating a lot of heat to form white solid of mass which cracks and crumbles into a white powder called slaked lime (calcium hydroxide)



Quick lime slaked lime

The group (II) metal oxides dissolve in acids with evolution of heat and formation of colourless solution which is a combination of water and the salt.eg



The reactivity of the oxides with dilute sulphuric acid decreases down the group because the sulphate become less soluble as you move down the group.

f) Carbonates and hydrogen carbonates

Carbonates of group (II) decompose on heating to form oxide and carbon dioxide while the group (I) carbonates do not decompose on heating except lithium carbonate.



(M = Be, Mg, Ca, Sr, Ba)

The hydrogen carbonates of group (II) elements are only known to exist in solution while those of group (I) elements exist in solid state except lithium which exists in solution.

The hydrogen carbonates of group (II) elements decompose on heating to liberate

carbondioxide and a metal carbonate and water are formed.e.g



On further heating, the metal carbonate decomposes to metal oxide and carbondioxide gas.



Decomposition temperature of group (II) carbonates

Metal carbonate	BeCO_3	MgCO_3	CaCO_3	SrCO_3	BaCO_3
Temperature/ $^{\circ}\text{C}$	25	540	900	1290	1300

The decomposition temperature of group (II) carbonates increases down the group.

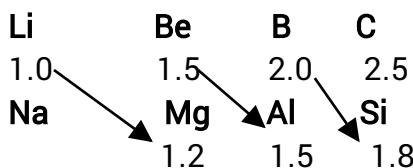
This is because down the group, the ionic radius (size of the cation) increases resulting into a decrease in the polarizing power of the cations.

BeCO_3 has low decomposition temperature because it is more polarized making it to have a greater covalent character hence low decomposition temperature.

Down the group the extent of polarization by the cations decreases resulting in to increase in ionic character and hence lattice energy. This makes BaCO_3 to have the highest decomposition temperature due to its high lattice energy as a result of increased ionic character.

3.04 Diagonal relationship

Electronegativity increases across the period and decreases down the group of the periodic table. So the elements connected diagonally in the periodic table tend to have similar electronegativity.



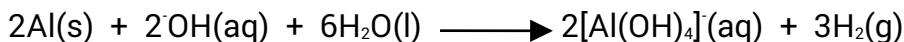
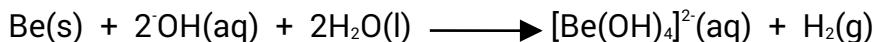
At the same time, atomic radius decreases across a period and increases down a group. This leads to elements existing along the diagonals in the periodic table to form ions with similar charge density. Therefore, these elements along diagonals have similar chemical properties especially properties that depend on electronegativity and polarizing power of the cations.

*The phenomenon of elements existing along diagonals in adjacent groups in the periodic table having similar chemical properties such as electronegativity, atomic radius, ionization energy and polarizing power is called **diagonal relationship**.*

It is also defined as the relationship in which the elements in the second period resemble the elements in the next higher group in the third period, and have an anomalous property in relation to other members of the group.

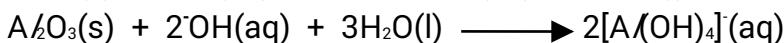
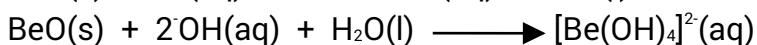
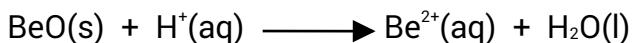
3.05 Properties in which beryllium resembles aluminium

- (i) Both metals react with aqueous alkali to liberate hydrogen gas. This is because they are amphoteric.

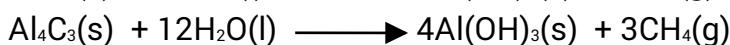


- (ii) Both metals are rendered passive by concentrated nitric acid due to formation of a film of an oxide layer around the metal which is impermeable to the acid.

- (iii) The hydroxides and oxides of both metals are amphoteric.



- (iii) Beryllium carbide, Be_2C and aluminium carbide, Al_4C_3 are hydrolyzed to form methane while the rest of group (II) carbides form ethyne.



- (iv) Both metals form covalent chlorides which fume in moist air liberating hydrogen chloride gas, HCl . This is due to hydrolysis and the chlorides are dimerised in vapour state.



- (v) Both metals have a tendency to form complex ions e.g. $[\text{BeF}_4]^{2-}$ and $[\text{AlF}_6]^{2-}$

3.06 Complex formation by group (II) elements

A complex is positive or negative ion in which an atom or group of atoms with negative charges or lone pair of electrons are coordinated with the central metal ion or atom which is normally a metal.

Complex formation is favoured by the following factors;

- (i) Small and highly charged cation.

- (ii) Presence of suitable empty orbital of appropriate energy level.

Group (II) elements have the tendency to form complexes but the ability to form complexes decreases down the group.

Beryllium at the top of the group is the smallest atom therefore; its ion is small and highly charged. This makes it able to form many complexes.

But down the group, the sizes of the cation increases which favors decrease in charge density and therefore the tendency to form complexes also decreases.

3.07 Effect of ionic radius of group (II) ions on the properties of their compounds

Group (II) ions are doubly charged hence they have small ionic radius than the group (I) metal cations which are singly charged. Consequently the group (II) cations have a high charge density and polarizing power than group (I) cations and this has the following effect on the properties of their compounds;

- 1) Solubility.

Group (II) salts are less soluble in water than group (I) salts. This is because group (II) cations have high charge density and hence high polarizing power than the group (I) cations.

Therefore compounds of group (II) elements are more polarized than those of group (I) compounds and this results in to a greater covalent character of group (II) compounds thus they are generally sparingly soluble in water while group (I) compounds are more soluble in water.

2) Thermal stability.

Group (II) salts thermally unstable than group (I) salts. This is due the covalent nature of group of (II) salts which makes them easily decomposed when heated. For example sodium carbonate does not decompose on heating while magnesium carbonate decomposes completely on heating to magnesium oxide, MgO and carbondioxide gas, CO₂.



3) Hydrolysis.

Aqueous solutions of some group (II) salts are acidic and this is due to hydrolysis. The hydrolysis is mainly undergone by beryllium salts and to some extent magnesium salts.

Basing on this, as you descend the group, the ability of group (II) salts to undergo hydrolysis decreases. This is because of reduced charge density with increasing ionic radius implying that barium salts shows no tendency towards hydrolysis. E.g. when beryllium chloride is dissolved in water, it ionizes to form hydrated beryllium ion, [Be(H₂O)₄]²⁺ which then undergoes hydrolysis.



3.08 Chemical test for group (II) cations

Reagent	Observations		
	Mg ²⁺	Ca ²⁺	Ba ²⁺
Addition of sodium hydroxide drop wise until in excess to solution having the metal ion.	White precipitate insoluble in excess.	White precipitate insoluble in excess.	White precipitate insoluble in excess.
Addition of ammonia solution drop wise until in excess to solution having the metal ion.	White precipitate insoluble in excess.	No precipitate is formed.	No precipitate is formed.
Addition of sodium	White precipitate	White precipitate	White

carbonate solution			precipitate
Addition of solid NH ₄ Cl, followed aqueous ammonia and finally disodium hydrogen phosphate, Na ₂ HPO ₄	White crystalline precipitate of magnesium ammonium phosphate (MgNH ₄ PO ₄ .6H ₂ O) NB (i) ammonia is to make the solution alkaline since Na ₂ HPO ₄ works under alkaline solution (ii) NH ₄ Cl is to prevent formation of Mg(OH) ₂ which is a white precipitate.		
Dilute sulphuric acid		A white precipitate of calcium sulphate is formed if the solution having calcium ion is concentrated.	
Potassium chromate		A yellow precipitate of calcium chromate is formed which is soluble in ethanoic acid if solution having calcium ion is concentrated.	
Ammonium oxalate solution		A white precipitate of calcium oxalate soluble in dilute HCl and HNO ₃ but insoluble in dilute ethanoic acid	A white precipitate of barium oxalate soluble in dilute HCl and HNO ₃ but also soluble in ethanoic acid
Potassium chromate solution			A yellow precipitate of BaCrO ₄ soluble in dilute HCl and HNO ₃ but insoluble in ethanoic acid

NB (I) with ammonia solution, no precipitate is formed with Ba²⁺ and Ca²⁺ because ammonia is a weak base and so the concentration of hydroxyl ions provided is not enough

to reach and exceed the solubility product of the metal hydroxides due to low ionization of the ammonia solution.

For Mg^{2+} , the ammonia provides hydroxyl ions for the ionic product to be reached and exceed the solubility value of $Mg(OH)_2$.

(II) Reaction equations for some of the reactions.

3.09 Group (II) chemistry sample questions

- 1) (a) Write the general outer electronic configuration of group (IIA) elements of the periodic table.
(b) The elements Be, Mg, Ca, Sr, and Ba are in group (II) of the periodic table. Explain how the following factors vary within the group;
 - (i) Atomic radius.
 - (ii) Ionization energy.
 - (iii) Electro positivity.
 - (iv) Melting point.
- 2) (a) Define the term diagonal relationship.
(b) State three pairs of elements that show diagonal relationship
(c) State six properties in which beryllium resembles aluminium but differs from the rest of group (II) elements.
(d) Give reasons for your answer in 2 (c).
- 3) (a) State what would be observed and write equations for the reaction which take place when;
 - (i) Magnesium is reacted with boiling water.
 - (ii) Barium is reacted with cold water.
(b) Compare the reaction of beryllium and barium with sulphuric acid under various conditions.
(c) Explain how the solubility of hydroxides and sulphates of the elements of group (II) of the periodic table vary down the group.
- 4) Zinc is a d-block element and magnesium is an s-block element. Discuss the chemistry of zinc and magnesium showing;
 - (a) Similarities.
 - (b) Differences. Illustrate your answers with equations (you should include reactions with water, acids and non metals)
- 5) (a) Discuss how the ionic radius of group (II) metals affects the properties of their compounds.
(b) Explain with equation(s) why an aqueous solution of beryllium chloride has a pH of less than 7.
(c) Explain why the decomposition temperature of beryllium carbonate is less than that of barium carbonate.
- 6) Name one reagent (s) that can be used to identify and confirm each of the following pairs of ions and each case state what is observed when each member of the pair is separately treated with that reagent named.
 - (a) Ba^{2+} and Ca^{2+}
 - (b) Mg^{2+} and Zn^{2+}

- (c) Pb^{2+} and Ba^{2+}
- (d) Ca^{2+} and Mg^{2+}
- (e) Pb^{2+} and Al^{3+}

- 7) (a) Describe and explain the trend in the thermal decomposition of group (II) nitrates from magnesium to barium writing equations where necessary.
- (b) Magnesium chloride and silicon chloride reacts differently with water. Describe and explain those differences, writing equations where necessary.
- (c) Burning barium metal in air forms an oxide which contains 81.1% of barium by mass.
- (i) What is the formula of the oxide?
- (ii) When this oxide of barium is added to water barium hydroxide and another compound formed when the solution is acidified, and added to potassium iodide solution. Explain these observations and write equations for the reaction occurring.
- 8) The elements beryllium, magnesium and barium belong to group (II) in the periodic table.
- (a) (i) State three chemical properties shown by the elements. For each property write an equation to illustrate your answer.
- (ii) Explain the trend in the solubilities of the hydroxides of the elements in waters.
- (b) Beryllium differs in some of its properties from the rest of the elements in the group.
- (i) State five properties in which beryllium differ from the rest of the members of the group.
- (ii) Give reasons why beryllium shows different properties from the rest of group (II) elements.
- (c) (i) Name one reagent that can be used to distinguish between magnesium ions and barium ions.
- (ii) State what would be observed in each case when the reagent in (c) is used.
- (iii) Write equation (s) for the reaction (s) that takes place in c (ii)
- (d) An aqueous solution of magnesium chloride has a pH of less than 7. Explain.
- 9) The decomposition temperatures of group (II) metal carbonates are given below.
- | Metal carbonate | BeCO_3 | MgCO_3 | CaCO_3 | SrCO_3 | BaCO_3 |
|-----------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Decomposition temperature/K | 370 | 470 | 1170 | 1550 | 1630 |
- a) Write the equation for the thermal decomposition of the carbonate ion giving state symbols.
- b) Suggest with reasons what causes the variation in the decomposition temperatures.

CHAPTER FOUR

4.00 GROUP (III) ELEMENTS

They include;

Elements	Symbol
Boron	B
Aluminium	Al
Gallium	Ga
Indium	In
Thallium	Tl

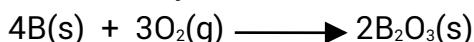
4.01 General properties

- The general outer electronic configuration is nS^2nP^1 .
- The common oxidation state exhibited by the group three elements is +3.
- Boron is a non-metal while the rest of the elements are metals.
- Boron does not occur freely in nature but it occurs as borax, $Na_2B_4O_7 \cdot 10H_2O$ and boric, H_3BO_3 acid respectively.

4.02 Chemical properties of group (III) elements

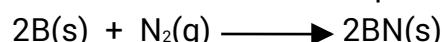
1) Reaction with oxygen.

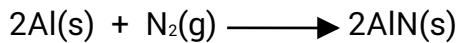
Boron readily burns when heated in oxygen to form diboron trioxide.



2) Reaction with nitrogen.

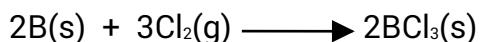
Both boron and aluminium burns when heated in nitrogen gas to form boron nitride and aluminium nitride respectively.





3) Reaction with chlorine.

Boron readily combines with chlorine when heated to form boron tri chloride,



4.03 Primary standard

Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$). This is a very good primary standard.

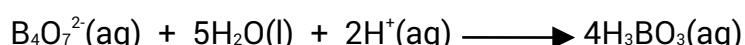
A primary standard is substance used to make a solution of accurately known and constant concentration.

Characteristics of a primary standard

- (i) It is chemically pure.
- (ii) It is stable that's must have a constant concentration.
- (iii) It must have a high relative molecular mass hence minimizing errors in weighing.
- (iv) It must be soluble in water.

A standard solution of borax is used to standardize solutions of hydrochloric acid and sulphuric acid in volumetric analysis.

The indicator used is mainly methyl orange because the boric acid formed has no effect on the indicator.



Mole ratio of $\text{B}_4\text{O}_7^{2-}\text{(aq)} : \text{H}^+ = 1:2$

4.04 Aluminum

a) Extraction of aluminium

The major ore from which aluminium is extracted is called Bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$). This ore has the following impurities;

- (i) Silica (silicon dioxide), SiO_2
- (ii) Titanium (IV) oxide, TiO_2
- (iii) Iron (III) oxide.

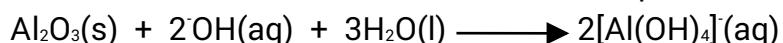
The two major stages involved in the extraction of aluminium are;

- (i) Purification of the Bauxite
- (ii) Electrolysis

Purification of the Bauxite

The bauxite is roasted to drive off the water of crystallization.

The roasted ore is then ground or pulverized into a fine powder and dissolved in hot concentrated sodium hydroxide solution to form soluble sodium aluminate. This is to dissolve free aluminium oxide since it is amphoteric in a process called leaching.



Since silica is acidic, it also dissolves to form sodium silicate (Na_2SiO_3)



Iron (III) oxide and titanium (IV) oxide remain undissolved because they are basic and

therefore they filtered off.

The filtrate is then seeded with freshly prepared aluminum hydroxide to precipitate the pure aluminium hydroxide.



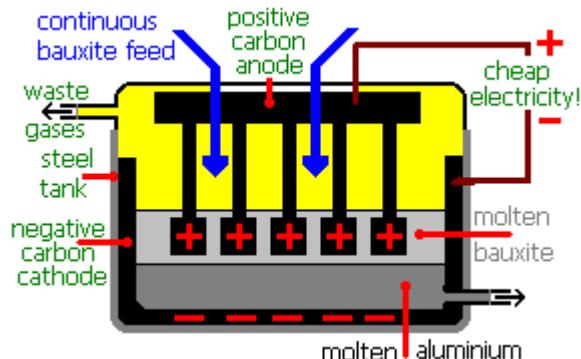
The aluminium hydroxide can also be precipitated by bubbling carbondioxide gas through the filtrate.



The aluminium hydroxide formed is then filtered out and strongly heated to obtain anhydrous aluminium oxide, Al_2O_3 .



Electrolysis of aluminum oxide



The purified ore is dissolved in molten cryolite (Na_3AlFe_6). Cryolite is used to lower the melting point of the aluminum oxide from 2050°C to 850°C .

The molten solution is then electrolyzed in a steel container lined with carbon acting as the cathode and graphite rod suspended in molten solution acting as the anode.

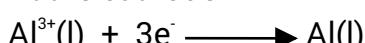
A low voltage and a high current density are used. The low voltage is used to avoid the decomposition of the cryolite while high current density is used because the process demands more energy.

Aluminium oxide ionizes as follows;



Aluminum is discharged at the cathode while at the anode oxygen is discharged.

At the cathode



At the anode



NB// Aluminium cannot be extracted by reduction of Al_2O_3 using carbon or carbon monoxide because Al_2O_3 is a very stable compound thus reduction requires a lot of energy which cannot be supplied during carbon or carbon monoxide reduction hence it can only be extracted by electrolysis.

The extraction of aluminum by the given process has the following shortcomings;

- The process demands a lot of energy. Therefore, usually carried out where there is high and cheap electric power. This makes it uneconomical.
- The anode needs replacement from time to time because it burns in oxygen produced to form oxides of carbon.

b) Uses of aluminium

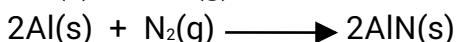
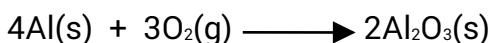
- (i) For making of domestic cooking utensils because it is a good conductor of heat.
- (ii) It is used in the wrapping of food because it has the ability to reflect heat and light.
- (iii) It is used to make overhead high tension cables for transmission of electricity. This is because it is a good conductor of electricity and is of low density.
- (iv) It is used to make aircraft bodies because it has a low density and high tensile strength.
- (v) Aluminium powder is used to make aluminium paints for painting of windows and roofs etc
- (vi) It is used in the thermitite process in the extraction of other metals e.g. chromium and iron. This is because it is highly electropositive.



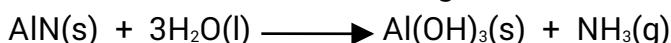
c) Chemical properties of aluminium

1) Reaction with air.

When heated in air, it burns to form a mixture of aluminium oxide and white solid of aluminium nitride.



The nitride liberates ammonia gas when cold water is added to it.



2) Reaction with water.

It does not react with water regardless of the condition because the oxide film on the metal surface prevents the interaction between the metal and the water.

3) Reaction with acids.

Aluminium does not react with dilute acids but react with concentrated acids.

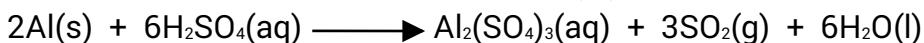
(i) Hydrochloric acid.

It reacts with fuming concentrated hydrochloric acid liberating hydrogen gas and a salt is formed.



(ii) Sulphuric acid.

It does not react with dilute sulphuric acid because the aluminium oxide is insoluble in sulphuric acid. However, it reacts with concentrated sulphuric acid liberating sulphur dioxide and forming aluminium (III) sulphate and water.

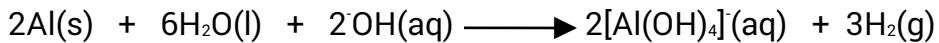


(iii) Nitric acid.

It does not react with aluminium at any concentration therefore rendered passive (forms oxide layer on aluminium). In this respect, aluminium resembles beryllium and chromium.

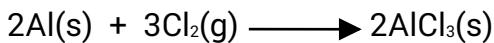
4) Reaction with alkalis.

Aluminium dissolves readily in aqueous alkali evolving hydrogen gas and with the formation of a complex that is soluble.



5) Reaction with halogens.

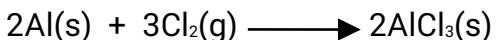
It is oxidized by dry chlorine when heated to form aluminium chloride which dimerises.



d) Compounds of aluminium

(i) Aluminium chloride.

It is prepared by passing dry chlorine gas or dry hydrogen chloride gas over heated aluminum metal.

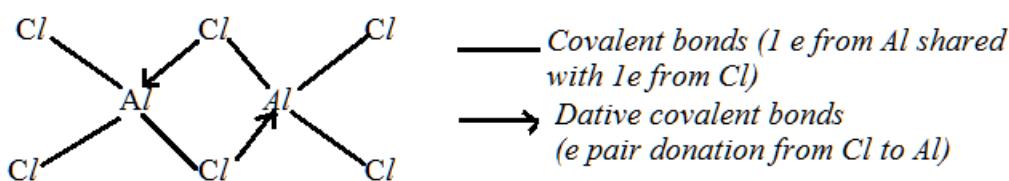


Aluminium exists in the hydrated form as $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$

Anhydrous AlCl_3 cannot be prepared by heating the hydrated AlCl_3 because it will undergo hydrolysis-producing fumes of hydrogen chloride gas and Al_2O_3 when heated.



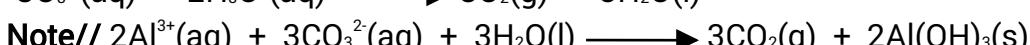
AlCl_3 also dimerises like BeCl_2 when heated.



(ii) Aluminium carbonate, $\text{Al}_2(\text{CO}_3)_3$

It does not exist because any attempt to prepare it results into the formation of aluminium hydroxide, $\text{Al}(\text{OH})_3$ and carbondioxide.

This is because in solution the aluminium ions, Al^{3+} are hydrated and they undergo hydrolysis to give solution of pH less than 7. Therefore, when an aqueous solution containing the carbonate ion, CO_3^{2-} is added to the above solution, the hydrogen ions produced due to the hydrolysis of Al^{3+} react with the carbonate to liberate carbondioxide.



Behaviour of Al^{3+} ions in water

Due to the small size and high charge of aluminium ion (+3) leading to high charge density of Al^{3+} . It is normally hydrated in aqueous solution and undergoes hydrolysis resulting into the release of hydrogen ions and this makes the solution to have a pH of less than 7.

Bonding in aluminium halides

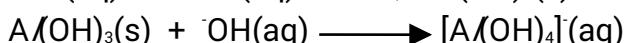
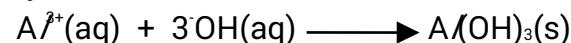
Aluminium shows an oxidation state of +3 in most of its compounds. The very high positive charge and small ionic radius causes distortion (polarization) of the electron clouds around the halide ion in contact with it.

The polarization is greatest as the size of the halide ion increases. Therefore, the iodide ion with the greatest size is the most polarized while fluoride ion experiences negligible polarization. This makes aluminium fluoride to be ionic while aluminium chloride to be intermediate between ionic and covalent.

4.05 Identification of Al^{3+} ions

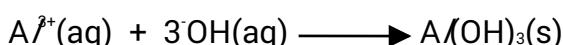
(i) Addition of sodium hydroxide solution.

When sodium hydroxide is added to solution containing Al^{3+} drop wise until in excess, a white precipitate of aluminium hydroxide is formed which dissolves in excess sodium hydroxide solution to form a colourless solution of aluminate.



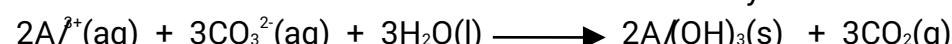
(ii) Addition of ammonia solution.

A white precipitate of aluminium hydroxide is formed which does not dissolve in excess ammonia solution.



(iii) Addition of sodium carbonate solution.

A white precipitate of aluminium hydroxide is formed with evolution of a colourless gas that turns moist blue litmus red and lime water milky.



The precipitate dissolves in excess of the reagent forming a colourless solution.



(iv) Addition of aluminon reagent (a solution of the ammonium salt of aurinetricarboxylic acid).

Here the Al^{3+} solution is first acidified with dilute hydrochloric acid followed by addition of few drops of the aluminon reagent and lastly sodium hydroxide solution drop wise. A bright red adsorption complex or pink lake is formed.

4.06 Group 3 chemistry sample questions

- 1) (a) The principal ore used for the extraction of aluminium is bauxite.
 - (i) Give the name and formula of the aluminium compound present in the bauxite.
 - (ii) Name two important impurities usually present in bauxite.
 - (iii) Outline the process by which pure aluminium oxide is obtained from bauxite, giving appropriate equations where applicable.
 - (iv) Indicate how the process deals with the two impurities you have named in (a) (ii) above.
- (b) (i) Briefly explain how aluminum can be obtained after the ore has been treated as in (a) (iii) above. Give appropriate equations.
- (ii) Explain why a low voltage and a high current density is used during the extraction of aluminium from its ore.
- (c) Write equations and state conditions under which aluminium react with;
 - (i) Air
 - (ii) Sodium hydroxide

- (iii) Hydrochloric acid
 - (iv) Sulphuric acid
- (d) Sodium carbonate was added to a solution of aluminium chloride drop wise until in excess.
- (i) State what was observed.
 - (ii) Explain your observation in (d) (i) above.
 - (iii) Write stepwise equations for the reactions that took place.
- (e) (i) Explain why aluminium utensils should not be washed using alkaline solutions.
- (iii) State with reasons five uses of aluminium metal.
- 2) Boron forms borax which is commonly used in volumetric analysis.
- (a) State five characteristics of Borax which makes it suitable for use in volumetric analysis.
 - (b) Write ionic for reaction that takes place between borax and dilute hydrochloric acid.
 - (c) Write equations and state conditions under which Boron reacts with;
 - (i) Chlorine
 - (ii) Oxygen.
- 3) Explain using appropriate equations the following observations.
- (a) Aluminium carbonate does not exist.
 - (b) Anhydrous aluminium chloride cannot be prepared by heating of hydrated aluminium chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$)

CHAPTER FIVE

5.00 GROUP (IV) ELEMENTS

The elements are;

Carbon } non-metals

Silicon }

Germanium metalloid

Tin }

Lead } metals

The general outer electronic configuration for the group (IV) elements is nS^2nP^2 where n is the principal quantum number.

5.01 General properties

- The metallic nature of group (IV) elements increase down the group. Carbon and silicon show many of their properties as non-metals eg they give acidic oxides.
- Germanium, tin and lead are amphoteric despite the fact that some lead oxides are basic.
- The common valency shown by group (IV) elements is four. Apart from carbon, the rest of the elements can have more than four bonds. This is because they have empty d-orbitals especially those of the outer shell to participate in bonding.
- The presence of empty d-orbitals in the elements other than carbon is responsible for the formation of complex ions such as SiF_6 .
- Some carbon compounds are less reactive than the corresponding compounds of the other elements e.g carbon tetrachloride does not react with water whereas silicon

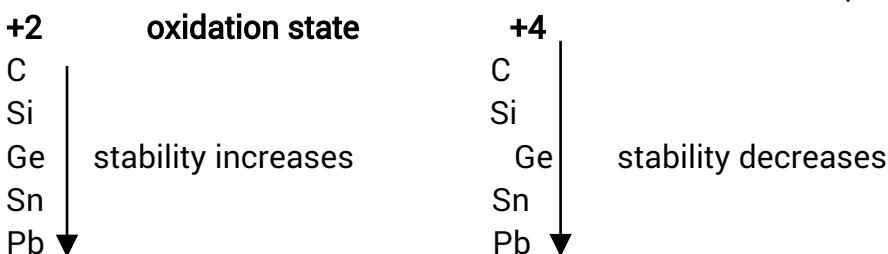
tetrachloride is readily hydrolysed.

5.02 Oxidation states

Group (IV) elements exhibit two oxidation states i.e. +2 and +4 oxidation states. The +2 oxidation state involves two electrons in the nP^2 sub shell while the +4 oxidation state involves two pairs of electrons in both the ns and np sub shell. i.e.

+2	ns ²	np ₂
+4	ns ²	np ₂

The stability of the two oxidation states is not the same for all the elements in the group. The stability of +2 oxidation state increases as you move down the group while that of +4 oxidation state decreases from carbon to lead due to inert pair effect.



Inert pair effect is the reluctance or inability of the valence electrons in s-orbital to take part in chemical bonding as the atomic number increases. This is because the s-electrons are more penetrating to the nucleus than the p-electrons hence they experience greater nuclear attraction and becomes relatively more stable and less available to be involved in chemical bonding.

The compounds of carbon and silicon are more stable in the +4 oxidation state and unstable in the +2 oxidation state e.g.

- Carbonmonoxide is unstable and therefore readily oxidized to carbondioxide

$$2\text{CO(g)} + \text{O}_2\text{(g)} \longrightarrow 2\text{CO}_2\text{(g)}$$
- Siliconmonoxide(SiO) is unstable and does not exist on its own while silicon dioxide(SiO_2) is very stable and exist on its own.
- Germanium (Ge) and tin (Sn) form compounds which are stable in both +2 and +4 oxidation state but compounds of Ge in the +4 oxidation state are relatively more stable than compounds of Sn in the +4 oxidation state in aqueous solution. Tin(II) is oxidized to Tin(IV) in solution

$$\text{Sn}^{2+}\text{(aq)} \longrightarrow \text{Sn}^{4+}\text{(aq)} + 2\text{e}$$
- Lead form compounds which are stable in +2 oxidation state while the compounds in the +4 oxidation state are unstable and highly oxidizing e.g. lead(II) oxide is more stable than lead(IV) oxide and when heated, it decomposes to lead(II) oxide and oxygen

$$2\text{PbO}_2\text{(s)} \longrightarrow 2\text{PbO(s)} + \text{O}_2\text{(g)}$$

When lead (IV) oxide is warmed with concentrated sulphuric acid, white solid of lead (II) sulphate, and water are formed with evolution of oxygen gas.



5.03 Trend in electropositivity

C	
Si	
Ge	Electropositivity increases
Sn	
Pb	

Explanation

Electropositivity increases down the group.

Down the group, both the nuclear charge as well as the screening effect increases.

However, the increase in screening effect outweighs the increase in nuclear charge. This is due to the increase in the number of full inner energy levels. Consequently the effective nuclear charge as well as the nuclear attraction of the outer electrons decreases thus the ease in electron loss or electropositivity increases.

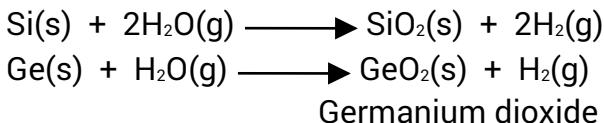
NB// carbon has a unique property from the rest of the group (IV) elements because it is small, has high electronegativity value and do not have electrons in the d sub shell. The properties in which carbon behaves differently from the rest of the group members are:

- (i) Carbon forms gaseous oxides at room temperature while the rest of the elements in the group form oxides which only exist in the solid state.
- (ii) Carbon forms stable multiple bonds with itself and with other non metals
e.g. $\text{C} \equiv \text{C}$, $\text{C} = \text{C}$, $\text{C} = \text{O}$, $\text{C} \equiv \text{N}$.
- (iii) Carbon forms compounds which are relatively inert e.g. carbon tetrachloride.
- (iv) Carbon exhibits catenation. Catenation is the direct bonding between atoms of the same element.
 $\text{C} - \text{C} - \text{C} - \text{C} - \text{C}$
- (v) Carbon does not show inert pair effect.
- (vi) Carbon is restricted to a coordination number of only 4 while the rest of the group members can have both a coordination number of 4 and 6.

5.04 Chemical properties of group (IV) elements

1) Reaction with water.

Carbon, silicon, and germanium do not react with cold water but when heated it reacts with steam. Carbon forms a monoxide and hydrogen gas while silicon and Germanium forms corresponding dioxide and hydrogen gas.

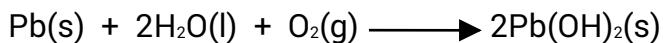


Tin reacts very slowly with cold water but readily with steam forming tin (IV) oxide and hydrogen gas.



Lead reacts with only pure water (soft water) producing sparingly soluble lead (II) hydroxide. It does not react with hard water because the sulphate and carbonate present

in it react with lead (II) ion to form insoluble lead (II) sulphate and lead (II) carbonate which forms protective layer on the metal thereby preventing further reaction. For this reason, it is unsafe to transport soft water using lead pipes because it results in to lead poisoning but it is safe to transport hard water using lead pipes.

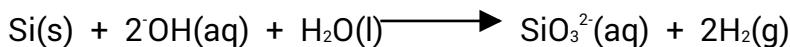


2) Reaction with alkalis

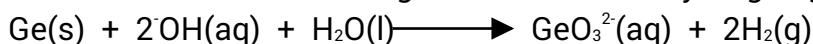
Carbon does not react with alkalis.

Silicon, germanium, and lead all react with hot concentrated alkalis.

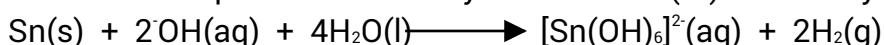
With silicon, a silicate and hydrogen gas is evolved. This reaction is possible because silicon is acidic.



Germanium reacts to form germinate ion and hydrogen gas

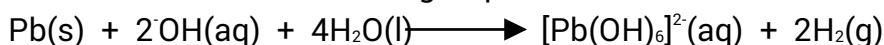


With tin a complex called hexahydroxostanate(IV) ion and hydrogen gas are formed



The reaction of lead is very slow to form hexahydroxoplumbate(IV) ion and hydrogen gas.

This is because of the increase in the basic character of the elements down the group i.e. lead is the most basic in the group.



3) Reaction with acids.

- Sulphuric acid.** Carbon, tin, and lead do not react with dilute sulphuric acid but react with concentrated sulphuric acid. During the reaction, concentrated sulphuric acid is reduced to sulphur dioxide and water while the elements are oxidized. Carbon, tin and lead is oxidized to carbondioxide, tin (II) sulphate and lead (II) sulphate respectively.



- Nitric acid.** Carbon, germanium, tin only react with concentrated nitric acid. Here the acid is reduced to nitrogendioxide and water and the elements oxidized to their corresponding dioxides.



The reaction of lead with concentrated nitric acid results into the formation of mixtures of oxides of nitrogen and lead (II) nitrate for which no simple equation can be written.

- Hydrochloric acid.** Both tin and lead react with hot dilute hydrochloric acid but more rapidly with hot concentrated hydrochloric acid to liberate hydrogen gas with the formation of tin (II) chloride and lead (II) chloride respectively. The rapid reaction is because solubility increases with temperature.



NB// silicon is resistant to the action of acids. However, it is attacked by hydrofluoric acid liberating hydrogen gas and forming hexafluorosilic acid.



5.05 Compounds of group (IV) elements

Group (IV) elements form two types of compounds i.e.

- (i) Compounds in the +2 oxidation state.
- (ii) Compounds in the +4 oxidation state.

The relative stability of the two types of compounds varies from one element to the next

a) Oxides group(IV) elements

There are two types of oxides i.e. monoxide (MO) and dioxides (MO_2)

<u>Monoxides</u>	<u>Dioxides</u>
CO	CO_2
SiO	SiO_2
GeO	GeO_2
SnO	SnO_2
PbO	PbO_2

Nature of the oxides

The oxides of carbon exist as gases while the other oxides of the elements of group (IV) exist as solids. Carbon dioxide is a gas at room temperature while the rest of the oxides exist as solids with high melting point.

Explanation

Carbon has a smaller atomic radius compared to the rest of the elements. Therefore both the carbon and oxygen closely approaches each other making their P orbitals to overlap leading to formation of stable multiple bonds between the carbon and oxygen atoms.

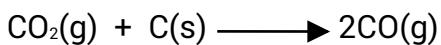
Because of this, carbon dioxide exist as discrete molecules being held by only weak vanderwaals forces of attraction which is easily overcome. However, in the rest of oxides, there is no overlap of P orbitals because of the large size of their atoms. As a result of this, other group (IV) elements can only form single bonds which are very strong with oxygen atoms. This gives them 3 dimensional or giant structures of solids which require a lot of energy to break.

Illustrations

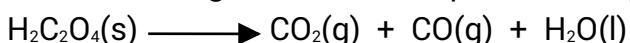
1) Monoxides

a) Carbonmonoxide.

It is prepared by passing carbon dioxide over heated coke in a combustion tube.

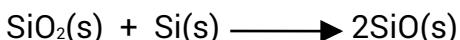


It can also be prepared by the dehydration of oxalic acid crystals using hot concentrated sulphuric acid .carbon dioxide is also formed but removed from the mixture by passing the mixture through concentrated potassium hydroxide solution.

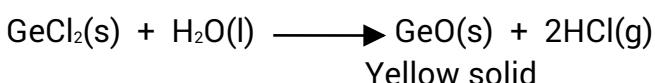


b) Silicon monoxide.

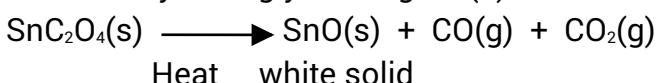
It is very unstable and prepared by strongly heating silicondioxide together with silicon.

**c) Germanium monoxide.**

It is made by the action of cold water on germanium (II) chloride. Hydrogen chloride gas is also formed.

**d) Tin (II) oxide.**

It is made by strongly heating tin (II) oxalate.

**e) Lead (II) oxide.**

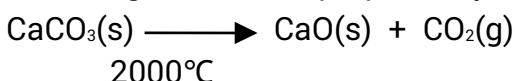
It is a yellow solid when cold and reddish brown when hot. It is made by heating lead (II) hydroxide.

**2) Dioxides****a) Carbon dioxide.**

It is prepared by the action of dilute hydrochloric acid on carbonates.



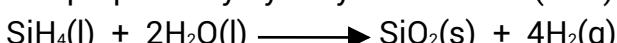
On a large scale, it is prepared by strongly heating limestone.



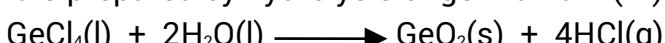
It is an acidic oxide therefore dissolves in aqueous alkalis.

b) Silicondioxide.

It is prepared by hydrolysis of silane (SiH_4) or silicon tetra hydride

**c) Germanium dioxide.**

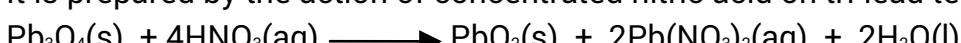
It is prepared by hydrolysis of germanium (IV) chloride.

**d) Tin (IV) oxide.**

It is amphoteric, therefore reacts with both acids and bases. This oxide is prepared by the action of concentrated nitric acid on tin metal.

**e) Lead (IV) oxide.**

It is prepared by the action of concentrated nitric acid on tri-lead tetraoxide

**Basicity of the oxides**

This refers to the acid base character of the elements and their compounds i.e. the reaction of the elements and their compounds with acids and bases.

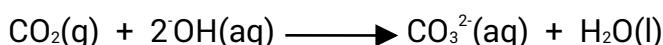
Generally, the basicity of the oxides increases down the group as the metallic character

increases. i.e. oxides of lead and tin in oxidation state of +2 do not react with alkalis but those in the +4 state react because they are acidic or less basic since acidity increases with oxidation state.

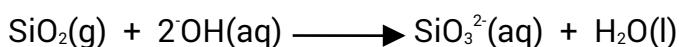
Reaction of dioxides with alkalis

Both carbon dioxide and silicon dioxide are acidic, therefore reacts with a base.

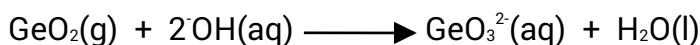
Carbon dioxide reacts to form a carbonate.



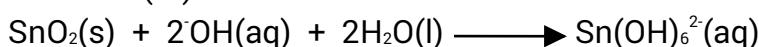
Silicon dioxide reacts to form a silicate



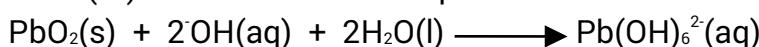
Germanium (IV) oxide is amphoteric, it reacts with aqueous alkalis to form the germanate ion



Tin (IV) oxide dissolves in aqueous alkalis to form stannate (IV) ions or hexahydroxo stannate (IV) ion.

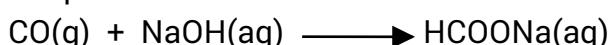


Lead (IV) oxide dissolves in aqueous alkalis to form the plumbate (IV) ion



Reaction of monoxides with alkalis

Carbon monoxide dissolves in aqueous alkali e.g. sodium hydroxide at very high temperature to form sodium methanoate.



Silicon monoxide does not exist.

Germanium oxide reacts with alkalis to form hexahydroxo germanate (II) ion.



Silicon monoxide and lead (IV) oxide do not react with aqueous alkalis because they are highly basic.

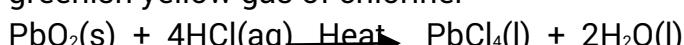
Oxides of lead

a) Lead (IV) oxide.

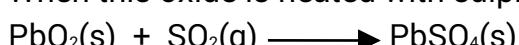
It is dark brown solid that react with concentrated sulphuric to form white crystals of lead (II) sulphate, water and oxygen.



When the oxide is heated with concentrated hydrochloric acid, a yellow oily liquid of lead (IV) chloride is formed which decomposes to a white solid of lead (II) chloride and greenish yellow gas of chlorine.

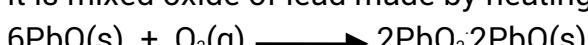


When this oxide is heated with sulphur dioxide, a white solid of lead (II) sulphate is formed.



b) Tri-lead tetraoxide.

It is mixed oxide of lead made by heating lead (II) oxide in air at 450°C.



It behaves as a mixed oxide containing lead (IV) oxide and lead (II) oxide.

When reacted with dilute nitric acid, it forms a dark solid and a colourless solution. The dark brown solid is lead (IV) oxide and the colourless solution contains lead (II) nitrate.



Orange solid Dark brown

With dilute hydrochloric acid, a white precipitate and a greenish yellow gas is obtained.

The greenish yellow gas is chlorine and the white solid is white precipitate of lead (II) chloride.



b) Chlorides of group (IV) elements

Group (IV) elements form two types of chlorides.

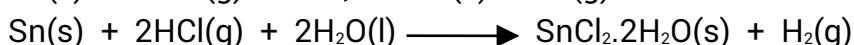
- Dichlorides, MCl_2
- Tetra chlorides, MCl_4

a) Dichlorides.

They are mainly formed by tin and lead. The rest of the elements do not form dichlorides because they would simply be oxidized to tetrachlorides due to high instability +2 oxidation state.

(i) Tin (II) chloride, SnCl_2 .

The anhydrous SnCl_2 is obtained by passing dry hydrogen chloride gas over heated tin metal while the hydrated SnCl_2 is obtained by reacting Sn with concentrated hydrochloric acid.



The anhydrous SnCl_2 cannot be obtained by heating hydrated SnCl_2 because it will undergo hydrolysis and give off basic $\text{Sn(OH)}\text{Cl}$



Chemical reactions of Tin (II) chloride

- When SnCl_2 is dissolved in water, it forms a cloudy or milky solution. This is due to the formation of basic SnCl_2 as a result of hydrolysis of Sn^{2+} in water.



- Reducing property of tin (II) chloride.

SnCl_2 acts as a reducing agent when dissolved in moderately concentrated hydrochloric acid because the conc HCl prevent it from undergoing hydrolysis to form basic tin (II) chloride. The Sn^{2+} ions in the solution loses electrons to form Sn^{4+} ions and these electrons are taken up by oxidizing agents such as iron (III), iodine dissolved in potassium iodide, acidified potassium dichromate, mercury (II) chloride solution etc. The half equation for the oxidation of Sn^{2+} to Sn^{4+} is given below.

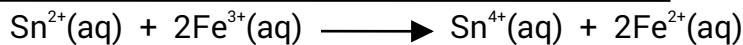
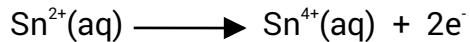


Examples

1) Iron (III).

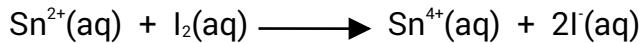
It reduces Fe^{3+} to Fe^{2+} .

The colour of the solution changes from brown to pale green.



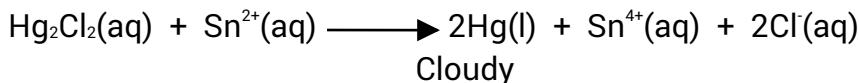
2) Iodine.

It reduces iodine dissolved in potassium iodide to iodide ions. The colour of the solution turns from brown to colourless.



3) Mercury (II) chloride.

It is reduced in stages to form mercury. The colour of the solution changes from colourless to cloudy due to the formation of mercury.



(ii) Lead (II) chloride, PbCl_2 .

It exists as a white crystalline solid obtained by treating any soluble salt of lead with hydrochloric acid or barium (II) chloride.e.g.



Lead (II) chloride is insoluble in cold water but readily dissolves in hot water.

Reason

Solubility of any ionic compound is determined by both lattice and hydration energy. Pb^{2+} ions has a large size and this leads to low charge density, consequently this leads to a low hydration energy which can not be offset by the high lattice energy hence insolubility in water. However in hot water, it suddenly undergoes hydrolysis to form basic lead (II) chloride which is soluble and when the solution is cooled the basic salt combines with more chloride to form lead (II) chloride which re-crystallizes.



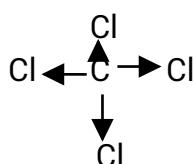
b) Tetra chlorides, MCl_4

- (i) Carbon tetrachloride, CCl_4 , it is prepared by chlorinating carbon disulphide in the presence of iodine or iron (III) chloride catalyst.



The bonds in CCl_4 are polar but CCl_4 molecule is non-polar.

Illustration



The bonds are polar because chlorine atoms are more electronegative than carbon atom, hence these chlorine atoms attract bonding electrons towards themselves and become partially negatively charged and the carbon atom partially positively charged. The unequal sharing of electrons is therefore responsible for the bond polarity.

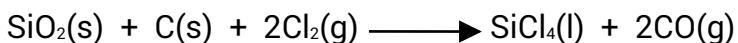
The CCl_4 molecule is non-polar because it has a tetrahedral shape in which the C-Cl bonds are symmetrically arranged since each pair of chlorine atoms attracts the bonding electrons in the opposite direction, the effect of the bonding polarity cancels out, and

consequently the whole molecule becomes non-polar inspite of having polar bonds.

Illustration

(ii) Silicon (IV) chloride.

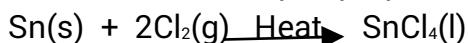
It is prepared by heating a mixture of silica and carbon in a current of dry chlorine gas.



It is a colourless volatile liquid at room temperature.

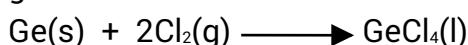
(iii) Tin (IV) chloride.

It is a colourless liquid prepared by passing dry chlorine gas over heated tin metal.



(iv) Germanium (IV) chloride.

It is a Colourless volatile liquid prepared by passing dry chlorine gas over heated germanium metal.



(v) Lead (IV) chloride.

It is prepared by the action of concentrated hydrochloric acid on lead (IV) oxide.



Lead does not form lead tetra bromide and lead tetra iodide but it forms lead tetra fluoride and PbCl_4 . The rest of the elements form tetra bromides and tetra iodides.

Lead tetra bromide and lead tetra iodide do not exist because bromine and iodine are weak oxidizing agents compared to fluorine and chlorine, hence they cannot oxidize lead (II) to lead (IV).

Properties of tetra chlorides

All tetra chlorides are generally colourless, volatile covalent liquids except CCl_4 which is not volatile. For this reason they tend to fume when exposed to moist air due to hydrolysis.

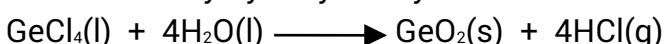
a) Reaction with water.

CCl_4 does not react with water. The rest of the tetra chlorides react with water due to hydrolysis to form white fumes of hydrogen chloride gas.

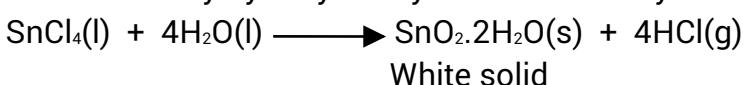
SiCl_4 is readily decomposed by water to form white fumes of hydrogen chloride gas and hydrated (IV) oxide.



GeCl_4 is readily hydrolysed by cold water to form germanium (IV) oxide and HCl gas.



SnCl_4 is readily hydrolyzed by water to form hydrated tin (IV) oxide



PbCl_4 is readily decomposed by water to form lead (IV) oxide which is a dark brown solid and fumes of HCl gas.



NB//. Carbon tetrachloride does not react while the rest of the tetrachlorides react with water.

Reason

Carbon cannot expand its octet while the rest of group (IV) elements can expand their octet and they all have vacant orbitals which can accept lone pair of electrons from water during hydrolysis. Water attacks Si because Si has got partial positive charge brought about by difference in electronegativity.

Illustration

All the four chlorine atoms are replaced in the same way by OH. This finally gives Si(OH)_4 which decomposes to SiO_2 . The over all reaction becomes;



b) Reaction with alkalis.

They react to form dioxides and chlorides.

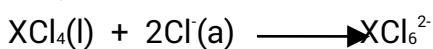


The oxide formed with lead is amphoteric and reacts to form a plumbate.

Eqn

c) Reaction with acids.

SnCl_4 and PbCl_4 react with concentrated hydrochloric acid to form complex of the form XCl_6^{2-}



(X = Sn or Pb)

Nature of tetra chlorides

They are liquids with low boiling points. This suggests that they are simple molecular compounds.

Chloride	Boiling point/°C
CCl_4	77
SiCl_4	58
GeCl_4	83
SnCl_4	114
PbCl_4	Decomposes

The boiling point generally increases down the group. This is because the molecules are held by weak vander waals which increases with increase in the molecular mass.

SiCl_4 has a lower boiling point than expected because the electronegativity difference between chlorine and silicon is small. Si is less electronegative than carbon, and thus the partial charge on Si is great leading to a greater repulsion.

Thermal stability

They are all stable except PbCl_4 which decomposes because as you move down the group

the +2 oxidation state becomes more stable +4 becomes less stable.

Bond energy(X-Cl) of the group (IV) chlorides

Tetrachlorid CCl₄ SiCl₄ GeCl₄ SnCl₄ PbCl₄

e

X-Cl/KJmol⁻¹ 327 404 339 314 233

Generally, bond energy decreases down the group. This is because of the continuous increase in the bond length which results into less and less attraction of the nuclei hence the bonds formed between the element and the chlorine atoms becomes weaker and weaker down the group.

Enthalpies of formation of group (IV) chlorides (XCl₄)

Tetrachlorid CCl₄ SiCl₄ GeCl₄ SnCl₄ PbCl₄

e

DH⁰/ KJmol⁻¹ -136 -640 -549 -511 -320

For CCl₄, C has a high enthalpy of atomization since it is a small atom. The enthalpy of formation becomes less exothermic as the strength of the covalent bond decreases due to the increase in the bond length down the group.

c) Hydrides of group (IV) elements

All the elements form hydrides with the formula MH₄. These hydrides include

Methane CH₄

Silane SiH₄

Germane GeH₄

Stannane SnH₄

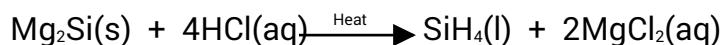
Plumbane PbH₄

Preparations of group (IV) hydrides

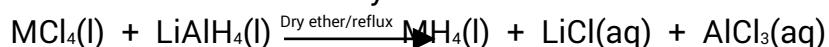
Methane is prepared by hydrolysis of aluminium carbide.



Silane is prepared by heating magnesium silicide with dilute hydrochloric acid in the absence of air.



Germane, stannane, and plumbane are prepared by reducing their tetrachlorides with lithium aluminium tetra hydride.



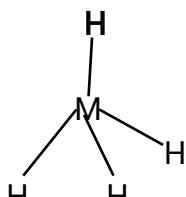
Physical properties of group (IV) hydrides

Methane is a gas and a covalent molecule while the rest of the tetrahydrides are covalent

liquids with intermolecular forces of attraction between their molecules. For this reason, they generally have low boiling point which increases in the order $\text{CH}_4 < \text{SiH}_4 < \text{GeH}_4 < \text{SnH}_4 < \text{PbH}_4$

The forces of attraction between the molecules of the group (IV) hydrides are the vanderwalls and these forces increases with increase in the relative molecular mass. Since the relative molecular mass increases down the group in the order $\text{PbH}_4 > \text{SnH}_4 > \text{GeH}_4 > \text{SiH}_4 > \text{CH}_4$. The boiling point of the hydrides deceases in the order, $\text{PbH}_4 > \text{SnH}_4 > \text{GeH}_4 > \text{SiH}_4 > \text{CH}_4$.

The structure adapted by the hydrides is tetrahedral



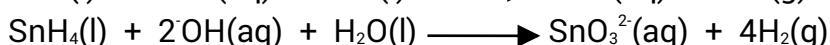
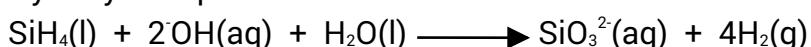
Hydrolysis of hydrides

The order of hydrolysis of the hydrides by a base is $\text{CH}_4 < \text{SiH}_4 < \text{GeH}_4 < \text{SnH}_4 < \text{PbH}_4$

And this order is determined by the electronegativity of the elements .If the elctronegativity of the element is high, the less is the hydrolysis of the hydride.

(C=2.6, Si = 1.9, Ge = 2.0, Sn = 1.9)

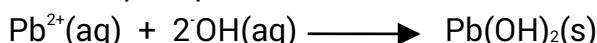
Hydrolysis equations



5.06 Testing for lead (II) ion, Pb^{2+}

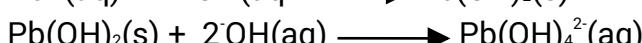
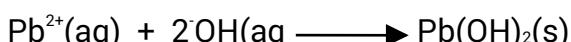
a) With ammonia solution.

A white precipitate insoluble in excess ammonia solution is formed.



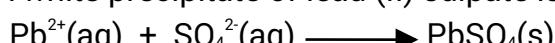
b) With sodium hydroxide solution

A White precipitate is formed that dissolve in excess sodium hydroxide forming a colourless solution.



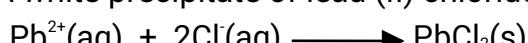
c) With dilute sulphuric acid.

A white precipitate of lead (II) sulphate is formed.



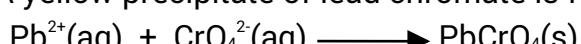
d) With dilute hydrochloric acid.

A white precipitate of lead (II) chloride is formed.



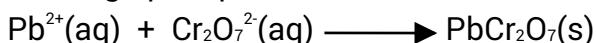
e) With potassium chromate solution.

A yellow precipitate of lead chromate is formed.



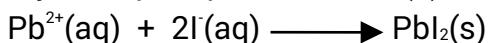
f) With potassium dichromate solution.

An orange precipitate of lead dichromate is formed.



g) With potassium iodide solution.

A yellow precipitate of lead (II) iodide is formed



5.07 Group 4 questions

- 1) (a) Write the general outer electronic configuration of group (IV) elements.
(b) Explain why carbon shows some differences from the rest of group (IV) elements.
(c) State the differences between the chemistry of carbon and the rest of group (IV) elements found in the periodic table.
- 2) Discuss the reactivity of group (IV) elements (carbon, germanium, tin and lead) of the periodic table with;
 - (a) Water
 - (b) Dilute acids
 - (c) Concentrated acids
 - (d) Alkalies
- 3) The elements; carbon, silicon, germanium, tin and lead belongs to group (IV) of the periodic table. Explain how the following properties vary down the group;
 - (a) Electropositivity
 - (b) Melting point
 - (c) Electrical conductivity
 - (d) Structure and bonding of the elements
 - (e) Stability of the oxidation states
- 4) Carbon, silicon, germanium, tin and lead are elements of group (IV) in the periodic table
 - (a) Discuss;
 - (i) The variation of the acid/base character of the oxides MO and MO_2 with increase in atomic number.
 - (ii) The differences in acid/base character of the oxides MO and MO_2 for any one element.
 - (iii) The reactivity of the tetrachlorides with water.
 - (iv) The relative stability of the dichlorides and terachlorides.
 - (b) Write equations and state the conditions to show how the following compounds of group (IV) elements can be prepared.
 - (i) Tetrachlorides (MCl_4)
 - (ii) Dioxides (MO_2)
 - (iii) Hydrides (MH_4)
- 5) Explain each of the following observations and write equations where applicable;
 - (a) The bonds in carbon tetrachloride are polar but carbon tetrachloride is a non polar molecule.
 - (b) Carbon dioxide is a gas at room temperature while silicon dioxide is a solid at room temperature.
 - (c) Lead (II) chloride is insoluble in dilute hydrochloric acid but soluble in concentrated hydrochloric acid.
 - (d) Silicon has a diamond type structure but is not as hard as diamond.

- (e) Tin (II) chloride fumes when exposed to moist air.
- (f) Lead forms only lead (II) chloride but not lead (II) bromide and lead (II) iodide. 7
- 6) State what is observed and write ionic equation for the reaction when aqueous tin (II) chloride solution is treated with;
- (a) Mercury (II) chloride solution.
- (b) Acidified potassium dichromate solution.
- (c) Iodine solution in potassium iodide.
- (d) Acidified potassium manganate (VII) solution.
- 7) Lead (II) oxide, lead (IV) oxide and tri-lead tetraoxide are oxides of lead. Write equations and state what is observed when the oxides of lead are separately treated with the following reagents;
- (a) Hot Concentrated hydrochloric acid.
- (b) Hot concentrated nitric acid.
- (c) Hot concentrated sulphuric acid.
- 8) State what is observed and write ionic equations for the reaction between lead (II) nitrate solution and;
- (a) Sodium hydroxide solution.
- (b) Ammonia solution.
- (c) Dilute sulphuric acid.
- (d) Potassium chromate solution.
- (e) Potassium dichromate solution.
- (f) Dilute hydrochloric acid.
- (g) Potassium iodide solution.
- (h) Ammonium sulphide solution.
- 9) Explain each of the following observations.
- (a) Lead (II) chloride is insoluble in ethanol where as lead (IV) chloride readily dissolves in the same solvent.
- (b) When water is added to lead (IV) chloride, white fumes are observed and a white precipitate is formed.
- (c) Lead (IV) chloride readily decomposes to lead (II) chloride and chlorine gas when heated but lead (II) chloride is not affected by heat.
- (d) Carbon which is in the same group as lead in the periodic table shows one valency of 4 in most of its compounds but lead shows valencies of both 2 and 4.
- (e) The solubility of lead (II) halides increases in the order $\text{PbI}_2 > \text{PbBr}_2 > \text{PbCl}_2$.
- (f) Crystals of lead (II) chloride can be prepared by in the laboratory by heating lead (II) oxide in dilute hydrochloric acid followed by cooling. When lead (II) oxide is heated under the same conditions no crystals are formed. Give reasons for these observations and illustrate your answer with appropriate equations.
- 10) (a) When red lead oxide, Pb_3O_4 was reacted with nitric acid, a solution and solid was formed.
- Write equation for the reaction.
- (b) The mixture from (a) was filtered and the residue warmed with concentrated hydrochloric acid.
- (i) State what was observed. Explain your observation.
- (ii) Write the equation (s) for the reaction (s).

- (c) The filtrate in (a) was divided in two portions;
- To the first portion was added aqueous potassium iodide.
State what was observed and write equations for the reaction that took place.
 - The second portion was evaporated to dryness and the strongly heated. Explain what was observed and write the equation for the reaction that took place.

CHAPTER SIX 6.00 GROUP (VII) ELEMENTS

The elements include

FluorineF

Chlorine.....Cl

Iodine.....I

Bromine.....Br

Astatine.....At

The general configuration is nS^2nP^5

Fluorine shows some differences in its properties from the rest of the elements due to the following reasons.

a) Fluorine atoms have the smallest atomic radii. This give rise to;

- Very high electronegativity.
- Low fluorine-fluorine bond energy.
- Strong covalent bonds with other elements.
- High lattice energy of ionic fluoride.
- High hydration energy of fluoride ions.
- High positive electrode potential.

b) Fluorine atoms lack underlying d-orbitals while the rest of the elements have the underlying d-orbitals.

The properties in which the chemistry of fluorine differs from the rest of group (VII) elements are;

- HF is strongly hydrogen bonded due to its polar H-F bond
- HF is a weaker acid than other HX acids.
- Fluorine being more electronegative than oxygen reacts differently from other halogens containing oxygen e.g. water and alkalis.
- Fluorine has only one oxidation state while other halogens have more than one oxidation state
- The solubility of fluorides in water differs markedly from the solubility of other halides of the same metal e.g. calcium fluoride is insoluble in water while $CaBr_2$, CaI_2 are very soluble in water, silver fluoride is soluble in water while chlorides, bromides, and iodide of silver are soluble in water.
- The hydrogen compounds of fluorine is associated (H_2F_2 to H_5H_8) and exists as liquid

at room temperature while the hydrides of chlorine, bromine, and iodine are all gaseous at room temperature.

- The ionic character of fluorides is normally high while other metal halides have low ionic character.
- Fluorine combines directly with carbon while other halogens do not.
- Other elements show their highest oxidation state when combined with fluorine than other halogens.

6.01 Physical properties

1) Boiling points

The boiling point increases down the group ie increases with increasing molecular mass or weight.

Reason.

The boiling point of covalent molecules is determined by the strength of the vanderwaals forces. As the molecular weight increases the vanderwaals forces of attraction between the molecules also increases hence this results in the boiling point as stated above.

Table showing trends in the boiling point.

Element	Boiling point/°C.
F ₂	-188
Cl ₂	-34.1
Br ₂	+58.8
I ₂	+187

2) Bond dissociation energy.

Table showing trends in the bond dissociation energy.

Element	BDE/KJmol ⁻¹
F ₂	79.1
Cl ₂	122
Br ₂	111
I ₂	106

Generally, the bond dissociation energy decrease down the group. However, fluorine has unexpectedly low bond dissociation energy. The bond dissociation energy is determined by the strength of the covalent bond which in turn depends on the size of the atoms. The smaller the atom, the stronger the bond and hence the higher is the bond dissociation energy and vice versa. In the above respect, chlorine forms a stronger covalent bond resulting into higher bond dissociation energy. In the case of iodine, it forms the weakest bond between its atoms resulting in to the lowest bond dissociation energy. In case of

fluorine, its atoms are abnormally small in size thus it forms the shortest covalent bond. This results into the lone pair of electrons on the fluorine atoms approaching each other very closely hence resulting into stronger repulsion between the atoms which tend to force the atoms apart i.e. little energy is required to separate the covalent bond.

3) Electron affinity

Table showing trend in the first electron affinity of group (VII) elements.

Element	EA/KJmol ⁻¹
F ₂	-334
Cl ₂	-370
Br ₂	-340
I ₂	-320

Generally, electron affinity decreases down the group i.e. it becomes less negative as you move from one element to the next. This is because of the decreasing effective nuclear charge due to the increased screening effect, which outweighs the increase in nuclear charge hence the incoming electrons are less attracted as you move from one element to the next, consequently less energy is released.

Fluorine has unexpectedly low electron affinity than chlorine because of the abnormally small size of fluorine atoms that creates a strong repulsive field around the fluorine atom. Hence, the incoming electron is strongly repelled by the lone pair of electrons of the fluorine atoms which are concentrated in a small area thus some energy which would have been released is used to overcome the repulsive force.

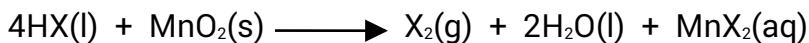
6.02 Preparation of halogens

- They are prepared by heating an alkali metal halide with concentrated sulphuric acid in the presence of manganese (IV) oxide.



(Where X = Cl, Br, I and M is an alkali).

- They can also be prepared by heating a concentrated solution of hydrogen halide with manganese (IV) oxide.



NB// fluorine cannot be prepared directly by chemical methods because of its great reactivity. However, it can only be prepared by electrolysis of fused fluorides e.g. calcium fluoride (fluorospars)

In the laboratory, chlorine gas can be prepared by the action of concentrated hydrochloric acid on crystals of potassium permanganate.



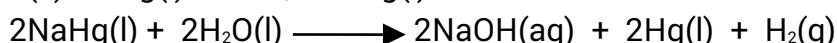
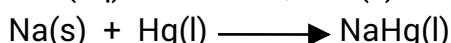
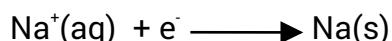
6.03 Industrial preparation of chlorine

Chlorine is obtained as a by-product during the manufacture of sodium hydroxide. In this process, concentrated sodium chloride (brine) is the electrolyte in the mercury cell with liquid mercury as the cathode and graphite as the anode.

In the solution of concentrated sodium chloride, the ions are Na^+ , H^+ , Cl^- , and OH^- . Due to the high concentration of chloride ions, it is discharged at the anode in preference to the OH^- .



At the cathode, Na^+ ions are discharged which forms an amalgam with mercury. The amalgam is removed and treated with water. The sodium in the amalgam reacts with water to form sodium hydroxide. The mercury formed is returned to the cell for further use.

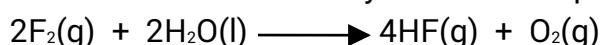


Downs cell for electrolysis of brine

6.04 Chemical reactions of the halogens

1) Reaction with water.

Fluorine reacts with water to liberate oxygen and hydrofluoric acid is formed. This reaction is violent and may result into explosion.



Chlorine reacts slowly with water to form chloric (I) acid also known as hypochlorous acid and hydrochloric acid.

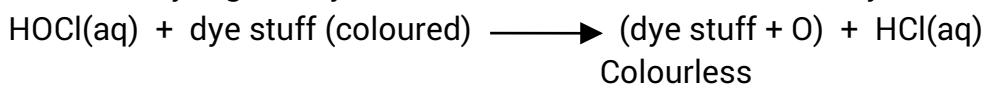


In the presence of sunlight, the hypochlorous acid formed decomposes slowly to liberate oxygen gas and hydrochloric acid is also formed.



Sunlight

The bleaching action of moist chlorine is due to the formation of hypochlorous acid which oxidizes any organic dye stuff to a colourless substance. Dry chlorine does not bleach.

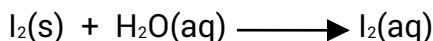


Bromine dissolves slowly in water forming hydrobromic acid and hypobromous acid and when exposed to light, the hypobromous acid decomposes to oxygen gas and hydrobromic acid

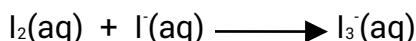




Iodine is sparingly soluble in water due to its covalent nature.



But when aqueous potassium iodide solution is added, the iodine molecules react with the iodide ions from potassium iodide to form a soluble complex of potassium tri-iodide.



2) Reaction with alkalis.

a) Cold dilute caustic alkali solution.

Fluorine reacts to produce oxygen difluoride gas, sodium fluoride and water.



Both chlorine and bromine reacts to produce pale yellow solution of sodium (or potassium) chloride, chlorate(I), water and potassium (or sodium) bromide, bromate (I) and water respectively.



At high temperature of about 70°C, the chlorate (I) and bromate (I) undergo disproportionation reaction producing halate ion, XO_3^- and halide ion X⁻



Eg

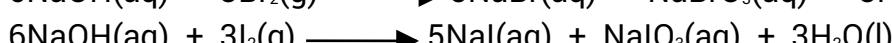
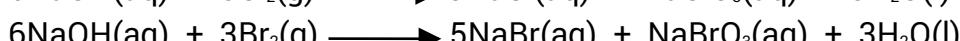


b) Reaction with concentrated alkali solutions.

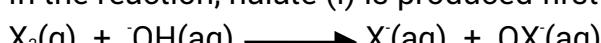
Fluorine reacts to produce oxygen gas, sodium fluoride and water.



Chlorine, bromine and iodine all reacts with hot concentrated solutions of alkali to produce colourles solution of halide ion, halate ion and water

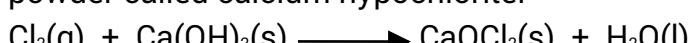


In the reaction, halate (I) is produced first which then disproportionates.



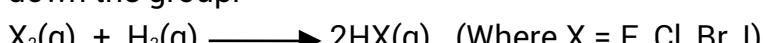
3) Reaction with calcium hydroxide (slaked lime)

Chlorine reacts with solid slaked lime at ordinary temperature to produce bleaching powder called calcium hypochlorite.



4) Reaction with hydrogen.

All halogens react with hydrogen to form hydrogen halides but the reactivity decreases down the group.



Fluorine explodes with hydrogen gas even in darkness.

Chlorine does not react in darkness, but reacts violently in the presence of ultraviolet light or sunlight. The reaction proceeds via a free radical mechanism

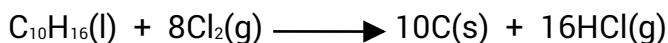
Bromine reacts with hydrogen only when heated at a temperature of about 200°C and in the presence of platinum catalyst.

Iodine reacts with hydrogen when heated at a temperature of about 400°C and the reaction is reversible and a catalyst is required.

The affinity of chlorine for hydrogen gives rise to reactions of the following kind.

(i) With turpentine

Filter paper soaked in warm turpentine and dropped in chlorine results into spontaneous combustion leading to the formation of black smoke ring of carbon particles and hydrogen chloride is also formed.

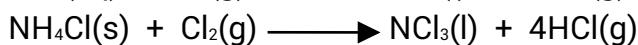
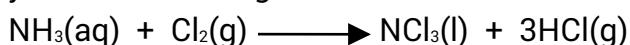


(ii) With ammonia

Addition of concentrated aqueous ammonia drop by drop inflames and burns with greenish flame, white fumes of ammonium chloride together with nitrogen gas are produced.



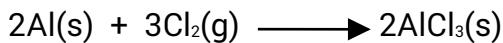
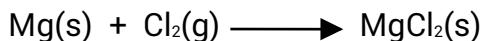
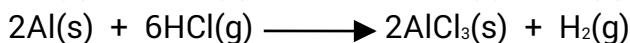
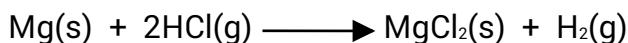
When the chlorine is in excess on ammonia, or ammonium chloride a dangerous explosive yellow oil of nitrogen chloride is formed.



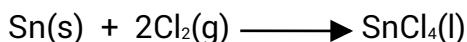
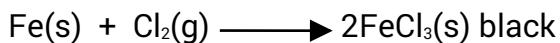
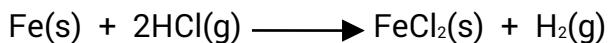
5) Reaction with metals.

All the halogens react with metals to form ionic halides but the reactivity decreases down the group. Fluorine is the most reactive and iodine reacts at a very high temperature.

For metals which show a constant oxidation number, only one chloride will be produced with either chlorine or hydrogen chloride e.g.

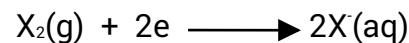


If the metal has variable oxidation number, the lower chloride is formed by hydrogen chloride and the higher chloride is given by chlorine.



6) Halogens as oxidizing agents.

Halogens readily accept electrons therefore acts as oxidizing agents.



The electrons are supplied by the reducing agents involved. Chlorine is the most powerful while iodine is the least in oxidizing behavior. Examples of oxidizing actions are;

(1) Oxidation of Iron (II) to Iron(III)

Chlorine or Bromine oxidizes pale green solution of iron (II) sulphate to yellow colour of iron (III) sulphate.



(ii) Reaction with hydrogen sulphide

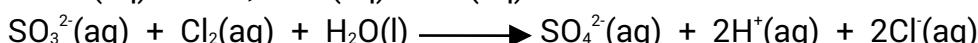
Passage of hydrogen sulphide gas into water containing chlorine, bromine or iodine

produces yellow precipitate of sulphur and the corresponding halogen acid.



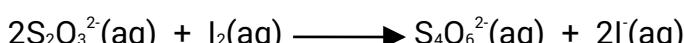
(iii) Sulphurdioxide, sulphurous acid or a soluble sulphite.

The above reagents are oxidized in aqueous solution by chlorine water. In the reaction the colour of chlorine water is discharged.



(iv) Reaction with sodium thiosulphate

Iodine dissolved in potassium iodide solution oxidizes sodium thiosulphate solutuion to sodium tetrathionate and the brown colour of iodine is discharged.



Chlorine in water oxidizes sodium thiosulphate to sulphate ion with precipitation of sulphur and if chlorine is in large excess, all the sulphur is converted to sulphate ion.



With excess chlorine,



7) Displacement reaction of halogens.

A halogen with a small relative molecular mass displaces another halogen with higher relative molecular mass in either solution or molten state e.g.



6.05 Compounds of group (VII) elements

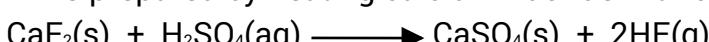
a) Hydrogen halides (HX)

They include;

- Hydrogen fluoride.
- Hydrogen chloride.
- Hydrogen bromide.
- Hydrogen iodide.

Preparation of hydrogen halides

HF is prepared by heating calcium fluoride with concentrated sulphuric acid.



Hydrogen chloride is prepared by heating concentrated sulphuric acid with sodium chloride.



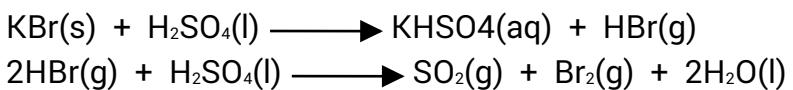
Hydrogen bromide is prepared by hydrolysis of phosphorus tribromide with water.



Hydrogen bromide cannot be prepared by heating an alkali metal eg KBr with conc H₂SO₄.

This is because the hydrogen bromide liberated further oxidized by concentrated sulphuric

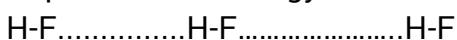
acid to sulphur dioxide, bromine gas and water. This is because concentrated sulphuric is a stronger oxidizing agent than bromine and iodine.



Physical properties of hydrogen halides

1) Boiling point

The boiling point of hydrogen halide increases with increasing molecular mass except for hydrogen fluoride which has abnormally high boiling point i.e. $\text{HCl} < \text{HBr} < \text{HI} < \text{HF}$. Hydrogen fluoride has abnormally high boiling point because its molecules associate through hydrogen bonding. This is possible due to the small size of fluorine atom making it more electronegative hence causing a big electron displacement towards itself in the H-F bond resulting into the formation of a strong hydrogen bond between its molecules which require a lot of energy to break i.e.



While for HBr, HI, their molecules are associated through weak vanderwaals forces which are easier to break. However the magnitude of the force increases with increasing relative molecular mass of the molecules hence this result into the increase of boiling point down the group i.e. with increasing molecular mass.

2) Acidic behaviour.

This arises from the ionization.



The acidity of the hydrogen halides is in the order $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$

The strength of the acid depends on the ease of release of a proton which in turn depends on the bond strength of the H-X bond and the size of the atom X. the larger the halogen atom, the weaker the H-X bond and the stronger is the acid and the smaller the halogen atom, the stronger the H-X bond and the weaker is the acid. Hence H-F is a weaker acid and H-I is a stronger acid.

NB//. Dilute solution of liquid hydrogen fluoride is a weak acid while concentrated solution of hydrogeb fluoride is a strong acid.

Explanation

Concentrated solution of liquid hydrogen fluoride contains more hydrogen fluoride molecules which undergoes self ionisation as shown below.



The fluoride ion formed combines with more HF molecules to form the species below;



This then makes the equilibrium position in (i) to shift to the right producing more hydrogen ions leading to the increased acidity.

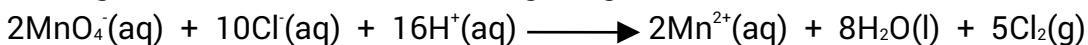
While in a dilute solution, ionisation of HF molecules is not energetically favourable due to the strong H-F bond as a result of small size of fluorine atom. This only causes a slight ionisation of HF molecules ie



Leading to reduced acidity.

3) Reaction of H-X with oxidizing agents.

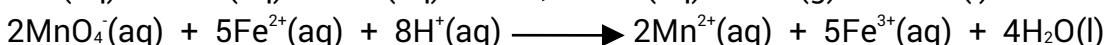
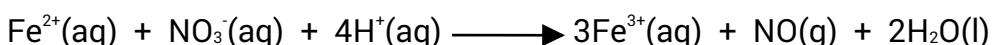
A stronger oxidizing agent such as acidified potassium permanganate oxidizes the H-X leading to the formation of free halogen eg



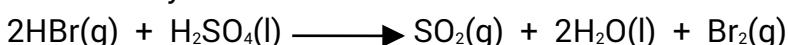
Potassium dichromate acts in a similar way like KMnO₄. For this reason, hydrochloric acid is not used to acidify titrations involving acidified KMnO₄ because the manganate would oxidize the chloride to chlorine since it is a powerful oxidizing agent.

Nitric acid is also not used because the nitrate is also a stronger oxidizing agent and therefore would compete with MnO₄⁻ during the reaction hence giving wrong titre value.

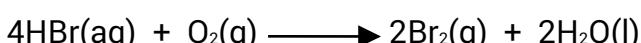
Reaction with Fe²⁺



However, weaker oxidizing agents such as concentrated sulphuric acid cannot oxidize HF and HCl because fluorine and chlorine are stronger oxidizing agents than concentrated sulphuric acid. For this reason concentrated sulphuric acid is not used to prepare HBr and HI because the acid oxidizes the HBr and HI to free bromine and iodine respectively immediately after their formation.



Hydrogen bromide reduces the acid to sulphur dioxide while the weaker reducing agent HI reduces the acid mainly to hydrogen sulphide for the same reason a solution of HBr and HI when exposed to air decomposes slowly releasing bromine and iodine due to aerial oxidation.



b) The oxy salts of chlorine

They include;

Hypochlorous acid, HOCl

Chlorous acid (chloric (II) acid), HClO₂

Chloric (V) acid, HClO₃

Perchloric acid, HClO₄

Acid strength of the oxy acids

The strength of the oxy acids is in the order HClO₄>HClO₃>HClO₂>HClO

Explanation

The strength of oxy acids is determined by the number of oxygen atoms attached to the chlorine atom. Oxygen has a greater electronegativity compared to chlorine atom hence it withdraws electrons from the chlorine atom. This effect is communicated through the chlorine atom to the OH bond. The magnitude of the partial positive charge on the hydrogen atom depends on the number of oxygen atoms in the molecule. The bigger the

partial positive charges on the hydrogen, the stronger the oxy acid and vice versa.

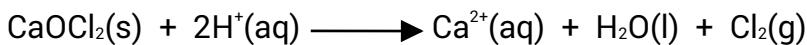
Alternatively

The strength of the oxy acid is determined by the stability of the oxy ion formed which in turn is determined by the extent to which the greater the negative charge is delocalised in the oxy ion.

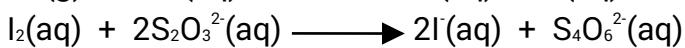
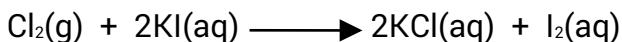
The greater the number of oxygen atoms the more stable the oxy ion and the stronger the acid. Hence the stability of oxy ion is in the order $\text{ClO}_4^- > \text{ClO}_3^- > \text{ClO}_2^- > \text{ClO}^-$ and therefore the strength of the acid increases in the order $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$

6.06 Estimation of percentage available of chlorine in bleaching powder (calcium hypochlorite)

Ethanoic acid or hydrochloric acid is added to the bleaching powder to liberate chlorine gas.



The chlorine gas evolved is bubbled through a solution of potassium iodide to liberate iodine solution which is then titrated with a standard solution of sodium thiosulphate using starch indicator.



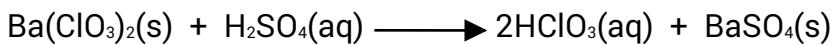
NB. A similar reaction can also be used to determine the percentage of available chlorine in liquid bleach e.g. jik which contains sodium hypochlorite, sodium chlorate (I)

In the presence of a proton, chlorate (I) ion reacts with iodide ion according to the equation.

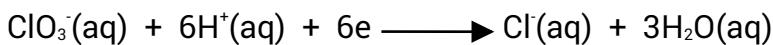


Halic acid, HClO_3

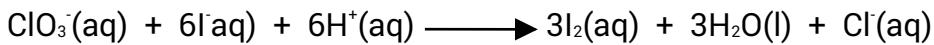
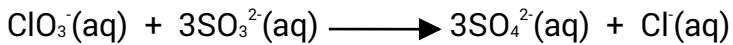
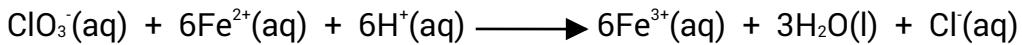
This is made from the reaction;



Chlorate (VI) ion can accept electrons from reducing agents and therefore acts as a very strong oxidizing agent in acidic medium.



Examples of oxidizing reactions of halic acid



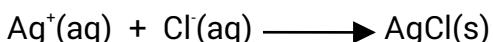
6.07 Testing for chloride, bromide and iodide ions

Reagents and observations

- (i) Addition of Silver nitrate solution and on dilute nitric acid.

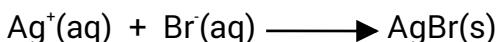
Cl^- .

A White precipitate silver chloride is formed but does not dissolve in excess of the reagent and soluble in dilute ammonia solution



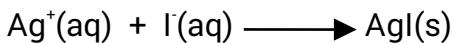
Br^- .

A Pale yellow precipitate of silver bromide is formed. The precipitate is insoluble in an acid but soluble in concentrated ammonia solution.



I^- .

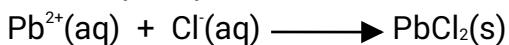
A yellow precipitate of silver iodide insoluble in both acid and ammonia solution is formed.



(ii) Addition of Lead nitrate solution.

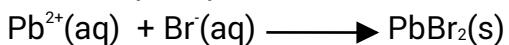
Cl^-

A white precipitate of lead chloride is formed.



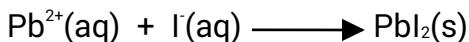
Br^-

A cream precipitate of lead bromide is formed.



I^-

A yellow precipitate of lead iodide is formed.



(iii) Addition of Concentrated sulphuric acid

Cl^- Produces hydrogen chloride gas

Br^- Produces hydrogen bromide gas

I^- Produces hydrogen iodide gas

(iv) Addition Concentrated sulphuric acid and manganese (IV) oxide

Cl^- . Greenish chlorine gas evolved.

Br^- . A reddish brown vapour of bromine gas is given out.

I^- . Dark solution of iodine is formed.

6.08 Group (VII) questions

1) (a) Write the general outer electron configuration of group VIIB elements of the periodic table.

(b) The elements; fluorine, chlorine, bromine and iodine belongs to group (VII) of the periodic table. State and explain how the following properties vary with increasing atomic number down the group;

(i) Boiling point.

(ii) First electron affinity

(iii) Oxidizing power.

(iv) Hydration energy

(V) Physical state.

- 2) (a) Write an equation stating the conditions for the reactions showing one general method for preparing halogens (excluding fluorine) in the laboratory.
- (b) Briefly describe how one of the halogen is produced on a large scale.
- (c) (i) Briefly describe how potassium chlorate (V) crystals can be prepared in the laboratory. Write equation where applicable.
- (ii) Briefly describe how potassium iodate can be prepared in the laboratory.
- (d) 2.0g of a mixture of potassium chloride and potassium chlorate (V) were dissolved in 250cm³ of water. 10.0cm³ of the solution was mixed with excess potassium iodide solution. The iodine liberated required 8.00cm³ of 0.2M sodium thiosulphate solution for complete reaction. Potassium chlorate and potassium chloride react according to equation;
- $$\text{ClO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 6\text{I}^-(\text{aq}) \longrightarrow 3\text{I}_2(\text{aq}) + \text{Cl}^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$$
- Calculate the percentage of potassium chlorate in the mixture.
- (e) Explain why chlorine is more soluble in dilute sodium hydroxide than in water.
- 3) (a) Fluorine shows some differences in its properties from the rest of the elements (chlorine, bromine, and iodine) of the periodic table. Explain.
- (b) State seven major differences between the chemistry of fluorine and the rest of the elements of group (VII) of the periodic table.
- (c) Explain why fluorine has abnormally low bond dissociation energy than chlorine.
- 4) Describe using equations and stating conditions for the reactivity of fluorine, chlorine and bromine with;
- (a) Water.
- (b) Dilute sodium hydroxide solution.
- (c) Concentrated sodium hydroxide solution.
- (d) Hydrogen gas.
- (e) Sodium metal.
- 5) (a) Hydrogen fluoride, hydrogen chloride, hydrogen bromide and hydrogen iodide are the hydrides of group (VII) elements.
- (i) State and explain the trend in the boiling points of the hydrides.
- (ii) Giving reasons explain the trend in acid strength of the hydrides.
- (iii) Using equations where possible explain what happens when concentrated sulphuric acid is mixed with each of the hydrides.
- (iv) HClO, HClO₂, HClO₃, and HClO₄ are oxy acids of chlorine. Giving reasons explain the trend in acid strength of the oxy acids of chlorine.
- (b) (i) briefly explain how the percentage of available chlorine in liquid bleaches such as JIK can be determined.
- (ii) Explain the use of chlorine in water treatment.
- (c) Describe how chlorine reacts with;
- (i) Hot aqueous sodium hydroxide solution.
- (ii) Aqueous potassium bromide.
- (iii) Ethene
- (iv) Benzene
- 6) Explain each of the following observations and where applicable write and equation to illustrate your answer.
- (a) Iodine is readily soluble in aqueous potassium iodide but sparingly soluble in water.

- (b) Hydrogen fluoride has a higher boiling point and is a weaker acid than hydrogen chloride.
- (c) Concentrated solution of hydrogen fluoride is a stronger acid than dilute solution of the same acid.
- (d) When concentrated sulphuric acid is added to solid potassium bromide, a brown gas is seen in addition to white fume of a colourless gas.
- 7) Name one reagent (s) that can be used to distinguish between the following pairs of compounds and in each case state what is observed when each member of the pair is separately treated with the named reagent. Write the ionic equation in each case.
- (a) Sodium chloride and sodium bromide.
 - (b) Potassium iodide and potassium bromide.
 - (c) Ammonium chloride and ammonium iodide.
 - (d) Iodocyclohexane and chlorocyclohexane.

CHAPTER SEVEN

7.00 CHEMICAL PROPERTIES OF PERIOD 2 AND 3 ELEMENTS AND THEIR COMPOUNDS

The reaction of these elements depends on the electro negativities and the electro negativity of both periods increase from alkali metals to the halogens.

The elements form ionic compounds when the difference between electro negativity is big. Usually when the bonding is between a metal and a non metal e.g. between sodium and chlorine in sodium chloride.

When the electronegativity difference between the elements decreases, the ionic character decreases and the covalent character increases for e.g. magnesium chloride (EN DIFF=1.8) is ionic while aluminum chloride (EN DIFF=1.5) is mainly covalent. This

explains why elements with high electro negativity form covalent compounds. Within any metal group, electronegativity decreases with increase in atomic number therefore the tendency to form ionic compound for any metal group also increases down the group also increase with increase in atomic number for e.g. BeCl₂ is mainly covalent and MgCl₂ is mainly ionic.

Period (ii) elements are restricted to not more than eight electrons in their outer most shell. They cannot expand their octate because the next orbital to 2p is of the lowest energy which is found in a different shell therefore the energy difference between the 2p and 2s is very big.

Group (II) elements have no empty orbital of close energy to enable expand their octate. Period (III) elements can expand their octate because they have 3d empty orbital which are close to the energy in the 3p orbital.

Question

Explain why phosphorus in the same group as nitrogen forms two chlorides PCl₃ and PCl₅ and nitrogen forms only NCl₃

The noble gas structure determines the lowest and upper limit of electrovalency. The more exothermic the compound, the more stable the product is than the reactant.

It determines how many electrons can be lost or generated during electrovalence because disruption of a noble gas structure cannot be compensated for by the ionization energy during formation of ionic compound.

7.01 Chemical properties of period two and three elements

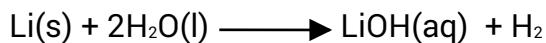
a) Reaction of the elements with water.

Metals displace hydrogen from water forming hydrogen gas and a hydroxide. Very reactive metals react in the cold. The other reacts extremely slowly with cold water depending on the solubility of the hydroxide formed e.g.

Sodium reacts vigorously with water darting on the water with hissing sound resulting in to formation of alkaline solution.



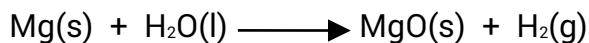
Lithium reacts less vigorously because its hydroxide is less soluble.



Magnesium reacts extremely slowly with cold water producing magnesium hydroxide and hydrogen gas.

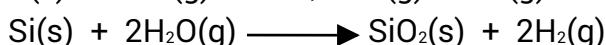
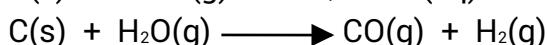
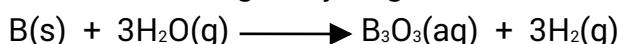


Magnesium burns in steam vigorously with its typical flame to produce white magnesium oxide.

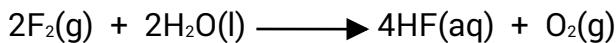


Beryllium does not react with water to a reasonable extent because it forms protective oxide. For similar reason aluminum does not react with water to any reasonable extent.

Giant molecular elements of period 2 and 3 i.e. boron and silicon react with water only when heated to give hydrogen.



Of the simple molecular elements of period 2 and 3, only halogens react with water. Fluorine oxidizes water to oxygen and hydrogen fluoride.



In the absence of sunlight chlorine reacts in the cold to form hypochlorous acid and hydrochloric acid.

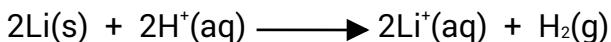


But in the presence of sunlight, hypochlorous acid decomposes to oxygen and hydrochloric acid.



b) Reaction of period 2 and 3 elements with dilute acids.

In period 2, only Li displaces hydrogen from dilute acids



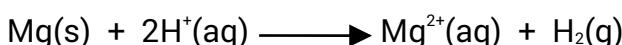
Be and Al has a protective oxide coating and only reacts when it's removed.

In period 3, it is only Na and Mg which reacts with dilute acids.

Na reacts violently



Mg dissolves in an acid giving a colourless gas that burns with a pop sound and a colourless solution is formed.



Calcium is slightly soluble.

Non metal do not react with dilute acids.

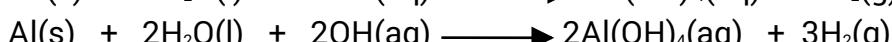
c) Reaction of period 2 and 3 elements with alkalis.

Na, Li and Mg do not react with alkali because if they are to react they would form alkali solution. However, if the alkali solution is dilute Na can react with water in solution.

Al and Be reacts vigorously with alkali, their protective oxide coating on them is amphoteric so it get removed by reacting with the alkali according to the equations:

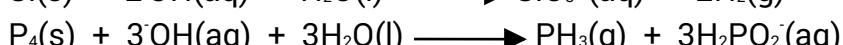
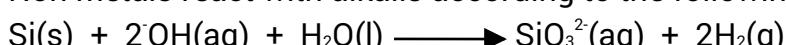


Then the elements react with the alkali according to the equations below.



d) Reaction of non metals with alkali.

Non metals react with alkalis according to the following equations.



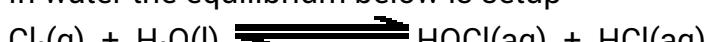
Sulphide sulphite

Cl₂ is quite more soluble in sodium hydroxide than in water because it is acidic.

In the cold



In water the equilibrium below is setup



The addition of OH ions shifts the equilibrium to the right because the alkali reacts with the acid.

At high temperature, the chlorate (I) formed disproportionate (the same species undergoing reduction and oxidation)



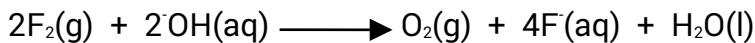
Chlorine reacts with hot concentrated sodium hydroxide to form sodium chloride and sodium chlorate (V).



F₂ reacts with alkali in the cold to form oxygen di-fluoride and fluoride.



When warmed with concentrated sodium hydroxide, oxygen gas and a fluoride are formed.



7.02 Compounds of period two and three elements

a) Oxides

Oxides of period 2

	Li_2O	BeO	B_2O_3	CO_2	NO_2	O_2	OF_2
Nature of oxide	basic	amphoteric	acidic	acidic	acidic	acidic	acidic
bonding	ionic	ionic	covalent	covalent	covalent	covalent	covalent
structure	Giant ionic	Giant ionic	Giant covalent	Simple molecular	Simple molecular	Simple molecular	Simple molecular
Enthalpies of formation / kJmol^{-1}	-596	-611	-424	-197	+17	-	+22

Oxides of period 3

	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
Nature of oxide	basic	basic	amphoteric			acidic	
bonding	ionic	ionic	ionic			covalent	
structure	Giant ionic	Giant ionic	Giant ionic	Giant covalent		Simple molecular	
Enthalpies of formation / kJmol^{-1}	-416	-602	-559	-455	-298	-132	+80

i) Structure and bonding of oxides of period and three elements

- The bonding is ionic for metal oxides and covalent for the non metal oxides. The ionic character decreases as you move from left to right of the period because the difference in electronegativity between oxygen and the element decreases in the same direction.
- The ionic character of the metal oxide can also be explained in terms of polarizing power of the cation. The greater the charge density of the cation the greater is the polarizing power and the more covalent is the oxide e.g. Na_2O is more ionic than Al_2O_3 .
- All ionic oxides have giant ionic structure while the covalent oxides have either giant ionic structure or simple molecular structure.

ii) Volatility of the oxides (melting and boiling point)

- The giant ionic oxides have high melting and boiling point because their ions are held together by strong electrostatic force of attraction which requires high temperature to overcome. The strength of electrostatic forces of attraction increases with charge of the ions and decrease in the size of the ions.
- Covalent oxides i.e. B_2O_3 and SiO_2 have high melting and boiling point because all their atoms are held by strong covalent bonds throughout the entire structure which require a lot of energy to overcome.
- Simple molecular oxides have low melting and boiling point because their molecules are held by weak vanderwaals forces of attraction which require little amount of energy to overcome .these forces increase with increase in molecular mass.

Note//. The smaller the atoms involved in bonding the stronger are the covalent bonds.

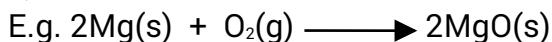
iii) Nature of the oxides of period 2 and 3

The oxides are classified as basic, amphoteric and acidic or neutral.

- The neutral oxides do not react with acids or bases and these are found in period 2 i.e. NO , CO , N_2O .
- Basic oxides. These are oxides of strongly electropositive metals (low electronegativity) e.g. Na_2O and MgO . As the electronegativity difference between the metal and oxygen decreases, the basic character also decreases. It can also be explained as; when the polarizing power of the cation increases, the basic character also decreases.
- Amphoteric oxides. These are oxides of less electropositive metals. They react with both acids and alkalis. The cations of such oxides have high polarizing power e .g Al_2O_3 and BeO .
- Acidic oxides. These are oxides of non metals. the higher the oxidation state of the element the more acidic is the oxide e.g. SO_3 is more acidic than SO_2

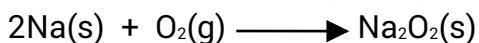
iv) Methods of preparation of the oxides

1) Heating the element in oxygen.

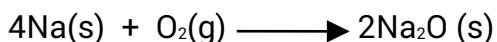


Magnesium burns with brilliant flame giving white powder of magnesium oxide as a residue.

Elements of very reactive element gives peroxide e.g. Na burns with a yellow flame to form sodium peroxide (Na_2O_2)

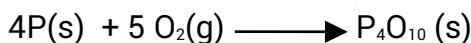


When there is insufficient supply of oxygen, Na forms the normal oxide.

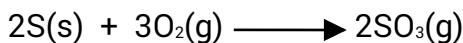


Al_2O_3 cannot be prepared by this method because it reacts with oxygen forming a protective oxide coating Al_2O_3 which prevents further reaction. However, when it is removed by dipping the Al_2O_3 in mercury chloride and hanged in air.

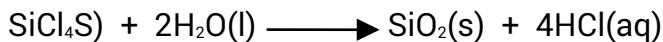
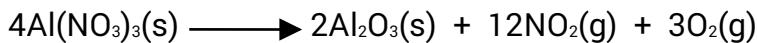
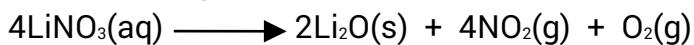
P_4O_{10} gives white flame (red flame)



Sulphur burns with purple flame to give $\text{SO}_3(\text{g})$



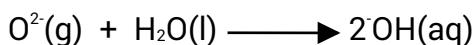
2) Thermal decomposition of hydroxides , carbonates , and nitrates of less reactive metals e.g.



v) Reaction of the oxides of period 2 and 3

1) Reaction With water.

The metal oxides have got the O^{2-} ion, a strong base which extracts a proton easily from water



They react with water to form metal hydroxide. The extent of the reaction depends on the solubility of the hydroxides formed i.e. if the OH^- is less soluble, the reaction goes to a small extent e.g.

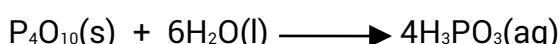


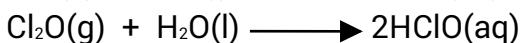
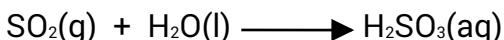
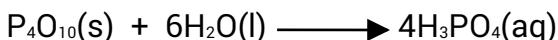
MgO dissolves to a small extent in water to form magnesium hydroxide.



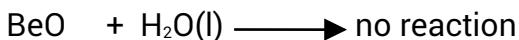
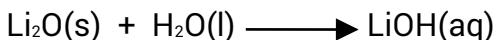
Al_2O_3 does not react with water.

Acidic oxides react with water to form acids. However, SiO_2 does not react with water because the water molecules can not penetrate the oxide of silicon to break the covalent bonds of the oxide.





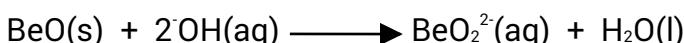
For oxides of period 2



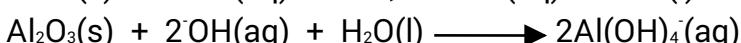
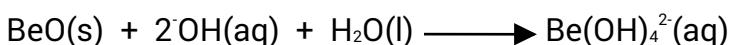
2) Reaction with alkalis.

Basic oxides do not react with alkalis.

Amphoteric oxides react with alkalis to form soluble complexes. In this way they behave like acids.



Or

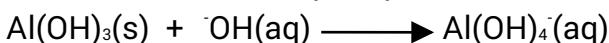


Note// amphoteric hydroxides also exist for these elements. They are made by adding alkalis to solution of their salts e.g. $\text{Al}(\text{OH})_3$ can be made by adding sodium hydroxide solution to aluminium (III) chloride solution.

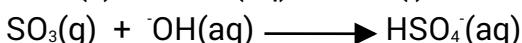


White precipitate

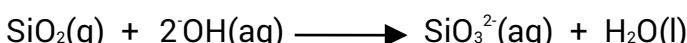
With excess OH^- , the precipitate dissolves due to the formation of the soluble complex



Acidic oxides react with alkalis to give salts of corresponding acid e.g.

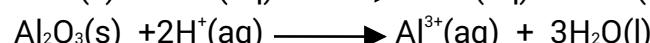


SiO_2 does not react with dilute alkalis but reacts with hot concentrated alkali to a silicate.



3) Reaction with acids.

Only basic and amphoteric oxides react with acids.



b) Chlorides of period 2 and 3

Chlorides of period 2



Boiling point/c	113 5	487	12	77	71	2	-101
bonding	ionic	Partially covalent				covalent	
structure	Giant ionic	linear			Simple molecular		
conductivity	good	poor			nil		

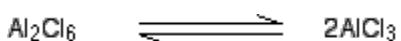
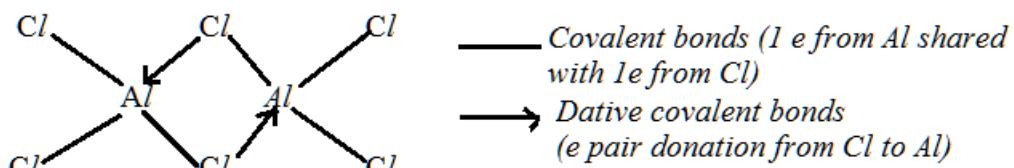
Chlorides of period 3

	NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₅	S ₂ Cl ₂	Cl ₂	General boiling points of the chlorides decreas- es across
Boiling point/c	148 5	1041.8	425	57	164	136	-35	
bonding	ionic	ionic	covalent			covalent		
structure	Giant ionic	Giant ionic			Simple molecular			
conductivity	good	good	poor			Non conducting		

the period indicating that the forces between the ions or between the molecules are weakened

NaCl and MgCl₂ have high boiling point because they are giant ionic and their ions are held by strong electrostatic forces of attraction. The rest of the chlorides are simple molecular and their molecules are held by weak vanderwaals forces of attraction which increase with increase in molar mass.

AlCl₃ is dimeric, it dimerises through coordinate bonding with chlorine using the vacant orbital on aluminium. This makes AlCl₃ to have a higher melting point than that of SiCl₄



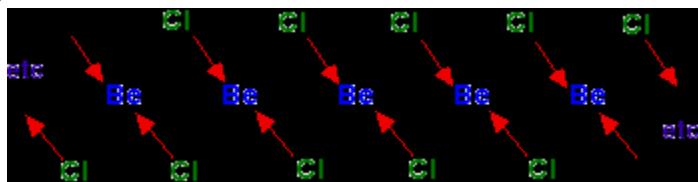
SiCl₄ is polar while PCl₅ is non polar

Diagram

For period 2

LiCl has a giant ionic structure and the ions are held by stronger electrostatic forces of attraction hence high boiling point

The boiling of BeCl₂ is rather high for a covalent compound. When Be uses its 2 valency electrons in covalent bonding, 2 orbitals are left vacant and these are used to form dative bonding with chlorine resulting in to a polymeric chain structure with relatively high molecular mass. This implies that the vanderwaals of attraction between its molecules are strong.



The rest of the chlorides in the period are simple molecular. Their molecules are held by weak vanderwaals of attraction and this increase with increase in molecular mass

Conductivity of period 2 and 3 chlorides

The ionic chlorides in period 2 and 3 (NaCl, MgCl₂ and LiCl) conducts electricity in molten state using their ions which are free to move. They do not conduct electricity in solid state because their ions are held by strong electrostatic forces of attraction and are not free to move.

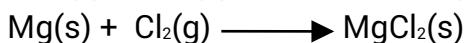
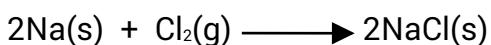
BeCl₂ and AlCl₃ are poor conducting in molten state because they form few ions in molten state and they are partially covalent.

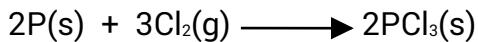
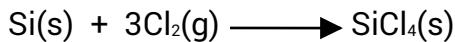
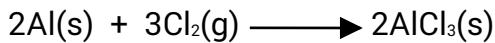
Simple molecular ions have no ions therefore they do not conduct electricity.

Methods of preparation of the chlorides

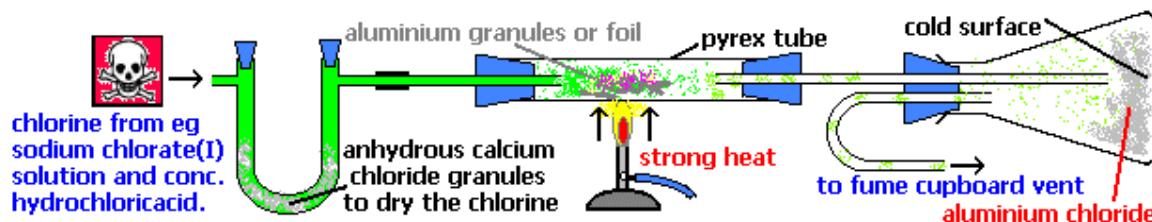
- 1) Generally they can be made by heating the element in chlorine. The apparatus below is suitable for preparing metal chlorides.

Diagram





The above apparatus is not suitable for preparing AlCl_3 because AlCl_3 sublimes. It needs a special apparatus like the one for preparing FeCl_3



The rest of the chlorides react slowly when heated to give the chlorides.

- 2) Metal chlorides can also be prepared by reaction of hot metals with hydrogen chloride gas .

Equations for the reactions are;



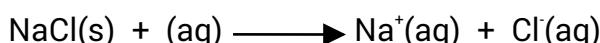
The reaction leading to the formation of SiCl_4 is slow and is catalyzed by AlCl_3 . For group 2, the methods of preparation of the chlorides are the same. However carbon does not react directly with chlorine and it is prepared by the action of chlorine gas on carbondiosulphide.



Reactions of the chlorides of period 2 and 3

1) Reaction with water

The ionic chlorides dissolve in water and dissociates into ions e.g



Metal chlorides where the cations has a high charge density undergo hydrolysis i.e they react with water thereby extracting hydroxyl ion from water and releasing proton into the solution resulting in to the formation of acidic solution when dissolved in water.

E.g. Both aluminium chloride and magnesium chloride when dissolved in forms acidic solution and each gives off white fumes of hydrogen chloride gas. This is because the magnesium ion and aluminium ion have high charge density and undergoes hydrolysis



The white fumes comes from Cl^- and H^+ due to the formation HCl

If complete hydrolysis, the products would be



This is not possible in the absence of a base.

Question

Explain the following observations: when a solution of aluminium salt is reacted with sodium carbonate, a white precipitate and a gas that turns lime water milky is evolved.

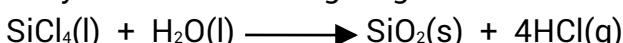
Answer

Aluminium is acidic, it undergoes hydrolysis producing H^+ when in solution, the salts react with CO_3^{2-} forming aluminium hydroxide which is seen as white precipitate with release of carbondioxide which turns lime water milky

Explain why aluminium carbonate does not exist

2) Reaction of non metallic chlorides with water

They react with water giving off white fumes of hydrogen chloride gas



When these chlorides are reacting with water the vacant orbitals in the chlorides of period 3 are used. The water molecules attack the central atom using the lone pairs of electrons on the oxygen atom. The lone pair of electron is donated to the vacant orbital in the central atom and this weakens the O-H bond in water and H-Cl bond in the chloride resulting in to the elimination of HCl.

Illustration

When the process repeats 3 more times we get $Si(OH)_4$ which decomposes to SiO_2



Carbon tetrachloride in period 2 does not undergo hydrolysis because:

- ✓ It does not have a vacant orbital to accept lone pair of electrons from water during reaction.
- ✓ Steric hinderance prevents the water molecules from reaching the carbon.

For period 2 chlorides

$LiCl$ dissolves in water to form ions



$BeCl_2$ dissolves in water and undergoes hydrolysis to form an acidic solution



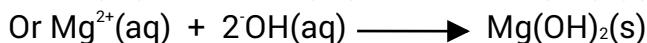
The other chlorides are chlorides of non metals and they all undergo hydrolysis except carbon tetrachloride.

**3) Reaction of metal chlorides with alkali**

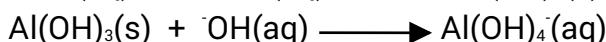
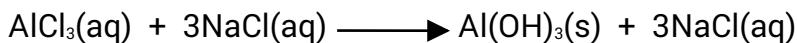
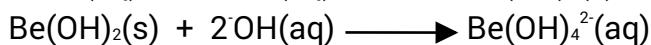
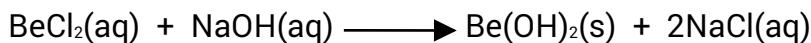
Only metal chlorides which form insoluble hydroxides react with alkali.

A solution of magnesium chloride reacts with sodium hydroxide to form a white

precipitate of magnesium hydroxide.



Berryllium and aluminium chlorides form precipitates which are amphoteric and can dissolve in excess alkali to form colourless solution

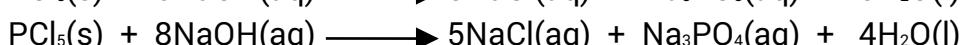


3) Reaction of non metallic chlorides with alkali.

Silicon tetrachloride reacts with concentrated solution of sodium hydroxide to form sodium silicate and chloride



Phosphorous chloride reacts with NaOH to form sodium phosphate 3 and sodium phosphate 5.



Sulphur(I)chloride (disulphur dichloride) reacts with sodium hydroxide forming sodium sulphide and sodium sulphite.



The reaction of chlorine with sodium hydroxide depends on the condition of reaction ie temperature and concentration.

Cold dilute sodium hydroxide reacts to give sodium hypocrite and sodium chloride.



When hot concentrated sodium hydroxide is used, chlorine reacts to give sodium chloride and sodium chlorate (V)



c) Hydrides of period 2 and 3 elements

	NaH	MgH ₂	AlH ₃	SiH ₄	PH ₃	H ₂ S	HCl	
Melting point	600	-	decomposes	-185	-163	-88	-114	
bonding	ionic	ionic	polymeric	Simple molecular				

Period 2 hydrides

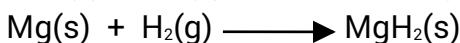
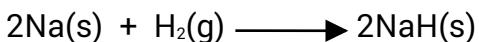
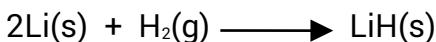
	LiH	BeH ₂	B ₂ H ₆	CH ₄	NH ₃	H ₂ O	HF
boiling point	decomposes	400	-9.3	-163	-33	-100	19
bonding	ionic	ionic	Simple molecular				

Beryllium hydride has relatively high boiling point because it is polymeric. The rest of the hydrides of period 2 are simple molecular. These molecules are held by weak vanderwaals forces of attraction which is very weak and requires little energy to overcome therefore they have low boiling points.

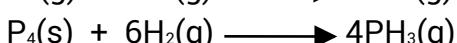
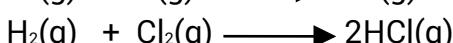
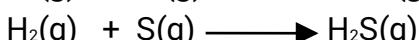
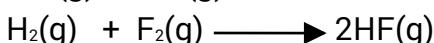
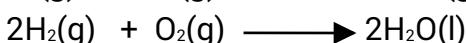
Ammonia, water and hydrogen fluoride have got relatively high boiling point when you consider their molecular masses in each of these hydrogen is bonded to very electronegative atom so they exhibit hydrogen bonding.

Methods of preparation of hydrides of period 2 and 3 elements

1) The ionic hydrides are made by heating the element in hydrogen.



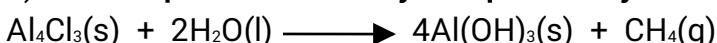
The covalent hydrides can be made by direct combination



2) Hydrides of less reactive metals of group (IV) can be made by reduction of their chlorides using lithium aluminium hydride in the presence of dry ether.

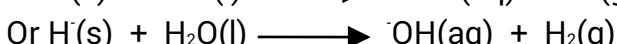
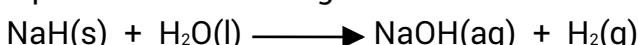


3) Decomposition of binary compounds by acids or water



Reactions of the hydrides with water

Ionic hydrides have got H- ion which acts as a strong base (electron donor). It can extract a proton from water eg



NaH reacts with water forming alkaline solution and a colorless gas which burns with a pop sound.

Other metal hydroxides of period 2 and 3 also react in the same way whether they are ionic or not forming a hydroxide and hydrogen



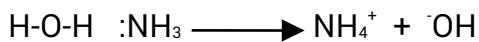
Boron hydride forms boric acid and hydrogen gas.



Methane does not react with water

Ammonia reacts with water to form an alkali because nitrogen is more electronegative than hydrogen. It has high electron density around its self and a lone pair of electrons. This makes it to act as an electron donor.

Illustration



In period 3

SiH_4 does not react with water because the electronegativity difference between silicon and hydrogen is small. This makes the silicon atom less positive but when there are traces of alkali, it forms SiO_2 and H_2



Phosphine does not almost dissolve in water because it is a weak base and the electronegativity difference between phosphorus and hydrogen is small.



Hydrogen sulphide and hydrogen fluoride are ionized by water.



Reaction of hydrides with alkalis and acids

7.03 Period 2 and 3 questions

1) The atomic number and melting points of some elements in period 3 of the periodic table are shown below

Element	N	Mg	Al	Si	P
	a				
Atomic number	11	12	13	14	15
Melting point/°C	98	650	660	141	4
				0	4

- (a) (i) Plot a graph of melting points against atomic number.
(ii) Explain the shape of the graph in (i).
- (b) Describe and explain how the oxides of magnesium and silicon react with;
(i) Sodium hydroxide.
(ii) Hydrochloric acid.
- (c) State the type of bonding in the oxides of sodium and phosphorous.
- 2) The elements Na, Mg, Al, Si, P and Cl are members of the third short period of the periodic table.
- (a) Write down the formulae of the principle chloride of each of the elements listed above.
- (b) Describe using equations how the chlorides in (a) above can be prepared.

(c) Which elements above form basic, acidic and neutral chlorides?

(d) Which two elements listed above form oxides of the type M_2O_3 ?

3) The elements Na, Mg, Al, P and Cl all belong to period three of the periodic table. discuss the reactions of each of these elements with;

- (a) Air
- (b) Water
- (c) Alkalies
- (d) Dilute acids

4) Study the table below and answer the questions that follow.

Oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_2	Cl_2O_7
Melting point/ $^{\circ}C$	119 3	307 5	230 0	172 8	563	30	-91

(a) Explain the observed melting points of each of the oxides above.

(b) Describe the reactions of each of the above oxides with;

- (i) Water
- (ii) Sodium hydroxide
- (iii) Hydrochloric acid

(Your answer should include the necessary equations).

(c) Write equations stating conditions leading to the formation of the above oxides.

5) Discuss briefly the structure and properties of the following oxides under the headings;

- (a) Structure and bonding
 - (b) Redox properties and
 - (c) Acid-base properties
- (i) H_2O_2 (ii) P_4O_{10} (iii) SiO_2 (iv) Na_2O

6) Below is table showing some of the physical properties of the chlorides of elements in period three of the periodic table.

Chloride	$NaCl$	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	S_2Cl_2	Cl_2
State	Solid	Solid	Solid	Liquid	Liquid	Liquid	Liquid
Melting point/ $^{\circ}C$	148	714	192	-68	92	-80	-181
Conductivity	Good	Good	Very poor	Nil	Nil	Nil	Nil

(a) Explain the trend in the physical properties of the chlorides.

(b) Discuss the reactions of the chlorides with water.

(c) The melting point of aluminium bromide is $97.5^{\circ}C$ whereas that of aluminum fluoride is $192^{\circ}C$. Explain.

7) (a) Name the classes of hydrides and in each case give an example.

(b) Write the formulae of the hydrides of Na, Al, P, Si and Cl. indicate the type of bonding in each case.

(c) Explain what happens when each of the hydrides given in (b) is added to water and

state whether the resultant solution is acidic, alkaline or neutral. Write equation in each case.

(d) State the observations and write equation when silicon tetrahydride (silane) reacts with;

- (i) $\text{Fe}^{3+}(\text{aq})$
- (ii) $\text{Cl}_2(\text{g})$

8) (a) The solid chloride of aluminium was found to be volatile when heated and had a vapour density of 133.5 at 350°C . The solid contains 80g of chlorine and reacted violently with water to give a solution which when treated with sodium hydroxide gave a white precipitate soluble in excess alkali.

(i) Calculate the molecular formula of the chloride ($\text{Cl} = 35.5$, $\text{Al} = 27$)

(ii) Write the structural formula showing the bonding in the chloride of aluminium

(b) When aluminium chloride was dissolved in sodium hydroxide there was a decrease in the freezing point depression of sodium hydroxide. Deduce whether the aluminium ion formed is $[\text{Al}(\text{OH})_4]^-$ or $[\text{Al}(\text{OH})_6]^{3-}$. Explain your observation.

(c) Write equation for the reaction of water with;

- (i) Aluminium nitride
- (ii) Aluminium carbide

9) The table below shows the melting points of chlorides of the elements from sodium to silicon.

Chloride name	Sodium chloride	Magnesium chloride	Aluminium chloride	Silicon tetrachloride
Melting point/°C	801	701	178	-70

(a) Write the formula of each of these chlorides.

(b) What type of chemical bonding is present in each of these chlorides

(c) How will these chlorides react with water? Write equation of reaction where appropriate

(d) The reaction of sulphur and chlorine forms a compound containing 31% sulphur.

(i) Determine its empirical formula.

(ii) Given that the molecular mass of the compound is 103.1, predict the shape of the molecule.

10) The metallic properties of elements in period three decreases from left to right.

(a) Using one property of the element and one property of its chloride, describe two pieces of evidence, which support each of the following statements.

(i) Sodium is a metal

(ii) Phosphorus is a non-metal

(b) The elements aluminium and silicon and their compounds have some metallic and non-metallic properties. Suggest an example of each of the following;

(i) a property of aluminium chloride that is typical of a non-metallic chloride.

(ii) a property of silicon that is characteristic of a metal.

(c) Aluminium hydroxide is amphoteric.

(i) Explain what amphoteric means.

(ii) Describe two reactions that show amphoteric behavior of aluminium hydroxide.

Write equations for these reactions and state which reaction is typical of a metal and which is typical of a non-metal.

11) Discuss the differences in the properties between the following pairs of compounds.

- (a) CCl_4 and SiCl_4
- (b) NH_3 and PH_3
- (c) HF and HCl
- (d) $\text{B}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$

Your answer should include relevant equation of reaction with water, acids and alkalis.

CHAPTER EIGHT

8.00 CHEMICAL PROCESSES

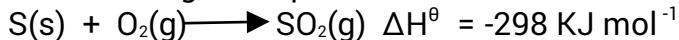
8.01 Manufacture of sulphuric acid

There are three main stages involved in the manufacture of sulphuric acid;

- (i) Burning sulphur to make sulphur dioxide.
- (ii) Converting sulphur dioxide and oxygen into sulphur trioxide.
- (iii) Absorbing sulphur trioxide in sulphuric acid to give highly concentrated sulphuric acid (oleum).

a) Making sulphur dioxide:

Air dried by concentrated sulphuric acid is passed through heated sulphur in a burning chamber to give sulphur dioxide.



b) Catalytic conversion:

Purified oxygen is heated together with the sulphur dioxide formed in the presence of vanadium (V) oxide catalyst to form sulphur trioxide.



Basing on the Lechatelier's principle, the production of sulphur trioxide is favoured by;

- Use of low temperature
- Use of high pressure
- Use of a catalyst

Problems faced in administering the above conditions include;

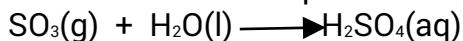
- Too much lowering of temperature slows down the rate of reaction to an extent that the yield of sulphur trioxide becomes minuscule.
- It is costly to build a chemical plant to work at high pressure.

A fairly good yield of sulphur trioxide is obtained by;

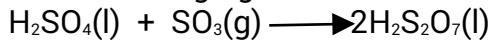
- Use of temperature of about 550°C .
- Use of pressure of about 150 to 200 atmospheres.
- Use of vanadium (V) oxide catalyst.

c) Absorbing sulphur trioxide:

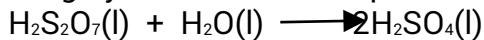
The sulphur trioxide is absorbed in water to give fuming sulphuric acid. But this technique is not suitable because the reaction is so violent that it would lead to a highly corrosive mist of sulphuric acid fumes being made and hence loss of the acid.



To obtain the best yield, sulphur trioxide is passed through sulphuric acid to give oleum which although gets hot does not vapourise at all easily.



The hot oleum is allowed to cool and mixed in a controlled amount of cold water to give a highly concentrated sulphuric acid (98%).



8.02 Uses of sulphuric acid

- Making of fertilizers e.g. superphosphate, ammonium sulphate.
- Processing of metal ores.
- Manufacture of detergents.
- Manufacture of rayon and other pigments.
- Manufacture of paper.
- Use as electrolyte in heavy duty batteries.
- Manufacture of paints and pigments.
- Use for industrial treatment of metals.
- Use as a laboratory reagent.

8.03 Manufacture of ammonia

The process leading to the production of ammonia is called the Haber process. The

process involves three main stages;

- i) Supply and purification of the reacting gases.
- ii) Compression of the gases and conversion into ammonia.
- iii) Recovery of ammonia.

a) Purification of the reacting gases:

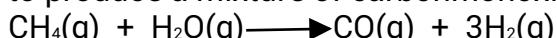
Haber process catalysts are easily poisoned especially by sulphur compounds and carbonmonoxide. It is for this reason that the nitrogen and hydrogen have to be thoroughly purified before they are used up.

The main source of nitrogen is naphtha (a mixture of hydrocarbons) from the oily industry or natural gas.

The sulphur compounds are removed from the hydrocarbons by passing them over zinc oxide or activated charcoal.

The purified hydrocarbon is subjected to primary and secondary reforming.

In the primary reforming, the hydrocarbons are reacted with steam over a nickel catalyst to produce a mixture of carbonmonoxide and hydrogen gas.



In the secondary reforming, the carbonmonoxide obtained from primary reforming combines with more steam to generate more hydrogen gas.



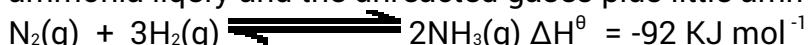
b) Compression and conversion:

Carbondioxide from the reforming stage is removed by washing with potassium carbonate solution and the remaining carbonmonoxide and carbondioxide is converted into methane in the methanator.

The purified gases ie hydrogen and nitrogen are comprssed and passed through a tower packed with finely divided iron catalyst mixed with promoters such as aluminium oxide, zirconium oxide and potassium oxide.

c) Recovery of ammonia:

The gases emerging from the converter are cooled and the pressure reduced, the ammonia liquefy and the unreacted gases plus little ammonia are recycled.



8.04 Uses of ammonia

- i) Manufacture of fertilizers.
- ii) Manufacture of nitric acid.
- iii) Manufacture of polymers.

8.05 Effects of temperature and pressure on the production of ammonia

The greatest yield of ammonia is achieved at low temperatures and high pressures.

However, the use of low temperature decrease the rate of reaction, therefore it is more profitable to use a higher temperature even though the maximum yield of ammonia is not obtained.

Similarly, the use of a plant that can withstand very high pressures will be much more expensive to build and run than the one which works at a lower pressure. Therefore it is economical to use a moderate pressure even though the maximum yield of ammonia is not obtained (pressure of between 150 and 300 atmospheres).

Illustration of effect of temperature and pressure on the production of ammonia



8.06 The manufacture of nitric acid

Nitric acid is prepared by the catalytic oxidation of ammonia as described below; Air containing about 10% of ammonia, at 230°C and 900kPa (9 atmospheres) is passed through a metal guaze made of platinum (about 90%) and rhodium (about 10%). The reaction gives nitrogen monoxide as the main product with evolution of a lot of heat.

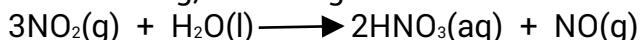
$$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g}) \Delta H^\theta = -904 \text{ KJmol}^{-1}$$

The hot nitrogen monoxide is cooled and converted to nitrogen dioxide by reaction with more purified oxygen.



According to Lechatelier's principle, the formation of nitrogen dioxide is favoured by use low temperature and high pressure. Usually a temperature of 150°C is used.

After cooling, the nitrogen dioxide is washed with water to give nitric acid (50-60%)



8.07 Uses of nitric acid

- i) Manufacture of fertilizers especially ammonium nitrate.
- ii) Nitration of organic compounds especially making of explosives and polymers eg nylon.
- iii) In the dyeing industry.
- iv) Treatment of metals.

8.08 Preparation of chlorine and sodium hydroxide

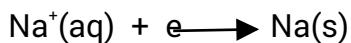
Chlorine and sodium hydroxide are made by the electrolysis of brine (concentrated sodium chloride or salt water)

Brine is continuously passed into a mercury cell that has graphite anodes and a moving stream of mercury as the cathode.

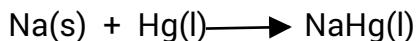
At the anode, the chloride ions are discharged in preference to the hydroxide ions in water.



And at the cathode, the sodium ions are discharged in preference to the hydrogen ions in water.

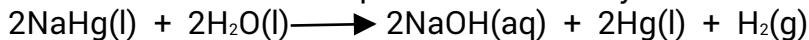


The sodium formed reacts with the mercury to form sodium amalgam (NaHg).



The amalgam travels with unused mercury out of the cell into a chamber containng water

where it reacts with it to produce sodium hydroxide.



NB//. The use of mercury cells has declined rapidly because of the damage, mercury and its compounds causes if they escape into the environment.

Mercury cell

8.09 Uses of chlorine

- i) Making solvents e.g. carbon tetrachloride.
- ii) Making of polyvinyl chloride.
- iii) Making of paper products.
- iv) Making of inorganic chemicals.
- v) Making of chloromethane.

8.10 Uses of sodium hydroxide

- i) Making of inorganic chemicals.
- ii) Making organic chemicals.
- iii) Making paper products.
- iv) Use in aluminium industry.
- v) Making of soap.

8.11 Manufacture of sodium carbonate

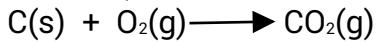
It is made by the Solvay process. In the Solvay process, the materials required are limestone, sodium chloride and ammonia solution. The procedures involved are outlined as follows;

a) Roasting of limestone:

The limestone mixed with coke is heated in Kilns through which a supply of air passes. Limestone decomposes to give off carbondioxide and calcium oxide remains.

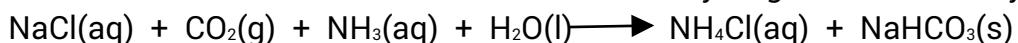


The coke burns in air to generate energy as well as more carbondioxide through the reaction;



b) The purified brine is passed down towers through which ammonia is passed.

The solution containing brine and ammonia is then passed down another series of towers against an upward moving current of carbondioxide. The different reactants combine to form ammonium chloride solution and sodium hydrogen carbonate crystals.



c) The particles of sodium hydrogen carbonate and ammonium chloride solution drop down to the bottom of the tower through slits at the edges of the plates and the ammonium chloride solution is filtered from the sodium hydrogen carbonate crystals.

d) Finally the sodium hydrogen carbonate crystals are heated in a rotary drier to convert it into sodium carbonate.



8.12 Uses of sodium carbonate (soda ash)

- i) Making of glass containers.
- ii) Making sodium phosphate.
- iii) Making alkaline cleaners.
- iv) Making of paper products.
- v) Making of glass products.

8.13 Cement

Cement is a complex mixture containing tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$), dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$) and tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$). Of these three components, $3\text{CaO}\cdot\text{SiO}_2$ is the most important. The following raw materials are used in the manufacture of cement:

- i) Limestone to provide calcium oxide.
- ii) Clay to provide alumina (Al_2O_3) and silicate (SiO_3)
- iii) Gypsum to provide calcium sulphate ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$)

There are two processes involved in the manufacture of cement;

- i) Dry process
- ii) Wet process

The main process used is the dry process. During this process, the following procedures are followed;

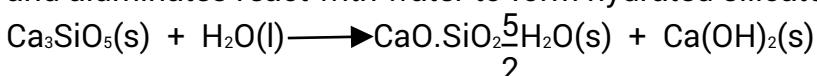
- a) Limestone and clay are mixed together in a ratio of 4:1 and this mixture is ground into a fine powder.
- b) The fine powder is first heated to drive off water from the mixture and later on the mixture is heated strongly to decompose limestone into calcium oxide (quick lime).
$$\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$$
- c) The mixture is further heated until it melts to form a complex grey coloured product called cement clinker.
- d) The cement clinker is then cooled to about 60 to 100°C. The powder formed is then mixed with gypsum (3-5) to give cement. Gypsum is meant to slow down the reaction between cement and water.

8.14 Uses of cement

- i) Used in the construction to make concretes and reinforced concretes.
- ii) Used in plastering of walls.
- iii) Used in construction of dams and bridges.

8.15 Setting of cement

Chemically the setting of cement is mainly due to the hydration of the molecules of its constituents and rearrangement. According to the crystalline theory, the calcium silicates and aluminates react with water to form hydrated silicates and aluminates.





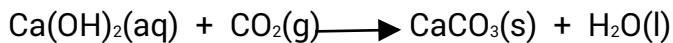
The products formed above crystallize and occupy the inner spaces within the mixture. This accounts for the hardness of the set cement.

8.16 Concrete

It is made by mixing cement, sand, gravel and water and the whole mass is allowed to set.

8.17 Mortar

Mortar is a mixture of slaked lime ($\text{Ca}(\text{OH})_2$) and sand in the ratio of one part of lime to three or four parts of sand which is made into paste by adding water to the mixture. Mortar gradually hardens owing to the crystallization of calcium carbonate by carbon dioxide of the air.



8.18 Fertilizers

Fertilizers are materials added to soil to improve its fertility. They contain essential elements which are plants requirements for growth. The three essential elements plants need are;

- i) Nitrogen
- ii) Phosphorous
- iii) Potassium

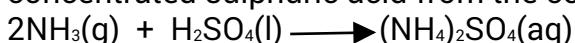
These elements are absorbed by plants as compounds e.g. nitrates, phosphates through the root system in the soil. There are two types of fertilizers;

- i) Artificial fertilizers
- ii) Natural fertilizers

Examples of artificial fertilizers;

1) Ammonium sulphate.

It is prepared by reaction of ammonia obtained from the Haber process with concentrated sulphuric acid from the contact process.



2) Phosphate fertilizer (super phosphate)

This fertilizer is obtained by reacting insoluble calcium phosphate with concentrated sulphuric acid.



CHAPTER NINE 9.00 TRANSITION ELEMENTS

These are elements with partially filled d or f sub shells in at least one of their oxidation states. There are 56 transition elements and they are divided into two blocks.

- The d block elements. These are elements with partially filled d-sub shells in at least one of their oxidation states.
- The f block elements. They are elements with partially filled f-sub shells in at least one of their oxidation states. They are called the inner transition elements. Consider the following elements.

Element	Atomic number	Electronic configuration
scandium	21	[Ar] 3d¹4s²
Titanium	22	[Ar] 3d²4s²
Vanadium	23	[Ar] 3d³4s²
Chromium	24	[Ar] 3d⁵4s¹
Manganese	25	[Ar] 3d⁵4s²
Iron	26	[Ar] 3d⁶4s²
Cobalt	27	[Ar] 3d⁷4s²
Nickel	28	[Ar] 3d⁸4s²
Copper	29	[Ar] 3d¹⁰4s¹
Zinc	30	[Ar] 3d¹⁰4s²

9.01 Physical properties of transition elements

a) Atomic radius.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radius	1.4	1.32	1.22	1.17	1.17	1.16	1.16	1.15	1.17	1.25

The atomic radius decreases slightly across the period. (Almost constant)

This is because the increase in screening effect of the inner electrons almost balances the increase nuclear charge as you built up the transition elements since the electrons are being added to an inner energy level (3d). This means the effective nuclear charge attraction changes slightly hence the trend.

b) Ionization energy.

Ionization energy decreases by a small amount as you go across the series. This is because the effective nuclear charge attraction is changing slightly as explained above.

There is a general slight increase in the 1st and 2nd ionization energy of the transition elements. This is because of the slight increase in the effective nuclear charge attraction. The rate of increase in the 3rd ionization energy across the series is faster than the rate of increase in the 1st and 2nd ionization energy across the series.

This because the electrons are being removed from the 3d sub-energy level were the increase in effective nuclear charge from one element is significant.

The 2nd ionization energy of chromium is higher than that of manganese because the 2nd electron in Cr is removed from a 3d⁵ subenergy level which is energetically stable yet the

2nd electron in Mn is removed from 4s¹ which is effectively shielded by the underlying 3d⁵.

c) Melting and boiling points.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
1 st										
I.E(KJmol ⁻¹)										

The transition metals generally have high melting points and boiling points because they have strong metallic bonds. The strength of the metallic bonds depends on the number of electrons free to participate in the bonding. Transition metals have got many electrons because the 3d and 4s sub-energy levels are close in energy.

The melting points generally decrease across the series because as the nuclear charge increases the electrons become less available for metallic bonding (the electrons are becoming more strongly held therefore less free to participate in metallic bonding)

However, the melting point of manganese is lower than expected because its electrons are less free to participate in bonding since the 3d sub-energy level is half-filled.

9.02 Characteristics of transition elements

The transition elements have the following general properties.

- (i) Variable oxidation states.
- (ii) Formation of coloured compounds or ions.
- (iii) Formation of complex ions.
- (iv) Catalytic activity.
- (v) Para magnetism.

a) Variable oxidation state.

Oxidation state is the charge left on the central atom when all the other atoms of a compound have been removed as ions.

Examples

1) Determine the oxidation state of chromium in the dichromate, Cr₂O₇²⁻.

The central atom is the chromium

The overall charge on the ion is -2

Let x be the charge on each chromium atom hence the summation of oxidation states is equal to charge.

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

Therefore x = +6

All the transition elements have variable oxidation states. This arises due to a small energy difference which exists between the 3d and 4s sub energy levels. Thus it is possible for the electrons in these 3d and 4s sub energy level to combine in various numbers during chemical reactions. This effect is commonly found in atoms with partially d-sub shells. Examples of oxidation states

Elements	oxidation states					
Scandium	+3					
Titanium	+2	+3	+4			

Vanadium	+2	+3	+4	+5		
Chromium	+2	+3	+4	+5	+6	
Manganese	+2	+3	+4	+5	+6	+7
Iron	+2	+3	+4		+6	
Cobalt	+2	+3	+4			
Nickel	+2	+3	+4			
Copper	+1	+2	+3			
Zinc	+2					

Stability of oxidation states

Some oxidation states are unstable and uncommon. The most stable ones are shown in bold.

In the lower oxidation states of +2 and +3 the elements forms mainly ionic compounds but in higher oxidation states of +6 and +7 the compounds formed are covalent and are very strong oxidizing agents.

The relative stability of oxidation states is determined by the following factors;

- (i) Stability of the electronic configuration.
- (ii) Heat change for the formation of the ion.
- (iii) The electrode potential.
- (iv) The pH of the medium.

1) Electronic configuration. An ion with a filled or half filled 3d sub shell is more stable than the one with a neither full nor half filled 3d sub shell. Consider the following;

- a) Fe..... $3d^64s^2$
 Fe^{2+} $3d^64s^0$
 Fe^{3+} $3d^54s^0$

Fe^{3+} is more stable than Fe^{2+} because it has a half filled $3d^5$ configuration while Fe^{2+} has a $3d^6$ configuration which is neither full nor half filled.

- b) Mn..... $3d^54s^2$
 Mn^{2+} $3d^54s^0$
 Mn^{3+} $3d^44s^0$
 Mn^{4+} $3d^34s^0$
 Mn^{7+} $3d^04s^0$

In the above case, Mn^{2+} is the most stable than the rest of the manganese ions because it has a half filled $3d^5$ configuration while the rest have configurations which is neither full nor half filled.

1) Heat change for the formation of ion.

Consider copper,

- Cu..... $3d^{10}4s^1$
 Cu^+ $3d^{10}4s^0$
 Cu^{2+} $3d^94s^0$

Cu^+ is expected to be more stable than Cu^{2+} but this is not true because the heat change for the formation of Cu^+ is less exothermic than the heat change for the formation of Cu^{2+} . This makes Cu^+ less stable than Cu^{2+} hence it tends to undergo disproportionation

reaction.



Disproportionation reaction is the simultaneous oxidation and reduction of anion or a compound. This process results into the attainment of stability of an ion or compound. NB//zinc and scandium are not regarded as typical transition elements because of the following reasons;

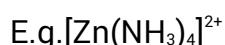
For scandium

- (i) The Sc^{3+} has a $3d^0$ configuration hence it cannot form coloured compounds since it lacks electrons in the $3d$ sub shell.
- (ii) It is limited to only one oxidation state of +3.

For zinc

- (i) In Zn^{2+} , the $3d^{10}$ configuration is fully occupied by electrons therefore it cannot form coloured compounds.
- (ii) It is also limited to a fixed oxidation state of +2.

However zinc resembles transition elements in that it is capable of forming complexes.



Most of the chemical properties of zinc are related to those of group (II) elements. The following are the properties in which zinc resembles group (II) elements;

- a) They both form normal oxides.
- b) They both have a fixed oxidation state of +2.
- c) They do not form coloured compounds.
- d) Zinc is capable of complex formation just like beryllium of group (II) elements.
- e) Zinc can undergo hydrolysis like the beryllium and magnesium in group (II).

b) Formation of coloured ions or compounds.

The majority of transition metal ions are coloured and in aqueous state these ions are normally hydrated. E.g.



Colour of transition metal is associated with the following factors;

- (i) Presence of unpaired of electrons.
- (ii) Nature of the group surrounding the metal ion (ligand).

The above factors can be explained as follows;

The unpaired d electrons in the ion absorb light energy and are temporarily raised to a higher energy level but these electrons quickly fall back to their stable condition of lower energy emitting light energy in the process. The wave length of the light emitted incase of transition metal ions falls in the wave band of the visible light whereas for most metals it lies in the ultraviolet range which is invisible.

The nature of the ligands surrounding the ion affects the colour of the ion in that it influences the amount of light absorbed. The presence of the ligands also causes electron repulsion which leads to the breaking or splitting of the unpaired d electrons due to groups

with significant difference in energy levels.

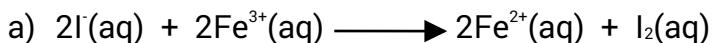
c) Catalytic activity

Catalytic activity of transition elements and their compounds is associated with their variable oxidation states. They function as catalysts by changing their oxidation states.

E.g. Fe^{3+} catalyses the reaction between iodide and peroxodisulphate ion



The reaction takes place in two stages.



Therefore the two reactions between the oppositely charged ions will be faster than one between the ions of the same charge.

Some of the examples of transition metal catalysts are;

(i) Vanadium (V) oxide, V_2O_5 used in the contact process to manufacture sulphuric acid.

(ii) Finely divided iron catalyst to manufacture ammonia in the Haber process.

(iii) Nickel catalyst. This is meant for hydrogenation of unsaturated compounds.

d) Exhibition of Paramagnetism in many of their compounds.

Paramagnetism is the tendency of a substance to be weakly attracted by strong magnetic field. Such substance is said to be paramagnetic, like many of the transition metal compounds are. In transition metal compounds, paramagnetism is caused by the presence of unpaired electrons in their metal atom $(n-1)d$ orbitals. These electrons are regarded as spinning on their axes hence generating a magnetic moment just as an electric wire generates a magnetic moment. The more the number of unpaired electrons, the stronger the attraction and vice versa.

Diamagnetism is the tendency of a substance to be weakly repelled by a strong magnetic field. This arises due to the absence of unpaired electrons on atoms of diamagnetic substance for example Zn is diamagnetic because it has no unpaired electrons in the $3d$ subshell.

e) Formation of many complex ions by the elements.

A metal complex is chemical species in which a metal atom is surrounded by a number of ions (usually anions) or neutral molecules. The bond formed between the metal atom and each of the surrounding ions or molecules is called a coordinate bond. This is basically an electrostatic attraction between the nucleus of the metal and electrons of the surrounding anions or molecules.

The formation of complex ions by transition elements is favoured by two factors;

- (i) Presence of empty or vacant d-subshell with appropriate energy which can accommodate electrons from ligands.
- (ii) The small size and high charge density of transition metal ions leads to formation of strong electrostatic bond between the metal ion and the ligands. This factor also applies to all ions with high charge density e.g. Al^{3+} , Be^{2+} .

Structure of complex ions

A complex ion is normally represented as $[\text{ML}_n]^{z \pm}$ where M is the central metal ion while L is the ligand surrounding the metal ion, n is the number of ligands (coordination number of the metal ion) and $\pm z$ is the charge on the complex.

A ligand is an atom or group of atoms with a negative charge or lone pair electrons that coordinate with the central metal ion or atom.

A ligand can be ionic or neutral.

A metal complex species is ionic when it has a net charge on it. For example chromium (III) cation, Cr^{3+} surrounded by six ammonia molecules (6NH_3), forms a cationic metal complex.

A neutral metal complex species is also possible when there is no net charge on the complex but has a lone pair of electrons. For example, a neutral nickel atom (Ni^0) surrounded by four carbon monoxide molecules (4CO) forms a neutral metal complex, $[\text{Ni}(\text{CO})_4]$.

The term coordination compound means a compound containing a species having the characteristics of a metal complex but capable of independent existence. Therefore a neutral complex like $[\text{Ni}(\text{CO})_4]$ is itself a coordination compound because it can independently exist.

Classification of ligands

Ligands are classified using the number of atoms on the ligand that can donate a pair of electrons. According to this classification we have the following;

- (i) **Unidentate ligand or monodentate ligand.** This is one with only donor atom per molecule for examples, Cl^- , NH_3 is also a unidentate ligand because it is only the nitrogen atom that can donate a pair electrons to the metal.
- (ii) **Polydentate ligands.** These are ligands with more than one donor atom per molecule and they make more than one bond with the central metal ion. For these ligands, a suffix replaces poly to indicate the number of donor atoms in such ligands. Thus the two, three, four, five and six donor atom ligands, are called bidentate, tridentate, tetradeinate, pentadentate, and hexadentate ligands, respectively. In **bidentate ligands** two bonds per molecule of ligand are formed with the central metal ion e.g. 1, 2-diammine ethane, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

Illustration

Coordination number and molecular formulae of complexes

The coordination number of a metal complex is the number of ligand donor atoms bonded directly to the metal atom. Thus it is referred to as the coordination number of the metal atom in a complex.

The molecular formula of a metal complex is written inside square brackets, the metal atom first followed by an appropriate number of ligands to satisfy its coordination number. For example, $[\text{FeF}_6]^{3-}$ is iron (III)-fluoride complex in which the coordination number of iron (III) is six. Another example is $[\text{Cr}(\text{NH}_3)_6]^{3+}$ in which the coordination number of chromium (III) is six. The formula of a neutral complex has zero net charge. For example, a neutral nickel atom coordinated by four carbon monoxide molecules has its complex written as $[\text{Ni}(\text{CO})_4]$.

Nomenclature of complex ions

The following rules are followed when naming complex ions;

- In an ionic coordination compound a cation is named first regardless of whether it is a complex or not.
 $K_4[Fe(CN)_6]$ Potassium hexacyanoferrate(II)
- Ligands are named in alphabetical order before the name of the metal atom.
- Prefixes are used to indicate the number of a particular ligand; di- for two, tri for three, tetra- for four, penta- for five, hexa- for six, etc; however, for complex ligands, bis-, tris-, tetrakis-, pentakis-, hexakis, are used to specify 2, 3, 4, 5 and 6 ligands respectively.
- Names of anionic ligands end with the suffix -o: for example, Cl^- chloro; O^{2-} oxo; HO^- hydroxo; SO_4^{2-} sulphato.
- Names of neutral ligands remain unchanged; however, there are some important exceptions, eg. NH_3 ammine, H_2O aqua, CO carbonyl; NO nitrosyl.
- For a cationic or neutral complex, the name of the metal atom is retained.
 $[Cu(NH_3)_4]^{2+}$ tetraamminecopper(II)ion
 $[Cr(H_2O)_5Cl]^{3+}$ chloropentaaquachromium(III)ion.
 $[Ni(NH_3)_5H_2O]^{2+}$ pentaammineaquanickel(II)ion
- For an anionic complex, the name of the metal atom ends with the suffix -ate, but where the suffixed English name sounds awkward, the latin stem of the name is used, eg; ferrate for an iron complex, argentate for a silver complex.
 $[CoCl_4]^{2-}$ tetrachlorocobaltate(II)ion
 $[Fe(CN)_6]^{3-}$ hexacyanoferrate(II)ion
- The oxidation state of the metal atom in the complex is shown by a roman numeral in parentheses after its name.
- A metal complex species is written as one word.

IUPAC names of some coordination compounds to illustrate the rules for naming the metal complex species.

Compound	Name
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)
$[Fe(H_2O)_6]SO_4$	Hexaquairon(II)sulphate
$[Cr(NH_3)_3Cl_3]$	Triaminetrichlorochromium(III)
$[Ni(CO)_4]$	Tetracarbonylnickel(0)
$[Cu(NH_3)_3(H_2O)Br_2]$	Triamminequadibromocupper(II)

Ligand exchange in a complex

This is the replacement of part or all the ligands of a metal complex ion by another ligand or group of ligands. This result into the change of the colour of the resulting complex formed. E.g. if concentrated hydrochloric acid is added to a solution of Cu^{2+} , the colour of the solution changes from blue to yellow due to the formation of terachlorocuprate(II).



Yellowish green

If dilute hydrochloric acid is added instead of concentrated hydrochloric acid, the solution turns green due to the presence of both $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{CuCl}_4]^{2-}$

Isomerism in complex ions

Isomerism is a phenomenon whereby compounds having the same number and kinds of atoms, have these atoms arranged either sequentially or spatially differently. These differences in atom to atom arrangements make them to possess' different properties. The compounds which are a consequence of isomerism are called isomers. Isomers of metal complexes can be divided into two major categories:

- Structural isomers
- Stereo isomers

Structural isomers are those isomers having different atom-to-atom bonding sequences, i.e. order of arrangement, relative to the metal atom. On the other hand stereo isomers have the same atom-to-atom bonding sequences, but their ligands are arranged differently in space relative to the metal.

Structural isomers

Structural isomers are divided into five well recognized classes:

- Coordination isomers.
- Hydration isomers;
- Hydrate isomers;
- Linkage isomers;
- Ligand isomers.

(i) **Coordination isomers.** These are isomers which occur in ionic coordination compounds whose cations and anions are both metal complex. They are a result of exchanging ligands between the metal atoms of the cationic and anionic complexes. The following are examples of pairs of coordination compounds.

- $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{C}_2\text{O}_4)_3]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{C}_2\text{O}_4)_3]$
- $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

(ii) **Ionization isomers.** These isomers are a result of exchange of anionic ligands inside and outside the coordination sphere. Examples of these isomers are provided by coordination compounds of chromium (III), cobalt (III) and platinum (IV) among others as shown below.

- $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$
- $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_2$
- $[\text{Cr}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Cr}(\text{NH}_3)_5\text{SO}_4]\text{Br}$
- $[\text{Pt}^{\text{II}}(\text{NH}_3)_4][\text{Pt}^{\text{IV}}\text{Cl}_6]$ and $[\text{Pt}^{\text{IV}}(\text{NH}_3)_4][\text{Pt}^{\text{II}}\text{Cl}_6]$

(iii) **Hydrate isomers.** These are isomers due to type of isomerism called hydration isomerism. It is similar to ionization isomerism in respect of exchange of species between those inside and outside the coordination sphere. The difference between the two is that in hydration isomerism the exchange is between water of hydration and anionic ligands. This means the anionic ligands become replaced by water molecules which become ligands and vice-versa.

Classical examples of hydrate isomers are the three crystalline isomers of chromium (III) chloride hexahydrate, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. The three isomers generated are;

$[\text{Cr}(\text{H}_2\text{O})_6]^{3+} 3\text{Cl}^-$	violet
$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+} 2\text{Cl}^- \text{H}_2\text{O}$	blue-green
$[\text{Cr}(\text{H}_2\text{O})_4 \text{Cl}_2]^+ \text{Cl}^- 2\text{H}_2\text{O}$	green

The isomers above differ in their conductivity properties and also in the number of moles of silver chloride precipitated when treated with silver nitrate solution.

Reaction with silver nitrate solution

- With, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} 3\text{Cl}^-$, three moles of silver chloride are formed. This shows that all the Cl^- are not coordinated to the chromium and has the highest conductivity. This is because it has 4 ions in its solution per molecule.
- $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+} 2\text{Cl}^- \text{H}_2\text{O}$, yields two molecules of silver chloride when treated with silver nitrate solution. This shows that two chloride ions are not coordinated to the central metal ion. Its conductivity is medium because it has 3 ions per molecule in solution.
- $[\text{Cr}(\text{H}_2\text{O})_4 \text{Cl}_2]^+ \text{Cl}^- 2\text{H}_2\text{O}$, yields only one molecule of AgCl and this shows that two chloride ions are coordinated to the chromium while one Cl^- is outside the coordination sphere. This isomer is the least conducting since it has only two moles per molecule in solution.

9.03 Chemistry of each of the elements

a) Titanium

Atomic number 22

Electronic configuration: $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^2 4\text{s}^2$

Chemical reactions of titanium

1) Reaction with oxygen.

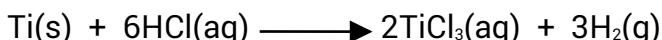
When heated in oxygen, titanium (IV) oxide is formed.



2) Reaction with acids.

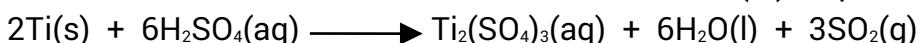
- Concentrated hydrochloric acid.

It reacts with hot concentrated hydrochloric acid to give titanium (III) chloride.



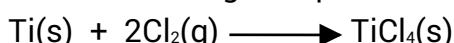
- Concentrated sulphuric acid.

It reacts with the metal when cold to form titanium (III) sulphate and sulphur dioxide.



3) Reaction with halogens

When chlorine gas is passed over heated titanium metal, titanium (IV) chloride is formed.



Compounds of titanium

The compounds formed by titanium shows oxidation states of +2, +3 and +4

$$\text{Ti}^{2+} \dots \dots \dots 1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$$

Ti³⁺ 1s²2s²2p⁶3s²3p⁶3d¹

T⁴⁺ 1s²2s²2p⁶3s²3p⁶

In the +2 oxidation state, the compounds are uncommon and unstable.

In the +3 oxidation state, titanium has one electron in the 3d sub shell and because of this unpaired electron the compounds of titanium (III) are coloured and paramagnetic.

In the +4 oxidation state, the 3d and 4s electrons are lost therefore it has no unpaired electrons and their compounds are neither coloured nor paramagnetic.

Compounds of titanium in the +2 oxidation state

Titanium (II) chloride

It is made by heating titanium (IV) chloride with titanium metal. It disproportionates on standing forming titanium (IV) chloride and the metal.



Titanium (IV) oxide is also known but since titanium (II) compounds are oxidized at once by water therefore it has no aqueous chemistry.

Compounds of titanium in the +3 oxidation state

In aqueous solution, it exists as $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ and is purple in colour. It is unstable therefore easily oxidized to +4 oxidation state compounds which are more stable.

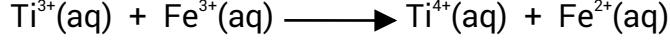
Solutions containing $[Ti(H_2O)_6]^{3+}$ are prepared by reduction of titanium (IV) compounds in acid with zinc e.g. Titanium (III) chloride is prepared by reduction of titanium (IV) chloride with zinc in the presence of hydrochloric acid.



NB//. Solutions of titanium (III) sulphate and titanium (III) chloride are used in volumetric analysis. The violet solution of $Ti_2(SO_4)_3$ is standardized by :

- Titration against acidified potassium permanganate solution at about 60°C.

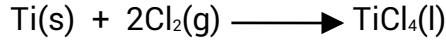
$$5\text{Ti}^{3+}(\text{aq}) + \text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) \longrightarrow 5\text{Ti}^{4+}(\text{aq}) + \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$$
 - Titration with iron (III) alum in presence of ammonium thiocyanate indicator.



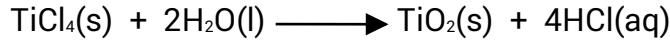
Compounds of titanium in the +4 oxidation state

Titanium (IV) chloride

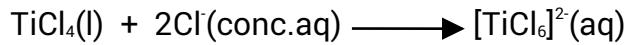
It is prepared by passing dry chlorine gas over heated titanium metal.



It is covalent colourless liquid and rapidly hydrolyzed by water and fumes in air.



It dissolves in concentrated hydrochloric acid to give the complex hexachlorotitanate (IV), $[\text{TiCl}_6]^{2-}$ just like lead (IV) chloride.



b) Vanadium

Atomic number, 23

Electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$

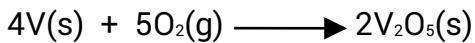
Oxidation states include;

+5 exist as VO_2^+	yellow or colourless.	$1s^2 2s^2 2p^6 3s^2 3p^6$
+4 exists as VO^{2+}	blue	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$
+3 exists as V^{3+}	green	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$
+2 exists as V^{2+}	purple or violet	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

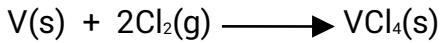
Properties of vanadium

At room temperature, it does not react with air, water, non oxidizing acids, and alkalis.

However when heated with oxygen gas, it forms vanadium (V) oxide.



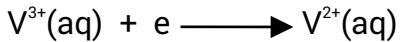
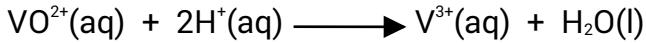
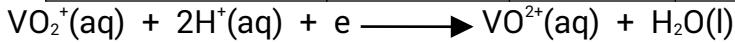
On heating with chlorine gas, vanadium (IV) chloride is formed.



All the oxidation states of vanadium can be observed in aqueous solution when a solution of ammonium vanadate (V) is reacted with dilute sulphuric acid and zinc metal.

The delightful sequence of colour changes can be used as an analytical test for vanadium.

Colour changes	Yellow	Blue	Green	Purple or violet
Cationic species	VO_2^+	VO^{2+}	V^{3+}	V^{2+}
Oxidation states	+5	+4	+3	+2



Compound in the +2 oxidation state

In solution, it exists as $[V(H_2O)_6]^{2+}$ and is violet in colour,

Vanadium (II) oxide, VO .

It is a black basic solid that is readily oxidized to the hydrated V^{3+} in air.

Compound in the +3 oxidation state

Vanadium (III) oxide. V_2O_3

V_2O_3 is a black solid prepared by passing dry hydrogen gas over heated V_2O_5 .

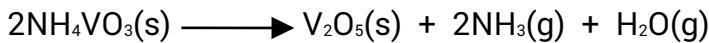


It is basic oxide therefore it dissolves in acids to form $[V(H_2O)_6]^{3+}$ which is green.

Compound in the +5 oxidation state

Vanadium (V) oxide, V_2O_5

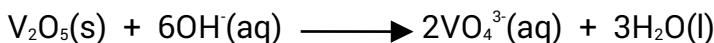
It is an orange solid made by heating ammonium vanadate.



This oxide is amphoteric; therefore it dissolves in strongly acidic solutions to form pale yellow VO^{2+}



It also dissolves in a strong alkali solution to form vanadate ion.



c) Chromium

Atomic number 24

Electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$

The oxidation states of chromium are +2, +3 and +6 with +3 being the most stable.



Extraction of chromium

Chromium metal can be obtained from a dichromate by first heating it to form to chromium (III) oxide and finally reducing the chromium (III) oxide with an electropositive metal e.g. aluminium, in a process called thermite process.

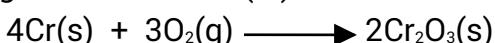


Properties of chromium

Chromium is a bluish-white metal with a melting point of 2163K. It has the following chemical properties.

1) Reaction with air.

Chromium is not affected by air at ordinary temperature. When heated, it is oxidized to green chromium (III) oxide



Green

2) Reaction with acids.

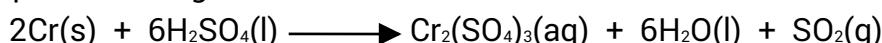
Chromium reacts slowly with both dilute hydrochloric acid and sulphuric acid but rapidly when heated to form blue solution of the corresponding chromium (II) salts.



Cr^{2+} is unstable therefore it is readily oxidized to green chromium (III) salts in the presence of air.



Hot concentrated sulphuric attacks chromium to give chromium (III) sulphate and sulphur dioxide gas.

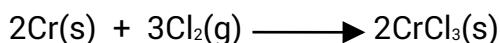


Dilute nitric acid does not attack chromium and when the acid is concentrated the metal

is rendered passive.

3) Reaction with chlorine.

Chromium combines directly with dry chlorine when heated to produce chromium (III) chloride.



Compounds of chromium

1) Chromium compounds in the +2 oxidation state.

This is the least stable oxidation state of chromium. Chromium compounds with this oxidation state tend to change to the most stable +3 oxidation state. A solution containing Cr^{2+} is blue but on oxidation it becomes green due to the formation of Cr^{3+} .

a) Chromium (II) oxide, CrO .

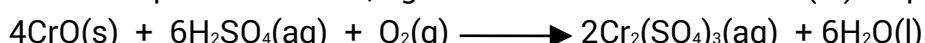
This is a black basic oxide prepared by heating chromium carbonate, CrCO_3 in the absence of air.



CrO dissolves in acids in the absence of air forming a blue solution of chromium (II) sulphate. E.g.

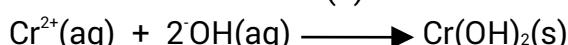


But in the presence of air, a green solution of chromium (III) sulphate is formed.



b) Chromium (II) hydroxide.

It is prepared as a yellow precipitate by addition of sodium hydroxide solution to the blue solution of chromium (II) salt.

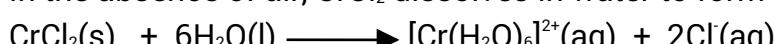


c) Chromium (II) chloride.

This is made by passing dry hydrogen chloride gas over heated chromium metal.



In the absence of air, CrCl_2 dissolves in water to form a blue solution of hydrated Cr^{2+} ions.



2) Chromium compounds in the +3 oxidation state.

In aqueous solution, chromium (III) compounds exists as $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and are the most stable of the tripositive ions formed by transition elements. $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ion is octahedral in shape and violet in colour. But it is often green due to the partial replacement of water molecules by other ligands. Other common stable octahedral complexes of chromium in the +3 oxidation state include $[\text{Cr}(\text{NH}_3)_6]^{3+}$, $[\text{CrCl}_6]^{3-}$.

Aqueous solution of chromium (III) is acidic because it undergoes hydrolysis reaction producing hydroxonium ions (H_3O^+). This is possible because of the small size and high charge density of Cr^{3+} ion. E.g.

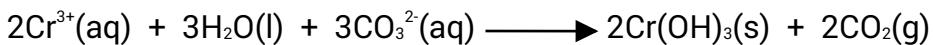


For complete hydrolysis



Addition of sodium carbonate solution to a solution of Cr^{3+} results into formation of a grey

green precipitate of chromium (III) hydroxide with evolution of a colourless gas which turns damp blue litmus paper red or pink.

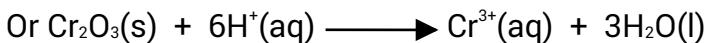
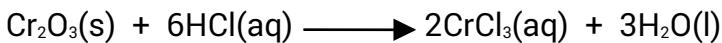


a) Chromium (III) oxide, Cr_2O_3 .

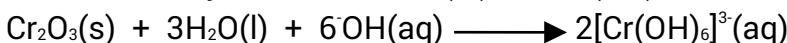
Cr_2O_3 is a dark green solid prepared by heating ammonium dichromate (VI). is amphoteric in nature



Cr_2O_3 is amphoteric; therefore its basic character is demonstrated by dissolving the oxide in an acid to form chromium (III) salt. E.g.

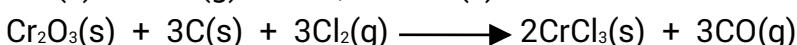
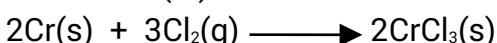


The acidic character is demonstrated by treatment of the oxide with excess caustic alkali to form hexahydroxochromate(III)ion, $[\text{Cr(OH)}_6]^{3-}$.



b) Chromium (III) chloride, CrCl_3 .

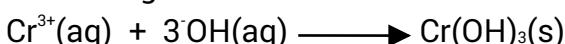
The anhydrous CrCl_3 exists as a violet solid when hydrated its green. It is prepared by passing dry chlorine gas over heated chromium metal or over an intimate mixture of chromium (III) oxide and carbon at red heat.



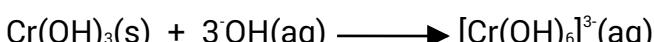
Hydrated chromium (III) chloride, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ exists in three isomeric forms discussed under isomerism exhibited by complexes.

c) Chromium (III) hydroxide.

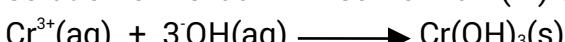
It is obtained as a grey green precipitate when an alkali solution is added to a solution containing Cr^{3+} ions.



But when the OH^- is in excess, a green solution of hexahydroxochromate(III)ion, $[\text{Cr(OH)}_6]^{3-}$, is formed.



But if ammonia solution is used instead of sodium hydroxide solution, a green precipitate of chromium (III) hydroxide is formed that dissolves in excess to form a pink or violet solution of hexaamminechromium(III)ion, $[\text{Cr(NH}_3)_6]^{3+}$.



Cr(OH)_3 decomposes to dark green solid of Cr_2O_3 and H_2O when heated

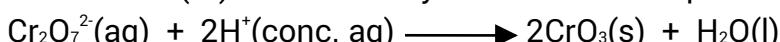


3) Chromium compounds in the +6 oxidation state.

Chromium (VI) is formed when all the six outer electrons are lost.

a) Chromium (VI) oxide, CrO_3 .

CrO_3 exists as red crystals and precipitated when a saturated solution of potassium dichromate (VI) is acidified by concentrated sulphuric acid and then cooled.



Orange

At 46K, CrO_3 melts and decomposes to Cr_2O_3 and oxygen.



CrO_3 is deliquescent therefore dissolves in water forming chromic (VI) acid

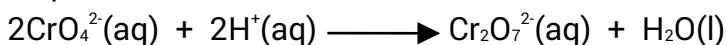


b) Dichromates, $\text{Cr}_2\text{O}_7^{2-}$.

These are orange coloured salts containing a dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$; common dichromates include; sodium dichromate which is deliquescent and potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$ which is not hence used as a primary standard in volumetric analysis.

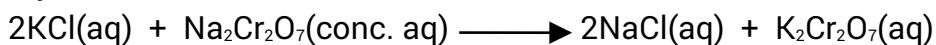
(i) Sodium dichromate (IV), $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$

It is made by making a solution of sodium chromate (VI) followed by acidification with sulphuric acid.



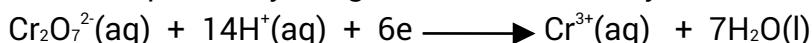
(ii) Potassium dichromate (IV), $\text{K}_2\text{Cr}_2\text{O}_7$

This is prepared by mixing hot saturated solution of sodium dichromate and potassium chloride. The sodium chloride precipitated is filtered off and the dichromate (VI) crystallizes as the solution cools.



Generally, dichromates are strong oxidizing agents in acidic solutions but they are not strong enough to oxidize Cl^- to Cl_2 . This implies that they can be acidified by hydrochloric acid.

Like all other oxidizing agents, it acts as an electron acceptor. The orange colour of $\text{Cr}_2\text{O}_7^{2-}$ is replaced by the green colour of the hydrated chromium (III) ion.



Examples of oxidizing reactions by $\text{Cr}_2\text{O}_7^{2-}$ in acidic solution are;

(a) Conversion of iron (II) in acidified solution to iron (III).

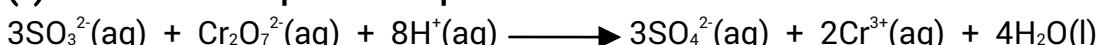
The pale green to yellow (brown) colour change of Fe^{2+} to Fe^{3+} is not visible against the marked colour change of orange to green (Cr^{3+}). This reaction can be used in the titration of iron (II) ion using diphenyl ammine indicator.



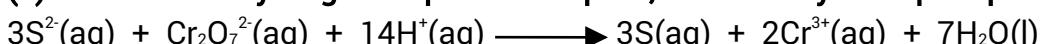
(b) Liberation of iodine from acidified potassium iodide.



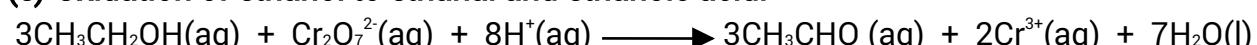
(c) Oxidation of sulphite to sulphate.



(d) Oxidation of hydrogen sulphite to sulphur, which is a yellow precipitate.



(e) Oxidation of ethanol to ethanal and ethanoic acid.



Relationship between chromates and dichromates

Addition of an acid to a yellow solution containing CrO_4^{2-} forms orange solution of a

dichromate, $\text{Cr}_2\text{O}_7^{2-}$



Yellow Orange

Addition of an alkali solution to a solution containing a dichromate forms a chromate.

Therefore the colour of the solution changes from orange to yellow.



Orange Yellow

NB//. The above reactions show that $\text{Cr}_2\text{O}_7^{2-}$ is stable in acidic solution while CrO_4^{2-} is stable in an alkaline solution.

Double salt of chromium

A double salt is one that shows all reactions of its constituent ions in solution. E.g.

- Chromium potassium sulphate, $K_2SO_4Cr_2(SO_4)_3 \cdot 24H_2O$ which is sometime known as chrome alum.
 - Ammonium iron (II) sulphate, $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 12H_2O$

A complex salt

A complex salt is one which dissolves in water to give a complex ion and simple ion. E.g. chromium (III) chloride hexahydrate, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ dissolves in water to give $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and 3Cl^-

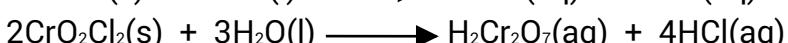


a) Chromium (VI) dichloride (chromyl chloride), CrO_2Cl_2

It is a dark red solid prepared by dissolving chromium (VI) oxide in slightly concentrated hydrochloric acid.



CrO_2Cl_2 is hydrolyzed by water to give chromic acid and hydrochloric acid.



Action of heat on dichromates

The dichromate (VI) of potassium and sodium when strongly heated produces the corresponding chromate (VI) oxide, chromium (III) oxide and oxygen gas.



For ammonium dichromate (VI), chromium (VI) oxide is left with liberation of nitrogen and steam.



Testing for chromium (III) ion, Cr³⁺

a) Addition of sodium hydroxide solution.

d) Manganese

Atomic number 25

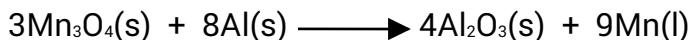
Electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

Manganese has an abnormally low melting point than any other transition metal. This is because in Mn, the 3d sub shell is half filled therefore the 3d electrons less available for delocalization in a metallic bond. This results into weak metallic bond in manganese hence low melting point.

Preparation of manganese

1) By thermite process (Goldschmidt)

Manganese (IV) oxide is heated to redness to give tri-manganese tetra-oxide, Mn_3O_4 . The oxide formed is then mixed with aluminium powder and fired by burning magnesium ribbon in contact with sodium peroxide or barium peroxide to give manganese and aluminium oxide.



2) By reduction with carbon.

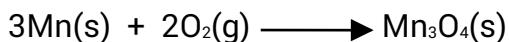
A mixture of manganese (IV) oxide, MnO_2 and carbon is heated at a very temperature in an electric furnace to form manganese which has some traces of carbon. Since reaction requires very high temperature and the manganese formed is not pure the method is not suitable for the preparation of manganese.



Chemical properties of manganese

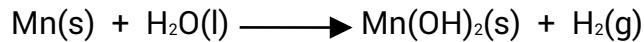
1) Reaction with air.

Pure manganese is not attacked by air at room temperature. However, it burns when strongly heated to produce tri-manganese tetra-oxide, Mn_3O_4 .



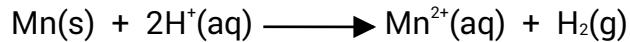
2) Reaction with water.

Pure manganese does not react with cold water but when heated it forms manganese (II) hydroxide and hydrogen gas.



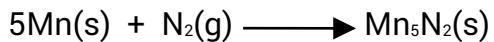
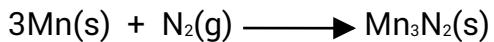
3) Reaction with acids.

Dilute hydrochloric acid and sulphuric acid both reacts with manganese to form the corresponding manganese (II) salts and hydrogen gas.



4) Reaction with non metals.

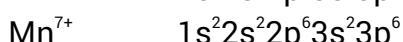
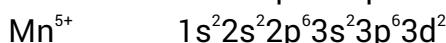
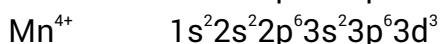
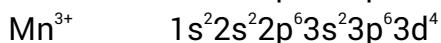
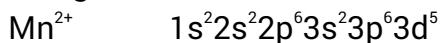
Mn reacts with nitrogen at white heat to form nitrides, Mn_5N_2 and Mn_3N_2



It also combines with chlorine carbon to form carbide, Mn_3C
Mn when heated reacts with chlorine and sulphur.

Compounds of manganese

Manganese can exist in the +2, +3, +4, +5, +6 and +7 oxidation states.



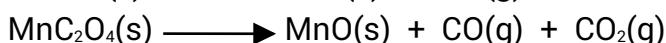
In the +2 oxidation state, the two 4s electrons are lost leading to half filled 3d-subshell which makes it posses some extra stability therefore the Mn(II) compounds are more stable than compounds of Ti, V or chromium in the +2 oxidation state.

Generally, as the oxidation number of Mn increases, the covalent nature of its compounds and acidity of its oxides also increases.

1) Manganese compounds in the +2 oxidation state.

a) Manganese (II) oxide, MnO .

MnO is a greenish powder obtained by heating manganese (II) carbonate or ethanedioate (oxalate) in the absence of air.

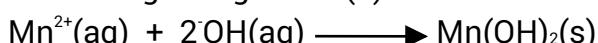


MnO is a basic oxide therefore it dissolves in acid to give manganese (II) salts.



b) Manganese (II) hydroxide.

It is obtained as a dirty white precipitate by addition of aqueous alkali to a solution containing manganese (II) salts.

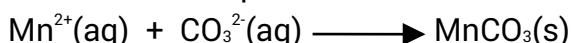


The dirty white precipitate is insoluble in excess of both sodium hydroxide solution and ammonia solution. However, the precipitate slowly turns to brown hydrated manganese (III) oxide on standing due to aerial oxidation by oxygen.



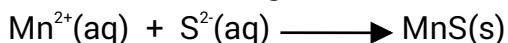
c) Manganese (II) carbonate.

It is obtained as a light yellow or reddish precipitate by addition of sodium carbonate solution to an aqueous solution of Mn^{2+}



d) Manganese (II) sulphide, MnS .

It is obtained as a brown or black precipitate when ammonium sulphide is added to a solution containing manganese (II) ions or by bubbling hydrogen sulphide into the solution containing Mn^{2+} .



The sulphide is readily soluble in dilute mineral acid.



2) Manganese compounds in the +3 oxidation state.

Manganese (III) compounds are relatively uncommon and they tend to disproportionate in aqueous solution to Mn²⁺ and brown solid of manganese (IV) oxide.



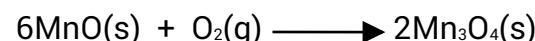
a) Manganese (III) oxide, Mn₂O₃.

This occurs as a brown solid and can be obtained by heating manganese (IV) oxide in the presence of ammonia gas.



b) Manganese (II) di-manganese (III) oxide, Mn₃O₄.

This is red oxide of manganese obtained by strongly heating any other oxide of the metal in air.



The oxide reacts with cold concentrated sulphuric acid to give manganese (II) and manganese (III) sulphates.



But in hot nitric acid, it precipitates manganese (IV) oxide due to disproportionation of Manganese (III).



3) Manganese compounds in the +4 oxidation state.

a) Manganese (IV) oxide, MnO₂ (pyrolusite).

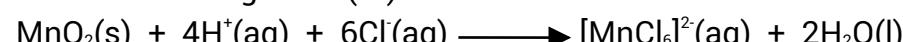
It is a black solid obtained by heating manganese (II) nitrate.



MnO₂ is not affected by dilute acids and the following are some of its reactions;

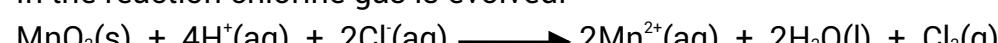
(i) Reaction with cold concentrated hydrochloric acid.

MnO₂ dissolves in the acid to form unstable octahedral complex called hexachloromanganate (IV) ion.



(ii) Reaction with warm concentrated hydrochloric acid.

In the reaction chlorine gas is evolved.



(iii) Oxidizing actions.

- It converts warm concentrated hydrochloric acid to chlorine gas.



- It oxidizes ethanedioic acid (Oxalic acid) to carbon dioxide in the presence with dilute sulphuric acid.



- It also oxidizes warm concentrated sulphuric acid to oxygen and manganese (II) sulphate



(vi) Action of heat on Manganese (IV) oxide, MnO₂.

MnO₂ liberates oxygen when strongly heated with the formation of tri-manganese tetra-oxide, Mn₃O₄.



NB//. MnO_2 is used as catalyst in the laboratory for the decomposition of both potassium chlorate (V) and hydrogen peroxide to produce oxygen gas.

4) Manganese compounds in the +5 oxidation state.

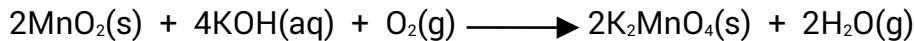
These compounds are of little importance. In solution it exists as MnO_4^{3-} and is blue in colour.

5) Manganese compounds in the +6 oxidation state.

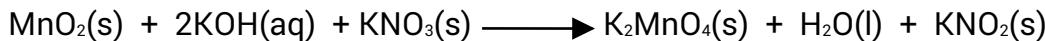
a) Potassium permanganate.

It exists as green solid prepared by the following ways;

- Heating manganese (IV) oxide and potassium hydroxide in excess oxygen.



- Heating manganese (IV) oxide, potassium hydroxide and potassium nitrate.

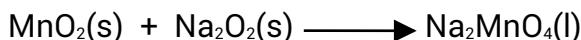


- Strongly heating potassium permanganate.

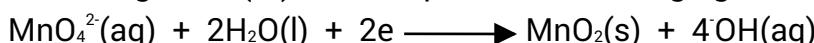


b) Sodium permanganate.

This obtained by fusing of manganese (IV) oxide with sodium peroxide.



The manganate (VI) ions are powerful oxidizing agents.



The manganates are only stable in the presence of alkali but in neutral or acid solution they disproportionate to produce manganese (VII) ions and manganese (IV) oxide. The colour of the solution changes from green to purple and a brown solid is formed.



When chlorine gas is bubbled through a solution of manganese (VI) ion, manganese (VII) ion is formed and the colour of the solution changes from green to purple.



6) Compounds of Manganese in the +7 oxidation state.

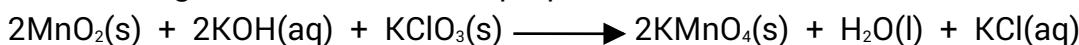
Potassium permanganate, KMnO_4

It exists as purple crystals.

Preparation of potassium permanganate

Potassium hydroxide and potassium chlorate (V) are fused in an iron (or nickel) crucible and manganese (IV) oxide is gradually stirred in with constant heating until the mass goes stiff.

The mixture is cooled, boiled with water and carbondioxide passed through the solution until all the green colour turned to purple.



Carbondioxide serves as an acid by converting any remaining manganate (VI) to manganate (VII) by disproportionation.



NB//. On a large scale, KMnO_4 is obtained by dissolving K_2MnO_4 in water which then disproportionates to form KMnO_4 and MnO_2 which is filtered out. The solution is

crystallizes to obtain KMnO_4 .

Properties of potassium permanganate

1) Action of heat.

When strongly heated it decomposes to manganate (VI), manganese (IV) oxide and oxygen gas.



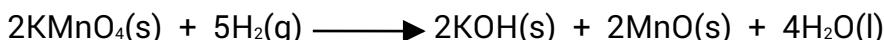
2) Reaction with concentrated hydrochloric acid.

The solid KMnO_4 oxidizes the acid to chlorine.



3) Reaction with hydrogen gas.

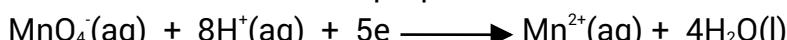
If heated in hydrogen gas, potassium hydroxide and manganese (II) oxide are formed.



Potassium permanganate is a strong oxidizing agent in solution. However, the oxidizing property is dependent on the medium in which it is used.

(i) In strongly acidic medium.

It is reduced to Mn^{2+} . The purple colour of the solution turns to pink or colourless.



(ii) In slightly acidic solution.

The purple colour of manganate (VII) changes to the brown solid of manganese (IV) oxide.



This reaction is catalyzed by light, which is why the reagent is normally kept in brown glass bottles.

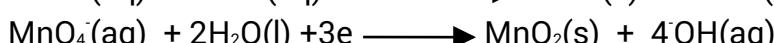
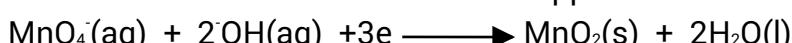
(iii) In strongly alkaline solution.

The purple colour of manganate (VII) solution changes to green due to the formation manganate (VI).



(iv) In weakly alkaline or neutral medium.

The MnO_4^- is reduced to MnO_2 which appears as brown solid.



Examples of oxidations involving potassium permanganate (VII) in strongly acidic solutions;



NB// the oxidation of iodide ion by manganate (VII) in neutral or fairly alkaline condition is given by the equation below.



Potassium permanganate is not a good primary standard compared to potassium dichromate. This is because a solution of KMnO_4 undergoes slow decomposition when exposed to light to produce manganese (IV) oxide, MnO_2 , oxygen gas and manganese (VI) ions therefore it is not suitable to be used as a primary standard. Although it is not primary standard, it is used in redox titrations because;

- (i) It acts as its own indicator.
- (ii) It can oxidize a fairly wide range of substances.

NB//. On a large scale it is used in the preparation of carboxylic acids, ketones and diols.

Practical applications of potassium permanganate in volumetric analysis

It is used to determine the percentage of iron in an ore of iron.

Procedure

A known mass of the iron ore is crushed and boiled with excess dilute sulphuric acid until no further reaction takes place.

The hot solution is cooled and filtered directly into a volumetric flask.

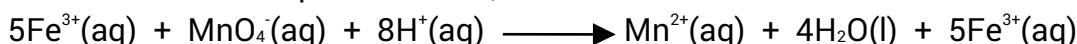
The residue in the filter paper is thoroughly washed with distilled water and the solution in the volumetric flask is made to the mark with distilled water.

A known volume of this solution is then pipetted into a conical flask, zinc dust added and it is boiled for about 10 minutes. This is to reduce Fe^{3+} to Fe^{2+}

The solution is cooled and titrated with a standard solution of acidified potassium permanganate from a burette.

NB//. The KMnO_4 solution is first acidified using dilute sulphuric acid.

From the reaction equation below;

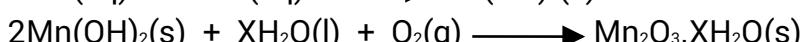
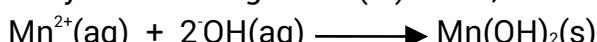


The percentage of iron in the ore can be calculated.

Test for manganese (II) ions, Mn^{2+} .

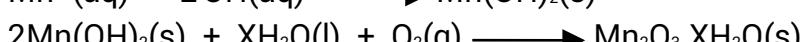
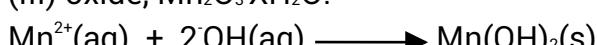
a) Addition sodium hydroxide solution.

A dirty white precipitate of manganese (II) hydroxide is formed insoluble in excess sodium hydroxide solution. The precipitate turns brown on standing due to the formation of hydrated manganese (III) oxide, $\text{Mn}_2\text{O}_3 \cdot \text{XH}_2\text{O}$.



b) Addition of ammonia solution.

A dirty white precipitate manganese (II) hydroxide which does not dissolve in excess ammonia solution and turns brown on standing due to oxidation to hydrated manganese (III) oxide, $\text{Mn}_2\text{O}_3 \cdot \text{XH}_2\text{O}$.



c) Addition of sodium bismuthate, NaBiO₃.

This reagent is used to confirm the presence of Mn²⁺.

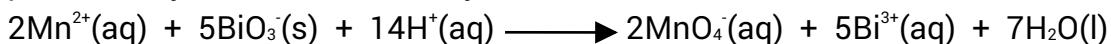
It can be used in solution or solid form and in order to get a proper observation, very small quantity must be used.

Procedure;

A little concentrated nitric acid is added to the solution containing Mn²⁺ ions followed by few grains of solid Bismuthate and the mixture warmed

Observation;

The solution immediately turns purple due to the formation of MnO₄⁻. The MnO₄⁻ is produced by oxidation of Mn²⁺ by Bismuthate ions.



d) Test with lead (IV) oxide, PbO₂.

It gives similar observation as bismuthate when added to Mn²⁺ ions in solution.

Procedure;

Add little concentrated nitric acid to the test solution followed by few grains of PbO₂ and warm the solution mixture.

Observation;

The solution turns purple due to the oxidation of Mn²⁺ to MnO₄⁻ by PbO₂.



e) Iron

Atomic number 26

Electronic configuration: 1s²2s²2p⁶3s²3p⁶3d⁶4s²

The main ores of iron are;

- (i) Haematite, Fe₂O₃.
- (ii) Magnetite, Fe₃O₄.
- (iii) Siderite (spathic iron), FeCO₃.
- (iv) Iron pyrite, FeS₂.

Extraction of iron

The raw materials used in the extraction of iron are iron ore, limestone, and coke.

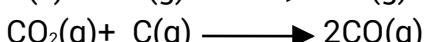
If iron pyrite is used, it is first converted to iron (III) oxide (haematite) by strongly heating the iron pyrite.



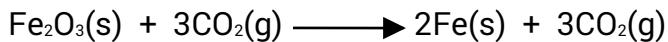
Stages in the extraction

The haematite, limestone and coke are added to the blast furnace from the top.

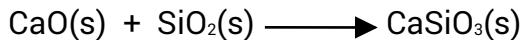
Hot air at 1600°C is fed from the bottom of the furnace which burns with the coke to form carbondioxide. The carbondioxide is reduced to carbonmonoxide by the unburnt coke.



At 700°C, haematite is reduced by the carbonmonoxide to spongy iron.



At 800°C, limestone is decomposed to calcium oxide which then reacts with sandy impurities like silica form slag (calcium silicate), CaSiO_3 .



The molten slag trickles down the furnace and floats on top of molten iron thus preventing the oxidation of iron by hot air.

The iron is removed and waste gas that includes CO_2 , CO , H_2 and N_2 are removed and burnt to produce hot air.

The iron formed is called **pig or cast iron**. It is spongy and brittle because it contains a lot of Impurities such as manganese, carbon, silicon. The pig or cast iron can be used for the following purposes;

For making of drainage pipes, street lamp standards, railway lines, gas stoves, and engine blocks.

Wrought iron

It is the purest form of iron obtained by oxidizing the impurities in pig or cast iron in a furnace lined with haematite. The haematite oxidizes carbon to carbonmonoxide and other impurities such as manganese, carbon silicon are oxidized and remains as slag. Wrought iron is ductile and malleable. Therefore it can be used for making iron sheets, chains, nails, coffins, etc.

Steel

It is an alloy of carbon and iron with a controlled amount of carbon. Addition of metals such as manganese, nickel, and chromium to steel forms a special steel called stainless steel.

Stainless steel is resistant to corrosion therefore it is used for making of cutleries.

Invar

This alloy of iron contains only nickel. It is resistant to thermal expansion hence used for making of watches.

Properties of iron

It is a grey solid when pure with a melting point of about 1800K. Its chemical properties are as follows;

1) Reaction with air/oxygen.

When heated it combines with oxygen to give iron (II) iron (III) oxide (tri ferric terraoxide)
 $3\text{Fe}(\text{s}) + 2\text{O}_2(\text{g}) \longrightarrow \text{Fe}_3\text{O}_4(\text{s})$

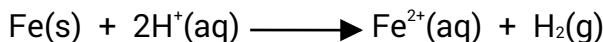
2) Reaction with water.

Iron does not react with cold water but on heating it reacts with steam to form iron (II) iron (III) oxide and hydrogen gas is liberated.

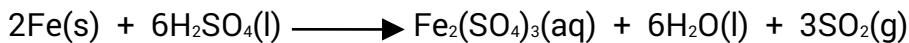


3) Reaction with acids.

It liberates hydrogen gas from both dilute sulphuric acid and hydrochloric acid and the corresponding iron (II) salts are formed.



But with concentrated sulphuric acid, it reacts when heated to form iron (III) sulphate, sulphur dioxide and water.



Concentrated nitric acid does not react with iron and instead it renders it passive due to the formation of a thin layer of iron (III) oxide.

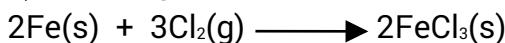
It does not react with concentrated hydrochloric acid because concentrated hydrochloric acid is not an oxidizing agent.

NB// iron precipitates copper from solution of its salts because of its comparatively strong electropositive character.

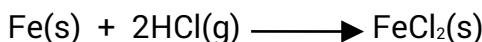


4) Reaction with non metals.

a) **Halogens.** It reacts with chlorine when heated to form iron (III) chloride.

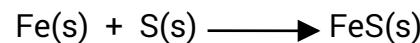


But when hydrogen chloride gas is used, iron (II) chloride is instead formed.



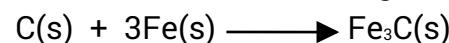
b) **Sulphur.**

It combines with sulphur when heated to form a black solid of iron (II) sulphide.



c) **Carbon.**

It forms iron carbide at high temperature.



Rusting of iron

This is the slow conversion of iron to hydrated iron (III) oxide in the presence of water, oxygen and impurities.

The process of rusting is electrochemical in nature in that it requires an electrolyte obtained by the dissolution of acidic gases found in the atmosphere in water.

Homogeneous iron with uniform surface does not rust.

Rusting results from the presence of anodic and cathodic points on the surface of the iron. These points are caused by lack of uniformity on the surface of the metal and also due to the presence of stress and impurities on the surface.

Anodic points are areas of high electrode potential and cathodic points are areas of low electrode potential. When this condition exists in the presence of a suitable condition a short circuited cell is created.

Mechanism of rusting

At the anodic points (areas of high electrode potential), the iron dissolves to form iron (II)

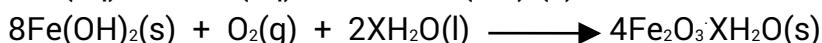
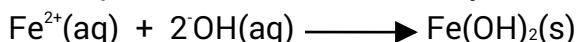
ions, Fe^{2+} and electrons. The Fe^{2+} and electrons travel along surface of the metal to the cathodic points (areas of low electrode potential)



At the cathodic points, water in presence of oxygen gains electrons from the anode points to form the hydroxyl ions.

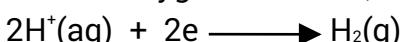


The hydroxyl ions then combine with the Fe^{2+} to iron (II) hydroxide which undergoes atmospheric oxidation to form hydrated iron (III) oxide, $\text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ which is rust.



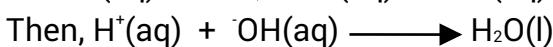
NB//.

- If oxygen is absent, the reaction below takes place.



The hydrogen gas produced clings at the surface of the metal polarizing the cell hence rusting is prevented.

- Carbon dioxide accelerates the process of rusting by making the solution acidic hence facilitating formation of Fe^{2+} ions.
- The presence of electrolyte like sodium chloride increases the rate of rusting by making water more conducting due to the increase in the concentration of the conducting ions.
- Addition of sodium hydroxide solution retards rusting by removing hydrogen ions hence the conducting particle decreases. I.e.



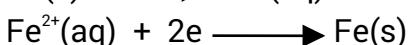
Methods of prevention of rusting

Various methods are used to provide a protective coating to iron metal in order to exclude oxygen and water from coming into contact with the iron metal. These include;

- (i) Painting.
- (ii) Greasing or oiling.
- (iii) Electroplating.

This is the process by which iron or steel objects are coated with metal higher than iron in the electrochemical series. This is done by dipping iron or steel object into a bath of the molten metal. For example galvanization and tin plating of the iron object.

- Galvanized iron or steel is the iron or steel coated with zinc metal. Galvanized iron resists rusting even if the zinc coating peels off or scratched. This is because zinc is more electropositive than iron and therefore it becomes anodic with respect to iron as given by the equations below.



And the iron becomes cathodic with respect to zinc by accepting the electrons to form iron metal. A thin layer of zinc carbonate is formed on the zinc thereby protecting it from rusting.

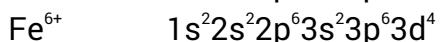
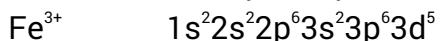
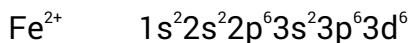
- Tin plated cannot resist rusting because tin is less electropositive than iron hence

when the tin layer is scratched, the iron becomes anodic with respect to tin therefore it corrodes faster than it would if tin were not present.

- Cathodic protection. This is the process of connecting an underground iron pipe at intervals to stripe of a more electropositive metal such as zinc, magnesium, and aluminium. The more reactive metal corrodes whereas iron does not. This results into the formation of hydrogen gas which prevents rusting by polarizing the cell.

Compounds of iron

The common oxidation states are +2, +3 and +6



The most stable oxidation state of iron is +3 due to the half filled 3d subshell.

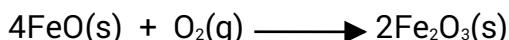
1) Compounds of iron in the +2 oxidation state.

a) Iron (II) oxide, FeO .

It is a black basic oxide made by heating ferrous oxalate (iron (II) oxalate), FeC_2O_4 in the absence of air.



When exposed to air, it is rapidly oxidized to iron (III) oxide

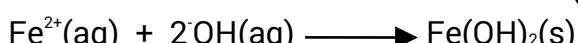


FeO dissolves in dilute acids to form the corresponding iron (II) salts which are readily oxidized to iron (III) salt on standing in air.



b) Iron (II) hydroxide (hydrated iron (II) oxide).

It is dark gelatinous green precipitate precipitated by the action of aqueous alkali or ammonia solution on a solution of iron (II) salt.

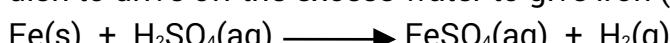


The precipitate rapidly turns brown on exposure to air by oxidation to iron (III) hydroxide.

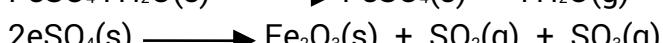


c) Iron (II) sulphate heptahydrate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

They exist as pale green crystals and are made by warming iron filings with dilute sulphuric acid to iron (II) sulphate solution. The solution is then boiled in an evaporating dish to drive off the excess water to give iron (II) sulphate heptahydrate.

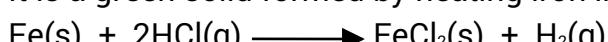


When the crystals are gently heated, water vapour is given off and on strong heating sulphur dioxide; white fumes of sulphur trioxide and iron (III) oxide are formed.



d) Iron (II) chloride.

It is a green solid formed by heating iron in a current of dry hydrogen chloride gas.



e) Ammonium iron (II) sulphate, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$.

It is a double salt deposited as pale green solid. It is salt is made by mixing hot equimolar

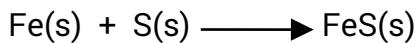
quantities of ammonium sulphate and iron (II) sulphate. This salt is quite pure and has two advantages over iron (II) sulphate.

- (i) It is not efflorescent.
- (ii) It is resistant to atmospheric oxidation.

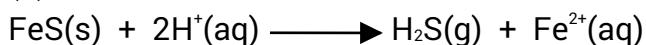
Basing on the above reasons, the salt is used as a redox standard in moderately precise volumetric analysis.

f) Iron (II) sulphide, FeS.

It is a black solid manufactured by heating equimolar quantities of iron fillings and sulphur



It reacts with concentrated hydrochloric acid to produce hydrogen sulphide gas and iron (II) chloride.



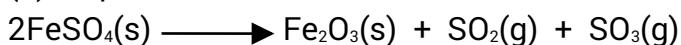
2) Compounds of iron in the +3 oxidation state.

In a strongly acidic solution, it exists as a pale purple ion $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$. The hydrated Fe^{3+} is acidic due to the hydrolysis reaction.

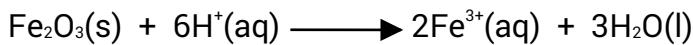


a) Iron (III) oxide, Fe_2O_3 .

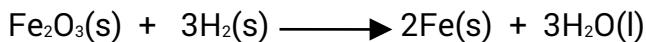
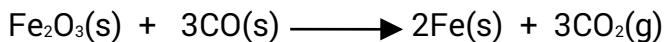
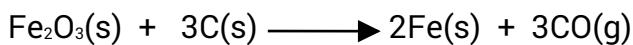
Fe_2O_3 is reddish brown in colour it occurs as haematite and can be made by heating iron (II) sulphate.



It is a basic oxide therefore dissolves in dilute acids forming the corresponding iron (III) salts.



Fe_2O_3 is reduced to iron when strongly heated with carbon or in current of carbon monoxide or hydrogen gas.

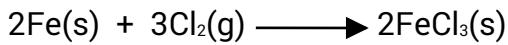


When Fe_2O_3 is heated strongly (1600K), it forms a black oxide of tri-iron tetraxoxide, Fe_3O_4 .



b) Iron (III) chloride, FeCl_3 .

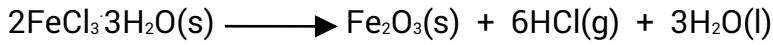
This is reddish brown when hydrated and black when anhydrous. The anhydrous FeCl_3 is made by passing dry chlorine gas over heated iron.



FeCl_3 dimerises when in the vapour phase.



FeCl_3 is covalent in character and the anhydrous form cannot be prepared by heating the hydrated iron (III) chloride because it undergoes hydrolysis leading to the formation of hydrogen chloride gas and iron (III) oxide.



When FeCl_3 is dissolved in water, it forms a yellow solution containing hydrated iron (III) ions.



The hydrated iron (III) undergoes hydrolysis releasing hydroxonium ions in solution

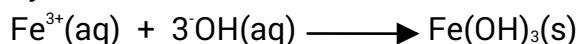
thereby making the solution acidic i.e. pH of solution is less than 7.



The hydrolysis is due to the small size and high charge density of Fe^{3+} .

c) Iron (III) hydroxide.

It is precipitated as a brown yellowish precipitate by addition of aqueous sodium hydroxide solution or ammonia solution to a solution of iron (III) salt.



When heated, Fe_2O_3 is formed.

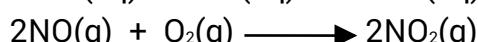


NB//. Fe_2O_3 is amphoteric like Cr_2O_3 and Al_2O_3 .

Examples of reactions leading to the conversion of iron (II) to iron (III)

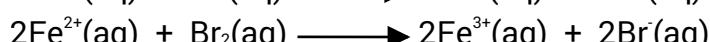
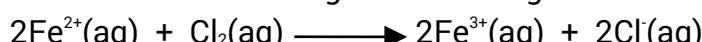
a) Reaction with concentrated nitric acid.

On heating the mixture, brown fumes of nitrogen dioxide gas is evolved.

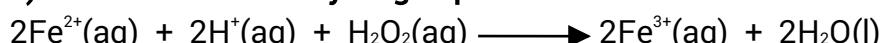


b) Reaction with chlorine or bromine water.

The colour of the halogen is discharged.



c) Reaction with hydrogen peroxide solution.



d) Reaction with acidified potassium manganate (VII) solution.

The purple colour of the manganate (VII) solution turns to colourless due to the formation of manganese (II) ions.



e) Reaction with acidified potassium dichromate (VI) solution.

The golden yellow dichromate (VI) solution turns dark green due to the formation of chromium (III).



Examples of reactions leading to the conversion of iron (III) to iron (II)

a) Reaction with zinc in presence.

The reaction takes place in the presence of dilute sulphuric acid or hydrochloric acid.



b) Reaction with hydrogen sulphide.

In the reaction, sulphur is precipitated as a yellow solid.

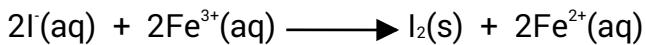


c) Reaction with sulphur dioxide dissolved in water.



d) Reaction with acidified potassium iodide solution.

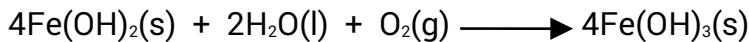
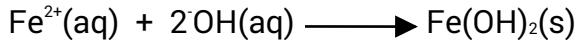
A brown solution of iodine is produced.



Test for iron (II) salts in solution

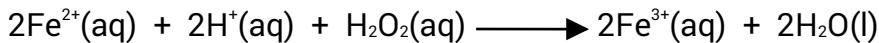
a) Addition of sodium hydroxide solution or ammonia solution.

A dirty green precipitate of iron (II) hydroxide is formed and it is insoluble in excess of the reagent. The precipitate turns brown on standing due to oxidation to iron (III) hydroxide.



b) Addition of hydrogen peroxide.

The colour of the solution turns from pale green to brown due to oxidation of Fe^{2+} to Fe^{3+} .



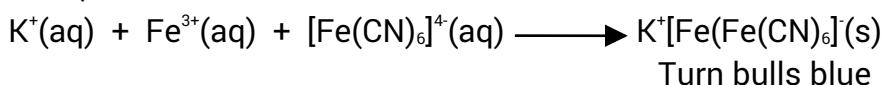
c) Addition of potassium ferricyanate (potassiumhexacyanoferrate(III) solution), $[\text{Fe}(\text{CN})_6]^{4-}$.



This reagent gives a dark blue precipitate of turn bulls' blue which is chemically the same as Prussian blue.



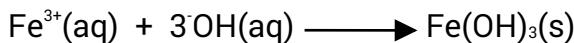
Then,



Test for iron (III) salts in solution

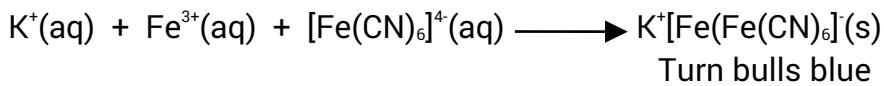
a) Addition of sodium hydroxide solution or ammonia solution.

A brown precipitate of iron (III) hydroxide insoluble in excess of the reagent is formed.



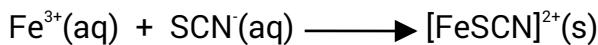
b) Addition of potassium hexacyanoferrate(II) or potassium ferrocyanide.

A dark blue precipitate or Prussian blue is formed.



c) Addition of potassium thiocyanate or ammonium thiocyanate.

A blood red solution is formed.



f) Cobalt

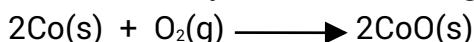
Atomic number 27

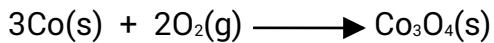
Electronic configuration: $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^7 4\text{s}^2$

Chemical reactions of cobalt

1) Reaction with oxygen.

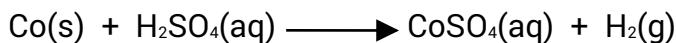
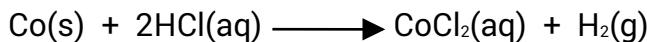
It reacts slowly when heated to give a mixture of cobalt (II) oxide and tri-cobalt tetraoxide.





2) Reaction with acids.

When heated with dilute hydrochloric acid or sulphuric acid, the corresponding cobalt (II) salt is formed.

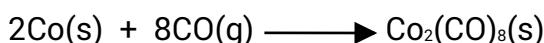


When reacted with dilute nitric acid, cobalt (II) nitrate and oxides of nitrogen are formed.

Concentrated nitric acid renders Co passive due to the formation of $\text{Co}_3\text{O}_4\text{(s)}$.

3) Reaction with carbonmonoxide.

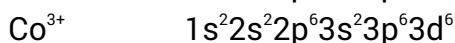
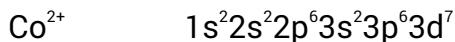
On heating under a pressure, an orange powder of cobalt carbonyl with oxidation state of zero is formed.



NB//. Cobalt does not react with alkalis, water and halogens.

Compounds of cobalt

Common oxidation states exhibited by cobalt are +2 and +3.



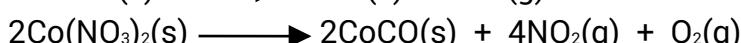
Compounds in the +2 oxidation state are the most stable while those in +3 oxidation state are uncommon except they are found in the complex ions of cobalt. The compounds in the +3 oxidation state are strong oxidizing i.e. easily changed to +2 oxidation state.

1) Cobalt (II) compounds.

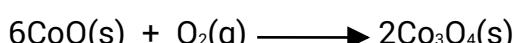
All cobalt (II) compounds in aqueous solution are pink and they exist as hydrated cobalt (II) ion i.e. $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.

a) Cobalt (II) oxide, CoO .

It is a greenish powder formed by heating cobalt (II) carbonate or nitrate in the absence of air.



In the presence of air, the oxide formed takes up oxygen forming cobalt (II)cobalt (III) oxide.

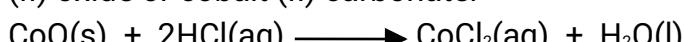


Cobalt (II) oxide is basic therefore dissolves in acids to form cobalt (II) ions.



b) Cobalt (II) chloride, CoCl_2 .

Cobalt (II) chloride is formed in solution by the action of dilute hydrochloric acid on cobalt (II) oxide or cobalt (II) carbonate.



The hydrated cobalt (II) chloride exists as red crystals while the anhydrous crystals as blue crystals.

When the hydrated $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ is strongly heated, it undergoes hydrolysis to give the metal oxide, hydrogen chloride gas and water vapour.

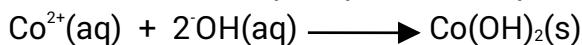


When dissolved in water, it gives a pink solution containing hydrated cobalt (II) ions which on treatment with concentrated hydrochloric acid forms blue solution due to the formation of a soluble complex called tetrachlorocobaltate (II) ions.



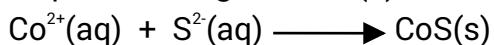
c) Cobalt (II) hydroxide, Co(OH)_2 .

It is a blue precipitate formed by addition of aqueous sodium hydroxide to cobalt (II) salt solution. The blue precipitate turns pink when left to stand in air.



d) Cobalt (II) sulphide, CuS .

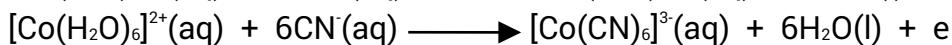
It is a black compound that does not dissolve in water. It is precipitated by the action of ammonium sulphide solution on a solution of cobalt (II) salt or by passing hydrogen sulphide through cobalt (II) salt solution.



NB//. The sulphide is not precipitated in the presence of an acid since CoS has a high solubility product value implying that sufficiently high concentration of the sulphide is required.

2) Cobalt (III) compounds.

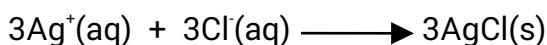
Cobalt (III) ions are powerful oxidizing agents and are only stable in the presence of stronger ligands such as cyanide ions or ammonia e.g.s of cobalt (III) complex include, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{CN})_6]^{3-}$



NB//. The isomers formed by cobalt (III) chloride with ammonia just like chromium (III) chloride has the empirical formula of $\text{CoCl}_3(\text{NH}_3)_6$. These isomers are;

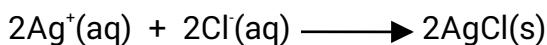
a) $[\text{Co}(\text{NH}_3)_6]^{3+}3\text{Cl}^-$.

This isomer is green in colour and has six ammonia molecules bonded to the Co^{3+} . On treatment with silver nitrate solution all the three free chloride ions are precipitated as silver chloride.



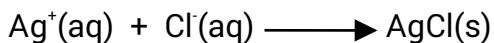
b) $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}2\text{Cl}^-$.

It is violet in colour. The isomer has two chlorides which are free therefore three ions conducting. When reacted with silver nitrate solution; two molecules of silver chloride are precipitated.



c) $[\text{Co}(\text{NH}_3)_42\text{Cl}]^+ \text{Cl}^-$.

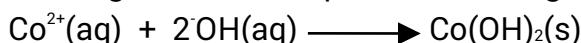
It is green isomer with two ions conducting and one free chloride ion. This means only one molecule of silver chloride is precipitated when reacted with silver nitrate solution.



Test for cobalt (II) ions in solution

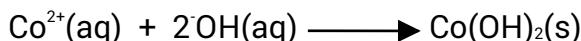
1) Addition of sodium hydroxide solution.

A blue precipitate of cobalt (II) hydroxide is formed which does not dissolve in excess of the reagent and turns pink on standing in air.

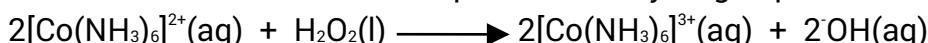


2) Addition of ammonia solution.

A green precipitate of cobalt (II) hydroxide is formed which dissolves in excess concentrated ammonia solution forming a brown solution. The brown solution turns dark brown on standing in air.

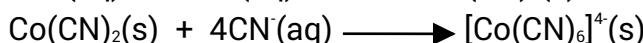
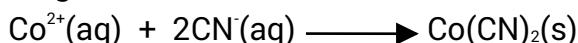


NB//. Oxidation is faster in the presence of hydrogen peroxide.

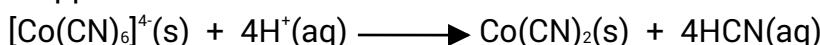


3) Addition of potassium cyanide solution (poison).

Reddish brown precipitate of cobalt (II) cyanide is formed which dissolves in excess of the reagent to form a brown solution of hexacyanocobaltate (II).

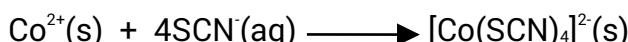


On acidification of the complex with cold dilute hydrochloric acid, the precipitate reappears.



4) Addition of ammonium thiocyanate or potassium thiocyanate.

Addition of few grains of the substance to a neutral or acid solution cobalt (II) salt results into the formation of a blue solution owing to the formation tetrathiocyanatocobaltate (II) ions.



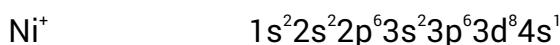
NB//. In the absence of the above test, the presence of Co^{2+} ions can be confirmed by addition of concentrated hydrochloric acid. The solution changes from pink to blue.

g) Nickel

Atomic number 28

Electronic configuration: $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^8 4\text{s}^2$

The common oxidation state exhibited by nickel is +2. Other oxidation states are +1, +3 and +4

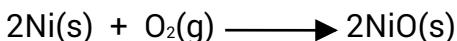


The +2 oxidation state is the most stable.

Chemical reactions of nickel

1) Reaction with air or oxygen.

It burns when heated to produce a green solid of nickel (II) oxide.



2) Reaction with water.

Nickel is not attacked by cold water. It reacts with steam at red heat forming nickel (II) oxide and hydrogen gas.



3) Reaction with acids.

It reacts less readily with dilute hydrochloric acid or sulphuric acid but rapidly with dilute nitric acid when heated to form the corresponding nickel (II) salt.



4) Reaction with chlorine.

Nickel forms nickel (II) chloride when heated in a current of dry current of chlorine.



5) Reaction with carbonmonoxide.

On heating nickel in a stream of dry carbonmonoxide, nickel carbonyl in the zero oxidation state is formed.



NB//. Nickel does not react with alkalis.

Compounds of nickel in the +2 oxidation state

a) Nickel (II) oxide, NiO.

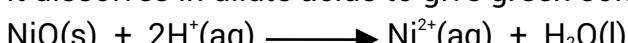
It is a green basic oxide prepared by heating nickel (II) carbonate or nickel (II) nitrate.



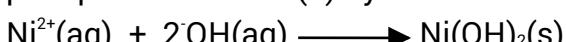
NiO is reduced to nickel metal when heated in a stream dry hydrogen gas.



It dissolves in dilute acids to give green solution containing Nickel (II) ions.



Addition of sodium hydroxide or ammonia solution to the green solution forms green precipitate of nickel (II) hydroxide.



The green precipitate is soluble in excess ammonia solution forming deep blue solution of octahedral complex called hexaaminenickel (II) ion.



b) Nickel (II) sulphate.

It exists as green crystals obtained by dissolving nickel (II) oxide in hot dilute sulphuric acid.



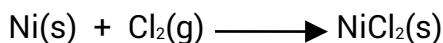
On strong heating, it decomposes completely to green solid of nickel (II) oxide and white fumes of sulphurtrioxide.



c) Nickel (II) chloride.

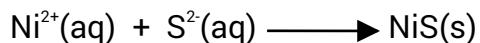
The anhydrous nickel (II) chloride is yellow in colour while the hydrated, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ is green and readily soluble in water.

The anhydrous form is prepared by heating nickel in dry chlorine gas.



d) Nickel (II) sulphide.

It is a black solid obtained by passing hydrogen sulphide through alkaline solution of nickel (II) ion.

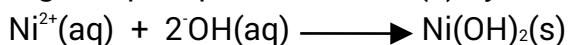


NB//. NiS does not dissolve in hydrochloric acid like CoS.

Test for nickel (II) ions in solution

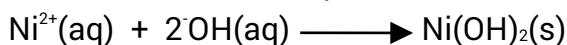
a) Addition of sodium hydroxide solution.

A green precipitate of nickel (II) hydroxide insoluble in excess of the reagent is formed.



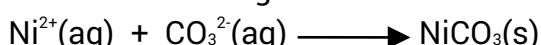
b) Addition of ammonia solution.

A green precipitate of nickel (II) hydroxide formed and it dissolves in excess ammonia solution to form a deep blue solution of hexaaminenickel (II) ion.



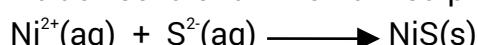
c) Addition of sodium carbonate solution.

A green precipitate of nickel (II) carbonate is formed. The precipitate does not dissolve in excess of the reagent.



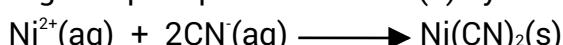
d) Addition of ammonium sulphide.

A black solid of ammonium sulphide is formed.

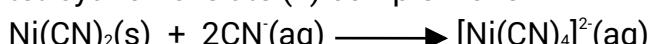


e) Addition of potassium cyanide solution (poison).

A green precipitate of nickel (II) cyanide is formed.



The precipitate dissolves in excess of the reagent giving a yellow solution of tetracyanonickelate (II) complex ions.



On addition of dilute hydrochloric acid, the complex breaks down and the green precipitate reappears.



f) Test with dimethylglyoxime.

To a solution containing Ni^{2+} , add few drops of ammonia solution to neutralize any acid present in the solution followed by addition of dimethylglyoxime.

A red precipitate is formed which confirms the presence of nickel (II) ion.

h) Copper

Atomic number 29

Electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

The main ores of copper are;

- (i) Copper pyrite, CuFeS_2 .
- (ii) Copper galance, Cu_2S .
- (iii) Malachite, $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$.

Extraction of copper

Copper is mainly extracted from copper pyrite. The ore is first concentrated by a process called froth floatation.

Concentration refers to the removal unwanted earthly materials from the impure ore in order to increase the amount of the ore. During the process, the impure ore is ground into fine powder and then mixed with water in a floatation tank to which a frothing agent is added.

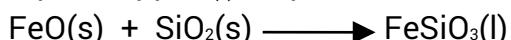
Air is blown into the mixture to produce froth. This causes the wetted earthly materials to sink to the bottom of the tank while the ore to rise and float on surface of the water.

The concentrated ore is skimmed off from the surface, dried and roasted in a supply of air to form iron (II) oxide, copper (I) sulphide and sulphur dioxide.



NB//. The sulphur dioxide formed is removed and can be converted to sulphuric acid.

The remaining mixture is heated with silica to form molten iron (II) silicate which floats on top of copper (I) sulphide and the iron (II) silicate removed as slag.



Air is then blown into the molten Cu_2S thereby oxidizing it to copper (I) oxide which reacts with the remaining copper (I) sulphide to produce an impure form of copper called blister copper and sulphur dioxide gas.



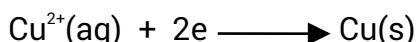
The impure copper is purified by electrolysis. During the process, the blister copper is made the anode in a solution of copper (II) sulphate acidified with dilute sulphuric acid and pure copper cathode.

The copper atoms at the anode ionize to form copper (II) ions which migrate to the cathode where they gain electrons and are deposited as brown solid. Hence the mass of the cathode increases while that of the anode decreases.

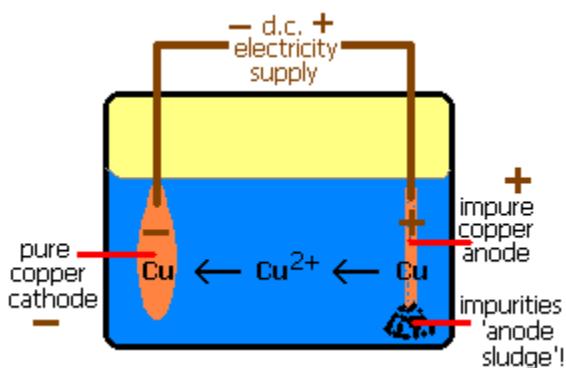
Reaction at the anode



Reaction at the cathode



Illustration

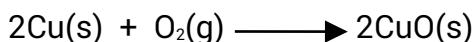


Properties of copper

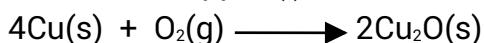
It is a reddish brown metal which is a good conductor of both heat and electricity. The following are the chemical properties of copper.

1) Reaction with air

When heated in dry air at 300°C, a black layer of copper (II) oxide is formed.



At 1000°C, copper (I) oxide is formed.



2) Reaction with acids.

It is less electropositive than hydrogen, so it cannot displace hydrogen from dilute acids or water. However, the metal reacts with concentrated oxidizing acids such as sulphuric acid and nitric acid.

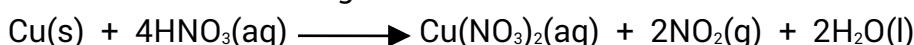
(i) Concentrated sulphuric acid.

It oxidizes copper to copper (II) sulphate and the acid is reduced to sulphur dioxide and water.



(ii) Nitric acid.

If the acid is highly concentrated, it oxidizes copper to copper (II) nitrate solution and the acid is reduced to nitrogendioxide and water.



With moderately concentrated acid, copper is oxidized to copper (II) nitrate and the acid reduced to nitrogendioxide and water.

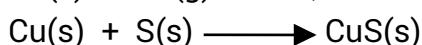
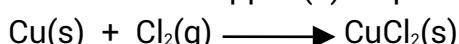


NB//. In solution, copper (I) compounds disproportionate to form stable copper (II) ions and solid copper.



3) Reaction with halogens and sulphur.

Copper reacts readily when heated with chlorine gas and sulphur to form copper (II) chloride and copper (II) sulphide respectively.



Compounds of copper

The oxidation states exhibited by copper compounds are +1, +2 and +3.



Copper (I) compounds are formed by loss of the 4s electron from the ground electronic state $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

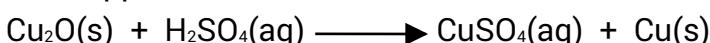
In the +1 oxidation state, copper possesses a full 3d sub shell. Therefore copper (I) compounds are diamagnetic.

Copper (II) compounds have the electronic structure; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$ in the configuration there is one unpaired electron hence making compounds of copper in +2 oxidation state paramagnetic and coloured.

1) Copper (I) compounds

a) Copper (I) oxide, Cu_2O .

It is a dark red oxide which dissolves in dilute sulphuric acid forming copper (II) sulphate and copper metal.



Cu_2O reacts with concentrated hydrochloric acid to form copper (I) chloride which forms dark brownish complex of dichlorocuprate (I) in excess of the acid.



Cu_2O is readily reduced to metallic copper when heated in a stream of dry hydrogen gas or carbon.



b) Copper (I) iodide, Cu_2I_2 .

It is white solid made by addition of potassium iodide solution to copper (II) sulphate solution.



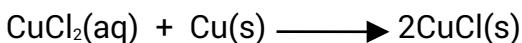
When sodium thiosulphate solution is added to the mixture, the brown colour of iodine turns colourless due to the reaction below.



NB//. The above reactions are used in volumetric analysis for quantitative determination of copper (II).

c) Copper (I) chloride, CuCl .

It is obtained by boiling a solution of copper (II) chloride with copper metal in the absence of air.



The copper (I) salt formed is only stable or held in solution in presence of concentrated hydrochloric acid due to complex formation.



Dilution of the complex causes it to break and precipitate copper (I) chloride.

Copper (I) chloride dissolves in ammonia solution forming a complex called diaminecopper (I), $[\text{Cu}(\text{NH}_3)_2]^+(\text{aq})$



This reaction resembles silver (I) chloride in that both are capable of similar complex formation.



2) Copper (II) compounds

a) Copper (II) oxide.

It is black solid prepared by thermal decomposition of copper (II) carbonate, copper (II) hydroxide or copper (II) nitrate.



The oxide is basic. It dissolves in acids e.g. hot dilute sulphuric acid forming blue solution of copper (II) sulphate.

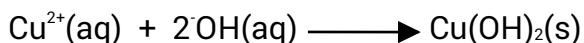


The oxide is also reduced to brown metal when heated in a stream of dry hydrogen gas or by heating with carbon or methane.



b) Copper (II) hydroxide, Cu(OH)₂.

It is prepared as a blue precipitate by the action of sodium or potassium hydroxide on a solution of copper (II) sulphate or by addition of few drops of ammonia solution to the salt.

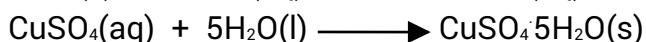


The precipitate does not dissolve in excess potassium or sodium hydroxide but soluble in excess ammonia solution forming a deep blue solution containing tetraamminecopper (II) ion.



c) Copper (II) sulphate, CuSO₄.5H₂O.

It exists as blue crystals obtained by dissolving copper (II) oxide in hot dilute sulphuric acid which crystallizes out to form copper (II) sulphate pentahydrate.



When the blue crystals are gently, white anhydrous copper (II) sulphate is formed and water vapour condenses to form water.

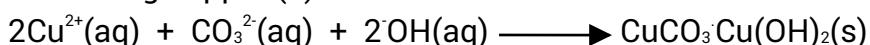


On strong heating, the white solid decomposes completely to black solid of copper (II) oxide and white fumes of sulphur trioxide.



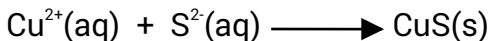
d) Copper (II) carbonate.

Copper does not form a blue carbonate but forms a basic carbonate which exists as a green solid. It is prepared by addition of sodium carbonate solution to a solution containing copper (II) ions.



e) Copper (II) sulphide, CuS.

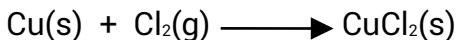
It is a black solid made by passing hydrogen sulphide through a solution of copper (II) sulphate.



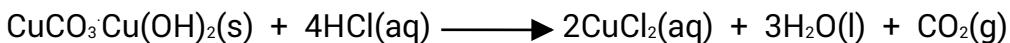
NB//. Ammonium sulphide can be used instead of hydrogen sulphide.

f) **Copper (II) chloride, CuCl₂.**

It is made by passing dry chlorine gas over heated copper.



It can also be prepared by dissolving copper (II) oxide or basic copper carbonate in hot dilute hydrochloric acid.



- At red heat, CuCl₂ dissociates into copper (I) chloride and chlorine.



- It is soluble in water forming a blue solution.



- Addition of concentrated hydrochloric acid or potassium chloride solution to copper (II) solution produces a yellow-brown complex ion of tetrachlorocuprate (II).



On dilution, the complex breaks up forming a blue solution of copper (II).



g) **Copper (II) ethanoate or acetate.**

It exists as green crystal made by treating concentrated ethanoic acid with copper (II) oxide.

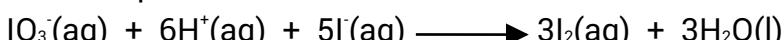


Determination of amount of copper in copper (II) iodate

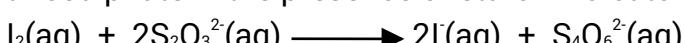
Copper (II) iodate is dissolved in water to give a solution containing copper (II) ion and iodate ion.



To the resultant solution is added excess potassium iodide solution in the presence of dilute sulphuric acid to liberate iodine solution.



The iodine solution produced is finally titrated with a standard solution of sodium thiosulphate in the presence of starch indicator.

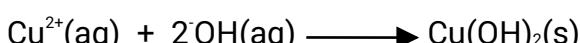


From the above equations, the amount of copper present can be determined.

Test for copper (II) ions in solution

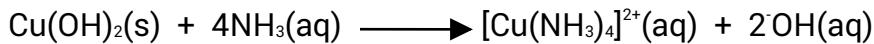
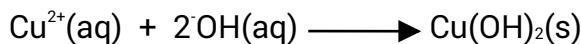
a) **Addition of sodium hydroxide solution.**

A blue precipitate of copper (II) hydroxide which does not dissolve in excess of the reagent is formed.



b) Addition of ammonia solution.

A blue precipitate of copper (II) hydroxide is formed which dissolves in excess of the reagent to form a deep blue solution of tetraaminecopper(II).



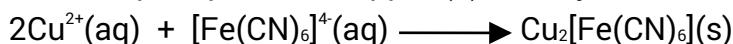
c) Addition of concentrated hydrochloric acid.

A yellowish green solution tetrachlorocuprate (II) is formed but turns blue on dilution with water.



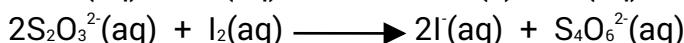
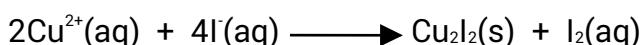
d) Addition of potassium hexacyanoferrate or potassium thiocyanate.

A brown precipitate of copper (II) hexacyanoferrate is formed.



e) Addition of potassium iodide solution.

A white precipitate in brown solution is formed but turns white when sodium thiosulphate solution is added to the mixture.



i) Zinc

Atomic number 30

Electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

The only oxidation state of zinc +2

Zinc is not regarded as a typical transition metal in that both the zinc atom and zinc ions have a full 3d sub energy level.

This results into most of its compounds being colourless and more so it has a fixed oxidation state of +2.

However, zinc resembles group (II) elements in the following ways;

- (i) It liberates hydrogen gas from dilute acids.
- (ii) It reacts with steam to form zinc oxide and hydrogen gas.
- (iii) It reacts with oxygen to form zinc (II) oxide.
- (iv) It reacts with the halogens e.g. chlorine to form zinc (II) chloride.
- (v) It reacts with sulphur to form zinc (II) sulphide.

Extraction of zinc

The ores of zinc are;

- (i) Calamine, ZnCO_3
- (ii) Zinc blende, ZnS
- (iii) Zincite, ZnO

The main ore is zinc blende.

Process of extraction

The zinc blende is ground into fine powder and to the powder is added water and oil. The mixture is agitated by blowing air through it.

The ore produced are carried to the surface of the froth after which it is removed and dried.

The concentrated ore is strongly heated in air to convert it to an oxide of zinc.



The ZnO is then mixed with coke in a blast furnace and hot air is blown through the mixture.

The ZnO is reduced to the metal which distills off and the crude zinc is purified by re-distillation.



Alternative method

The zinc oxide obtained is leached with dilute sulphuric acid and the solution treated with calcium hydroxide which precipitates out all the insoluble hydroxides.



The precipitated hydroxide is filtered off and heated with zinc powder and then acidified.

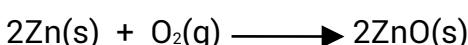
It is then electrolyzed using aluminium cathode and.

At the cathode, zinc ions migrate and are deposited.

Chemical properties of zinc

1) Reaction with air.

It burns when heated in air with a bluish flame forming zinc (II) oxide which is yellow when hot and white when cold.



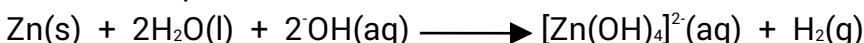
2) Reaction with water.

It does not react with cold water but when heated it reacts with steam to give hydrogen gas and zinc (II) oxide.



3) Reaction with alkali.

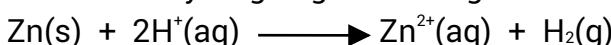
It reacts with hot aqueous sodium hydroxide liberating hydrogen gas and forming a soluble complex of zincate.



4) Reaction with acids.

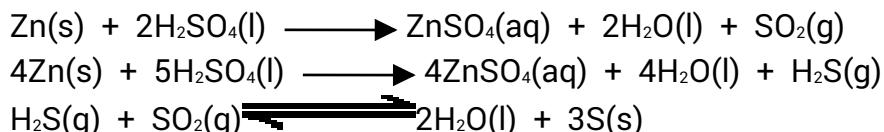
- Dilute hydrochloric acid and dilute sulphuric acid.**

It liberates hydrogen gas forming the corresponding zinc (II) salt.



- Concentrated sulphuric acid.**

It reacts only when hot to give mixed products.

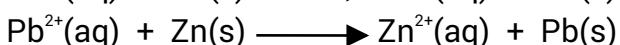


- **Nitric acid.**

Variable products are formed depending on the concentration and temperature of the acid.

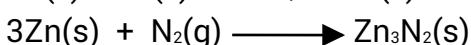
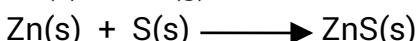
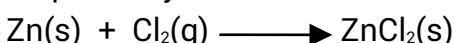
5) Displacement reactions.

Zinc is strongly electropositive hence it displaces less electropositive metals from their aqueous solutions.



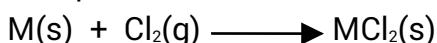
6) Reaction with chlorine, sulphur and nitrogen.

They all react when heated to form zinc (II) chloride, zinc (II) sulphide and zinc nitride respectively.



Reactions in which zinc resembles magnesium

(i) Both metals react with chlorine forming metal chlorides that are partially covalent, deliquescent and whose solutions are slightly acidic due to hydrolysis.



(ii) Both solutions containing Zn^{2+} and Mg^{2+} ions precipitates basic carbonate from sodium carbonate solution.

(iii) Both metals form nitrides on heating in nitrogen gas.

(iv) They easily form complexes.

Compounds of zinc

Zinc (II) compounds

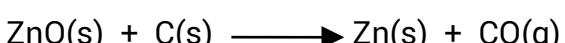
a) Zinc (II) oxide.

It exists as a white solid when cold and yellow when hot.

It is predominantly covalent and amphoteric i.e. dissolves in both acids and alkalis.

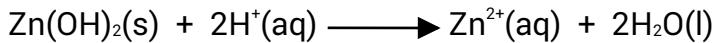


ZnO is reduced by either excess carbon or carbonmonoxide at red heat but the reduction with carbonmonoxide is not suitable since the reaction is reversible.

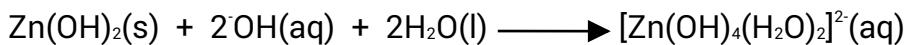


b) Zinc (II) hydroxide, Zn(OH)_2 .

It is amphoteric in nature. It reacts readily with acids forming the corresponding zinc (II) salts.



With alkalis, zincate ion is formed.

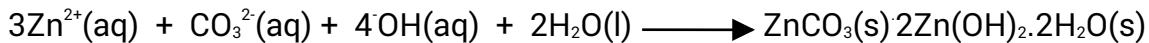


c) Zinc (II) carbonate.

It is a white precipitate formed by addition of sodium hydrogen carbonate solution to a solution containing zinc (II) ions.

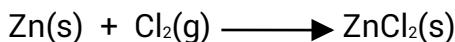


Sodium carbonate solution is not used to precipitate zinc carbonate because it is so much hydrolyzed in solution that always precipitates out basic carbonates.



d) Zinc (II) chloride.

The anhydrous is obtained by heating zinc in either chlorine gas or hydrogen chloride gas.



e) Zinc (II) sulphate.

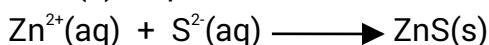
They appear as clear crystals.

On heating it decomposes to zinc oxide and white fumes of sulphurtrioxide.



f) Zinc (II) sulphide.

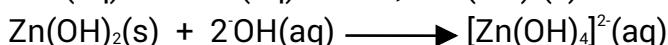
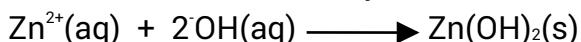
It is a white crystalline solid prepared by passing hydrogen sulphide through a solution of zinc (II) sulphate.



Test for zinc (II) ions in solution

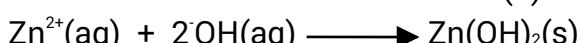
a) Addition of sodium hydroxide solution.

A white precipitate of zinc (II) hydroxide is formed and dissolves in excess forming a colourless solution terahydroxozincate (II) ion.



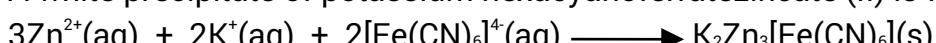
b) Addition of ammonia solution.

A white precipitate of zinc (II) hydroxide is soluble in excess of the reagent forming a colourless solution teraaminezinc (II) ion.

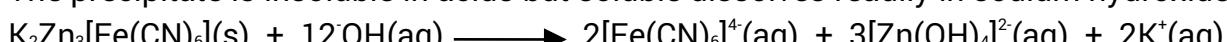


c) Addition of potassium hexacyanoferrate (II) solution.

A white precipitate of potassium hexacyanoferratezincate (II) is formed



The precipitate is insoluble in acids but soluble dissolves readily in sodium hydroxide.



This reaction can be used to distinguish zinc (II) ion from aluminium (II) ion.

d) Addition of disodium hydrogen phosphate solution.

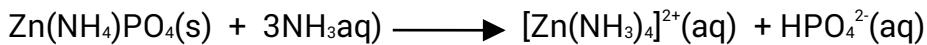
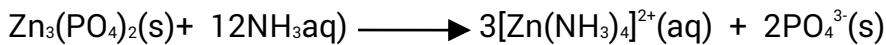
A white precipitate of zinc phosphate is formed.



In the presence of ammonium ions, a white precipitate of zinc ammonium phosphate is formed.



Both precipitates are soluble in dilute acids and aqueous ammonia.



e) Ammonium sulphide solution.

A white precipitate which dissolves in dilute hydrochloric acid is formed.

9.04 Sample questions

- 1) (a) Define the term transition element.

- (b) Distinguish between d and f-block elements.

- (c) Write the electronic configurations of the following elements:

(i) Copper

(ii) Chromium

(iii) Scandium

- (d) The atomic number, atomic radii, melting point and first ionisation energy of transition elements are shown in the table.

Element s	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radii										
Melting point										
1 st I.E										

Explain the variation in the;

- (i) Melting point of the transition elements from Sc to Zn

- (ii) 1st ionisation of transition elements from Sc to Zn.

- (e) Manganese has the highest melting point compared to the rest of the transition elements.

- (f) (i) Plot a graph of atomic radii against atomic number.

- (ii) Explain the shape of your graph.

- 2) (a) The second ionisation energy of chromium is higher than that of manganese. Explain.

- (b) (i) Define the term oxidation of an atom.

- (ii) Calculate the oxidation state of manganese and chromium in the following compounds.

- MnO_4^{2-}
- Mn_2O_3
- Cr_2O_3
- CrO_4^{2-}

- (c) Explain how the following factors influence the stability of oxidation state of an element (illustrate with examples).

- (i) Electronic configuration.
 - (ii) Heat change for the formation of ion.
 - (iii) pH of the medium
 - (iv) Electrode potential.
- (d) Explain what is meant by the term disproportionation reaction.
- 3) (a) State;
- (i) Two reasons why scandium is not regarded as a typical transition element.
 - (ii) Two reasons why zinc is sometimes not regarded as a transition element.
- (b) (i) Give a reason why zinc is sometimes regarded as a transition element.
- (ii) Mention five properties in which the chemistry of zinc resembles the chemistry of group (II) elements.
- (c) Explain how the following are brought about in transition elements:
- (i) Formation of coloured compounds.
 - (ii) Catalytic activity.
- 4) (a) (i) Explain the difference between paramagnetism and diamagnetism.
- (ii) Chromium is paramagnetic while zinc is not diamagnetic. Explain.
- (b) With reference to transition elements, explain the following terms:
- (i) Complex ion
 - (ii) Ligand
 - (iii) Bidentate ligands
 - (iv) Coordination number
 - (v) Ligand exchange in a complex.
- (c) Name the following complexes according to the I.U.P.A.C systems of naming complexes and in each case give the coordination number of the complex.
- (i) $[\text{Cr}(\text{NH}_3)_5\text{SO}_4]\text{Br}$
- (ii) $\text{Cr}(\text{H}_2\text{O})_4 \text{Cl}_2]^+\text{Cl}^- \cdot 2\text{H}_2\text{O}$
- (iii) $[\text{Cu}(\text{NH}_3)_3(\text{H}_2\text{O})\text{Br}_2]$
- (iv) $[\text{Fe}(\text{H}_2\text{O})_6]\text{SO}_4$
- 5) (a) Hydrated chromium (III) chloride, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ exists as three structural isomers.
- (i) Write down the structural formulae of the isomers.
 - (ii) State and explain the type of bonding which occurs between chromium and water.
 - (iii) Describe how the isomers in (i) can be distinguished.
 - (iv) Which one of the isomers in (i) can exist as geometrical isomers.
- (b) A chromium salt, X, contains 19.96% Cr, 39.19% NH_3 and 40.88% chlorine by mass.
- (i) Calculate the empirical formula of compound X.
 - (ii) Name the reagent required to be added to hydrated chromium (III) chloride in order to form compound X?
 - (iii) State the conditions necessary to ensure that all the ligands in X are identical.
- (c) Cobalt forms two isomeric complexes with structural formulae $[\text{Cr}(\text{H}_2\text{O})_5 \text{Br}] \text{SO}_4$ and $[\text{Cr}(\text{H}_2\text{O})_5 \text{SO}_4]\text{Br}$.
- (i) Deduce the oxidation state of cobalt in either of the complexes.
 - (ii) State what would be observed when an aqueous solution of each isomer was

separately treated with barium nitrate solution. Explain your observations.

(iii) Name the reagent that could be used to distinguish between the two isomers and state what would be observed when a solution of each isomer is treated with the reagent named.

6) (a) (i) Write the electronic configuration of the atom of titanium (atomic number =22).

(ii) State all the possible oxidation numbers exhibited by titanium in its compounds.

(iii) For each of the oxidation states you have stated in (b), write the formula of a species in which titanium shows the oxidation state.

(b) (i) Explain why compounds of Titanium in +3 oxidation state are coloured and paramagnetic while titanium compounds in +4 oxidation state are not coloured and paramagnetic.

(ii) State two applications of titanium (II) sulphate and Titanium (III) chloride solution in volumetric analysis (illustrate with equations).

(c) Write equation of reaction between the following;

(i) Titanium metal and chlorine.

(ii) Titanium (IV) chloride and water.

(iii) Titanium (IV) chloride and concentrated hydrochloric acid.

(iv) Titanium (IV) chloride and titanium metal.

7) (a) The atomic number of iron is 26.

(i) Write the electronic configuration of iron.

(ii) Give two main ores from which iron can be extracted.

(b) Describe how pig/cast iron can be obtained from one of the ores mentioned above. (Reaction equations must be written)

(c) (i) Name one alloy that is made up of iron.

(ii) Name the other component (s) present in the alloy mentioned above.

(iii) Give two important uses of the alloy in (c) (i) above.

(d) Discuss the reaction of iron metal with;

(i) Sulphuric acid

(ii) Copper (II) sulphate solution

(iii) Water

8) (a) Describe with the help of equations the mechanism through which an iron metal can acquire brown coatings on its surface under suitable conditions.

(b) State the effect of the following towards the rusting process of iron metal;.

(i) Carbondioxide

(ii) Sodium hydroxide solution

(iii) Absence of oxygen

(iv) Sodium chloride solution

(c) Explain why;

(i) Galvanized iron resists rusting even if the zinc coating peels off.

(ii) Tin plated iron cannot resist rusting if the tin coating peels off.

(d) Explain what is meant by the term cathodic protection.

9) (a) Explain why iron (III) compounds are more stable than iron (II) and iron (VI) compounds.

(b) Explain the following observations;

(i) Addition of sodium hydroxide solution to any iron (II) salt results into formation a dirty green precipitate insoluble in excess and turns to brown when left

to stand in air.

- (ii) Iron (III) chloride solution has a pH of less than 7.
- (c) (i) State two reasons why ammonium iron (II) sulphate is preferred for use as a redox standard in volumetric analysis.
(ii) Iron (II) sulphate heptahydrate was heated gently and then strongly. State what was observed and write equations of reactions that took place.
- (d) Write equation of reaction between the following substances;
- (i) Iron (III) oxide and sulphuric acid
 - (ii) Iron (II) sulphide and concentrated hydrochloric acid.
- 10) Describe how the following reagents can be used distinguish between iron (II) and iron (III) salts in solution. (illustrate with equations)
- (a) Sodium hydroxide solution
 - (b) Potassium hexacyanoferrate (III) solution
 - (c) Potassium thiocyanate solution.
- 11) State what would be observed and write equation of reaction if;
- (a) Zinc crystals are added to iron (III) chloride solution in the presence of dilute hydrochloric acid or sulphuric acid.
 - (b) Chlorine gas is bubbled through a solution of iron (II) chloride.
 - (c) Potassium iodide solution is added to iron (III) salt solution.
 - (d) Acidified potassium permanganate solution is added to iron (II) sulphate solution.
- 12) (a) Cobalt has an atomic number of 27.
- (i) Write its electronic configuration.
- (ii) Discuss the reaction of cobalt with;
- Dilute sulphuric acid
 - Dilute hydrochloric acid
 - Oxygen
- (b) Write equation for the decomposition of cobalt (II) nitrate in the absence of air.
- (c) To a solution of cobalt (II) nitrate was ammonia solution drop wise until in excess.
- (i) State what was observed.
 - (ii) Write equation (s) for the reactions that took place.
- (d) Describe how the following can be used to test for the presence of cobalt (II) ions in solution (indicate observations and relevant equations).
- (i) Potassium cyanide solution.
 - (ii) Ammonium thiocyanide solution.

13) (a) Cobalt (III) chloride has an empirical formula of $\text{CrCl}_3(\text{NH}_3)_6$.

(i) Write the three possible isomers of cobalt (III) chloride.

(ii) State two ways through which the isomers above can be differentiated.

(iii) State the observation in each case if the above techniques are employed.

(b) Write equation of reaction between the following.

(i) Cobalt (II) chloride solution and dilute hydrochloric acid

(ii) Cobalt (II) chloride solution and concentrated hydrochloric acid.

(c) Addition of ammonium sulphide solution to cobalt (II) sulphate solution in the presence of an acid does not form any precipitate but precipitate forms when there is no acid. Explain.

14) (a) Concentrated hydrochloric acid was added drop-wise until in excess to an aqueous solution of cobalt (II) chloride.

(i) State what was observed.

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

(b) The resultant solution in (a) was diluted.

(i) State what was observed.

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

(c) A solution of cobalt (II) chloride was reacted with aqueous ammonia and ammonium chloride and a current of air was passed through the mixture. State what was observed and explain the observation.

15) A solution of cobalt (II) chloride was reacted with ammonia and ammonium chloride and a current of air was blown through the mixture. A red compound, Y, was produced which contained the following composition by mass; cobalt 23.6%, ammonia 33.9% and chlorine 42.5%.

(a) (i) Calculate the empirical formula of Y.

(ii) Determine the molecular formula of Y. (RFM of Y = 250.4)

(b) A sample of Y of mass 1.00g was reacted with silver nitrate solution and 1.15g of silver chloride was formed.

(i) Calculate the number of moles of free chloride ions per mole of Y. ($\text{Ag} = 108$, $\text{Cl} = 35.5$)

(ii) Hence deduce the formula of the complex ion in Y.

(c) Explain the role of air, the ammonia and the ammonium chloride in the formation of Y giving equations where appropriate.

16) When a pale green solid P was heated, it decomposed to a green solid Q and a gas that turned lime water milky was evolved. Q dissolved in dilute nitric acid to give a green solution R. on addition of sodium hydroxide solution to R, a green precipitate S, insoluble in excess alkali was obtained. S dissolved in aqueous ammonia to give a purple blue solution.

(a) Identify compounds P, Q, S and solution R.

(b) Write equation for the reaction between;

(i) Q and nitric acid

(ii) R and sodium hydroxide

(iii) S and aqueous ammonia

17) (a) (i) State the most common oxidation state exhibited by nickel.

(ii) Write the formulae of two species in which nickel shows the oxidation state you have stated in (a) (i).

(b) State three properties of nickel which are typical of transition metal.

(c) Compare the reactions of cobalt and nickel with the following (include equations where applicable)

(i) Carbonmonoxide

(ii) Chlorine

(iii) Dilute acids

18) (a) State two properties in which zinc shows similarity to group (II) elements.

(b) Discuss the reactions in which zinc resembles magnesium and include equations for the reactions.

(c) Compare the chemistry of zinc and magnesium with respect to the following properties.

(i) Thermal stability

(ii) Complex formation

(d) Beryllium and zinc can both react with sodium hydroxide solution. Other group (II) elements do not. Write equations for reactions of beryllium and zinc with sodium hydroxide solution.

- 19) (a) Name and write the formula of two ores from which zinc can be extracted.
- (b) With the help of equations, describe how zinc can be extracted from one of the ores mentioned in (a) above.
- (c) Write equation of reaction between zinc and the following;
- (i) Steam
 - (ii) Nitrogen
- 20) (a) Discuss the reactions of zinc with;
- (i) Dilute acids
 - (ii) Air
 - (iii) Copper (II) nitrate solution
 - (iv) Sodium hydroxide
 - (v) Concentrated sulphuric acid
- (b) State three ways in which the chemistry of zinc is similar to that of magnesium.
- (c) (i) State what is observed when dilute aqueous ammonia is added drop wise to a solution of zinc (II) chloride.
- (ii) Write equation (s) for the reactions that took place in (c) (i).
- 21) (a) (i) What is meant by the term primary standard?
- (ii) Explain why potassium permanganate is not a good primary standard while potassium dichromate is a good primary standard?
- (b) Give two reasons why acidified potassium permanganate is used in redox titrations despite the fact that it is not a good primary standard.
- (c) Describe in details how a given amount of pure iron can be determined in an ore of iron. (Use relevant equations)
- (d) State what is observed and equations for reactions if aqueous solution of manganese (II) salt is separately treated with the reagents below.
- i) Sodium hydroxide solution.
 - ii) Ammonia solution.
 - iii) Conc. nitric acid and solid sodium bismuthate.
 - iv) Concentrated Nitric acid and solid lead (IV) oxide.
- 22) Manganese has an atomic number of 25
- (a) (i) Write the electronic configuration for the element.
- (ii) State the different oxidation states exhibited by manganese and in each case give an example of the compound in the different oxidation states.
- (iii) Apart from variable oxidation states, give three reasons that enable manganese to be classified as a transition element.
- (b) Describe briefly how manganese is manufactured using the thermitite process.
- (c) Discuss the reaction of the manganese with ,

- (i) Water.
(ii) Dilute acids.
- (d) How does the compound of manganese in +7 oxidation state differ from those in the +3 oxidation state?
- 23) (a) Write equation for the decomposition of Mn^{+3} in aqueous solutions and state clearly the observations made.
- (b) State what is observed and write equation for the reaction if either manganese (II) carbonate or oxalate is heated and the resultant product dissolved in an acid.
- (c) (i) write an equation to show how manganese (IV)oxide can be prepared in the laboratory.
(ii) Discuss the reactions of manganese (IV) oxide with hydrochloric acid under suitable conditions of the acid.
(iii) Write separate equation for the reaction in which manganese (IV) oxide behaves as an oxidizing agent with concentrated sulphuric acid and oxalate.
- (d) (i) Describe the nature and how potassium manganate(vi) can be obtained in the laboratory.
(ii) Manganate (VI) is known to exist as a powerful oxidizing agent.
 - Write equation in which it behaves as an oxidizing agent.
 - Define the term disproportionation reaction and illustrate it using manganate(VI) in either neutral or acid solution .
(e) (i) Describe how potassium permanganate can be made in an ordinary laboratory.
(ii) Write equation for the reaction when potassium permanganate is strongly heated.
(iii) Give one reason why potassium permanganate reagent is kept in brown glass bottles.
(iv) With the help of equations discuss the behavior of potassium permanganate solutions in,
 - Strongly acidic medium.
 - Slightly acidic solution.
 - Strongly alkaline solution.
 - And slightly alkaline or neutral medium.
- 24) (a) (i) Give the formula and name any three ores of copper.
(ii) Using equations only show how pure copper meal can be extracted from one of the ores in (a) (i).
(iii) State giving examples, three properties of copper that are characteristic of transition metals.
- (b) Explain the following observations.
(i) Aqueous solution of copper (II) sulphate turns litmus paper red.
(ii) Addition of concentrated hydrochloric acid to a solution of copper (II) chloride solution turns the solution from blue to greenish yellow colour.
(c) 6.35g of copper (II) salt, $CuY \cdot nH_2O$ were dissolved and made up to 250 cm³ with water. 25.0 cm³ of the solution formed was treated with excess potassium iodide solution and the iodine liberated required 25.25 cm³ of 0.1 M sodium thiosulphate solution.
(i) Write the ionic equation of reaction of copper (II) ion with potassium iodide.
(ii) Calculate the percentage of water of crystallization copper in $CuY \cdot nH_2O$. the mass of Y is 96.
- 25) (a) (i) write an equation to show why aqueous chromium (III) chloride is

acidic.

- (ii) Explain why aqueous chromium (III) chloride is more acidic than aqueous chromium (II) chloride.
- (b) The addition of sodium hydroxide or sodium carbonate to aqueous chromium (III) chloride results in the formation of the same green precipitate.
- (i) Identify this green precipitate.
 - (ii) Write the equation (s) leading to the above observation.
 - (iii) State the role shown by both sodium hydroxide and sodium carbonate in the formation of this green precipitate.
 - (iv) Identify the gas evolved when carbonate ions react with aqueous chromium (III) ions and write an equation for the reaction occurring.
- (c) State the reagents which could be used to convert aqueous chromium (III) ions into chromate (VI) ions and write the equation of reaction.
- 26) (a) The two common oxidation states exhibited by copper are +1 and +2.
- (i) Write the electronic configuration of copper in the two oxidation states.
 - (ii) Give a reason why compounds of copper in the +1 oxidation state are neither paramagnetic nor coloured while those in the +2 oxidation states are coloured and paramagnetic.
- (b) Dilute sulphuric acid was added to copper (I) oxide.
- (i) State what was observed.
 - (ii) Write the equation of reaction.
 - (iii) Identify the type of reaction that took place.
- (c) Explain what would be observed if;
- (i) Hydrogen gas is passed over heated copper (I) oxide.
 - (ii) Copper (II) nitrate crystals are strongly heated.
 - (iii) Potassium iodide solution is added to copper (II) sulphate solution and sodium thiosulphate solution added to the resultant mixture.
- 27) (a) Discuss the reaction of copper with the following (illustrate with equations where applicable).
- (i) Nitric acid
 - (ii) Sulphuric acid
 - (iii) Hydrochloric acid
- (b) Excess concentrated hydrochloric acid was added to copper (I) oxide drop wise until in excess.
- (i) State what was observed.
 - (ii) Write equation(s) of reaction (s) that took place.
- (c) Illustrate with equations the reaction in which the chemistry of copper (I) chloride is similar to that of silver chloride.
- 28) (a) State what would be observed and write equation of reaction which will take place if the following reagents are added drop wise to a solution of copper (II) sulphate until in excess.
- (i) Ammonia solution
 - (ii) Concentrated sodium hydroxide solution
 - (iii) Potassium hexacyanoferrate solution
- (b) Addition of iron filings to aqueous copper (II) sulphate forms a solid and a solution containing an ion which can be separated by filtration.
- (i) Identify the solid

- (ii) State the observations made and write the ionic equation for the reaction.
- (c) Sodium hydroxide solution was added drop wise until in excess to the solution having the ion in (b) above.
- (i) State what was observed
- (ii) The resultant product in (c) was heated. Write equation of reaction that took place.
- 29) (a) Describe briefly how the amount of copper in an ore of copper (II) iodate can be precisely determined in the laboratory.
- (b)
- 30)

CHAPTER TEN

QUALITATIVE INORGANIC ANALYSIS

Preliminary tests for anions

The appearance of substances

It is always advisable to take note of the physical properties of a substance. This can provide a clue about the substance and inference can be made. Thus physical properties like appearance, colour, smell or solubility in water could lead to useful inferences as described below and hence one is guided as to the possible identity of the substance.

1) Colour

a) If a compound and its aqueous solution are colourless, it probably means absence of

- transition metal ion.
- b) If the substance is a black solid, presence of an oxide or a sulphide could be inferred.
- c) If the substance is a solid, and/or its aqueous solution is coloured, probably a transition metal ion is present. The following are some typical characteristic colours of some cations.

Colour	Cation
Very dark purple	Mn (VII) as in MnO_4^-
Dark blue-green	Mn(VI)
Very pale pink, not visible in solution	Mn^{2+}
Pale blue-green	Fe^{2+}
Golden yellow or brown in solution	Fe^{3+}
Green	Ni^{2+}
Blue, blue-green or green	Cu^{2+}
Blue-green, green or pale violet	Cr^{3+}
Yellow or orange	Cr(VI) as in $\text{Cr}_2\text{O}_7^{2-}$

2) Smells

Usually on heating a sample of unknown substance or occasionally even at room temperature, the following smells may be detected.

Observation	Inference
Smell of ammonia	Ammonium salt
Smell of SO_2	Sulphite
Smell of H_2S	Sulphide

3) Solubility in water

When a solid does not dissolve in water, it is generally right to infer the presence of such compounds like CO_3^{2-} , SO_4^{2-} , OH^- or O^{2-} other than group (I) metals, Cl^- , I^- , or Br^- of lead or silver etc.

4) The action of heat

Certain compounds are thermally unstable and will therefore decompose on heating. The experimental procedure is to heat a little (say one micro-spatula end-full) of the unknown solid in a dry and hard-glass or Pyrex test tube (an ignition tube is always best; first gently and then more strongly afterwards until no further change occurs. In the majority of cases, a gas is evolved during the heating, which includes water vapour. If a gas is evolved, it must be carefully and properly identified by its smell, action on moist litmus paper, action on lime-water, action on splint and the usual confirmatory test (see under tests for gases).

Always make sure to observe the residue as well since useful information may be obtained from it. Evidence may be obtained from;

a)

Gas evolved	Inference
NH_3	From NH_4^+ salt
HCl	From hydrated Cl^- (excluding group (I) chlorides or BaCl_2)
Br_2/I_2	From Br^- or I^-
$\text{SO}_2/\text{H}_2\text{S}$	From various sulphur compounds e.g. HSO_3^- , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$ and even certain SO_4^{2-} or hydrated S^{2-}
SO_3	From SO_4^{2-} (not of group (I), calcium or barium)

NO_2 and O_2	From NO_3^- other than group (I) or NH_4^+
O_2	From nitrate of group (I) and other oxygen rich compounds like chlorates, peroxides or manganate (VII) or higher oxides
CO_2	From HCO_3^- or CO_3^{2-} and some oxalate excluding group (I) and barium carbonates
H_2O vapour	From hydrated salts or hydroxides
CH_3COCH_3	From ethanoates (the vapour has sweet smell and burns)

b) Sublimate

This may be the original substance, implying covalent character, or an ammonium salt (white sublimate). A yellow sublimate which melts easily infers sulphur.

c) Residue

In many cases this is an oxide of the metal ion present. The following are typical examples;

Observation	Inference
Yellow (hot), white (cold)	Zinc oxide (ZnO)
Brownish (hot), yellow or yellowish brown (cold)	Lead (II) oxide (PbO)
Black (hot), reddish brown (cold)	Iron (III) oxide (Fe_2O_3)
Black	Copper (II) oxide (CuO)
'charring' or uneven blackening	Presence of carbon
Dark brown	Lead (IV) oxide (PbO_2)

5) Test for gases

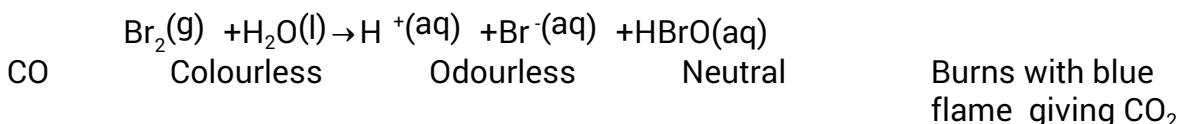
When a gas is evolved during an experiment, it MUST be tested so that it can be identified completely. It is wise to OBSERVE, SMELL and finally TEST THE GAS CHEMICALLY. This is because the human organs of sight and smell are much more sensitive than simple chemical tests. So use your nose and eyes first and foremost. When using chemical reagents like lime water, solutions of silver nitrate or potassium manganate (VII) for testing gases, remember to take small quantities of reagents because they are thus more sensitive.

Tests in which a solution changes colour, for example $\text{KMnO}_4(\text{aq})$ from purple to colourless or $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ from orange to green (test for SO_2) or $\text{KI}(\text{aq})$ from colourless to dark-brown (test for Cl_2) are best done using a small strip of "filter" paper whose tip has been dipped in the test reagent.

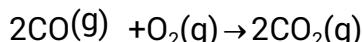
The following properties may be used to identify the gases specified.

Gas	Appearance or colour	Smell	Effect on litmus	Confirmatory test
Br_2	Deep brown (red), turns to liquid	Pungent	Bleaches	Forms a brown solution in a drop of tetrachloromethane on a glass rod

Explanation: HBrO is the bleaching agent as it is formed according to the equation

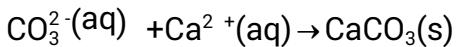
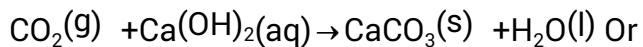


Explanation: Gas is combustible in air according to the equation



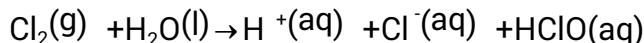
CO_2	Colourless	odourless	Acidic	Turns lime-water milky
---------------	------------	-----------	--------	------------------------

Explanation: Forms a white insoluble calcium carbonate



Cl_2	Pale green	Pungent	Acidic and bleaches	Potassium iodide solution turned brown
---------------	------------	---------	---------------------	----------------------------------------

Explanation: 1) Acids formed in aqueous solution of which HClO is the bleaching agent



2) Chlorine is more electronegative than iodine so it oxidizes iodide ion to iodine.

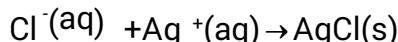
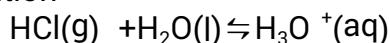
H_2	2 $\text{I}^-(\text{aq}) + \text{Cl}_2(\text{g}) \rightarrow \text{I}_2(\text{aq}) + 2\text{Cl}^-(\text{aq})$	Colourless	Odourless	Neutral	Gives a mild explosion when lit in air and ignites
--------------	---------------------------------------------------------------------------------------------------------------	------------	-----------	---------	----------------------------------------------------

Explanation: 1) Hydrogen is combustible: $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ or (g)

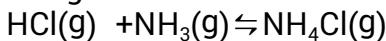
2) Explosion is mild due to the small proportion of oxygen in air

HCl	Misty or steamy fumes	Pungent and chocking	Acidic	Turns $\text{AgNO}_3(\text{aq})$ milky (same for HBr, HI). Gives dense white fumes with con NH_3 solution
--------------	--------------------------	-------------------------	--------	----------------------------------------------------------------------------------------------------------------------------------------------------

Explanation: 1) Dissociates almost completely to hydrogen and chloride ions in its aqueous solution

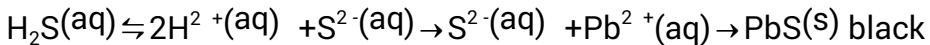


2) The gas neutralizes ammonia to give NH_4Cl , which shows as white fumes



H_2S	Colourless	Like rotten eggs	Weakly acidic	Darkens a solution containing Pb^{2+} ions
----------------------	------------	------------------	---------------	-----------------------------------------------------

Explanation: Hydrogen sulphide dissociates in solution as follows



I_2	Purple vapour, Black solid	Pungent	Bleaches slowly	Give blue colour with starch solution and gives purple colour in CCl_4 (see Br_2)
--------------	-------------------------------	---------	-----------------	------------------------------------------------------------------------------------------------------

Explanation: The blue colour formed with starch is due to adsorption of iodine onto the starch-iodine complex. The purple colour is a solution of iodine in CCl_4

N_2	Colourless	Odourless	Neutral	Very unreactive, Mg burns in it to give white ash
--------------	------------	-----------	---------	---------------------------------------------------

(Mn_3N_2) , which dissolves in cold water giving off NH_3 gas

Explanation: Nitrogen is very unreactive gas due to the stability of the $\text{N} \equiv \text{N}$ triple bond. But the bond can be broken by very high energy like from the flame of burning magnesium.

$\text{N}_2(\text{g}) + 3\text{Mg}(\text{s}) \rightarrow \text{Mn}_3\text{N}_2(\text{s})$				
$\text{Mn}_3\text{N}_2(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow 3\text{Mg}(\text{OH})_2(\text{aq}) + 2\text{NH}_3(\text{g})$				
NH_3	Colourless	Pungent(smell of goat's urine)	Alkaline	Forms dense white fumes with conc HCl and turns $\text{CuSO}_4(\text{aq})$ more intensely blue
$\text{Cu}^{2+}(\text{aq}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+}(\text{aq})$				
N_2O	Colourless	Sweetish	Neutral	Rekindles a glowing splint

Explanation: Nitrogen (IV) oxide is very readily decomposed by heat. Besides, it is an endothermic compound, thus the oxygen produced on decomposition supports combustion.

NO	Colourless but turns to brown when exposed to air	Smell of NO_2	Neutral though NO_2 is acidic	Darkens iron (II) sulphate solution
NO_2				
complex				
NO_2	Brown	Strong and unpleasant	Acidic	Darkens FeSO_4 solution; does not form a liquid or bleach litmus

Explanation: NO_2 is the anhydride of HNO_3 and HNO_2

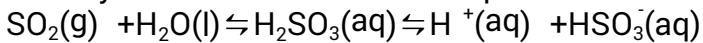
$2\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{HNO}_2(\text{aq})$				
PH_3	Colourless	Like rotten fish	Neutral	Very inf;amable, sometimes burns without ignition, giving white fumes.

Explanation: The spontaneous ignition is probably due to P_2H_4 and the white fumes are P_4O_{10}

$4\text{PH}_3(\text{g}) + 8\text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_{10}(\text{g}) + 6\text{H}_2\text{O}(\text{l})$				
O_2	Colourles	Odourles	Neutral	Rekindles a

				glowing splint
Explanation: Combustion is faster in pure oxygen compared to ordinary air.	SO ₂	Colourless	Sharp and choking smell of burning sulphur	Acidic and bleaches Decolourises KMnO ₄ (aq) or turns Cr ₂ O ₇ ²⁻ (aq)

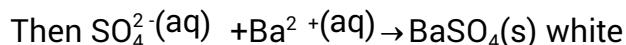
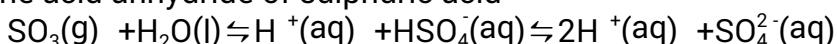
Explanation: Acidity is due to formation of sulphurous acid



Sulphurous acid is readily oxidized to sulphuric acid while Mn(VII) and Cr(VI) are reduced to Mn(II) and Cr (III) respectively

		H ₂ SO ₃ (aq) + (O) → H ₂ SO ₄ (aq)		
SO ₃	Smoky white fumes	Choking	Acidic	Turns BaCl ₂ or Ba(NO ₃) ₂ solution on glass rod milky

Explanation: This is the acid anhydride of sulphuric acid



H ₂ O vapour	Colourless condenses into colourless liquid droplets	Odourless	Neutral	Turns anhydrous copper (II) sulphate blue, turns cobalt (II) chloride paper pink
-------------------------	------------------------------------------------------	-----------	---------	----------------------------------------------------------------------------------

Explanation: Water vapour hydrates copper (II) sulphate and cobalt (II) chloride

6) Actions of acids

a) Dilute hydrochloric acid

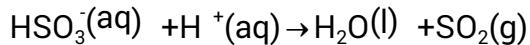
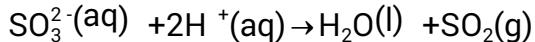
Dilute hydrochloric acid is a strong acid. It therefore liberates various acids from the anions of their salts. In two cases a volatile free acid is liberated. Viz: (H₂S and CH₃COOH). In other cases the free acid so liberated readily decomposes. Thus when dilute hydrochloric acid is added to a substance the following can be observed.

Observation

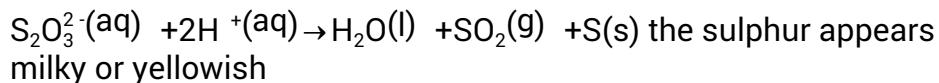


Inference

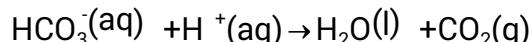
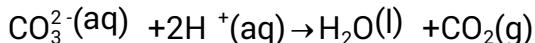
From SO₃²⁻ or HSO₃⁻



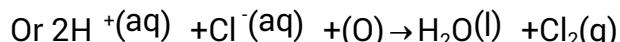
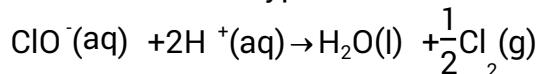
From S₂O₃²⁻ thus:



From CO₃²⁻ or HCO₃⁻, generally with effervescence



From hypochlorites, or from a strong oxidising agent acting on HCl acid. If the test is positive, repeat using dilute nitric acid, if Cl₂ is again evolved, the unknown is a hypochlorite

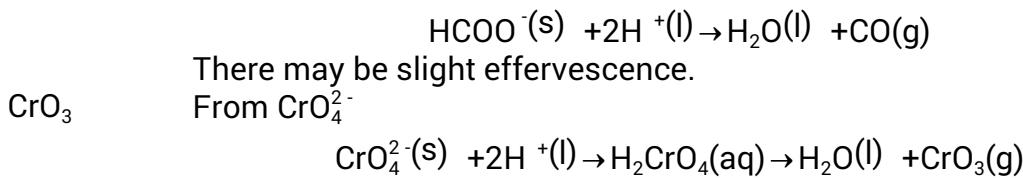


NO and NO ₂	From strong oxidizing agent From NO ₂ . A blue solution may be present.
2NO ₂ ⁻ (aq) + 2H ⁺ (aq) → H ₂ O(l) + NO(g) + NO ₂ (g)	the blue solution is due to N ₂ O ₃
H ₂ S	From S ²⁻ .
CH ₃ COOH	From ethanoates; ethanoic acid has a faint sharp smell CH ₃ COO ⁻ (aq) + H ⁺ (aq) → CH ₃ COOH(aq)

b) Concentrated sulphuric acid

Sulphuric acid is a very strong acid. As such it will add protons readily to the anions of almost all other acids thus displacing the corresponding acids from their salts. It is also a strong oxidizing and dehydrating agent. So in some cases the free acid is liberated. Expels of free acids liberated are hydrochloric acid and nitric acids. In other cases the acid is dehydrated. Examples of acid dehydrated by sulphuric acid are methanoic acid (HCOOH), ethane dioc acid (COO)₂ or C₂H₂O₄ and chromic acid, H₂CrO₄. In yet other cases oxidation occurs e.g. HBr and HI. During the actual experiment a little concentrated sulphuric acid is added to some of the unknown solid. The mixture is warmed, if necessary, but do not boil. The evolution of sulphur dioxide or sulphur trioxide indicates nothing. Otherwise the following may be observed;

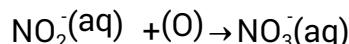
Observation	Inference
HCl	From chloride Cl ⁻ (aq) + H ₂ SO ₄ (l) → HCl(g) + HSO ₄ ⁻ (aq)
HBr and Br ₂	From bromide Br ⁻ (aq) + H ₂ SO ₄ (l) → HBr(g) + HSO ₄ ⁻ (aq) some HBr is oxidised to Br ₂ according to the equation Br ⁻ (aq) → Br ₂ (g) + 2e ⁻
HI and I ₂	From iodide I ⁻ (aq) + H ⁺ (l) → HI(g) Some HI is oxidized to I ₂ in a similar way to HBr. Iodine appears as a purple vapour and a brownish solid. The hydrogen iodide or hydriodic acid evolved is a powerful reducing agent. It reduces sulphuric acid largely to hydrogen sulphide and itself oxidized to hydrogen
HNO ₃	From nitrate: NO ₃ ⁻ (aq) + H ⁺ (l) → HNO ₃ (g) or NO ₃ ⁻ (aq) + H ₂ SO ₄ (l) → HNO ₃ (g) + HSO ₄ ⁻ (aq) The nitric acid appears as very pale brown steamy fumes. If a little of Devarda's alloy, or copper turnings, brown fumes of nitrogen (IV) oxide confirms a nitrate. Devarda's alloy is an Al/Zn/Cu alloy. The alloy or copper reduces nitric acid as shown below; Al(s) + 6HNO ₃ (l) → Al(NO ₃) ₃ (aq) + 3H ₂ O(l) + 3NO ₂ (g) Cu(s) + 4HNO ₃ (l) → Cu(NO ₃) ₂ (aq) + 2H ₂ O(l) + 2NO ₂ (g)
CO ₂ and CO	From ethanedioate C ₂ O ₄ ²⁻ (s) + 2H ⁺ (l) → (COOH) ₂ (g) → H ₂ O(l) + CO ₂ (g) + CO(g) Test for CO ₂ first because the burning of CO produces CO ₂
CO	From methanoate:



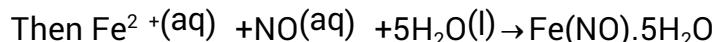
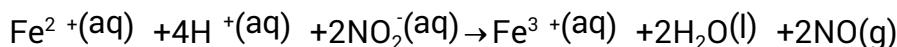
Further (confirmatory tests for anions)

a) Nitrite, NO_2^- ion

- 1) This is a reducing agent. After oxidation the solution contains nitrate ions. Oxidizing agents include aqueous manganate (VII), hydrogen peroxide or potassium dichromate solution.

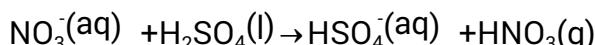


- 2) To a solution of nitrite, add freshly prepared aqueous iron (II) sulphate followed by dilute ethanoic acid. Formation of brown solution of penta aquonitrosyl iron (II) complex ion, $\text{Fe}(\text{NO})_5\text{H}_2\text{O}$ confirms a nitrite.

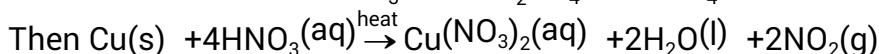
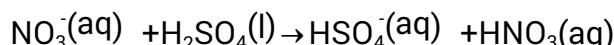


b) Nitrate ion, NO_3^-

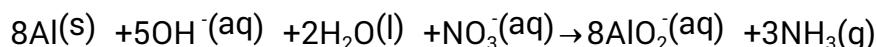
- 1) To the unknown solid, add concentrated sulphuric acid and warm if necessary. Evolution of brown fumes which condense into oily liquid at the sides of the test-tube indicates that a nitrate may be present.



- 2) To an aqueous solution of the unknown, add aqueous solution of freshly prepared iron (II) sulphate followed by a few drops of concentrated sulphuric acid added carefully down the sides of the test-tube. If a brown ring forms at the aqueous layer/acid junction, a nitrate is confirmed. (see under nitrite)
- 3) To the unknown solid, add a few pieces of copper turnings followed by about 5 cm³ of concentrated sulphuric acid and heat the mixture. Evolution of brown fumes of nitrogen dioxide confirms a nitrate.



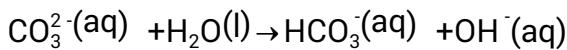
- 4) To a solution of the unknown or solid, add sodium hydroxide solution followed by zinc or aluminium powder and heat the mixture. Evolution of ammonia gas confirms a nitrate (see Devarda's alloy test described under preliminary tests for anions).



Note: This test requires exclusion of a nitrite

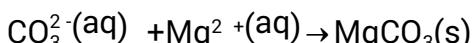
c) Carbonate, CO_3^{2-} ion

- 1) Most carbonates are insoluble in water. Hence an insoluble solid which gives carbon dioxide with effervescence on addition of dilute hydrochloric acid certainly implies presence of a carbonate ion.
- 2) If a carbonate is soluble, add a few drops of phenolphthalein solution, if a pink colouration appears it implies presence of carbonate ion because the carbonates are hydrolysed readily in water as follows:



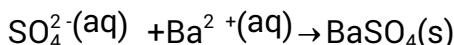
The pink colour is due to OH⁻

- 3) Add aqueous magnesium sulphate to the solution of carbonate. If a white precipitate forms, CO₃²⁻ is confirmed because magnesium carbonate is formed as follows:



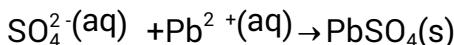
d) **Tetraoxosulphur (VI), (sulphate) ion: SO₄²⁻**

- 1) To the solution of the unknown add aqueous barium nitrate followed by excess dilute nitric acid. A white precipitate insoluble in acid confirms a sulphate.



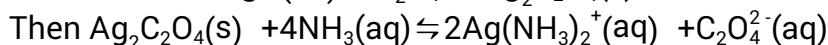
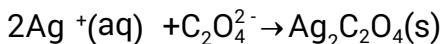
NB//. Aqueous barium chloride and dilute hydrochloric acid may be used instead of barium nitrate and dilute nitric acid respectively.

- 2) To the solution of the unknown add an aqueous solution of lead (II) ethanoate or lead (II) nitrate followed by dilute nitric acid. Formation of a white precipitate of lead (II) sulphate insoluble in nitric acid confirms a sulphate.

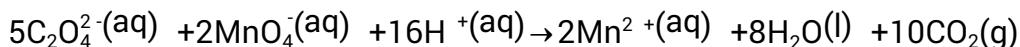


e) **Ethanedioate (oxalate), C₂O₄²⁻ ion**

- 1) To an aqueous solution of the unknown, add 2-3 drops of silver nitrate solution followed by excess aqueous ammonia. A white precipitate soluble in excess ammonia confirms ethanedioate ion.



- 2) To the solution of the unknown, add dilute sulphuric acid drop wise until the solution is acidic. Heat the mixture to about 60°C; just uncomfortable to touch. Then add drops of aqueous potassium manganate (VII) to the hot solution. If the manganate is immediately decolourised with gas bubbles, the ethanedioate is confirmed. This is because the ion reduces manganese (VII) to manganese (II) in acid medium thus;



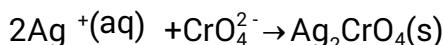
f) **Chromates (CrO₄²⁻) and dichromate (Cr₂O₇²⁻)**

Tetraoxo chromium (VI) or chromate ion is usually yellow when in neutral aqueous solution. But in the presence of strong acids the solution is orange due to formation of dichromate.

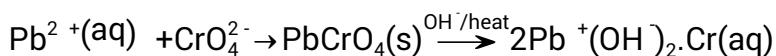
- 1) To the solution of the unknown, add aqueous barium chloride (or nitrate). A yellow precipitate soluble in dilute acid confirms CrO₄²⁻.



- 2) To the solution of the unknown, add aqueous silver nitrate followed by aqueous ammonia or nitric acid. A red precipitate soluble in both alkali and nitric acid confirms CrO₄²⁻.



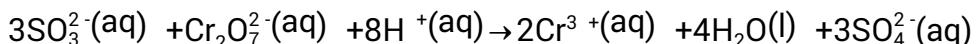
- 3) To the solution of the unknown, add aqueous lead (II) ethanoate followed by aqueous sodium hydroxide and boil. A yellow precipitate which turns red on boiling confirms chromate ion.



- 4) Dichromate ion is identified by using reducing agents in acid medium as exemplified

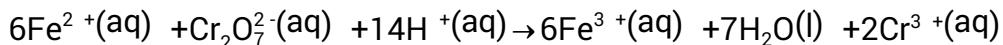
below;

- (i) To an aqueous solution of the unknown, add dilute sulphuric acid until the solution is acidic followed by few drops of sodium sulphite solution and heat. Colour change of orange $\text{Cr}_2\text{O}_7^{2-}$ to green Cr^{3+} confirms presence of dichromate ion.



The Cr^{3+} ion may be confirmed further using amyl alcohol (see under tests for Cr^{3+} ion)

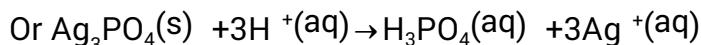
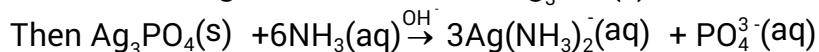
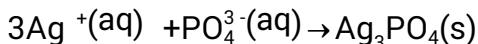
- (ii) To an aqueous solution of the unknown, add dilute sulphuric acid drop-wise till the solution is acidic. Add a few drops of iron (II) chloride solution and heat. A deep red colouration which turns brown on boiling confirms presence of dichromate.



Note that any reagent that causes reduction of the dichromate ion could be used.

g) Tetraoxo phosphorous (IV) (phosphate), PO_4^{3-} ion

- 1) To the solution of unknown, add an aqueous silver nitrate solution followed by excess aqueous ammonia or nitric acid. A yellow precipitate soluble in excess alkali or acid confirms phosphate.

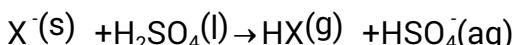


- 2) To about 1cm³ of the solution of the unknown, add dilute nitric till acidified and add up to 10cm³ or more ammonium molydate solution and warm to 40°C. A yellow crystalline precipitate soluble in aqueous ammonia or sodium hydroxide confirms presence of phosphate ion.
- 3) To the unknown solid, add magnesium powder and heat in an ignition tube, cool and add cold water. Formation of phosphine gas (smell of rotten fish) and ignites, confirms presence of phosphate ion.

h) Halides: chloride (Cl⁻), bromide (Br⁻) and iodide (I⁻) ion

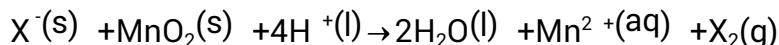
- 1) To the unknown solid add a few drops of concentrated sulphuric acid and warm if necessary.

- (i) Evolution of hydrogen chloride gas confirms chloride ion
(ii) Evolution of hydrogen bromide confirms bromide ion
(iii) Evolution of hydrogen iodide confirms iodide ion

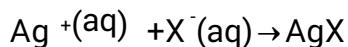


- 2) To the unknown solid add some manganese (IV) oxide followed by concentrated sulphuric acid and heat.

- (i) Evolution of chlorine gas confirms chloride ion
(ii) Evolution of bromine gas confirms bromide ion
(iii) Evolution of iodine vapour confirms iodide ion

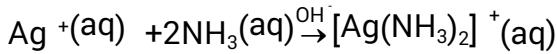


- 3) To a solution of the unknown, add 2-3 drops of aqueous silver nitrate followed by excess dilute nitric acid. Formation of a precipitate of silver halide confirms presence of a halide ion according to the equation.



NOTE:

- (i) The silver halides may be differentiated by their colours. AgCl is white, AgBr is pale yellow and AgI is yellow. The Ag-X bond is not very strong. The bond is broken by solar energy and therefore precipitates of the silver halides tend to darken on standing.
- (ii) Silver chloride and silver bromide dissolve in excess aqueous ammonia. This is because the concentration of the silver ions required to precipitate AgCl and AgBr is greatly reduced in the presence of ammonia since ammonia forms a complex ion with silver ion.

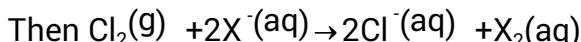
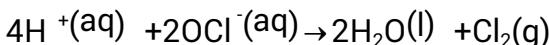


However AgI does not dissolve in aqueous ammonia because though the AgI is the least soluble, it provides still enough silver ions to cause the much lower solubility product of the halide to be exceeded.

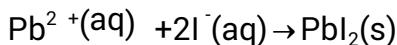
- 4) To a solution of the unknown, add bleaching powder then dilute nitric acid (or add chlorine water) followed by 2-3 drops of tetrachloromethane.

- (i) If the tetrachloromethane remains colourless, a chloride ion is confirmed.
- (ii) If a brown or red liquid forms in tetrachloromethane layer, a bromide ion is confirmed.
- (iii) If however a purple liquid develops in the tetrachloromethane layer, iodide ion is confirmed.

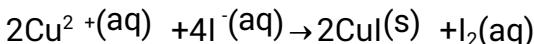
The acidified bleaching powder or chlorine water is an oxidising agent. Free chlorine is therefore produced. It is the chlorine which oxidizes the bromide or iodide ions to their respective halogens. The halogens being covalent, separate in the organic solvent (tetrachloromethane), and therefore express their respective colours.



- 5) To a solution of the unknown halide, add aqueous solution containing lead (II) ions (usually lead (II) ethanoate). A yellow precipitate lead (II) iodide confirms presence of iodide ion.

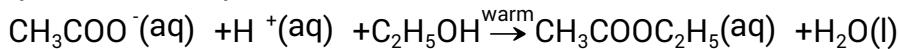


- 6) To a solution of the unknown halide, add aqueous solution of copper (II) sulphate. Formation of a brown precipitate of copper (I) iodide confirms presence of iodide ion. This is a redox reaction.

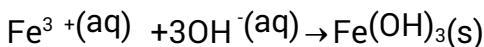
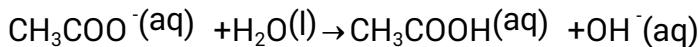


i) Ethanoate, CH_3COO^- ion

- 1) To a sample of the unknown, add about 2cm³ of ethanol followed by 2-3 drops of concentrated sulphuric acid. Warm the mixture. If a sweet smelling liquid (ethyl ethanoate) is produced, the presence of ethanoate ion is confirmed.



- 2) To an aqueous solution of the ethanoate, add 1-2 drops of iron (III) chloride in neutral solution. A red colouration infers ethanoate ion. Being the anion of a weak acid, the ethanoate ion is hydrolysed, though slightly in solution according to the equation.



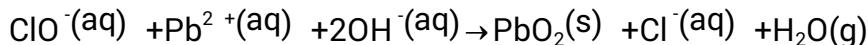
It is iron (III) hydroxide, which forms as a colloidal solution which accounts for the red colouration.

j) Oxo chloride (hypochlorite), ClO^- ion

1) Add cobalt (II) nitrate solution to a solution of the unknown. If a black precipitate of cobalt (II) (III) oxide forms accompanied by evolution of oxygen gas, the presence of oxochloride ion is confirmed. Oxygen is formed because cobalt (II) oxide catalyses decomposition of the anion according to following equation;

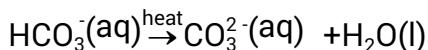


2) To the solution of the unknown, add aqueous solution of lead (II) ethanoate and boil the mixture. Formation of a brown precipitate of lead (IV) oxide confirms presence of the oxo chloride. This is because oxochloride oxidizes lead (II) to lead (IV) as follows;

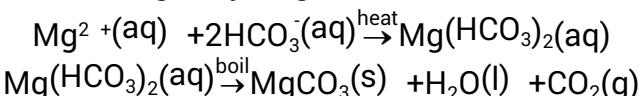


k) Hydrogen carbonate, HCO_3^- ion

1) An aqueous solution of hydrogen carbonate is almost neutral. On boiling a hydrogen carbonate solution, carbon dioxide is evolved and the resultant solution is alkaline to phenolphthalein. This is due to decomposition of the hydrogen carbonate to a normal carbonate thus:



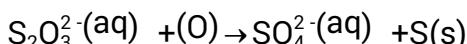
2) Add aqueous magnesium sulphate to a solution of a hydrogen carbonate and boil. If a white precipitate forms on boiling, a hydrogen carbonate ion is confirmed.



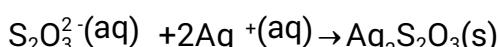
It should be noted that all other hydrogen carbonates except those of group (I) metal ions are liquids or non-existence because they are highly unstable.

l) Trioxosulphur (II) (thiosulphate) ion; $\text{S}_2\text{O}_3^{2-}$

1) This is another reducing agent. When aqueous solution of potassium manganate (VII) acidified with aqueous sulphuric acid is added to the solution of the unknown, a pale yellow or white suspension of sulphur is formed.

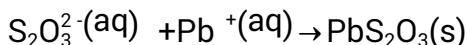


2) To an aqueous solution of $\text{S}_2\text{O}_3^{2-}$, add aqueous solution of silver nitrate, a white precipitate of $\text{Ag}_2\text{S}_2\text{O}_3$ confirms thiosulphate ions.

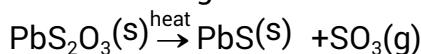


The precipitate turns brown because silver thiosulphate rapidly tends to decompose into silver sulphide. It also dissolves in excess silver nitrate due to formation of complex ions like $[\text{AgS}_2\text{O}_3]^-$ or $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{2-}$.

3) To an aqueous solution of $\text{S}_2\text{O}_3^{2-}$, add aqueous solution of lead (II) ethanoate. Formation of a white precipitate of lead thiosulphate soluble in excess reagent confirms presence of $\text{S}_2\text{O}_3^{2-}$.



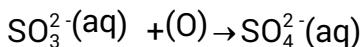
The precipitate forms complex ion, $\text{PbS}_2\text{O}_3^{2-}$ which is soluble in excess lead (II) ethanoate. The precipitate turns grey on boiling because lead (II) thiosulphate decomposes to lead (II) sulphide on heating.



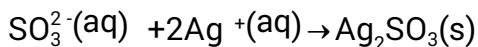
m) Trioxosulphur (IV) (sulphite): SO_3^{2-}

1) The anion is a reducing agent. It may be oxidized using oxidizing agents like hydrogen peroxide, halogens or iodates. After oxidation, the solution contains the

sulphate ion, which may be tested (see under sulphate ion)



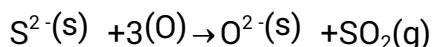
- 2) To a solution of the unknown add aqueous silver nitrate drop wise until in excess, a white precipitate of silver sulphite readily soluble in excess silver nitrate confirms sulphite.



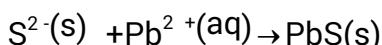
The silver sulphite is very soluble in excess silver nitrate solution due to formation of complex ions like $[\text{AgSO}_3]$ or $[\text{Ag}(\text{SO}_3)_2]^{2-}$

n) Sulphide ion, S^{2-}

- 1) Mix the solid with an excess of manganese (IV) oxide and heat. Evolution of sulphur dioxide shows the presence of sulphide ion except sulphides of group (I) metals.



- 2) If the unknown is soluble in water, test the aqueous solution with a solution containing lead (II) ions e.g. aqueous lead (II) nitrate or lead (II) ethanoate solution. Formation of a black precipitate of lead (II) sulphide confirms presence of sulphide ion.



- 3) Mix the unknown solid with Devarda's alloy. Add dilute hydrochloric acid to the mixture and warm the mixture. If hydrogen sulphide is evolved, the presence of sulphide ion is confirmed. (this test is most appropriate for insoluble sulphides)

Tests for cations

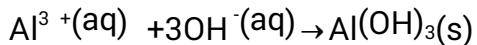
Cations can be identified when they are in their aqueous solutions by converting them to their respective hydroxides. Most hydroxides, except those of ammonium ion and group (I) metal ions are insoluble because of their strong basic characters. They are therefore usually identified by their colours when formed as precipitates. Some are amphoteric and so they dissolve in excess sodium hydroxide solution which is a stronger base. But the precipitates so formed dissolve when excess ammonia is added.

When any hydroxide formation does not serve to completely distinguish a cation from others, more specific tests are necessary in order to confirm the presence of the cation. The following tests are those often used in order to identify cations.

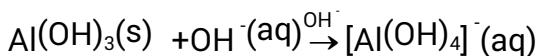
a) Aluminium ion, Al^{3+}

- 1) With aqueous sodium hydroxide

Add dilute sodium hydroxide solution drop-wise to an aqueous solution of the unknown until in excess. A white gelatinous precipitate of aluminium hydroxide soluble in excess sodium hydroxide implies aluminium ion present.



Aluminum hydroxide is amphoteric so reacts with the stronger base to form a complex salt which is soluble.



2) With aqueous ammonia

Aluminum hydroxide is formed as a white precipitate as in the case of sodium hydroxide. However, the precipitate is insoluble in excess ammonia solution.

3) With alizarin solution

To the solution of the unknown, add aqueous ammonia drop-wise until the solution is alkaline; then add 1-2 drops of alizarin solution. A pink colouration confirms presence of aluminum ion.

b) Ammonium ion, NH₄⁺

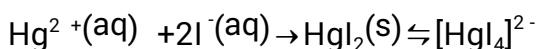
1) Reaction with aqueous sodium hydroxide

To about 1 cm³ of a solution containing the unknown cation, add 2-3 drops of dilute sodium hydroxide and then continue adding sodium hydroxide drop-wise until it is in excess. Warm the mixture if no precipitate forms. If ammonia gas is evolved, ammonium ion is confirmed.



2) With mercury (II) chloride solution

To an aqueous solution of the unknown cation, add a few drops of mercury (II) chloride solution followed by potassium iodide solution added until the red precipitate of mercury (II) iodide just dissolves due to the formation of the tetraiodomercury (II) ion thus;



Now add aqueous sodium hydroxide until in excess. Formation of a yellow or brown precipitate or brown solution of oxydimercuriammonium iodide, (OH)₂NH₂I confirms the presence of ammonium ion.

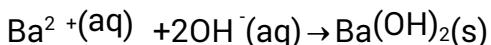
c) Barium ion, Ba²⁺

1) Flame test

Barium ion imparts a pale yellowish green colour of flame.

2) With aqueous sodium hydroxide

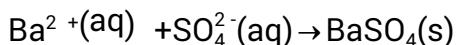
To the solution of the unknown, add aqueous sodium hydroxide drop-wise until in excess. A white precipitate insoluble in excess sodium hydroxide implies that barium ions may be present.



NB: Does not form precipitate with aqueous ammonia (see under Ca²⁺)

3) With dilute sulphuric acid (or sodium sulphate)

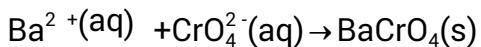
To the solution of the unknown, add 2-3 drops of dilute sulphuric acid or sodium sulphate solution. Formation of a heavy white precipitate of barium sulphate confirms presence of barium ions.



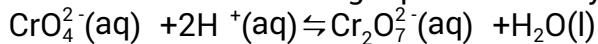
NB//. Barium ion should be contrasted with lead (II) ion, which shows the same results. Use of aqueous sodium hydroxide may help.

4) With chromate (VI) ion

To the aqueous solution of the unknown, add 2-3 drops of aqueous potassium chromate followed by ethanoic acid. A yellow precipitate insoluble in ethanoic acid confirms barium ions.



NB: In acid solution the following equilibrium may exist:



Even then, the presence of dilute ethanoic acid, around pH 3, there is still sufficient concentration of chromate ions to cause precipitation of barium (II) chromate; unlike calcium chromate, which is more soluble. Thus, although calcium ions may form a precipitate with chromate ions in case calcium ion is present in a fairly high concentration, the precipitate soon dissolves in ethanoic acid. Hence the difference between calcium and barium ions.

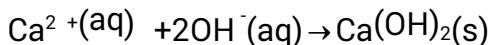
d) Calcium ion, Ca^{2+}

1) Flame test

Imparts a short-lasting orange-red colour flame.

2) With aqueous sodium hydroxide

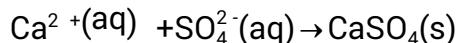
To the solution of the unknown, add dilute sodium hydroxide solution drop-wise until in excess. A white precipitate insoluble in excess sodium hydroxide implies that calcium ion may be present.



NB//. Calcium ion does not form a precipitate with aqueous ammonia because ammonia is a weak base. So it does not provide hydroxide ions in sufficient quantity to exceed the solubility product of calcium hydroxide, which is quite high.

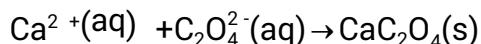
3) With dilute sulphuric acid or aqueous sodium sulphate

To the solution of the unknown, add 2-3 drops of dilute sulphuric acid or sodium sulphate solution. A white precipitate of calcium sulphate confirms presence of the calcium ion.



4) With ammonium ethanedioate solution

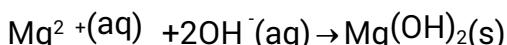
To the aqueous solution of the unknown, add aqueous ammonia until the solution is alkaline, and then add a few drops of ammonium ethanedioate to the mixture. A white precipitate of calcium ethanedioate confirms presence of calcium ions.



e) Magnesium ion, Mg^{2+}

a) With sodium hydroxide solution.

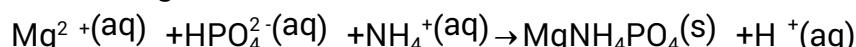
To the aqueous solution of the unknown, add aqueous sodium hydroxide drop-wise until in excess. If the white precipitate insoluble in excess sodium hydroxide is formed, magnesium ion is suspected.



NB//. Similar observation is made with ammonia. Although because of the weak basic character of ammonia, the precipitate may not show.

2) With disodium monohydrogen phosphate

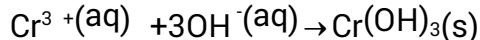
To aqueous solution of the unknown, add solid ammonium chloride followed by 3-4 drops of di-sodium monohydrogen orthophosphate (sodium phosphate) then aqueous ammonia added till in excess. A white crystalline precipitate insoluble in ammonia confirms presence of magnesium ion.



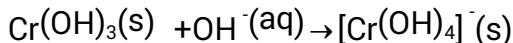
f) chromium (II) ion, Cr^{3+}

1) with sodium hydroxide

To the solution of the unknown, add aqueous sodium hydroxide drop-wise until in excess. A grey-green gelatinous precipitate soluble in excess sodium hydroxide to form a green solution implies chromium (III) ion.



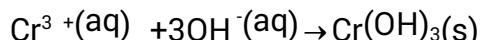
The chromium (III) hydroxide is amphoteric so reacts with stronger base, sodium hydroxide, forming a soluble chromite salt.



NB//. In this respect, chromium (III) hydroxide resembles aluminium in group (III).

2) with dilute ammonia solution

To the solution of the unknown, add a few drops of aqueous ammonium chloride followed by aqueous ammonia drop-wise until in excess. A green gelatinous precipitate soluble in excess ammonia solution to give a green solution implies chromium (III) ion.

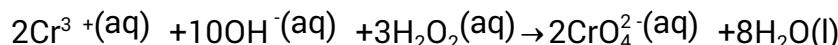


Chromium (III) ion complexes with ammonia thus resulting into the observed dissolution of chromium (III) hydroxide.



3) with hydrogen peroxide/lead (II) ethanoate

To the solution of the unknown add dilute sodium hydroxide until the solution is alkaline; then add hydrogen peroxide solution to the mixture followed by lead (II) ethanoate solution. A yellow solution formed on adding hydrogen peroxide which gives a yellow precipitate when lead (II) ethanoate is added confirms chromium (III) ion.

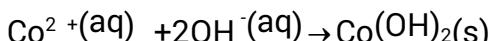


NB//. Instead of adding lead (II) ethanoate to the resultant solution above, if amyl alcohol is added followed by dilute sulphuric acid, a blue colour would form in the alcohol layer, which confirms chromium (III) ion. The blue colour is due to chromium peroxide, CrO_5 , which is stabilized to some extent in organic solvent. It is also derived from chromium (VI) i.e. $\text{Cr}_2\text{O}_7^{2-}$ (see under $\text{Cr}_2\text{O}_7^{2-}$)

g) cobalt (II) ion, Co^{2+}

1) with aqueous sodium hydroxide

Add aqueous sodium hydroxide drop-wise to a solution of cobalt (II) until the alkali is in excess. Warm the mixture. A blue precipitate, which turns pink on warming in excess alkali indicates presence of cobalt (II) ion.



The precipitate goes to dark brown on standing due to oxidation of cobalt (II) hydroxide to cobalt (II) hydroxide by air (oxygen)

The precipitate does not form when ammonium chloride is added prior to adding the aqueous alkali.

2) with aqueous ammonia

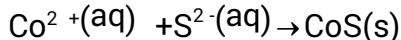
Add aqueous ammonia drop-wise to the suspected cobalt (II) ion; then add 2-3 drops of hydrogen peroxide solution.

A blue precipitate soluble in excess ammonia or aqueous ammonium chloride shows presence of cobalt (II) ion. The ammonia complexes with the cation. On standing or add

hydrogen peroxide, the ammoniacal solution turns red as various complexes are formed through oxidation.

3) with aqueous ammonium sulphide

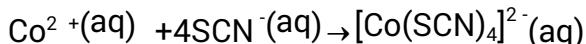
Add 2-3 drops of aqueous ammonium sulphide to the suspected cobalt (II) solution. Formation of a black precipitate indicates presence of cobalt (II) ion.



The same reaction occurs when aqueous cobalt (II) solution is treated with aqueous ammonia or ammonium chloride followed by passage of hydrogen sulphide gas. The precipitate of cobalt (II) sulphide insoluble in dilute hydrochloric acid although it reacts slowly with hot concentrated hydrochloric acid.

4) with a strong solution of potassium or ammonium thiocyanate

To about 1 cm³ of aqueous cobalt (II), add 2-3 drops of a fairly concentrated potassium or ammonium thiocyanate solution. A blue solution of potassium thiocyanatocobaltate(II) confirms presence of cobalt (II) ion.

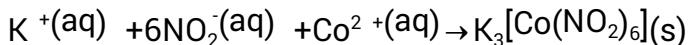


5) borax bead test

Heat a small loop of platinum wire to red hot and quickly us it to pick the borax. Heat the borax in the loop of wire until it swells and forms a colourless transparent bead. Allow the bead to cool and spray a little water to moisten it. Use the moist bead to pick a minute quantity of the suspected cobalt (II) compound. Heat the bead first in the reducing zone of the Bunsen burner and later in the oxidizing zone. A blue colour of the borax bead confirms cobalt (II) ion.

6) with potassium nitrite in the presence of ethanoic acid

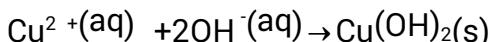
Add ethanoic acid to an aqueous solution of cobalt (II) ion until the solution is added; then add 2-3 drops of potassium nitrite solution and shake the mixture. A yellow crystalline precipitate confirms presence of cobalt (II) ion.



h) copper (II) ion, Cu²⁺

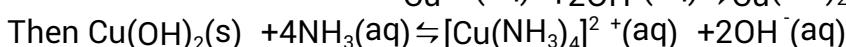
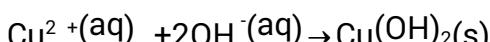
1) with sodium hydroxide

To the solution of copper (II), add sodium hydroxide drop-wise until in excess. A light blue (almost white) precipitate of copper (II) hydroxide insoluble in excess sodium hydroxide implies presence of copper (II) ion.



2) with aqueous ammonia

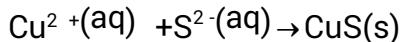
Add dilute ammonia solution to the solution of the unknown drop-wise until ammonia is in excess. A pale blue precipitate of copper (II) hydroxide which dissolves in excess ammonia giving a deep blue solution of the tetramminecopper(II) complex ion confirms copper (II) ion.



3) with hydrogen sulphide

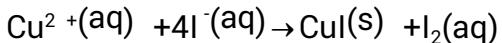
Add dilute hydrochloric acid to the solution of the unknown until the solution is acidic. Warm the mixture and pass hydrogen sulphide through the hot acidified mixture. A black

precipitate of copper (II) sulphide confirms copper (II) ion.



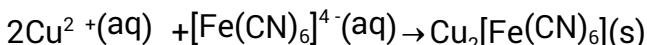
4) with potassium iodide

To the solution of the unknown add few drops of aqueous potassium iodide. Formation of a brown colour and an off-white precipitate of copper (I) confirms presence of copper (II) ion.



5) with potassium hexacyanoferrate (II)

Add 2-3 drops of aqueous potassium hexacyanoferrate (II) to the solution of the unknown. A brown precipitate of copper (II) hexacyanoferrate (II) confirms presence of copper (II) ion.

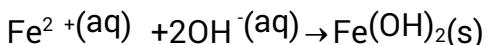


NB//. The reaction is a delicate test for copper (II) ion in solution. In very dilute solution only a purplish-brown colour and no precipitate is obtained.

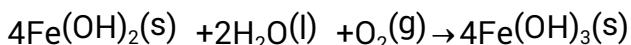
i) Iron (II) ion, Fe^{2+}

1) With dilute sodium hydroxide

Add dilute sodium hydroxide drop-wise to a solution of the unknown until in excess. A green gelatinous precipitate of iron (III) hydroxide insoluble in excess sodium hydroxide implies presence of iron (II).



iron (II)hydroxide is Purely basic and so does not dissolve in excess sodium hydroxide. But it slowly turns brown on exposure to air due to oxidation to iron (III) hydroxide by atmospheric oxygen.

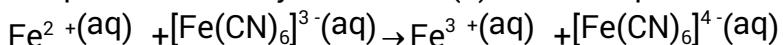


2) With aqueous ammonia

Same observation as in the case of sodium hydroxide.

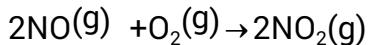
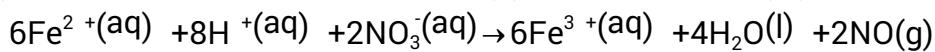
3) With potassium hexacyanoferrate (III)

To the aqueous solution of the unknown, add 2-3 drops of aqueous hexacyanoferrate (III). A dark blue precipitate of hexacyanoferrate (II) confirms presence of iron (II).



4) With concentrated nitric acid or any oxidizing agent

Add concentrated nitric acid to the solution of the unknown and boil the mixture. Formation of a yellow or brown solution of iron (II) and evolution of brown fumes of nitrogen (IV) oxide confirms presence of iron (II) oxidized to iron (III).

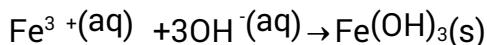


Other oxidizing agents, including chlorine or bromine-water, hydrogen peroxide, potassium dichromate convert iron (II) to iron (III), hence colour changes from green to yellow (brown) are observed on appropriate treatment.

j) Iron (III) ion, Fe^{3+}

1) With sodium hydroxide

Add dilute sodium hydroxide solution drop-wise to the aqueous solution of the unknown until sodium hydroxide is in excess. A rust-brown (red) gelatinous precipitate implies iron (III) ion.



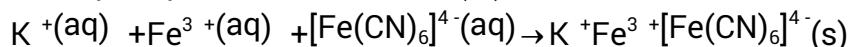
Iron (III)hydroxide is purely basic and therefore is not soluble in excess sodium hydroxide.

2) With aqueous ammonia

Same as for sodium hydroxide solution.

3) With potassium hexacyanoferrate(II) solution

To the solution of the unknown, add 2-3 drops of potassium hexacyanoferrate(II) solution. A dark blue precipitate confirms iron (III) ion.



4) With potassium thiocyanate solution

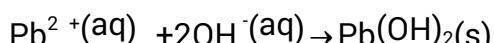
Add 2-3 drops of potassium thiocyanate solution to the solution of the unknown. A blood-red colour of pentaquo iron (II) thiocyanate confirms iron (III) ion.



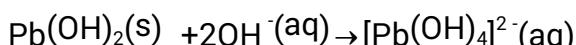
k) Lead (II) ion, Pb^{2+}

1) with dilute sodium hydroxide

To the solution of the unknown, add sodium hydroxide drop-wise until in excess. A white precipitate of lead (II) hydroxide soluble in excess sodium hydroxide implies lead (II) ions.

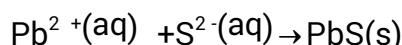


Lead (II) hydroxide is amphoteric and so is acted upon by stronger base, NaOH, forming a soluble salt of lead.

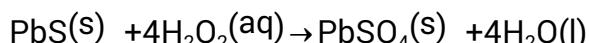


2) with hydrogen sulphide

To the solution of the unknown, add dilute hydrochloric acid and then heat fairly strongly. Pass hydrogen sulphide through the hot acidified solution. A dark brown precipitate of lead (II) sulphide insoluble in yellow ammonium sulphide confirms lead (II) ion.

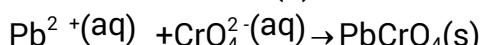


NB//. The precipitate turns white when treated with hydrogen peroxide due to oxidation of sulphide to lead (II) sulphate.



3) with potassium chromate

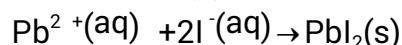
To the solution of the unknown, add 2-3 drops of aqueous potassium chromate. A yellow precipitate of lead (II) chromate confirms lead (II) ion.



4) with potassium iodide

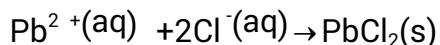
To the solution of the unknown, add 2-3 drops of potassium iodide. A yellow shiny

precipitate of lead (II) iodide confirms lead (II) ion.



5) with hydrochloric acid (or aqueous sodium chloride)

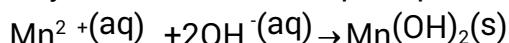
To the aqueous solution of the unknown, add 3-4 drops of dilute hydrochloric acid or aqueous solution of sodium chloride. Heat the mixture. Formation of white needle-like and shiny crystals of lead (II) chloride soluble in hot water but recrystallises on cooling confirms lead (II) ion.



I) Manganese (II) ion, Mn^{2+}

1) With sodium hydroxide

To the solution of the unknown, add dilute sodium hydroxide solution drop-wise till in excess. An off-white precipitate of manganese (II) hydroxide is formed which is insoluble in excess sodium hydroxide solution implies presence of manganese (II) ion.

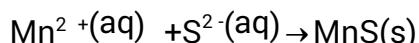


2) With dilute ammonia solution

Same observation as with sodium hydroxide

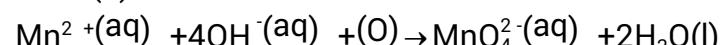
3) With hydrogen sulphide

Add aqueous ammonia to the solution of the unknown until it is alkaline. Bubble hydrogen sulphide through the resultant solution. A dirty white or pink (flesh coloured) precipitate of manganese (II) sulphide implies presence of manganese (II) ion.



4) With sodium bismuthate

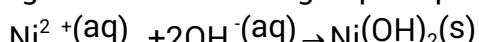
To the solution of the unknown (or solid) add few drops of concentrated nitric acid followed by a small quantity of solid sodium bismuthate and boil the mixture for some time. A violet (purple) colouration which forms and may settle as a precipitate confirms presence of manganese (II) ion.



m) Nickel (II) ion, Ni^{2+}

1) With dilute sodiumhydroxide

To the solution of the unknown, add dilute sodium hydroxide solution drop-wise until it in excess. A light green precipitate of nickel (II) hydroxide insoluble in excess sodium hydroxide and does not change colour on heating implies presence of nickel (II) ion.



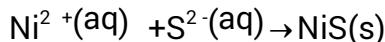
2) With dilute ammonia solution

Same precipitate as in the case of sodium, hydroxide forms, but the precipitate dissolves in excess ammonia solution to give a blue solution due to complexation of nickel (II) ion with ammonia.



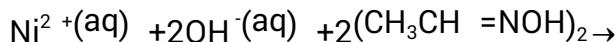
3) With hydrogen sulphide

To the solution of nickel (II) ion add ammonia solution until the solution is alkaline; then pass hydrogen sulphide through the alkaline solution. A black precipitate of nickel (II) sulphide implies presence of nickel (II) ion.



4) With dimethylglyoxime

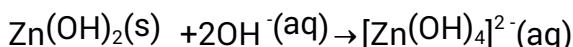
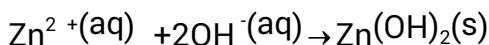
Add aqueous ammonia to the solution of the unknown until the solution is alkaline; then add 1-2 drops of dimethylglyoxime to the alkaline mixture. A red precipitate of nickel (II) dimethylglyoxime complex confirms presence of nickel (II).



n) Zinc (II) ion

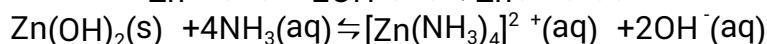
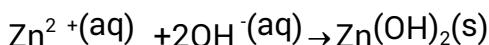
1) With aqueous sodium hydroxide

To the aqueous solution of the unknown, add dilute sodium hydroxide drop-wise until sodium hydroxide is in excess. A gelatinous white precipitate soluble in excess sodium hydroxide implies presence of zinc.



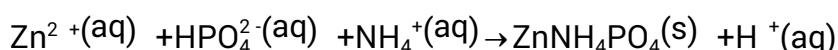
2) With aqueous ammonia

To the solution of the unknown, add aqueous ammonia drop-wise until ammonia is in excess. Formation of a white gelatinous precipitate soluble in excess ammonia implies presence of zinc ions.



3) With disodium monohydrogen phosphate

To the solution of the unknown, add solid ammonium chloride followed by 2-3 drops of disodium monohydrogen phosphate (sodium phosphate) solution followed by excess ammonia solution. A white precipitate soluble in aqueous ammonia confirms presence of zinc ions.

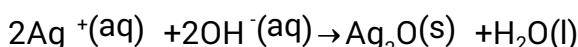


NB//. The presence of aqueous ammonia causes the zinc ion to be largely converted to $[\text{Zn(NH}_3)_6]^{2+}(\text{aq})$ thus reducing the concentration of zinc (II) ions to the level below that required to reach and exceed the solubility product of zinc ammonium phosphate thus the solid dissolves.

o) Silver ion, Ag^+

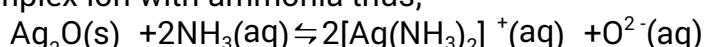
1) With sodium hydroxide solution

To the solution of the unknown, add aqueous sodium hydroxide drop-wise till in excess. A dark brown or black precipitate of silver oxide insoluble in excess sodium hydroxide implies silver ion.



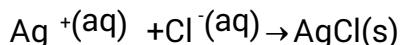
2) With aqueous ammonia

Same precipitate as above but dissolves in excess ammonia because silver ion forms diammine silver complex ion with ammonia thus;



3) With dilute hydrochloric acid

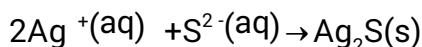
Add 2-3 drops of dilute hydrochloric acid (or chloride) solution to the solution of the unknown. A white precipitate which turns purple or dark in air and dissolves in ammonia solution confirms presence of silver ion.



The darkening is due to the partial decomposition of the weak Ag-Cl bond to metallic silver. It dissolves in ammonia due to the formation of the complex ion $[\text{Ag}(\text{NH}_3)_2]^+$ as seen above.

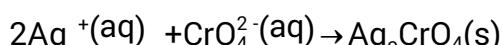
4) With hydrogen sulphide

To the solution of the unknown, add nitric acid until the solution is acidic and pass hydrogen sulphide through the acidified mixture. A black precipitate of silver sulphide confirms silver ion.



5) With potassium chromate

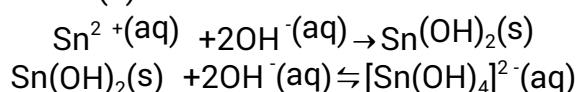
Add 2-3 drops of aqueous potassium chromate to the solution of the unknown. A dark red precipitate of silver chromate confirms silver ion.



p) Tin (II) ion, Sn^{2+}

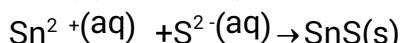
1) With dilute sodium hydroxide

To the solution of the unknown, add aqueous sodium hydroxide drop-wise until in excess. A white precipitate of tin (II) hydroxide soluble in excess due to its amphoteric nature implies presence of tin (II) ion.

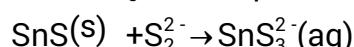


2) With hydrogen sulphide

To the solution of the unknown, add dilute hydrochloric acid until the solution is acidic. Heat the solution and bubble hydrogen sulphide into the hot solution. A brown precipitate (probably the hydro tin (II) sulphide) confirms presence of tin (II) ion.

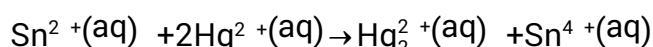


The precipitate dissolves in yellow ammonium sulphide due to oxidation of the tin (II) sulphide by the disulphide, S_2^{2-} contained in ammonium sulphide, forming thiostannate ion, SnS_3^{2-} , a complex.

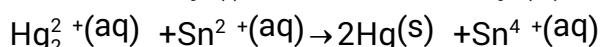


3) With aqueous mercury (II) chloride

To the solution of the unknown, add 2-3 drops of aqueous mercury (II) chloride. A white precipitate of mercury (I) chloride, which slowly turns grey, confirms presence of tin (II) ion.



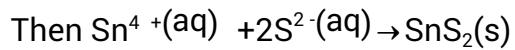
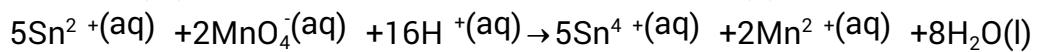
The excess $\text{Sn}^{2+}(\text{aq})$ reduce mercury (I) to further mercury (0), the grey metal.



This indicates behavior tin (II) as a strong reducing agent.

4) With acidified potassium permanganate or hydrogen sulphide

To the aqueous solution of the unknown, add dilute sulphuric acid until the solution is acidic followed by aqueous potassium permanganate added until no further decolourisation of the manganate solution occurs. Formation of a dirty yellow precipitate of tin (IV) sulphide confirms the presence of tin (II)



CHAPTER ELEVEN

SAMPLE QUESTIONS AND ANSWERS

Question 1

Suggest explanations for each of the following observations.

- (a) Lithium is the only alkali metal to react readily with nitrogen.
- (b) Of the chlorides of the group (II) elements only beryllium is covalent.
- (c) When aqueous sodium carbonate is added to a solution of aluminium ions, a white precipitate of aluminum hydroxide is formed.
- (d) Silicon tetrachloride is readily hydrolysed by water, but tetrachloromethane is not, in spite of the fact that energy would be liberated in each reaction.
- (e) The acids HCO , HClO_2 , HClO_3 and HClO_4 have different strengths in aqueous solution.

Question 2

- (a) (i) Explain what is meant by amphoteric character for an oxide or a hydroxide.

- (ii) Indicate which of the following oxides show amphoteric character.

Na_2O , BaO_2 , Al_2O_3 , P_4O_{10} , SnO , SiO_2 .

- (iii) State two chemical differences between the oxides of metals and non-metals.

- (b) (i) State which one of the oxides listed in (a) (ii) above, on treatment with dilute sulphuric acid, liberate hydrogen peroxide.

- (ii) Explain why this particular oxide is especially suitable for the preparation in this way solution of hydrogen peroxide.

- (i) Give a balanced equation for the reaction in (b) (i) above.

Question 3

- (a) (i) State the conditions under which magnesium and calcium will react with water, and write balanced equations for the reactions.

- (ii) Explain any differences between the two reactions in terms of atomic properties of the two metals.

(b) Compare the chemistries of magnesium and calcium with reference to the following:

- (i) The solubilities of their sulphates in water.
- (ii) The thermal stabilities of their carbonates;
- (iii) The reaction of their oxides with water.

Question 4

(a) Give the electronic configurations of boron and aluminium.

(b) Explain why;

- (i) Boron does not form simple compounds containing B^{3+} ion.
- (ii) Aluminium chloride is predominantly covalent whereas aluminium fluoride is predominantly ionic.
- (c) (i) How do the hydroxides of aluminium and boron differ in their acid-base character.
(ii) Briefly explain this difference in behavior.
- (d) Give and explain the structures of the chlorides of aluminium at temperatures just above their vaporization points.

Question 5

(a) (i) State and explain the term that link up the chemistry of boron and silicon.

(ii) State three similarities in which the chemistry of boron is similar to that of silicon but differ from the chemistry of other group (III) elements.

(iii) Name two other pairs of elements capable of exhibiting the term identified above.

(iv) Give the similarities shown by one of the pairs of elements given above.

(v) Explain why the different pairs of elements above are capable of exhibiting the identified term.

(b) Lithium chloride, lithium bromide and lithium iodide are salts of lithium.

(i) Explain why lithium salts have a greater degree of covalent character than the other halides of group (I) elements.

(ii) Identify the most covalent halide. Explain.

(iii) Explain why it is that although the lithium ion, Li^+ , is far smaller than the other metal ions, it moves through a solution less rapidly than the others.

(iv) Suggest a reason why lithium fluoride has the lowest solubility of the group (I) halides.

(c) Write equation to show the action of heat on the following;

(i) Lithium hydroxide.

(ii) Lithium nitrate.

Solution

(a) (i) Diagonal relationship

This is the existence of elements along the diagonals of period 2 and 3 of the periodic

table to show similar chemical and physical properties. The similarity arises due to similarity in atomic number, electronegativity, metallic and non-metallic nature of the elements along the diagonals.

(ii)

- Both form a wide variety of unstable hydrides, the boranes and the silanes e.g. BH_4 , B_2H_6 , SiH_4 , Si_2H_6 . While the rest of group (III) elements form stable hydrides.
- Both are weakly acidic while the rest of group (III) elements are strongly acidic.
- The chlorides of both are volatile and readily undergo hydrolysis to give acidic solutions which is not the case with the rest of group (III) elements.
- Both are non-metals whereas other group (III) elements are metals.
- They form oxide with giant covalent lattice structure while the rest of group 3 elements are mainly ionic.
- They readily form covalent hydrides while the rest of group (III) elements do not readily form hydrides and the hydrides formed are mainly ionic.

(iii)

- Beryllium and aluminium
- Lithium and magnesium

(iv)

Beryllium and aluminium

- Both metals are rendered passive by concentrated nitric acid.
- Both dissolve in concentrated alkali solution liberating hydrogen gas.
- Both metals are amphoteric i.e. react with both acid and base.
- The oxides and hydroxides of both metals are amphoteric.
- The chlorides of both elements electron deficient therefore acts as Lewis acid.
- The compounds of both elements are mainly covalent in nature.
- Both metals are not attacked by water because they form protective oxide coating.
- Both elements are capable of forming complexes.
- The chlorides of both elements are readily hydrolyzed to give acidic solution.

Magnesium and lithium

- Both form ionic nitride when burnt in nitrogen.
- Their hydrogen carbonates exist in only solution and not in the solid state.
- Both form monoxides when burnt in air.

- Hydroxides, carbonates and nitrates of Li and Mg decompose to oxides when heated.
- Hydroxide of Li and Mg are not deliquescent.

(b)

Question 6

This question concerns the chemistry of fluorine and chlorine and some of their compounds.

(a) The fluorine molecule has a shorter bond length (0.142 nm) than chlorine (0.199 nm), yet its bond dissociation enthalpy (158 kJ mol^{-1}) is much lower than that of chlorine (244 kJ mol^{-1}). Explain why fluorine has an unexpectedly low bond dissociation enthalpy and predict the effect that this low value has on the reactivity of fluorine compared with chlorine.

(b) Fluorine reacts immediately with cold water to form an acidic solution and oxygen gas. It reacts with cold dilute alkali to produce oxygen difluoride, OF_2 , and fluoride ions.

(i) Construct equations for these reactions and compare them with the reactions of chlorine with water and dilute alkali.

(ii) Explain, in terms of reduction-oxidation what has happened in each of the reactions that you have written in part (b)(i).

(iii) Deduce the shape of the oxygen difluoride molecule and suggest its physical state at room temperature.

(c) Suggest, in terms of the structure and bonding, why aluminium fluoride has a relatively high melting temperature (1563 K), but aluminium chloride sublimes at a much lower temperature (466 K).

(d) Hydrogen fluoride and hydrogen chloride are both colourless acidic gases at 298 K.

(i) Explain why the boiling temperature of hydrogen fluoride (293 K) is much higher than that of hydrogen chloride (188 K).

(ii) Explain why, in aqueous solution, the acid dissociation constant of hydrogen fluoride ($\text{p}K_a = 3.10$) is very different from that of hydrogen chloride ($\text{p}K_a = 7.20$).

(e) Many interhalogen compounds and ions are known. Deduce the shapes of, and draw structures for, BrF_2^+ , BrF_5 , ICl_2^- , ClF_3 and ClF_4^- .

Question 7

(a) Why are the elements sodium to argon placed in Period 3 of the Periodic Table? Describe and explain the trends in electronegativity and atomic radius across Period 3 from sodium to sulphur.

(b) Describe the trend in pH of the solutions formed when the oxides of the Period 3 elements, sodium to sulphur, are added separately to water. Explain this trend by reference to the structure and bonding in the oxides and by writing equations for the reactions with water.

Solution

(a) Outer electrons are in third shell (1) (allow 3s, 3p etc NOT 3d)
electronegativity is the power to attract electrons in a covalent bond (or shared pair) (1)

electronegativity increases from Na to S (1)

because number of protons in the nucleus (or nuclear charge) increases (1)

and the electrons are in the same shell (or experience the same shielding) (1)

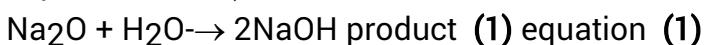
atomic radius decreases from Na to S (1)

because number of protons in the nucleus (or nuclear charge) increases (1)

and the electrons are in the same shell (or experience the same shielding) (1)

(for 'the same reasons as electronegativity increases' scores one only)

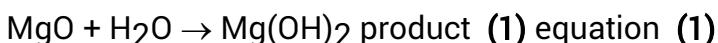
(b) the trend is a decrease in pH (or from alkaline to acid) (1)(can be implied from separate values)



(allow Na^+ OH^- , ignore state symbols)

Na_2O is ionic lattice (1)

(if lattice is not mentioned lose mark only once ie allow ionic for MgO , Al_2O_3)



(allow Mg^{2+} 2OH^-)

MgO is ionic lattice (1)

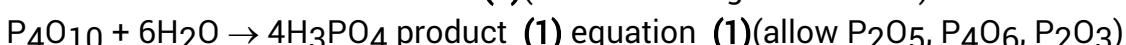
MgO sparingly soluble (1)

Al_2O_3 is ionic lattice or covalent macromolecular (1)(if covalent not mentioned lose mark only once)

insoluble in water or no reaction (1)(if formula wrong lose one mark)

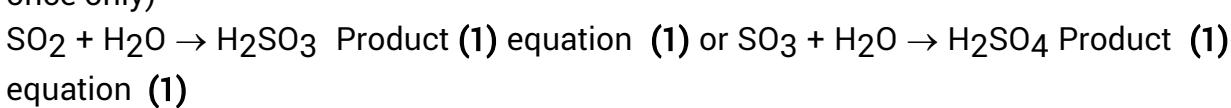
SiO_2 is covalent macromolecular (1)(if covalent not mentioned lose mark only once)

insoluble in water or no reaction (1)(formula wrong lose 1 mark)



H_3PO_4 is a strong acid or very acidic (1)

P_4O_{10} is covalent molecular (1)(if covalent or molecular not mentioned lose mark once only)



H_2SO_3 is a weak acid (1) H_2SO_4 is a strong acid or very acidic (1)

SO_2 is covalent molecular (1) SO_3 is covalent molecular (1)

Question 8

(a) In the table below, give the formulae of the chlorides of the elements of period 3, other than silicon.

Element	Na	Mg	Al	Si	P	S
Formula of chloride				SiCl_4		

(b) Calculate the percentage by mass of silicon in silicon tetrachloride.

(c) (i) Draw a dot and cross diagram to show the bonding in silicon tetrachloride.

(ii) Draw the shape of this molecule.

Explain your answer in terms of the Electron Pair Repulsion Theory.

(iii) State the shape of a molecule of AlCl_3 and explain why it is different from that of SiCl_4 .

(d) (i) Give an equation for the reaction of SiCl_4 with cold water.

(ii) How does the behaviour of carbon tetrachloride with cold water compare with this?

Explain any differences.

Solution

(a)

Element	Na	Mg	Al	Si	P	S
Formula of chloride	NaCl	MgCl_2	AlCl_3	SiCl_4	PCl_3	SCl_2

(b) 1 mole of SiCl_4 contains 1 mole of Si

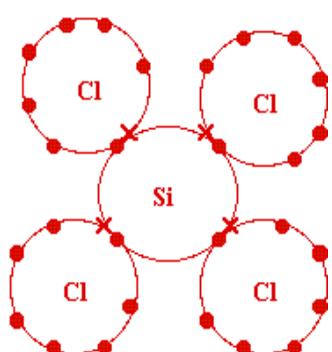
mass of 1 mole of Si = 28.0g

mass of 1 mole of SiCl_4 = $28.0 + (4 \times 35.5) = 170\text{g}$

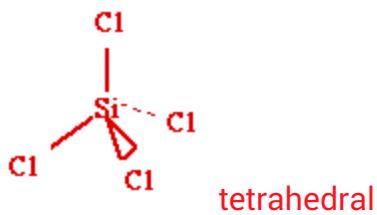
so % mass of Si = $28.0 \times 100 / 170$

% mass of Si = 16.5%

(c) (i)



(ii)



The molecule has 4 bonding pairs of electrons

A tetrahedral shape gives the maximum separation for 4 electron pairs

(ii) Trigonal planar

AlCl_3 has 3 bonding pairs of electrons

(d) (i) $\text{SiCl}_4 + \text{H}_2\text{O} \longrightarrow \text{SiO}_2 + 4\text{HCl}$

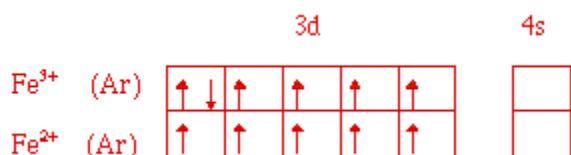
(ii) Carbon tetrachloride does not react with water

Carbon does not have vacant d orbitals like silicon

so carbon cannot accept a lone pair from an oxygen atom in water

Question 9

(a) Give the electronic configuration of the following ions.



(b) Outline, giving the reagent, the essential conditions and the equation, how a sample of anhydrous iron(II) chloride could be made from iron.

(c) Give the formula and name of the metal-containing ion formed when iron(II) chloride is dissolved in water. State the shape of this ion.

(d) (i) Describe what you would observe if dilute sodium hydroxide is added to the solution in (c).

(ii) Give an equation for this reaction and state the type of reaction occurring.

(e) (i) What further change would you observe if the product from (d)(i) was allowed to stand in air?

(ii) What type of reaction is occurring in the change?

(iii) Explain briefly, in the light of your answer to (a), why you might expect this reaction to occur.

Solution

(a)

	3d	4s												
Fe ³⁺ (Ar)	<table border="1" style="margin-left: auto; margin-right: auto;"> <tr><td>↑</td><td>↓</td><td>↑</td><td>↑</td><td>↑</td><td>↑</td></tr> <tr><td>↑</td><td>↑</td><td>↑</td><td>↑</td><td>↑</td><td>↑</td></tr> </table>	↑	↓	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	
↑	↓	↑	↑	↑	↑									
↑	↑	↑	↑	↑	↑									
Fe ²⁺ (Ar)	<table border="1" style="margin-left: auto; margin-right: auto;"> <tr><td>↑</td><td>↑</td><td>↑</td><td>↑</td><td>↑</td><td>↑</td></tr> <tr><td>↑</td><td>↑</td><td>↑</td><td>↑</td><td>↑</td><td>↑</td></tr> </table>	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	
↑	↑	↑	↑	↑	↑									
↑	↑	↑	↑	↑	↑									

- (b) Pass dry HCl gas over heated iron.



- (c) Formula: $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

Name: hexaaquairon(II)

Shape: octahedral

- (d) (i) A green precipitate forms which is insoluble in excess NaOH



Type of reaction: deprotonation

- (e) (i) The colour would slowly change to red-brown

- (ii) Redox

- (iii) Iron (III) is more stable than iron (II) because iron (III) has a stable 3d5 configuration.

Question 10

The chlor-alkali industry is very important in the production of many chemicals; its principal feedstock is sodium chloride, which is electrolysed under various conditions.

- (a) (i) Under what conditions is sodium metal made from sodium chloride?

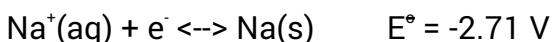
- (ii) Write equations for the reactions which occur at each electrode, identifying which is an oxidation and which is a reduction.

- (iii) The sodium metal produced can be used for the production of titanium from purified titanium (IV) chloride. Suggest an equation for such a reaction.

- (iv) Titanium (IV) chloride has a melting temperature of 248 K and a boiling temperature of 410K. Suggest how it might be purified industrially.

- (b) Electrolysis of aqueous sodium chloride in a diaphragm cell gives sodium hydroxide.

- (i) Explain, in terms of the standard electrode potential for sodium and for hydrogen, why the metal is not discharged from aqueous solutions of sodium ions;



- (ii) What is the main impurity in the sodium hydroxide solution produced from the diaphragm cell, and how is it removed?

- (iii) There are two products other than sodium hydroxide obtained from the diaphragm

cell. Identify these products and state one for each in industry.

(c) Sodium hydroxide is used in large quantities for the purification of bauxite.

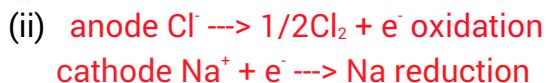
(i) Give an equation for a reaction in which sodium hydroxide is used in this purification.

(ii) Outline how aluminium metal is obtained from purified bauxite.

(iii) Explain in terms of bonding why aluminium is produced from aluminium oxide rather than from aluminium chloride.

Solution

(a) (i) The electrolysis of molten NaCl



(iv) fractional distillation

(b) (i) hydrogen has a standard electrode potential of 0.00 V

The standard electrode potential of sodium is more negative than that of hydrogen
. so hydrogen is more easily reduced and is discharged in place of sodium

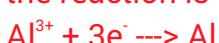
(ii) Sodium chloride is the main impurity. It is removed by crystallization

(iii) Chlorine; used as a disinfectant in swimming pool water.....

Hydrogen; used as a fuel in rocket engines

(c) (i) $\text{Al}_2\text{O}_3(\text{s}) + 2\text{OH}^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2[\text{Al}(\text{OH})_4]^{(\text{aq})}$

(ii) The purified bauxite is dissolved in molten cryolite and electrolysed. The cathode is made of carbon and aluminium forms here during the electrolysis. At the cathode the reaction is



(iii) Aluminium chloride is covalent and so contains no ions and so cannot undergo electrolysis

Question 11

(b) The table below gives some information about the sulphates of elements in Group 2.

Sulphate	Solubility/mol dm ⁻³	Lattice enthalpy/kJ mol ⁻¹	Hydration enthalpy of M ²⁺ /kJ mol ⁻¹
CaSO ₄	4.6*10 ⁻²	-2480	-1650
SrSO ₄	7.1*10 ⁻⁴	-2484	-1480
BaSO ₄	9.4*10 ⁻⁶	-2374	-1360

- (i) Suggest an explanation for the trend in the hydration enthalpies of the cations.
- (ii) Comment on the trend in the solubilities of these sulphates in relation to the lattice and hydration enthalpies given in the table.
- (iii) Barium sulphate, which is opaque to X-rays, is used for the "barium meal" to enable X-ray pictures to be taken of the gut. Barium ions are very toxic; why is this not a problem here?
- (iv) Give the equation for the reaction of barium with cold water.
- (v) Suggest the practical procedure by which you might convert the solution of the product in reaction (iv) into a reasonably pure sample of barium sulphate.

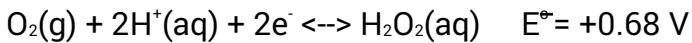
Solution

b) (i) The hydration enthalpy becomes less exothermic as the cation size increases because the charge density decreases

- (i) The solubility decreases down the group.
Solubility depends on enthalpy of solution and
enthalpy of solution = enthalpy of hydration - lattice enthalpy
Enthalpy of hydration changes more quickly than lattice enthalpy so.
Enthalpy of hydration has a more dominant effect
- (ii) Barium sulphate is insoluble
- (iii) $\text{Ba} + 2\text{H}_2\text{O} \rightarrow \text{Ba(OH)}_2 + \text{H}_2$
- (iv) Add sodium sulphate solution to the product
Filter the precipitate then wash and dry it

Question 12

(a) Hydrogen peroxide reacts both as an oxidising agent and as a reducing agent, depending on the conditions. Hydrogen peroxide reduces potassium dichromate(VI) in acidic solution to chromium(III) ions. Hydrogen peroxide will oxidise chromium(III) ions back to chromate(VI) ions in alkaline solution.

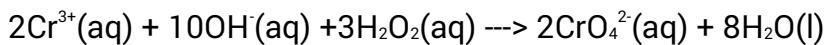


- (i) Deduce the overall equation for the reaction between hydrogen peroxide and dichromate(VI) ions using the data above.
- (ii) Calculate the standard potential of the cell which could be formed from these two half cells.

(iii) How would you determine in the laboratory the standard potential of the dichromate(VI)/chromium(III) electrode using a hydrogen electrode?

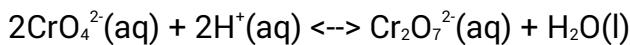
(iv) Why is it necessary to operate electrochemical cells under conditions where virtually no current is drawn from them when finding the cell e.m.f.?

(b) In alkaline solution the reaction of hydrogen peroxide with chromium(III) ions is



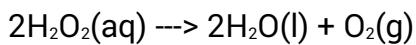
This reaction is used to prepare potassium dichromate(VI) from chromium(III) chloride and hydrogen peroxide in potassium hydroxide solution. The mixture is boiled until it is bright yellow. Boiling is continued until excess hydrogen peroxide has been destroyed. The solution is then cooled, and acidified with ethanoic acid.

(i) The reaction occurring on acidification with ethanoic acid is:



Show that this is not a redox reaction.

(ii) Hydrogen peroxide on heating reacts as follows:



Suggest how you would know when all the hydrogen peroxide has been destroyed in the reaction mixture.

(iii) Why is it essential to destroy all the hydrogen peroxide in the mixture before it is acidified?

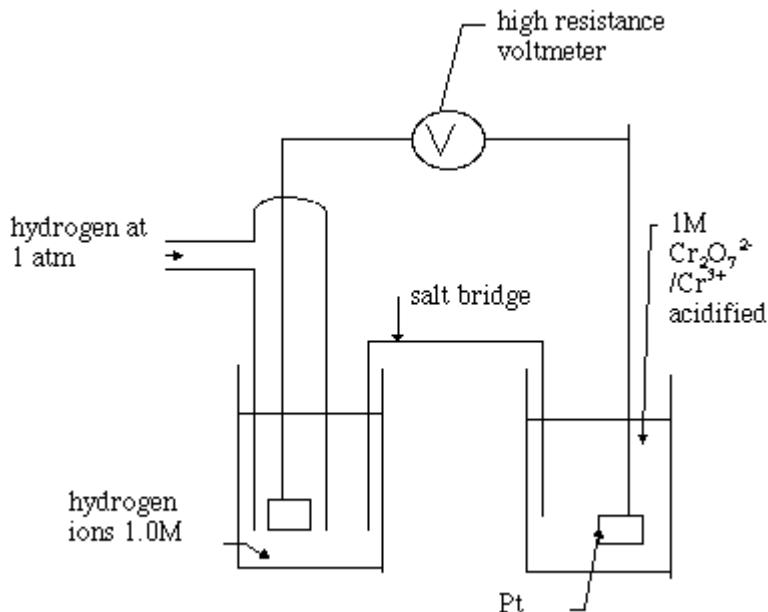
(iv) Derive the two half equations which together give the overall equation for the reaction between hydrogen peroxide and chromium(III) ions in alkaline solution.

Solution



(ii) $E_{\text{cell}} = E^{\circ}_{\text{Right}} - E^{\circ}_{\text{Left}} \dots E_{\text{cell}} = 1.33 - (+0.68) = 0.65\text{V}$

(iii)



(iv) This avoids a voltage drop across the internal resistance of the cell

(b) (i) chromate and dichromate both contain chromium (+6)

(ii) Effervescence stops when the hydrogen peroxide has been destroyed

(iii) Acid converts chromate to dichromate

The dichromate formed oxidises hydrogen peroxide

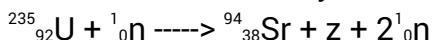
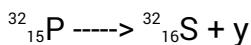
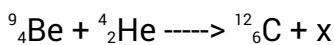
The chromium (III) formed reduces the yield



Question 13

(a) Define the term **isotope**.

(b) Identify x, y, and z in the following nuclear processes:

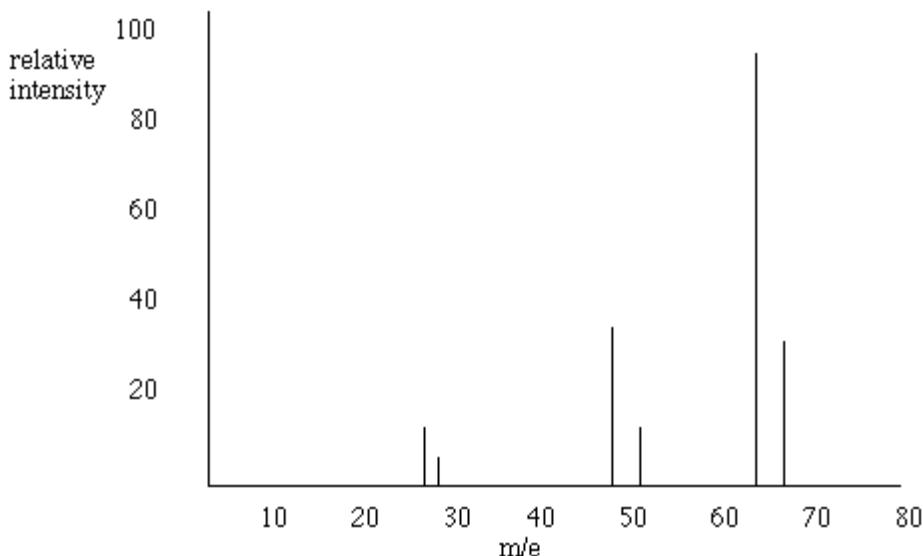


(c) The third of these reactions is the basis for the nuclear power industry.

What feature makes this possible?

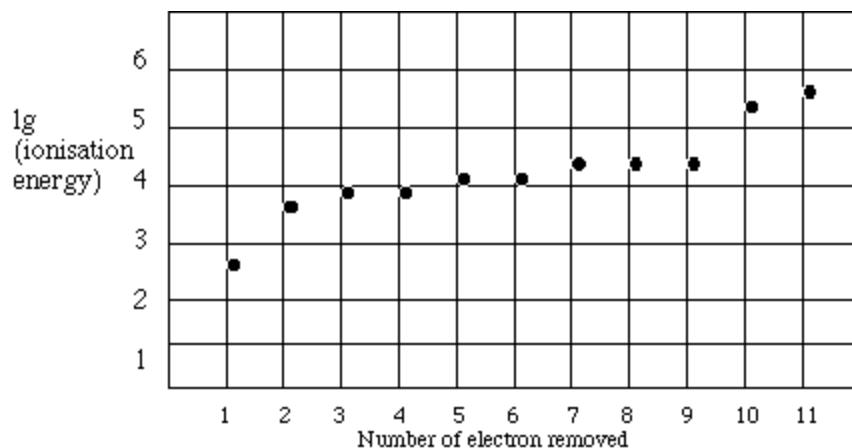
(d) The diagram shows part of the mass spectrum for chloroethane, $\text{C}_2\text{H}_5\text{Cl}$.

What ions are responsible for the peaks at m/e 66 and 64, and 29 and 28?



(e) Define the term **first ionisation energy**.

(f) The graph shows a plot of $\lg(\text{ionisation energy})$ vs number of the electron removed for sodium. Explain the form of this graph in terms of the electron structure of sodium.



solution

(a) Isotopes are atoms of the same element with different numbers of neutrons .

(b) x: a neutron

y: an electron

z: $^{140}_{54}\text{Xe}$

(c) This is a fission reaction in which 1 more neutron is formed than is used.

(d) 66: . $\text{C}_2\text{H}_5\text{Cl}^+$ with the isotope chlorine 37

64: $\text{C}_2\text{H}_5\text{Cl}^+$ with the isotope chlorine 35

29: C_2H_5^+

28: C_2H_4^+

(e) The enthalpy change when 1 mole of gaseous ions each with a single positive charge, are formed from gaseous atoms of an element.

(f) Electrons 10 and 11 are in the same energy level close to the nucleus so have the

highest ionisation energy. The next 8 are in a shell further away from the nucleus so are easier to remove. Electron 1 is in a shell furthest from the nucleus so has the lowest ionisation energy

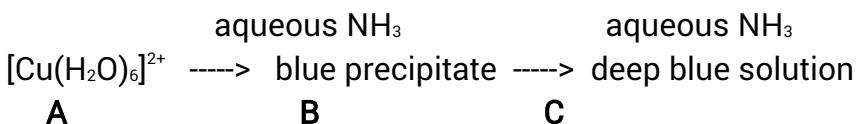
Question 14

- (a) Define **oxidation** in terms of electron transfer.
(b) State **three** properties which distinguish transition metals from main group metals.
(c) Give the electronic configuration for Fe and for Fe^{3+} in the table below.

	3d					4s
Fe: (Ar)						
Fe^{3+} : (Ar)	↑↓	↑	↑	↑	↑	↑↓

Suggest why Fe^{3+} is a more stable ion than Fe^{2+} under normal conditions.

- (d) (i) Name the types of reaction involved in the following changes:



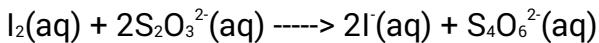
- (ii) Give the formula of compound **B**.

- (iii) Draw the structure of the ion responsible for the colour in solution **C** and show its shape.

- (e) Addition of aqueous copper(II) ions to aqueous iodide ions gives a precipitate of copper(I) iodide and liberates iodine; the iodine can be titrated with aqueous sodium thiosulphate, so these reactions form the basis for a volumetric analysis of copper, for example in metal alloys.

- (i) Write an ionic equation for the reaction of copper (II) ions with iodide ions.

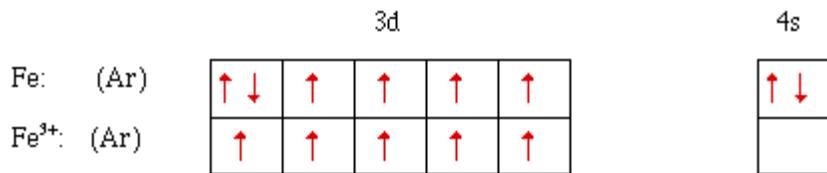
- (ii) Given that the reaction of iodine with sodium thiosulphate is



find the volume of sodium thiosulphate solution of concentration 1.00 mol dm^{-3} needed to react with the iodine liberated by copper ions from a brass screw of mass 2.00g, containing 60% of copper by mass.

Solution

- (a) Oxidation is the loss of electrons.
 (b) They form coloured ions or compounds
 They have variable valencies or oxidation states
 They show catalytic behaviour
 (c) Fe^{3+} is stable due to its half filled 3d sub-shell



(d) (i) A to B deprotonation and B to C ligand exchange

(ii) $\text{Cu}(\text{OH})_2$

(e) (i) $2\text{Cu}^{2+}(\text{aq}) + 4\text{I}^-(\text{aq}) \rightarrow 2\text{CuI}(\text{s}) + \text{I}_2(\text{aq})$

(ii) mass of copper = 60% of 2.00 = 1.20g

amount of copper = mass/molar mass = $1.20\text{g}/63.5\text{g mol}^{-1} = 0.0189\text{mol}$

so amount of copper(II) ions = 0.0189mol

amount of I_2 formed/amount of Cu^{2+} reacting = 1/2

so amount of I_2 formed = $2 \times \text{amount of } \text{Cu}^{2+} = 0.5 \times 0.0189\text{mol} = 0.00945\text{mol}$

amount of thiosulphate/amount of iodine = 2/1

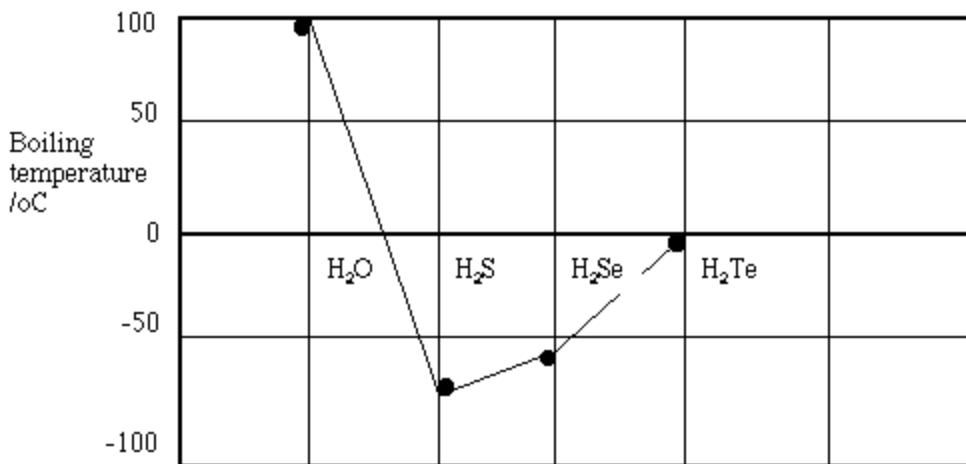
so amount of thiosulphate = $2 \times \text{amount of iodine} = 2 \times 0.00945 = 0.0189\text{mol}$

volume of thiosulphate = amount/concentration = $0.0189\text{mol}/1.00\text{mol dm}^{-3} = 0.0189\text{dm}^{-3}$

so volume of thiosulphate = 18.9cm⁻³

Question 15 .

(a) The graph shows the boiling temperatures of the hydrides of Group 6.



Why is the boiling temperature of water higher than would be expected from the group trend?

- (b) Why is solid water less dense than liquid water?
- (c) Silicon tetrachloride, SiCl₄, is a colourless liquid; its bonds are polar, but the molecule is not. Explain.
- (d) Silicon tetrachloride, SiCl₄, reacts with water to give silicon dioxide, SiO₂, and HCl; it will react with atmospheric moisture unless kept in a sealed tube. 1.00g of a poorly-kept sample of SiCl₄ was added cautiously to water. When reaction was complete the solution was made up to 250cm³ with pure water. 25.0cm³ portions of this required on average 21.6cm³ of 0.100 mol dm⁻³ sodium hydroxide solution for neutralisation. What percentage of the sample analysed was SiCl₄?
- (e) Single crystals of metals conduct electricity equally well in all directions, but a single crystal of graphite will conduct in only one direction. Suggest an explanation in terms of the structures of these materials.

Solution

- (a) Hydrogen bonding is present in water but not the other hydrides so water molecules need more energy to separate them.
- (b) Hydrogen bonds in ice hold molecules far apart in an open structure with low density. When melted many of these bonds are broken so the structures collapses and the water molecules become closer giving a higher density
- (c) SiCl₄ is tetrahedral so the dipoles in each bond cancel out.
- (d) amount of NaOH = concentration * volume = 0.100mol dm⁻³ * 21.6/1000dm³ = 2.16*10⁻³mol
 amount of HCl in 25cm³ = amount of NaOH = 2.16*10⁻³mol
 amount of HCl in 250cm³ = 10 * 2.16*10⁻³mol = 2.16*10⁻²mol
 $\text{SiCl}_4 + 2\text{H}_2\text{O} \longrightarrow \text{SiO}_2 + 4\text{HCl}$
 so amount of SiCl₄ / amount of HCl = 1/4

amount of $\text{SiCl}_4 = 0.25 * 2.16 \times 10^{-2} \text{ mol} = 5.40 \times 10^{-3} \text{ mol}$

mass of $\text{SiCl}_4 = \text{amount} * \text{molar mass} = 5.40 \times 10^{-3} \text{ mol} * 170 \text{ g/mol} = 0.918 \text{ g}$

so % of in original sample = $0.918 \times 100 / 1 = 91.8\%$

- (e) A metal has free electrons between atoms which are able to move in any direction. Graphite has free electrons between layers which are only able to move in the layers.

Question 16

- (a) Enter the formulae of the oxides for the elements shown in the empty boxes in the top two rows of the table. Indicate in the bottom row of boxes the acid-base nature of these oxides.

Na	Mg	Al	Si	P	S	Cl

- (b) Group 4 elements show a trend from non-metallic to metallic behaviour with increasing atomic number. How is this shown by the acid base properties of carbon dioxide, CO_2 , silicon dioxide, SiO_2 , and lead(II) oxide, PbO ? Write equations to illustrate this behaviour.

- (c) PbO and PbO_2 differ strikingly in their properties. Illustrate this by giving the reactions between these two oxides and concentrated HCl, stating the nature of each reaction.

- (d) The +2 oxidation state of tin is reducing. Give a reaction illustrate this property.

Solution

- (a)

Na	Mg	Al	Si	P	S	Cl
Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6	SO_2	Cl_2O
				P_4O_{10}	SO_3	
basic	basic	amphoteric	acidic	acidic	acidic	acidic

- (b) Carbon dioxide and silicon dioxide are acidic but lead (II) oxide is amphoteric.



- (c) For PbO :

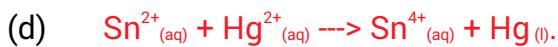


nature of reaction: acid-base.

For PbO₂:



nature of reaction: redox



Question 17

- (a) (i) Name the three classes of elements in the periodic table.
(ii) Describe briefly the structure and bonding in elements in the classes mentioned in (a)
(i) above
(b) Define (i) Melting point
 (ii) Density
(c) Describe and discuss the change in density and melting point;
 (i) Across a period of the periodic table.
 (ii) Down a group of the periodic table.

Solution

(a)

(i)

- Metals
- Semi-metals (metalloids)
- Non-metals

(ii)

- Metals have metallic crystal structures with high coordination numbers. The usual coordination number of twelve as in close packed structures or eight in as in body centered cubic structures.
- The non-metals form covalent bonded molecules (eg Cl₂, N₂, O₂ etc) with very small coordination numbers. This is usually one or two. They form volatile molecular solids in which the inter molecular bonding is due to weak van der waals forces.
- The metalloids (semi metals) form giant molecules in which the coordination number is small (< 4).

The giant molecules may have layers or long chain lattice structures. Example, in diamond, carbon forms three dimensional giant lattice structures with strong covalent bonds between the atoms of carbon. In graphite, carbon forms 2-dimentiosional infinite layers of molecules with covalent bonds within the layers and vanderwaals forces between the layers and the chains.

(b)

- (i) Melting point is the constant temperature at which a pure solid is in equilibrium

- with pure liquid at atmospheric pressure.
- (ii) Density is the mass per unit volume.
- (c)

- (i) **Across a period of the periodic table.**

Density

Along any period (2 or 3) of the periodic table, there is a general increase in density. From one element to the next, the effective nuclear charge increases as there is increased nuclear attraction on the outer electrons and yet no new shell is being added. As a result atomic radius decreases from left to right. The atomic mass increases across any period, therefore increasing atomic mass as atomic radius decreases leads to increase in density across a period.

Melting point

Melting point depends upon the type of structure and the strength of bonding forces which are a periodic function of electronic configuration.

Along (across) a period, structural changes are abrupt (not gradual) i.e. changes from metallic-giant molecular –simple molecular. The stronger the Metallic bonding the higher the metallic bonding. This depends on the number of valence electrons involved in metallic bonding.

In giant molecules such as silicon, where strong covalent bonds are between the silicon atoms, many of the bonds have to be broken before melting can occur, very high temperatures are needed and therefore melting point are very high.

In molecular crystals, where intermolecular bonding is weak(van der waals), relatively low melting points are observed.

- (ii) **Down a group**

Density

On descending any group in the periodic table, elemental structures are the same ie the number outer most electrons remains constant. But from one element to the next atomic radius increases. The increase in atomic mass tends to increase the density. Atomic volume also increases from element to the next. The increase in atomic volume tends to decrease the density. But the in atomic mass outweighs the increase in atomic volume and this favours increase in density down a group in the periodic table.

Melting point

In any group the structure of the elements are the same or similar. The melting point depend on the relative strength of bonding forces.

In group (I) (alkali metals) which are held in close packed structure by metallic bonding, the metallic bond becomes weaker as the size increases from one element to the next on descending the group. Therefore the melting point decreases down the group.

The halogens have molecular crystals in the solid state held together by weak van der waals forces. These forces increases from one element to the next on descending the group (as the atomic size increases) and therefore the melting point increases down the group.

In group (IIIB)-(VIB), the variation of the melting point is complicated because of the great structural changes which occur on descending the group.

Question 18

One characteristic property of transition metals is variable oxidation state.

- (a) For each of the following processes, write two equations to show how the transition metal catalyst reacts and is reformed. Identify the different oxidation states shown by the transition metal catalyst in each process.
- (i) The contact process catalysed by vanadium (V) oxide
 - (ii) The oxidation of ethanedioate ions by acidified potassium manganate (VII) autocatalysed by Mn^{2+} ions.
- (b) Cobalt (II) ions cannot easily be oxidized to cobalt (III) ions in water. Suggest why this oxidation can be carried out in aqueous ammonia and identify a suitable oxidizing agent.
- (c) Metal ions Q^{2+} in acidified aqueous solution can be oxidized by aqueous potassium dichromate (VI).

In a titration, an acidified 25.0cm^3 sample of 0.140mol dm^{-3} solution of $Q^{2+}(\text{aq})$ required 29.2cm^3 of a 0.030mol dm^{-3} solution of potassium dichromate(VI) for complete reaction.

Determine the oxidation state of the metal Q after the reaction with the potassium dichromate (VI).

Question 19

- (a) Explain, by referring to electrons, the meaning of the terms reduction and reducing agent.
- (b) Iodide ions can reduce sulphuric acid to three different products.
- (i) Name the three reduction products and give the oxidation state of sulphur in each of these products.
 - (ii) Describe how the observations of the reaction between solid potassium iodide and concentrated sulphuric acid can be used to indicate the presence of any two of these reduction products.
 - (iii) Write half equations to show how two of these products are formed by reduction of sulphuric acid.
- (c) Write equation an equation for the reaction that occurs when chlorine is added to cold water.
State whether or not the water is oxidised and explain your answer.

Question 20

- (a) State four main types of atomic radii.
- (b) Describe and discuss the changes in atomic radius
- (i) Across a period
 - (ii) Down a group
 - (iii) Along a transition series

Solution

(a) Types of atomic radii

- Ionic radius
- Covalent radius
- Metallic radius
- Van der waals radius

(b)

(i) Across a period

Atomic radius decreases across a period of the periodic table.

From one element to the next, no new shell is added since electrons are being added to the same principal quantum number. This leads to increased nuclear attraction on the outermost electrons which is not exactly balanced by the extra electron added since electrons in the same shell do not screen each other well from the nucleus. As a result the nuclear attraction is greater than the screening effect and electron-electron repulsions. So, the outer most electrons are pulled in closer to the nucleus.

(ii) Down a group

On descending a group in the periodic table, the number of outer most electrons remains constant but from one element to the next, there is added a full shell. The screening effect of the added full shell more than balances the increased nuclear attraction for the outermost electrons. This causes increase in atomic radius down a group.

(iii) Along a transition series

Both nuclear charge and the number of d-electrons increase across the series. The added inner electron screens each other from the nucleus much better than an additional outer electron (i.e. d-electrons screen each other from nuclear attraction poorly and also repels each other rather weakly). The net effect is a slight increase in effective nuclear charge which causes a little decrease in atomic size along any transition series.

Question 21

(a) What is meant by

- (i) Electronegativity
- (ii) Ionization energy

(b) Describe and discuss the changes in electronegativity and ionization energy

- (i) Across a period
- (ii) Down a group in the periodic table

Solution

(a)

- (i) Electronegativity is the relative ability of an atom to attract bonding electrons to become negatively charged in a covalent bonded compound.
- (ii) Ionization energy is the energy evolved when an electron is completely removed

from one mole of a gaseous atom to form one mole of a positively charged gaseous ion.

(b) Electronegativity

(i) Across a period

Electronegativity increases sharply across the S and P elements in the periodic table.

Effective nuclear charge increases from one element to the next across the period. This is because electrons are being added to the same shell and are shielding each other badly from the extra nuclear charge

(ii) Down a group

Electronegativity generally decreases down a group. On descending a group, the number of outermost electrons remains constant but the effective nuclear charge decreases. This is because of increasing screening effect of added new shells which outweighs the increase in nuclear attraction.

Ionization energy

(i) Across a period

Ionization energy generally increases across a period. From one element to the next across a period, electrons are being successively added to the same shell (no new shell being filled). And the nuclear charge is screening such added electrons. Such electrons shield each other poorly from the increasing nuclear charge. This causes a decrease in atomic radius and the increase in ionization energy along the series.

(ii) Down a group

Ionization energy decreases down a group. The effective nuclear charge decreases down a group. This is because, from one element to the next, a new shell is added and the screening effect of the added full shell outweighs the increased nuclear attraction for the outer most electrons leading to increase in atomic radius and consequently decrease in ionization energy down a group.

Question 22

(a) (i) What is meant by lattice energy.

(ii) Discuss the factors which determine the magnitude or trend of lattice energy in the periodic table

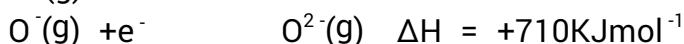
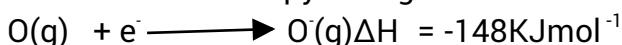
(b) Describe and discuss the changes in thermal conductivity

(i) Across a period

(ii) Down a group of the periodic table.

(c) (i) Define electron affinity.

(ii) Consider the enthalpy change for the reactions,



Comment on the sign of the electron affinities of oxygen.

Solution

(a) (i) Lattice energy is the change in internal energy when one mole of the solid crystal is converted to separate ions in the gas phase.

- (ii) Lattice energy depends upon the charge, ionic radius and electronic configuration of the constituent ions

These three factors determine both type of bonding in the crystal structure and the magnitude of the lattice energy if the bonding is mainly ionic.

- Lattice energy depends upon the reciprocal of distance between the ions ie $\frac{1}{r_+ + r_-}$.

Therefore for any given negative ion, the lattice energy decreases as the size of the positive ion (cation) increases down a group e.g. lattice energy for group (II) metal hydroxide decreases in the order $Mg(OH)_2 > Ca(OH)_2 > Sr(OH)_2$. Similarly for a given cation, lattice energy decreases as the size of the anion (negative ion) increases e.g. lattice energy decreases in the order $NaCl > NaBr > NaI$

- Lattice energy depends upon the charge on the ions ie the greater the charge on the ion, the greater the lattice energy. Example $MgCl_2$ has greater lattice energy than LiF .
- The electronic configuration also determines the magnitude of lattice energy. For example, with d10 configuration as in copper (I), since copper (I) has large lattice energies than predicted from ionic model. This is because, of the poor shielding effect of d^{10} electrons, with the effective nuclear charge being greater than expected

- (b) The mode of heat transfer is by free electrons which increase with atomic or molecular vibrations but the latter is more rapid.

(i) Across a period

Elements in which the bonding is metallic are good conductors of heat and conductivity increases with increase in number of valency electrons involved in the metallic bonding. So conductivity increases across a period as the number of valence valency electrons increases. The delocalized electrons conduct heat rapidly. When the bonding changes from metallic to covalent, there is a sharp drop in conductivity since there are no free electrons in covalent compounds e.g. a sharp drop in conductivity between Al and Si.

(ii) Down a group

For elements in which the bonding is metallic, the thermal conductivity decreases down a given group.

Non-metals have their high energy valence electrons localized in covalent bonds and are therefore poor thermal conductors.

- (c) (i) Electron affinity of an element is enthalpy change when one mole of isolated neutral atoms of an element in the gaseous state gains an electron.
 (ii) The first electron affinity of oxygen is negative. But the second electron affinity is $+710\text{KJmol}^{-1}$. This is because work has to be done to overcome the repulsion between the singly negatively charged oxygen atom $O^-(g)$ and the incoming electron.

Question 23

- (i) What is meant by enthalpy of hydration?
 (ii) The enthalpy of hydration of group IIA elements are given as

Ion	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
-----	-----------	-----------	-----------	-----------	-----------

$\Delta H_{\text{hydration}}$	-2425	-189	-156	-1414	-1273
	1	2			

Explain the trend

- (i) What is meant by electrode potential?
- (ii) State two factors which affect electrode potentials.
- State the table below

Electrode	Li^+/Li	Cs^+/Cs	K^+/K	Ba^{2+}/Ba	Ca^{2+}/Ca	Na^+/Na	Mg^{2+}/Mg	Zn^{2+}/Zn	H^+/H	Cu^{2+}/Cu	$\text{Fe}^{3+}/\text{F}^{e^{2+}}$	F_2/F
	-3.6 4	-2.9 5	-2. 92	-2.90	-2.87	-2.71	-2.37	-0.76	0.0 0	+0.3 4	+0.71	+2. 87

Explain each of the following

- The alkali metals have the highest negative electrode potentials.
- Lithium has the most negative electrode potential.
- Barium and calcium both in group IIA of the periodic table have negative potential than sodium.
- The electrode potential of beryllium is less negative than other group IIA elements.
- The electrode potentials of copper and iron (transition elements) is less negative than those of group IIA elements.

Solution

- (a) (i) Enthalpy of hydration is the enthalpy change when one mole of a gaseous ion is hydrated
- (ii) Enthalpy of hydration depends on three factors i.e. the charge on the ion, the ionic radius and the nature of the electronic core (or effective nuclear charge). In group (IIA) elements, the ionic radius increases from Be^{2+} down the group to Ba^{2+} . Effective nuclear charge decreases down the group because of greater shielding by added new shells from one element to the next. This leads to decreasing attraction (less attraction) for water molecules causing a decrease in enthalpy of hydration down the group.
- (b) (i) Electrode potential is the driving force for a member (metal dipped into solution of its ions) to change from one oxidation state to another. It is a quantitative measure of tendency of reactants in their standard states to form product in their states for a particular reactant.
- (ii)
- Enthalpy of atomization
 - Ionization energy
 - Salvation energy (hydration energy) of gaseous metal ions.

(c)

- The alkali metals have relatively low enthalpies of atomization and low ionization energy. This causes electrode potential to be large and negative despite their low enthalpies of hydration.
- The lithium ion is small in size and therefore is strongly hydrated leading to much larger enthalpy of hydration than any of the alkali metals. Therefore lithium has the

most negative electrode potential.

(iii) The ionization energies of barium and calcium are higher than that of sodium. Although the ionization is, their enthalpies of atomization are fairly small and their hydration energies are very large due to high charge density compared to sodium. Therefore Ba^{2+} and Ca^{2+} ions have negative potential than sodium ion.

(iv) Beryllium is a small atom with exceptionally high ionization energy than any of the group (IIA) elements. This makes the electrode potential of beryllium to be less negative than other elements of group (IIA).

(v) The transition elements (copper and iron) have a high ionization energy and very large atomization energy which despite their high enthalpy of hydration, reduces their electrode potentials below the group (IIA) elements.

Question 24

The elements Na, Mg, Al, P and Cl all belong to period three of the periodic table. Discuss the reactions of each of these elements with

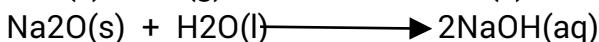
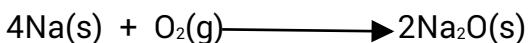
- (a) Air
- (b) Water

Solution

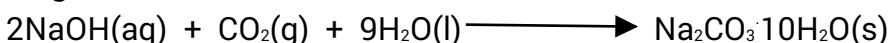
(a) Reactions with air

The metals react with oxygen to form oxides which are formed on the surface of the metal and whether the reaction continues depends on the film formed. I.e. if the oxide is protective (oxide with low solubility in water), then the reaction may not continue.

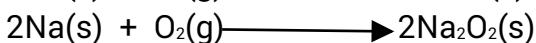
▪ Sodium almost does not react with dry air (very little attacked by dry air). But when exposed to moist air, sodium reacts to form sodium monoxide. This oxide is deliquescent; it absorbs water from air and dissolves to form sodium hydroxide solution.



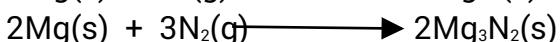
The alkaline solution absorbs carbondioxide from air and forms crystalline mass of sodium carbonate which may loose its water to form a white powder if left exposed for a long time.



When sodium is heated in air, a mixture of monoxide and peroxide are formed

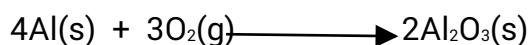


▪ Magnesium does not react with dry air. It reacts slowly with moist air forming a layer of oxide. The oxide later changes to hydroxide and finally a carbonate. When heated, magnesium burns with a brilliant flame forming magnesium oxide and nitride.



▪ When aluminium is exposed to air, it acquires a thin layer of oxide layer which protects further reaction. But when heated to high temperature it forms a mixture of oxide

and nitride.



- Non-metals do not react with air at room temperature except phosphorous. Phosphorous reacts slowly with moist air at room temperature and burns vigorously in air at higher temperatures.

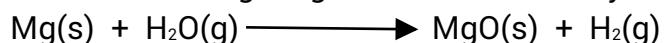


(b) Reaction with water

- Sodium and magnesium react with water displacing hydrogen and forming hydroxides. The reactivity decreases from sodium to magnesium. Na reacts rapidly with cold water.



- Clean magnesium reacts with cold water only very slowly. It burns brilliantly if heated in steam forming magnesium oxide and hydrogen gas.



- Chlorine is a sparingly soluble in water. It dissolves to form hydrochloric acid and hypochlorous acid.



Question 25

The elements Na, Mg, Al, P, Si, S and CL are in period three of the periodic table.

Discuss the;

- Structure and physical properties
- Acid-base character of the oxides of each of the elements.

Solution

(a) The oxides Na_2O , MgO , Al_2O_3 and SiO_2 have giant structures. Na_2O , MgO and Al_2O_3 are ionic. Therefore are solids at room temperature with high melting points and boiling points. They are conductors of electricity in molten state.

The oxides of P_4O_{10} , SO_3 and Cl_2O_7 have simple molecular structures consisting of discrete small molecules. They have low boiling points (more volatile than the ionic oxide) they do not conduct electricity in the liquid state. The change in the structure and bond type from ionic oxides to simple molecular oxides across the period is due to decreasing electronegativity difference between the element and oxygen.

(b) The gradation in structure of the oxides from ionic through giant molecules to simple molecules leads to differences in the way in which oxides react with water and alkalis. Na_2O is ionic and contains O^{2-} , it reacts vigorously with water forming alkaline solution.



It reacts more vigorously with acids forming aqueous solutions of Na^+ (aq) ions.



MgO does not react so readily with water or acids. This is because of the large charge density on the Mg^{2+} ion which holds the O^{2-} ion more firmly. Therefore MgO is only

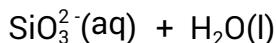
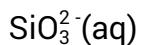
slightly soluble in water. It reacts readily with acids to form solutions of $Mg^{2+}(aq)$ ions.



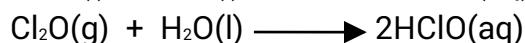
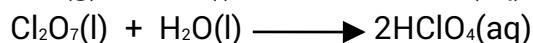
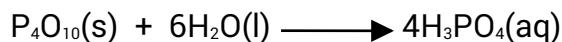
Al_2O_3 is amphoteric. It does not react with water but reacts with both acid (H^+) and alkalis (OH^-).



SiO_2 does not react with water but it reacts with concentrated alkalis forming silicates,



The oxides of P_4O_{10} , SO_3 and Cl_2O_7 except Cl_2O are acidic. They react readily with water forming strong acids.



Question 26

Some physical properties of the chlorides of elements in period three are presented in the table below.

Chloride	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	S_2Cl_2	Cl_2
State	Solid	Solid	Solid	Liquid	Liquid	Liquid	Gas
Melting point	148	714	192	-68	-92	-80	-101
Conductivity	Good	Good	V.poor	Nil	Nil	Nil	Nil

(a) Explain the trend in the physical properties.

(b) Discuss the reactions of these chlorides with water.

(c) The melting point of aluminium bromide is $97.5^\circ C$ whereas that of aluminium fluoride is $192^\circ C$

Solution

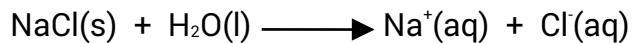
(a) Melting point generally decreases across the period. $NaCl$ and $MgCl_2$ have giant structures composed of oppositely charged ions attracted to each other by strong electrostatic forces in ionic bonds. $NaCl$ is mainly ionic and the three dimensional lattice structures consist of discrete ions. $MgCl_2$ forms a layer lattice. Therefore the melting points are high and in molten state, they are conductors of electricity because the ions are able to move freely.

The other chlorides have simple molecular structures composed of small discrete molecules attracted to each other by weak van der waals forces.

AlCl_3 form a layer lattice of intermediate type of bonding between ionic and covalent. SiCl_4 has a lattice which consists of discrete molecules but in which the bonds are more polar than those in PCl_3 and S_2Cl_2 . Cl_2 has no ionic character. Therefore the melting points of these chlorides are low and as liquids they will not conduct electricity.

(b) Reaction with water

NaCl and MgCl_2 are ionic and readily dissolve in water. NaCl dissolves forming single aquated ions.



The solution is neutral ($\text{pH} = 7$)



The resulting solution has a $\text{pH} \approx 6.5$

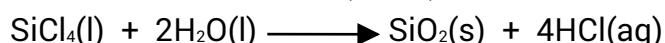
AlCl_3 dissolves in water to give a solution which is acidic

In aqueous solution the Al^{3+} ion is attracted to six water molecules, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$

However, the electric field associated with the small and highly charged Al^{3+} ion, is so intense that it draws electrons from the O-H bond of the water molecules surrounding it. This leads to loss of proton by the water molecule. Hence the solution is acidic.



The nonmetal chlorides, SiCl_4 , PCl_3 and S_2Cl_2 react with water forming acidic solutions.



- (c) The bromine atom is larger than the fluorine atom. The strong electric field associated with the small highly charged Al^{3+} ion is able to polarize the Al-Br bond. But this is not possible with the small fluorine atom. Therefore AlF_3 is predominantly ionic whereas AlBr_3 is covalent which easily polymerises into Al_2Br_6 . Hence the melting point of AlF_3 is greater than that of AlBr_3 .

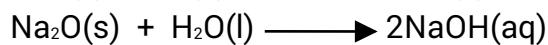
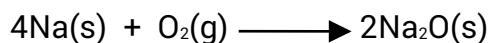
Question 27

Explain each of the following.

- When sodium metal is left exposed to air for a long time, a white powder is formed.
- When magnesium is heated in air and the product shaken with water and warmed, ammonia is evolved.
- Magnesium oxide is slightly soluble in water.
- Aluminium chloride dissolves in water to give solution of pH less than 7.

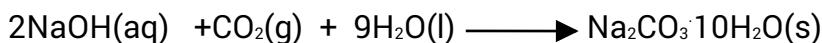
Solution

- (a) Sodium reacts with oxygen forming sodium monoxide. Sodium monoxide is deliquescent thereby absorbs water from air forming a solution of sodium hydroxide.



The alkaline solution absorbs carbon dioxide from the air forming a crystalline mass of

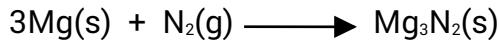
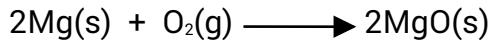
sodium carbonate.



If left exposed for a long time, the hydrated sodium carbonate loses water and leaves a white powder of sodium carbonate monohydrate.



- (b) Magnesium burns with a brilliant bluish-white flame when heated. It combines with oxygen to form magnesium oxide and with nitrogen in the air to form magnesium nitride.



If the product is shaken with water and warmed, ammonia is evolved.



- (c) The Mg^{2+} ion is a small ion and highly charged (i.e. large charge density). This large charge density holds the O^{2-} ion more firmly (strongly) such that the lattice energy for magnesium oxide is high. This lattice energy cannot be offset by the hydration energy. Therefore magnesium oxide is only slightly soluble in water.



- (d) When aluminium chloride is dissolved in water, the aluminium ion, Al^{3+} is surrounded (attracted) by six water molecules as in $[\text{Al}(\text{H}_2\text{O}_6)]^{3+}$. The small Al^{3+} ion is highly charged and therefore a high electric field exists around the Al^{3+} ion. This electric field is intense that it draws electrons in the O-H bond of water molecule enabling the water molecule to loose a proton. Hence it is acidic ($\text{pH} < 7$)



Question 28

- (a) (i) What is meant by concentration of ore.
(ii) Give the ores of aluminium and state one impurity.
(iii) Describe how one of the ores you have named in (a) (ii) above can be concentrated.
- (b) State the observation and write equations for the reactions of aluminium with
(i) Aqueous sodium hydroxide
(ii) Sulfuric acid
(iii) Sulphur
(iv) chlorine
- (c) (i) Aluminium oxide is amphoteric. Explain.
(ii) State the observation and write equations when aqueous sodium hydroxide is added to $[\text{Al}(\text{H}_2\text{O}_6)]^{3+}(\text{aq})$

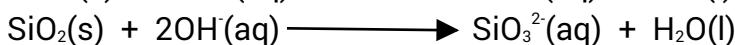
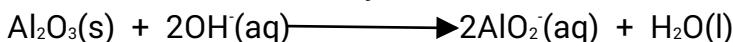
Solution

- (a) (i) Concentration is the process of removing the unwanted earthly (gangue) material and other impurities from an ore of a metal before reduction and purification.
- (ii) Bauxite $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$

Impurities

- Iron (III) oxide
- Silicondioxide
- Titanium oxide

(iii) Bauxite is reacted with hot concentrated caustic soda (NaOH). This removes alumina and silica as they are soluble.



The insoluble impurities like iron (III) oxide are filtered and the solution of sodium aluminate diluted with water so as to precipitate aluminium hydroxide.



The aluminium hydroxide is filtered off, washed and dried. It is heated to give aluminium oxide, Al_2O_3 .



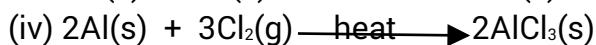
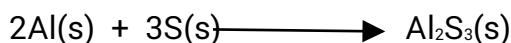
The aluminum oxide is reduced by electrolysis to aluminium metal using carbon electrodes.



(ii) Sulphuric acid- hot and concentrated



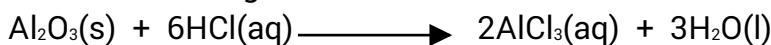
(iii) Aluminium to be heated



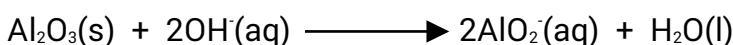
(c) (i) Aluminium oxide is an oxide which exhibits both acidic and basic properties.

Aluminium oxide reacts with acids e.g. hydrochloric acid to form salt and water.

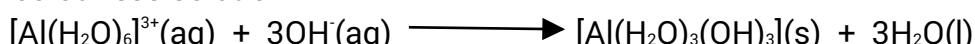
Thus behaving as a basic oxide.



Aluminium oxide reacts with sodium hydroxide to form a salt. Thus behaving as an acidic oxide.

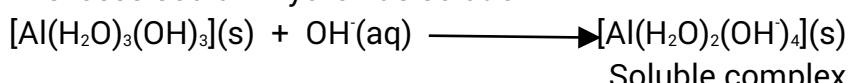


(ii) White precipitates which dissolves in excess aqueous sodium hydroxide forming a colourless solution



White precipitate

In excess sodium hydroxide solution



(iii)

Use

- Cooking utensils
- Reflector
- Aluminium paint
- Air craft bodies
- Wrapping materials

Property

- Good conductors of heat
- Resistant to corrosion, does not tarnish and reflects heat
- Prevents corrosion
- Light metal
- Resistant to corrosion

Question 29

- (a) Name the three classes of hydrides and in each case give an example.
- (b) Write the formula of the hydrides of Na, Al, P, Si and Cl. Indicate the type of bonding in each case.
- (c) Explain what happens when each of the hydrides given in (b) above are added to water and state whether the resultant solution is acidic, alkaline or neutral. Write equations in each case.
- (d) State the observations and write equation when silane reacts with
- Iron (III) solution
 - Chlorine gas

Solution

(a)

- Ionic hydride eg NaH
- Covalent hydrides eg HCl, H₂S
- Metallic hydride eg NiH₂

(b)

- NaH, ionic
- PH₃, covalent
- SiH₄, covalent
- HCl, covalent

(c) NaH reacts with water forming hydrogen gas and an alkaline solution. The resultant solution is alkaline



AlH₃ reacts with water forming hydrogen and an alkaline solution.



SiH₄ does not react with water. This is because the Si-H bond is strong.

PH₃ is almost insoluble in water and a solution in water is neutral to litmus.

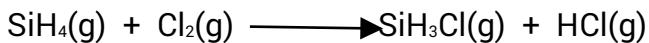
HCl reacts with water to form an acidic solution (pH<7)



(d) (i) solution changes from reddish brown to greenish



(ii) Greenish yellow colour fades and white fumes are observed



Question 30

(a) The solid chloride of aluminium was found to be volatile when heated and had a vapour density of 133.5 at 350 °C . The solid contains 80g of chlorine and reacted violently with water to give a solution which when treated with sodium hydroxide gave a white precipitate soluble in excess alkali.

(i) Calculate the molecular formula of the chloride (Cl = 35.5, Al = 27)

(ii) Write the structural formula showing the bonding in the chloride of aluminium

- (iii) Explain all the observations above
- (b) When aluminium chloride was dissolved in sodium hydroxide there was a decrease in the freezing point depression of sodium hydroxide. Deduce whether the aluminium ion formed is $[Al(OH)_4]^-$ or $[Al(OH)_6]^{3-}$. Explain your reasoning.
- (c) Explain each of the following
- Solutions of simple aluminium (III) salts are acidic.
 - Aluminium utensils should not be washed in strongly alkaline solution.
- (d) Write equations for the reaction of water with
- Aluminium nitride
 - Aluminium carbide

Solution

(a)

(i) Molecular mass = 2 × vapour density = 2 × 133.5 = 267

$$Al_xCl_y = 267$$

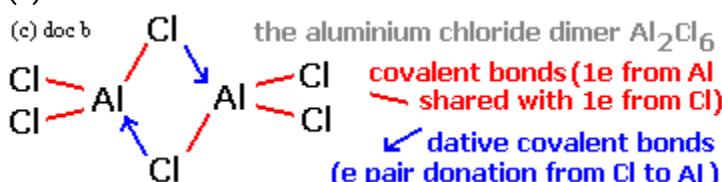
$$\frac{(y \times 35.5)}{267} \times 100 = 80\% \\ y = \frac{80 \times 267}{35.5 \times 100} = 6$$

$$Al_xCl_y = 267$$

$$27x + 6(35.5) = 267 \\ x = 2$$

Therefore the chloride is Al_2Cl_6

(ii) Structural formula



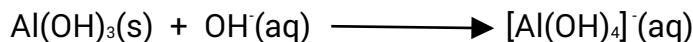
(iii) On heating aluminium chloride, it dissociates to give aluminium chloride, $AlCl_3$.



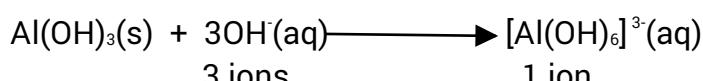
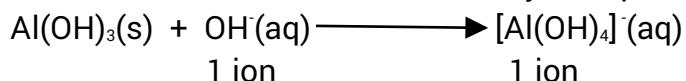
It reacts violently with water to give hydrated aluminium ions, $[Al(H_2O)_6]^{3+}$ and chloride ions, Cl^- .



The white precipitate is aluminium hydroxide which dissolves in excess alkali.



(b) The formation of aluminate ions may be represented by the following equations



The freezing point depression depends on the total number of particles present in solution. In the formation of $[Al(OH)_4]^{-}(aq)$ there is no change in the number of ions and

therefore no change in the freezing point depression of sodium hydroxide on the addition of aluminium hydroxide.

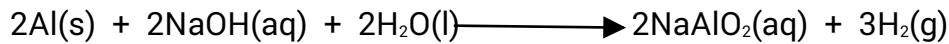
However, in the formation of $[\text{Al}(\text{OH})_6]^{3-}$ (aq), there is a change (decrease) in the number of ions. This would lead to a decrease in the freezing point depression of sodium hydroxide on adding aluminium hydroxide. Therefore the formula of the aluminate ion is $[\text{Al}(\text{OH})_6]^{3-}$ (aq)

- (c) (i) Aluminium salts are hydrolysed in water according to the following equation.



This is possible because of the high electric field around the small Al^{3+} ion which weakens the O-H bond in water such that H^+ ions are produced and the solution is acidic.

- (ii) Strong alkaline solutions dissolve aluminium to form aluminate.



- (d) (i) $\text{AlN}(\text{s}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow \text{Al}(\text{OH})_3(\text{s}) + \text{NH}_3(\text{g})$



Question 31

- (a) The calculated and experimental lattice energy of sodium salts of the halogens is given in the table below.

Salt	NaF	NaCl	NaBr	NaI
Calculated	-904	-779	-736	-701
lattice energy (KJmol ⁻¹)				
Experimental	-904	-777	-720	-674
lattice energy (KJmol ⁻¹)				

Explain the trend in the discrepancy

- (b) The vapour pressure of AlF_3 , AlCl_3 and AlBr_3 reach the value of 1 atmosphere at 1564K, 696K and 530K respectively. Explain.

- (c) Study the table below.

Salt	Solubility g/100g of water
NaCl	0.615
NaF	0.099(insoluble)
AgCl	1.33×10^{-6} (insoluble)
AgF	1.42

Explain each of the following

- (i) NaCl and AgF are soluble
(ii) NaF and AgCl are insoluble

- (d) The melting point of NaCl, CaO, CCl_4 and SiO_2 are 8008, 2480, 23 and 1610 respectively.
Explain

Solution

(a) The polarizing power of an ion depends on the strength of its electrical field (charge density). An ion with a low polarizing power will have a high polarisability because its electric field is low. Therefore it will be more easily distorted by other fields. The anion size increases from fluorine to iodine. As anions have high polarisabilities but low polarizing power, the polarisability increases as the size of anion increases from F⁻ to I⁻. This is because as the anion becomes larger, electrons become more diffusely spread and further from the nucleus. The increase in polarisability leads to a high distortion of electron cloud and introduces some covalency causing discrepancy between measured and calculated lattice energy. NaF is purely ionic and so both measured and calculated lattice energy are the same. Covalent character in the crystal lattice of sodium halides increase in the order NaCl < NaBr < NaI and so discrepancy between measured and calculated lattice energy increases in the same order.

(b) In boiling, the binding forces within a liquid have to be broken down and the particles are separated. Energy is absorbed by the particles in the liquid until it is ready to break up at its boiling point. A liquid will boil when its vapour pressure equals prevailing atmospheric pressure of 1 atmosphere.

Fluorine is a small anion not polarized and therefore AlF₃ is purely ionic with strong electrostatic forces between Al³⁺ ion and F⁻ ion. A lot of energy has to be absorbed to break these forces and the vapour pressure will reach 1 atmosphere at high temperature.

The Cl⁻ ion is intermediate in size and partly polarized. The bonding in AlCl₃ is intermediate between ionic and covalent, less energy is needed and the vapour pressure will reach 1 atmosphere at a lower temperature.

The Br⁻ ion is large, easily polarized and therefore AlBr₃ is covalent with a simple molecular structure. The weak intermolecular forces can easily be overcome by supplying low energy and therefore its vapour pressure will reach 1 atmosphere at a lower temperature.

(c) (i) Both NaCl and AgF are purely ionic and the high lattice energy is easily overcome by the high hydration energy. Therefore the two salts are soluble.

(ii) In AgCl, due to the large size of the chloride ion, which is partly polarized, the ionic bonding in AgCl is strengthened by covalent character. This leads to a very high hydration energy which cannot easily be offset by the hydration energy. Similarly due to the small of fluoride ion, there is a strong electrostatic force of attraction in the ionic crystal of NaF with high lattice energy which cannot be offset by the hydration energy. Therefore both AgCl and NaF are insoluble in water.

(d) In melting of a solid the binding forces are broken down by increase in temperature.

NaCl and CaO are ionic solids with strong electrostatic forces holding the ions together. Therefore they have high melting points. The electrostatic forces are higher in CaO due to the high charge on Ca²⁺ ion and O²⁻ ion leading to a much higher melting point of CaO than for NaCl.

CCl₄ is a covalent compound which is non polar with a simple molecular structure. The molecules are held together by weak van der waals forces. Therefore it has very low melting point.

The bonding in SiO₂ is covalent with a giant structure. High energy is needed to

overcome these forces hence high melting point.

Question 32

The elements C, Si, Ge, Sn and Pb belong to group (IVB) of the periodic table.

- (a) The chemistry of carbon and its compounds differ from that of other elements in the group. Illustrate this statement with two examples.
- (b) Carbon has two allotropes
 - (i) What is meant by the term allotrope.
 - (ii) Describe the structure of the allotropes of carbon and explain the effect on the physical properties.
 - (iii) State two uses of each allotrope.
 - (iv) Describe briefly an experiment to show that the two substances are allotropes of carbon.
- (c) Write equation for the reaction of sulphuric acid with;
 - (i) Carbon
 - (ii) Tin
- (d) Ethanoic acid reacts in the presence of air with lead. Write the equation of reaction.

Solution

(a)

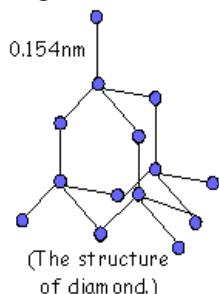
- Carbon has the property of direct bonding with itself as in linear chains, rings. In the chains or rings carbon may have single or multiple bonds. Example in ethane, benzene etc.
- Carbon is the only element in the group which forms stable multiple bonds with itself and other non-metals (nitrogen and oxygen). Example, in alkenes, aldehydes, ketones, nitriles etc.
- Carbon forms gaseous oxides, whereas the other elements of the group do not. E.g. CO_2 , CO is gases but the rest of the oxides of group (IV) are not gaseous.
- Carbon has a maximum covalency of four. It cannot have more than eight electrons in its outer shell. Examples CCl_4 , CH_4 etc.
- Carbon compounds are relatively inert. Example, CCl_4 does not undergo hydrolysis whereas SiCl_4 hydrolyses readily.
- Carbon does not show inert pair effect. Because of this, there are no stable compounds in which carbon has an oxidation state of +2.
- Carbon in general, forms stronger bonds to other elements than do the other elements of group (IVB). Therefore, its compounds tend to be more stable with respect to dissociation into elements.
- Carbon has a much higher electronegativity than the rest of the elements in group (IVB). It is able to form anions e.g. C_2^{2-} and C^4- .

(b)

- (i) Allotropes are two or more substances (elements or compounds) which can exist in more than one form.
- (ii) Carbon has two allotropes, namely diamond and graphite.

Structure of diamond

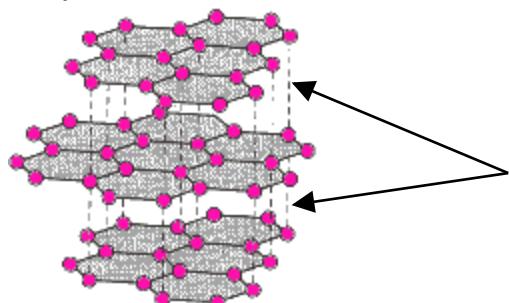
In diamond each carbon atom is covalently bonded to four other carbon atoms arranged tetrahedrally. This gives a three dimensional giant atomic structure.



Because of the compactness, strength and uniformity of the covalent bonds, diamond is very hard, transparent and non-volatile liquid (high melting point). There are no free electrons and therefore diamond does not conduct electricity.

Structure of graphite

In graphite each atom is bonded to two other carbon atoms forming a two dimensional layer structure. The carbon atoms lie in parallel planes in which the atoms are bonded through sp^2 covalent bond in a network of regular hexagons. Each layer is held to another by weak van der waals force. The unused p-electrons are delocalized between the planes.



Graphite is therefore soft, can slide along layers. It is a conductor of heat and electricity because of the delocalized electrons.

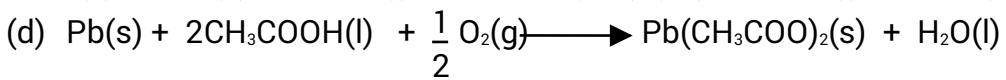
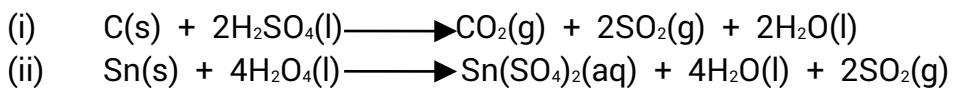
(iii) Uses of diamond

- As jewels.
- In oil-well drills.
- Cutting tools.
- Glass cutters.
- Watch bearings.
- Dyes and abrasives etc.

Uses of graphite

- In making pencils.
- In making electrodes, graphite crucibles.
- In making brushes for electric motors.
- As lubricant etc.

(c)



Question 33

For the chlorides of the elements C, Si, Sn and Pb

(a) Describe the structure and the molecular shape

(b) Discuss

(a) Volatility

(ii) Thermal stability

(iii) And hydrolysis of the chlorides

(c) Write equation (s) for the preparation of

(i) $SiCl_4$

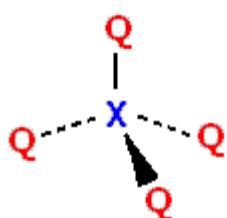
(ii) CCl_4

(iii) $PbCl_4$

(d) State two observations when aqueous iodine is added to tin (II) chloride.

Solution

(a) In all the tetrachloride, each element is bonded to four atoms of chlorine through covalent bond. The four atoms of chlorine are arranged tetrahedrally giving a three dimensional structure.



Weak van der waals forces exist between molecules and therefore the chlorides have simple molecular structure.

(b)

(i) Volatility

All the chlorides, XQ_4 have low melting points and boiling points. They are volatile liquids at room temperature. The melting point and boiling point is a measure of the intermolecular forces. The melting point and boiling point increase in the order $CCl_4 < SiCl_4 < GeCl_4 < SnCl_4 < PbCl_4$. This is because the molecular masses increase in the same order.

(ii) Thermal stability

Thermal stability is a measure of the strength of the bonding forces. The size of cation increases from carbon to lead and this leads to the X-Q bond becoming weaker down the group. The weaker the X-Q bond, the less stable is the chloride. Therefore CCl_4 , $SiCl_4$ and $GeCl_4$ are stable even at high temperatures. $SnCl_4$ decomposes on heating to form $SnCl_2$ and Cl_2 .

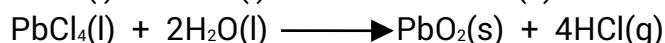
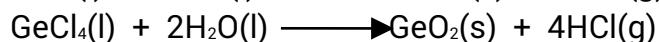
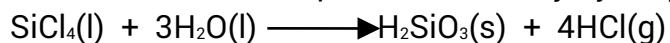


$PbCl_4$ is unstable and decomposes readily to form $PbCl_2$ and Cl_2 .



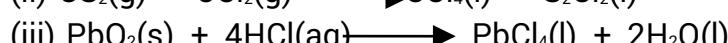
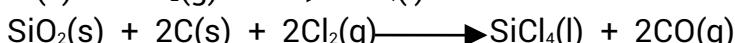
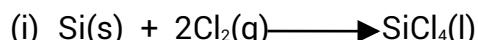
(iii) Hydrolysis of chloride

All the chlorides except CCl_4 are readily hydrolysed to form hydroxyl compounds.

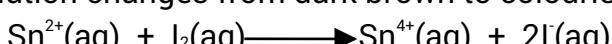


The tendency to undergo hydrolysis is in the order $\text{SiCl}_4 > \text{GeCl}_4 > \text{SnCl}_4 > \text{PbCl}_4$.

(c)



(d) Solution changes from dark brown to colourless.



Question 34

C, Si, Ge, Sn and Pb are elements of group (IVB) in the periodic table.

- (a) (i) Describe the type of chlorides formed by these elements.
(ii) Show how the chlorides of the elements react with water
(iii) Lead (II) chloride is more soluble in concentrated hydrochloric acid than in water.
Explain.
- (b) (i) Describe the trend in the basicity of the oxides of these elements.
(iii) Write equations to show how the oxides of carbon, silicon and germanium react with sodium hydroxide.
- (c) State observation and write equation when concentrated sulphuric acid is heated with lead (IV) oxide.

Solution

(a)

(i) All the elements of group (IVB) form chlorides of the type MCl_4 which are liquids and covalent.

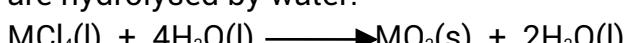
I.e. each element in the group is bonded to four atoms of chlorine through covalent bonding.

Tin forms stable chloride, SnCl_4 which is mainly covalent.

Lead forms stable chloride, PbCl_2 which is mainly ionic.

Carbon and silicon also form chlorides of the type $\text{M}_n\text{H}_{2n+1}\text{Cl}$ which are mainly covalent.

(ii) CCl_4 does not react with water but all the other chlorides of group (IVB) elements are hydrolysed by water.



Where M = Si, Ge, Sn and Pb

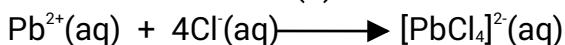
The tendency to undergo hydrolysis is in the order, $\text{SiCl}_4 > \text{GeCl}_4 > \text{SnCl}_4 > \text{PbCl}_4$.

Tin (II) chloride is soluble in water whereas lead (II) chloride is sparingly soluble in cold water but soluble in hot water.

(iii) Lead (II) chloride is soluble in water and the following equilibrium is formed.



In the presence of concentrated hydrochloric acid, the chloride ions from the acid combines with lead (II) ions to form a complex.



The formation of this complex reduces the concentration of lead (II) ions thereby altering the above equilibrium from left to right. Therefore lead (II) chloride dissolves.

(b)

(i) Trend in basicity of oxides

Oxides in oxidation state +2

Carbonmonoxide, CO is weakly acidic (or neutral)

Sicon (II) oxide, SiO is unstable

Germanium (II) oxide, GeO is amphoteric

Lead (II) oxide, PbO is mainly basic

Oxides in oxidation state +4

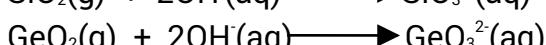
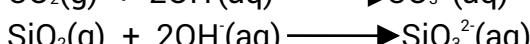
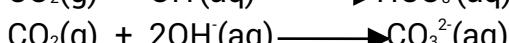
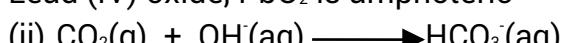
Carbondioxide, CO₂ is acidic

Silicon (IV) oxide, SiO₂ is acidic

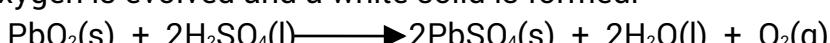
Germanium (IV) oxide, GeO₂ is amphoteric

Tin (IV) oxide, SnO₂ is amphoteric

Lead (IV) oxide, PbO₂ is amphoteric



(c) Oxygen is evolved and a white solid is formed.



Question 35

Explain each of the following

- The bonds in tetra chloromethane are polar but tetra chloromethane molecules are not polar.
- The boiling points of the hydrides of group (IVB) elements in the periodic table are in the order.
 $\text{CH}_4 < \text{SiH}_4 < \text{GeH}_4 < \text{SnH}_4$
- Lead (IV) chloride is very unstable and a powerful oxidising agent decomposing to lead (II) chloride.
- Tin (IV) chloride which is less stable than tin (II) chloride is a powerful reducing agent in aqueous solution is hydrolysed by cold water whereas carbon tetrachloride is not hydrolysed.
- The melting point of C (diamond), Si, Ge, Sn and Pb are 3730 °C, 1410 °C, 232 °C and 327 °C respectively.

Solution

(a) The chlorine atom is more electronegative than the carbon atom. The chlorine atom tends to attract the bonding electrons in C-Cl bond more towards itself. This leads to the chlorine atom acquiring a partial negative charge leaving the carbon atom with a partial positive charge causing distortion of the electron distribution between the carbon atom and chlorine atom. This unequal distribution of bond electrons is responsible for the bond polarity in tetrachloromethane. However, the C-Cl bonds are symmetrical in the tetrachloromethane because the chlorine atoms are tetrahedrally arranged around the carbon atom. The bond polarity effects cancel each other so that the molecule has a net dipole moment of zero. Therefore the whole molecule is non-polar.

(b) The boiling point of a substance is a measure of the strength of molecular forces of attraction which have to be overcome. The boiling points of compounds increase with increase in molecular mass and polarity of the molecules. The molecular mass of the hydrides of group (IVB) increase in the order $\text{CH}_4 < \text{SiH}_4 < \text{GeH}_4 < \text{SnH}_4$. Therefore boiling points vary in the same order.

(c) Lead (IV) chloride is a covalent liquid and unstable. The M-Cl bond in lead (IV) chloride is the weakest compared to the tetrachlorides of group (IVB) elements. Therefore lead (IV) chloride is unstable and easily decomposes to lead (II) chloride and chlorine.



Lead (IV) chloride readily accepts electrons thereby behaving as a strong oxidizing agent. In lead (II) chloride which is ionic, the lead (II) ion is formed by loss of two p-electrons in the outer shell, while the two s-electrons remain relatively stable and unreactive (inert pair effect). Therefore lead (II) chloride is more stable than lead (IV) chloride.

(d) $\text{SnCl}_4(\text{l})$ is covalent liquid and unstable due to the weakness of the Sn-Cl bond. It is thus less stable than tin (II) chloride and decomposes on heating to tin (II) chloride and chlorine gas.



Tin (II) chloride is ionic and in aqueous solution it readily loses electrons and becomes tin (IV) chloride thereby behaving as a strong reducing agent.



Carbon does not have d-orbitals whereas tin has d-orbitals. The non-bonding electrons on the oxygen of water molecule interact with the vacant d-orbitals in tin through dative covalency. This interaction leads to weakening of the Sn-Cl bond so that chlorine atom is lost as hydrogen chloride gas. Such an interaction is not possible with carbon which lacks a d-orbital. Therefore SnCl_4 undergoes hydrolysis whereas CCl_4 does not.

(e) The melting point of a substance indicates the strength of the forces holding the particles together within the solid of the substance.

The metallic (electropositive) character and non-metallic character decreases as atomic number increases down the group (IVB) elements. Atomic size increases from carbon to lead and this leads to increase in atomic radius, and weakening of interatomic bonding causing a decrease in the attraction of neighboring nuclei for intervening electrons. The decrease in interatomic forces results in a change in

bonding from covalent to metallic down the group. In diamond the carbon atoms are held by strong covalent bond bonds arranged tetrahedrally giving it a 3-dimensional giant molecular structure. Silicon and germanium also have giant molecular structures similar to diamond, but the strength of covalent bond decreases to germanium. Therefore melting point decreases from diamond (very high) to tin (lowest). Tin and lead have giant metallic structures but because lead is more electropositive (more metallic) than tin, the melting point of tin is lower than that of lead.

Question 36

- (a) (i) What is meant by the 'inert pair effect'
(ii) Describe briefly the preparation of lead (II) chloride from lead nitrate.
- (b) A red solid oxide of lead Q was treated separately with dilute nitric acid and concentrated sulphuric acid. The results are summarized in the table below.
- | Reagent | Observation |
|--------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Dilute nitric acid was added to Q and heated | -a dark brown precipitate was formed.
-when concentrated HCl was added to the dark brown precipitate, a greenish-yellow gas was evolved and a white precipitate was formed. |
| Concentrated sulphuric acid was added and heated | -A colourless gas which rekindled a glowing splint was evolved and a white precipitate was formed. |
- (i) Explain all the observations above.
(ii) State the observation and write the equation when the dark brown precipitate is heated strongly.
(iii) Write equation when Q is reacted with hot potassium hydroxide.
- (c) When a mixture of carbon and an oxide of a group (II) element was heated to a very high temperature, a compound A was formed. A reacted with cold water to give a gas B which decolourised chlorine water.
(i) Identify the element in group (II) and the substances A and B.
(ii) Write equation for the reactions leading to the formation of gas B.
- (d) Describe the preparation of the dark brown solid lead (IV) oxide from bleaching powder.

Solution

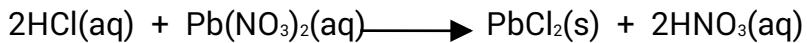
(a)

(i) Inert pair effect

The elements of group (IVB) can use the s and p electrons in chemical bonding. The decreasing tendency down the group of the s-electrons to be involved in chemical bonding is called **inert pair effect**. This leads to the oxidation state +2 becoming more stable down the group than compounds in oxidation state +4. Example lead (IV) oxide is unstable but lead (II) oxide is stable. Carbonmonoxide is unstable but carbondioxide is stable.

(ii) Preparation of lead (II) chloride.

Dilute hydrochloric acid is placed in a beaker and lead (II) nitrate solution is added until in excess. A white precipitate is formed. The precipitate is filtered, washed two or three times with cold distilled water and dried on a porous plate.



(b)

(i) The red oxide is Pb_3O_4

When it is treated with dilute nitric acid and warmed, lead (IV) oxide is formed as dark brown precipitates and a clear solution.



The brown solid (lead (IV) oxide) when warmed with concentrated hydrochloric acid liberates chlorine gas (greenish-yellow gas) and lead (II) chloride formed as a white precipitate.



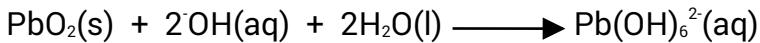
When Q is warmed with concentrated sulphuric acid, oxygen is evolved and a white precipitate of lead (II) sulphate is formed.



(ii) Oxygen is evolved and a yellow solid is formed.



(iii) Solid dissolves in aqueous hydroxide



(c)

(i) The element in group (IIA) is calcium.

A is calcium oxide, CaO .

B is ethyne, $\text{HC} \equiv \text{CH}$

(ii) $\text{CaO}(\text{s}) + 3\text{C}(\text{s}) \longrightarrow \text{CaC}_2(\text{s}) + \text{CO}(\text{g})$



(d) Bleaching powder is placed in beaker. It is shaken with water and the mixture filtered.

The clear liquid which contains $\text{OCl}(\text{aq})$ ions is added to a solution of lead nitrate or lead acetate and the mixture heated. Lead (IV) oxide precipitates as a dark brown powder. It is filtered off, washed with warm distilled water (2 or 3 times) and allowed to dry.

Question 37

C, Si, Ge, Sn and Pb are elements of group (IVB) in the periodic table.

(a) (i) Describe the type of hydrides formed by these elements.

(ii) Describe the shape/structure, the volatility and thermal stability of the hydrides of these elements.

(iii) Write equation for the preparation of SiH_4 and SnH_4 .

(b) (i) Describe briefly the preparation lead (IV) oxide from red lead oxide, Pb_3O_4 .

(ii) Write the structure of lead (IV) oxide.

(iii) Lead (IV) oxide shows acidic properties and oxidizing properties. Write equations in each case to illustrate these properties.

(c) When concentrated hydrochloric acid is cooled in ice-salt lead (IV) oxide, slowly stirred

and filtered a bright yellow liquid is formed.

(i) Explain the formation of the yellow liquid.

(ii) State the observation and write equation when concentrated solution of ammonium chloride is added to the yellow liquid.

Solution

(a)

(i) All the elements of group (IVB) in the periodic table form hydrides of the type MH_4 . They are all volatile and gases at room temperature, silicon and germanium form other hydride of the type M_nH_{2n+2} . All these hydrides are covalent.

(ii) Shape/structure

In all the tetrahydrides, each element (group (IVB) is bonded to four hydrogen atoms through covalent bond. The hydrogen atoms are arranged tetrahedrally giving a 3-dimensional molecular structure. Weak van der waals exist between molecules.

Volatility

Melting point and boiling point is a measure of the strength of intermolecular forces. All the hydrides having simple molecular structure are volatile gases at room temperature with very low boiling point and melting point. The boiling points of these hydrides increase in the order $CH_4 < SiH_4 < GeH_4 < SnH_4 < PbH_4$. This is because the molecular mass increases in the same order.

Thermal stability

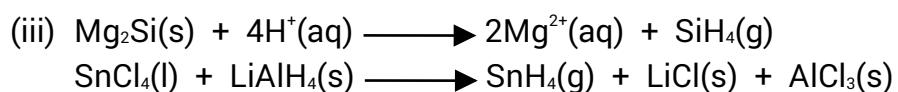
Atomic size increases from carbon to lead although electronegativity decreases. This leads to increase in the length of M-H bond (weakening of bond length) in the order $CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$. The weaker the M-H bond, the less stable the hydride.

CH_4 is very stable

SiH_4 is moderately stable

GeH_4 decomposes on gentle heating

PbH_4 is very unstable at room temperature.



(b)

(i) Preparation of lead (II) oxide.

Dilute nitric acid is placed in a beaker and warmed. Red lead is added by means of a spatula a little at a time. As the red lead oxide reacts with nitric acid, a brown powder is precipitated and a solution of lead (II) nitrate is formed. The mixture is filtered and the residue in the filter paper is washed two or three times with hot distilled water. It is allowed to dry.

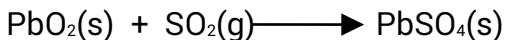
(ii) Structure, O =Pb =O

(iii) Acidic properties

- Lead (IV) oxide reacts with sodium hydroxide

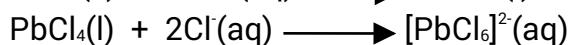


- Oxidizing property

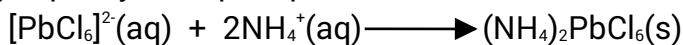


(c)

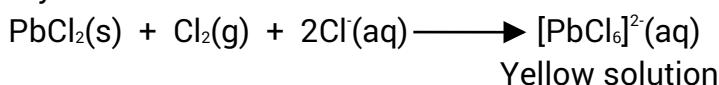
- (i) Lead (IV) oxide reacts with concentrated hydrochloric acid to form lead (IV) chloride which then reacts with more (excess) chloride ions to form a complex which is a yellow liquid.



- (ii) A pale yellow precipitate is formed.



(d) A yellow solution is formed.



Question 38

(a) Carbon and lead form oxides with oxygen.

- (i) Write the formula and oxidation states of all oxides of carbon and lead.

- (ii) Comment on the stability of the oxides in (i) above.

- (iii) Describe the structure and bonding of carbondioxide.

(b) (i) Describe briefly the laboratory preparation of carbondioxide.

- (ii) State the observation and write equations when carbondioxide is bubbled in lime water for a long time.

(c) You are provided with two solutions.

Solution A: is suspected to contain either a carbonate, CO_3^{2-} or hydrogencarbonate, HCO_3^-

Solution B: contains a mixture of a carbonate, CO_3^{2-} and a hydrogen carbonate, HCO_3^- .

- (i) When magnesium sulphate was added to a solution A and the mixture boiled, white precipitate was formed. Write equation for the reaction that has taken place.

- (ii) Describe briefly how you would prove (show) that solution B contains both, CO_3^{2-} and HCO_3^- ions.

(d) Explain each of the following observation.

- (i) The C-O bond lengths in CO_3^{2-} ion are all equal.

- (ii) Barium carbonate readily decomposes when heated whereas calcium carbonate does not.

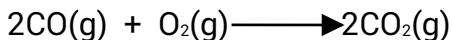
Solution

(a)

(i)

Oxide	Oxidation state
CO	+2
CO_2	+4
PbO	+2
PbO_2	+4

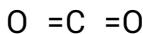
- (ii) CO is less stable and is readily oxidized to CO_2 .



PbO is stable which is only oxidized by strong oxidizing agents. PbO₂ is thermally unstable decomposing to PbO and O₂.



(iii) Structure of CO₂

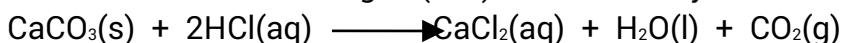


The carbon atom is sp³ hybridised and all the four electrons are used in multiple covalent bond formation with the two oxygen atoms. Each oxygen atom has two pairs of non-bonding electrons which are equal. This gives carbondioxide a linear molecular structure with weak van der waals forces between the molecules.

(b)

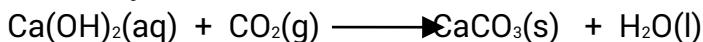
- (i) Calcium carbonate (marble chips) is placed in a flask fitted to dropping funnel (thistle funnel).

Dilute Hydrochloric acid is added from the funnel on to the marble. Effervescence occurs and a colourless gas (CO₂) is collected by downward delivery.

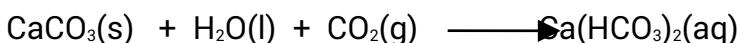


- (ii) The solution of lime water first turns milky and then becomes clear again.

The milky solution is due to the formation of calcium carbonate.

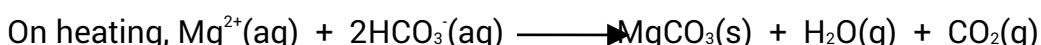


The solution becomes clear again due to the formation of calcium hydrogen carbonate which is soluble.

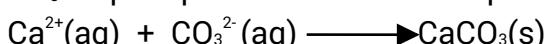


(c)

- (i) A whit precipitate on boiling indicates a hydrogen carbonate ion because magnesium ion and hydrogen carbonate ions are soluble; a soluble combination in the cold.



- (ii) First add calcium chloride solution in excess to solution B. the normal carbonate, CO₃²⁻ is precipitated as chalk. The precipitate is filtered off.

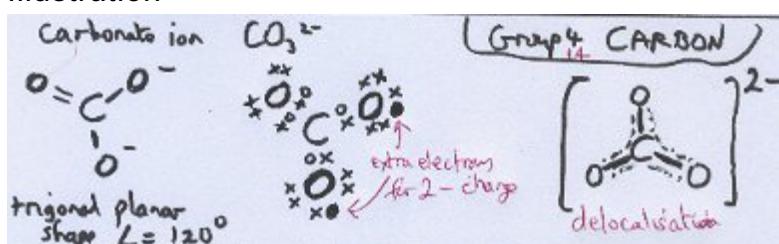


Dilute ammonia solution is then added to the filtrate and a white precipitate of calcium carbonate indicate the presence of hydrogen carbonate ions in solution B.

(d)

- (i) The CO₃²⁻ ions has discrete planar structure. The extra electrons on the oxygen are involved in resonance with the pi-electrons of the C = O bond so that the ion is a resonance hybrid containing equal contributions from three forms.

Illustration



This results in all the C-O bond lengths being identical (equal)

- (ii) The beryllium cation, Be²⁺(aq) is smaller than the calcium cation, Ca²⁺. Due to the

strong electric field around Be^{2+} ion, the carbonate ion, CO_3^{2-} ion is greatly polarized (i.e. small cation with high charge) causes greater polarization of a large anion. This causes BeCO_3 to have a covalent character and therefore is easily decomposed by heat. The Ca^{2+} ion being large does not cause great polarization of the CO_3^{2-} and therefore CaCO_3 is ionic with strong electrostatic forces in the crystal and more stable to decomposition by heat.

Question 39

(a) Explain each of the following

- (i) Graphite is an electrical conductor whereas diamond is not.
- (ii) Lead (II) chloride is insoluble in cold water but dissolves in hot water.
- (iii) Tin (IV) chloride fumes when left exposed to air.
- (iv) Tin (II) oxide is amphoteric.

(b) State the observation and write equation when any two of the following reagents were added to tin (II) chloride.

- (i) Iron (III) chloride solution
- (ii) Mercury (II) chloride solution
- (iii) Water (in excess)

(c) The density and enthalpy of combustion of diamond and graphite is given in the table below.

Property	Allotrope	
	Diamond	Graphite
Density	3.51	2.25
Enthalpy of combustion KJ/mol	-395.4	-393.4

Graphite is converted to diamond.

- (i) Calculate the enthalpy change for the conversion and comment on your value.
- (ii) Calculate the change in volume when one gram of graphite is converted completely into graphite.
- (iii) What would happen to the total volume of the system if a give mass of diamond is converted completely into graphite. Explain your answer.
- (iv) Graphite is more reactive than diamond. Explain.

Solution

(a)

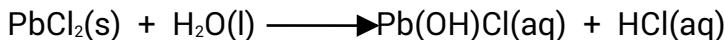
- (i) In graphite, each carbon atom is bonded to three other carbon atoms through covalent bonding (sp^2) leaving each carbon atom with an extra p-electron. This arrangement gives a 2-dimensional layer structure in which the carbon atoms are arranged in corners of a regular hexagon with each layer being held to another by weak van der waals forces. The extra p-electrons are delocalized between the layers and are responsible for the electrical conductivity of graphite. In diamond each carbon is bonded to four other carbon atoms through strong

covalent bonds (sp³ hybridised orbitals) arranged tetrahedrally. This arrangement gives a 3-dimensional structure with no free electrons and therefore diamond is a non-conductor of electricity.

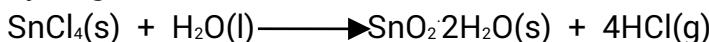
- (ii) Lead (II) chloride is ionic with high lattice energy. In cold water, the hydration energy cannot offset lattice energy and therefore lead (II) chloride is insoluble in cold water.



In hot water lead (II) chloride undergoes hydrolysis to form a basic salt which is soluble.



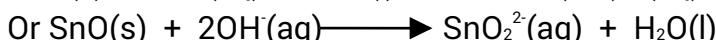
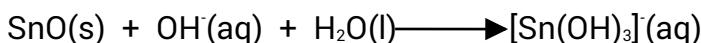
Tin (IV) chloride is readily hydrolysed by water to a basic oxide and white fumes of hydrogen chloride.



This reaction causes tin (IV) chloride to fume in air.

- (iii) Tin (II) oxide is an oxide which exhibits both acidic and basic properties.

It reacts with sodium hydroxide solution to form a salt thus behaving as an acidic oxide.



It reacts with hydrogen ions (acid) to form a salt and water thus behaving as a basic oxide.

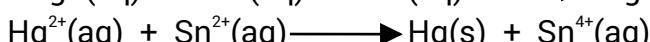
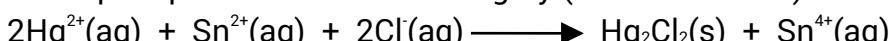


(b)

- (i) Solution changes from yellow (brown) to pale green.



- (ii) White precipitate which becomes grey (black in excess)

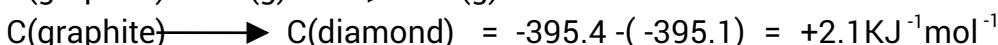


- (iii) A white precipitate is formed.



(c)

- (i)



Graphite is more stable than diamond because the conversion is endothermic process. However the conversion of diamond to graphite is exothermic as the change involves the initial breaking of a large number of strong covalent bonds (large activation energy).

$$\text{(ii) Volume of diamond} = \frac{1}{3.51} = 0.2849$$

$$\text{Volume of graphite} = \frac{1}{2.25} = 0.4444$$

$$\text{Change in volume} = 0.4444 - 0.2849 = 0.16 \text{ cm}^3$$

- (iii)

- High pressure needed because the conversion proceeds by decrease in volume.
 - High temperature because conversion is endothermic.
- (iv) The volume increases because; the density of the graphite is less than that of diamond.
- (v) The open structure of graphite enables reagents to penetrate the layers and react whereas the closed structure of diamond prohibits this therefore activation energies are lower and corresponding reactions proceed more quickly with graphite than for diamond. Therefore graphite is more reactive.

Question 40

- (a) (i) State two important oxidation states exhibited by carbon, silicon, tin and lead.
(ii) Describe how the stability of the two oxidation states varies from carbon to lead.
- (b) Explain each of the following
(i) Lead (II) chloride is insoluble in ethanol whereas lead (IV) chloride readily dissolves in the same solvent.
(ii) When water is added to lead (IV) chloride, white fumes are observed and a brown precipitate is formed but when lead (IV) chloride is heated, it readily decomposes to lead (II) chloride and chlorine.
(iii) Lead does not form lead tetra bromide.
(iv) The bondings in tetravalent compounds are predominantly covalent.
- (c) (i) State two uses of carbondioxide
(ii) State the observation and write equation when aqueous sodium hydroxide is added to lead (II) oxide.

Solution

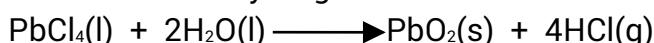
- (a)
- (i) All these elements which belong to group (IVB) exhibit oxidation state of +2 and +4.
(ii) The stability of oxidation state +2 increases from carbon to lead while that of +4 decreases. This is due to inert pair effect ie the tendency of s-electrons to be involved in chemical bonding decreases from carbon to lead. Carbonmonoxide, CO is unstable and is readily oxidized in air to carbondioxide.
- $$2\text{CO(g)} + \text{O}_2\text{(g)} \longrightarrow 2\text{CO}_2\text{(g)}$$
- SiO is not known but SiO₂ is widely distributed.
Sn is readily oxidized in air to SnO₂.
- $$2\text{SnO(s)} \longrightarrow 2\text{SnO}_2\text{(s)}$$
- PbO is a stable oxide of lead which is only oxidized by strong oxidizing agents to lead (IV) oxide.
Lead (IV) oxide, PbO₂ is thermally unstable and easily decomposes to lead (II) oxide and oxygen.
- $$2\text{PbO}_2\text{(s)} \longrightarrow 2\text{PbO(s)} + \text{O}_2\text{(g)}$$
- (b)
- (i) In lead (II) chloride, the lead (II) ions, Pb²⁺ formed by loss of two p-electrons and the chloride ions, Cl⁻ are held by electrostatic forces. Therefore the crystals of lead (II)

chloride are ionic.

The molecules of ethanol are associated through hydrogen bonding in addition to weak van der waals forces. The intermolecular forces in ethanol can not interact with the electrostatic forces in PbCl_2 as they are not of the same nature. Therefore PbCl_2 is insoluble in water.

Lead (IV) chloride is a covalent liquid having a simple molecular structure with weak van der waals forces between their molecules. These forces are able to interact with the intermolecular forces in ethanol. Therefore lead (IV) chloride dissolves in ethanol.

- (ii) Lead (IV) chloride readily undergoes hydrolysis with water. This is because of the weakness of the Pb-Cl bond and the presence of d-orbitals. The hydrolysis gives white fumes of hydrogen chloride and brown lead (IV) oxide.



However, lead (IV) chloride is unstable and readily decomposes to chlorine and lead (II) chloride when warmed.



- (iii) Lead in oxidation state +4 (Pb^{4+}) is a strong oxidizing agent and therefore the bromide ion, Br^- with a reducing action is not strong oxidizing to convert lead (II) to lead (IV). Hence lead tetrabromide does not exist.

- (iv) All the elements of group (IVB) have four electrons in the outermost shell (ns^2np^2). They do not form cations of M^{4+} in the solid compounds because of the high ionization energy involved in removing four electrons from an atom. Therefore the four electrons are involved in chemical bonding through sharing of electrons hence tetravalent compounds are predominantly covalent.

(c)

- (i) Uses of carbon dioxide

- In production of mineral waters eg fizzy drinks.
- As a refrigerant.
- In fire extinguishers.
- In the manufacture of sodium carbonate by solvay process.

- (ii) It dissolves to give a colourless solution



Question 41

- (a) Explain each of the following.

- (i) The solubilities of lead (II) halides increase in the order $\text{PbI}_2 < \text{PbBr}_2 < \text{PbCl}_2$.
- (ii) There is a steady increase in stability of the lower oxidation states relative to higher oxidation states from carbon to lead in group (IVB) elements of the periodic table.
- (iii) The C-C bond lengths in ethane, ethene and benzene are 0.154nm, 0.134nm and 0.139nm respectively.

- (b) State what would happen and write equations when CCl_4 , SiCl_4 , SnCl_4 and PbCl_4 are separately shaken with water.

(c)

- (i) Write equation giving conditions for the laboratory preparation of lead (IV) chloride.
 (ii) State the type of bonding in lead (II) chloride and give the physical property which is typical of the bond type.

Question 42

The elements F, Cl, Br and I belong to the same group of the periodic table.

- (a) (i) State the properties of fluorine that resemble those of oxygen.
 (ii) Fluorine is the most reactive among all the halogens. Give two reasons.
 (b) Explain each of the following.
 (i) The melting points of the halogens decrease in the order.
 $I_2 > Br_2 > Cl_2 > F_2$
 (ii) The temperatures at which the molecules dissociate into atoms decrease in the order.
 $Cl_2 > Br_2 > I_2$
 (iii) The enthalpy of atomization of fluorine and chlorine are 75.1 and 122 KJmol⁻¹ respectively.
 (c) (i) State three differences between the chemistry of fluorine and the rest of the elements in the group.
 (ii) Describe briefly how dry chlorine can be prepared in the laboratory.
 (iii) How does chlorine react with sulphur dioxide?

Solution

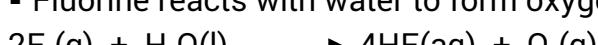
- (a) (i)
- The hydrides are associated through hydrogen bonding e.g. HF and H₂O.
 - Oxygen and fluorine combine directly with carbon.
- $$C(s) + O_2(g) \longrightarrow CO_2(g)$$
- $$2F_2(g) + O_2(g) \longrightarrow CF_4(g)$$
- The solubility, melting point and boiling points of fluorides are generally close in magnitude to the corresponding oxides than they are in the chloride.
- (ii)
- Fluorine has abnormally size and high electronegativity.
 - It has abnormally low bond dissociation energy.
 - The hydration energy of the fluoride ion is the most negative.
 - The lattice energy of its compounds is greater than those of the other halides.
- (b) (i) Atomic number increases from fluorine to iodine. The number of electrons also increases. This leads to increase in polarisability i.e. the greater the number of electrons, the greater the polarization. Increased polarisability results in increased intermolecular attractions (van der waals forces). Hence increase energy required to separate the molecules of the elements. Melting points therefore decreases in the order $I_2 > Br_2 > Cl_2 > F_2$.
- (ii) The smaller the atomic size, the stronger the covalent bond between the atoms. Atomic size increases from chlorine to iodine. Chlorine being the smallest forms a stronger covalent bond and requires a lot of energy to break the bond between the atoms. Bromine is next to chlorine in size, therefore less energy is required to break the bond

between its atoms than for chlorine. Iodine has the largest atomic size with the weakest bond between its atoms therefore lesser energy is required to break the bonds between the atoms.

(iii) Fluorine is a small atom and therefore forms a short covalent bond with itself. The three pairs of non-bonded electrons (lone pairs of electrons) on the fluorine atom approach each other very closely and therefore experience a strong repulsion. This repulsion tends to force the atom apart and assists in dissociating the molecule. Therefore the fluorine molecule has an abnormally low enthalpy of atomization. Chlorine is bigger than fluorine and therefore forms a stronger covalent bond with itself than fluorine.

(c) (i)

- Fluorine is more reactive and its compounds are more stable.
- The solubility of fluorine compounds differs from that of the corresponding chlorine compounds e.g. AgF is soluble but AgCl is insoluble, CaF_2 is insoluble but CaCl_2 is insoluble.
- Fluorides are more ionic e.g. AlF_3 is ionic but AlCl_3 is covalent.
- Fluorine reacts with water to form oxygen and hydrofluoric acid.

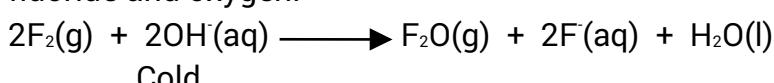


The other elements dissolve in water forming hydrohalic acid and hypohalous acids.

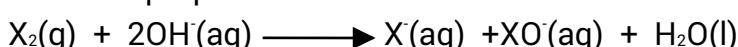


Where $\text{X} = \text{Cl}, \text{Br}, \text{I}$

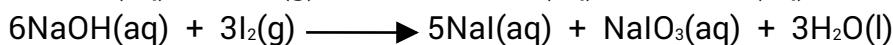
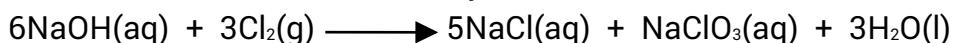
- Fluorine reacts with cold, dilute and also with hot concentrated sodium hydroxide to fluoride and oxygen.



The other halogens react with cold dilute sodium hydroxide to form halide and hypohalite which disproportionate.

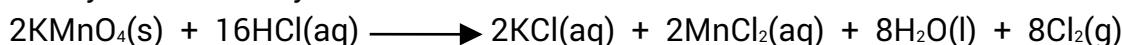


With hot concentrated sodium hydroxide



- Fluorine compounds are often more inert e.g. SF_6 .
- Fluorine forms strong hydrogen bond e.g. HF has anomalous properties.
- Fluorine brings out the highest oxidation (coordination) numbers from other elements and has a maximum valence of 1.

(ii) Potassium manganate (VII) placed in flat bottom flask. Concentrated hydrochloric acid is added from a thistle funnel. The gas is passed through water to remove fumes of hydrogen chloride and dried by passing it through concentrated sulphuric acid. It is collected by down delivery.



Or from manganese (IV) oxide (heat is required)



(iii) Cl_2 reacts with $\text{SO}_2(\text{g})$ in solution



Question 43

For the elements F, Cl, Br and I which belong to the same group in the periodic table.

(a) Discuss the reactions of these elements

- (i) With hydrogen
- (ii) With metals
- (iii) With non-metals
- (iv) As oxidizing agents

(b) (i) The oxidizing power of these elements decrease in the order $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$. Explain.

(ii) State two uses of the halogens.

(c) Aqueous hydrogen fluoride ionizes in dilute solution and concentrated solution. But in the one of the two solutions, hydrogen fluoride is expected to be relatively acidic.

(i) Write equations for the ionization of aqueous hydrogen fluoride in the two solutions.

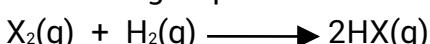
(ii) State and explain which solution is expected to be more acidic.

Solution

(a)

(i) Reaction with hydrogen

All the halides react with hydrogen to form hydrogen halides but the reactivity decreases down the group.



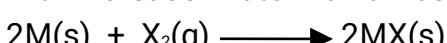
Fluorine and hydrogen explode in the dark. Chlorine does not react at room temperature but reacts explosively in sunlight or ultraviolet light. The reaction is explosive because it proceeds via the formation of free radicals.

Bromine and hydrogen react on heating or in the presence of platinum catalyst at about 200°C . Iodine combines with hydrogen at 400°C in the presence of a catalyst (platinum) and the reaction is reversible.



(ii) Reaction with metals

All these elements are very reactive with metals to form halides. The reactivity decreases with increase in atomic number down the group.



Fluorine is the most reactive and combines readily with all metals while iodine reacts slowly even at high temperatures.

(iii) Reaction with other non-metals

Fluorine reacts directly with all non-metals except nitrogen, helium, and neon. Chlorine and bromine react with all non-metals except carbon, oxygen, nitrogen and noble gases. The reactivity of the halogens with non-metals decreases from fluorine to iodine.

(iv) Reaction as oxidizing agents.

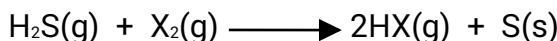
Fluorine is the strongest oxidizing agent and it oxidizes all the other halide ions,



Chlorine will oxidize Br^- (aq) ions and I^- (aq) ions, Bromine will oxidize I^- (aq) ions and iodine will not oxidize any halide ions.

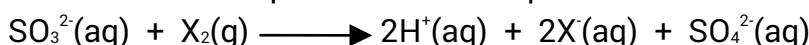
Fluorine oxidizes too violently to be useful. Typical oxidation reactions of chlorine, bromine and iodine are;

- Oxidation of hydrogen sulphide to sulphur.

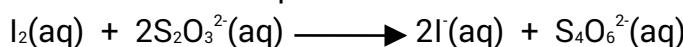


X = Cl, Br, I

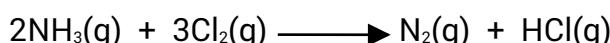
- Oxidation of sulphur dioxide to sulphuric acid.



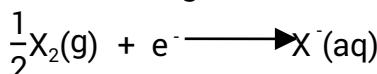
- Oxidation of thiosulphate ions to tetrathionate ions by iodine.



- Others are



(b) (i) The oxidizing reaction of the halogens involves the following reaction.

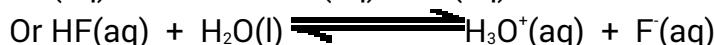


This reaction involves enthalpies of atomization, electron affinity and enthalpy of hydration. Both enthalpy of hydration and electron affinity increase (become more endothermic) from fluorine to iodine. Atomization energy decreases from Cl to I and fluorine having the lowest value. The sum of these energy terms favours oxidising power in the order $F_2 > Cl_2 > Br_2 > I_2$.

(ii) Uses of halogens

- Chlorine is used in the manufacture of organic chemicals e.g. DDT, tetrachloromethane, bleaching agents.
- It is also used to sterilize water.
- Bromine is used for the manufacture of 1,2-dibromoethane which is added to petrol with tetraethyl lead as an anti knock.
- It is also used in the making of dyestuffs and drugs and in photography/
- Iodine is used as an antiseptic and in photography.

(c) (i) In dilute solution.



In concentrated solution



(ii) The concentrated solution is expected to be relatively more acidic. The $F^-(aq)$ ions combine HF to form $HF_2^-(aq)$. This upsets the equilibrium and thus promoting more dissociation of HF to form more $H^+(aq)$ ions.

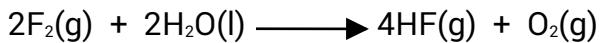
Question 44

F_2 , Cl_2 , Br_2 and I_2 belong to group (VIIB) of the periodic table. Discuss the reactions of each of these elements with;

- (a) Water
- (b) Aqueous sodium hydroxide.

Solution

(a) Fluorine fumes in moist air. It reacts with water to form oxygen and hydrofluoric acid.



The other elements (Cl_2 , Br_2 , I_2) are sparingly soluble in water. Chlorine and bromine are moderately soluble in water (bromine more so than chlorine), while iodine is only sparingly soluble. The solubility is in the order $Br_2 > Cl_2 > I_2$. When they dissolve they form hydrohalic acid and hypohalous acid



Where $X = Cl$, Br or I

(b) With cold dilute sodium hydroxide

Fluorine reacts with cold dilute sodium hydroxide to form the fluoride and oxygen difluoride.



Chlorine, bromine and iodine react with dilute sodium hydroxide to form the halide (chloride, bromide, and iodide) and hypohalite (hypochlorite, hypobromite and hypoiodite) respectively.



Where $X = Cl$, Br or I

All the hypohalites disproportionate although the rate of varies. $ClO^-(aq)$ slowly disporionates to $Cl^-(aq)$ and $ClO_3^-(aq)$ at room temperature.

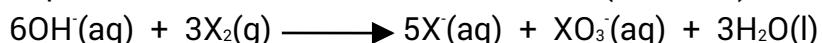
BrO^- and IO^- rapidly disproportionate to the halide (Br^- , I^-) and halate (BrO_3^- or IO_3^-)

With hot concentrated sodium hydroxide solution.

Fluorine reacts wiith hot concentrated sodium hydroxide to form fluoride and oxygen.

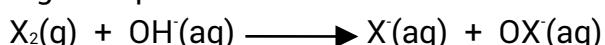


Chlorine, bromine and iodine react with hot concentrated solutions of sodium hydroxide to produce colourless solutions of halide (Br^- , Cl^- , I^-) and halite (ClO_3^- , BrO_3^- or IO_3^-)



Where $X = Cl$, Br or I

Essentially, the halite is produced at first and then disproportionate rapidly due to the high temperature.



Question 45

- (a) (i) Explain what is meant by **disproportionation**.
(ii) Chlorine dissolves to a much greater extent in water in the presence of hydroxyl ions i.e. alkaline solution. Explain.
- (b) Explain the trend in boiling point and acidity of the hydrides of group (VIIIB) elements.
(i) The trend in boiling point $\text{HCl} < \text{HBr} < \text{HI} < \text{HF}$
(ii) Trend in acidity $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$
- (c) Explain the trend in melting point and solubility of the sodium salts of elements in group (VIIIB)
(i) Trend in melting point $\text{NaCl} > \text{NaBr} > \text{NaI}$
(ii) Trend in solubility $\text{NaF} < \text{NaCl} < \text{NaBr} < \text{NaI}$.

Solution

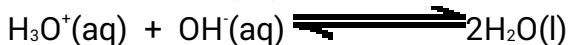
- (a) (i) Disproportionation is the breaking down of an ion or compound into two different products, one in a higher and the other in a lower oxidation state. E.g.



- (ii) Chlorine is sparingly soluble in water. It dissolves to form hydrochloric acid and hypochlorous acid.



In the presence of hydroxyl ions, the hydroxonium ions combine with the hydroxyl ions to form water and the hypochlorous acid reacts with the hydroxyl ions to form water and ClO^- (aq).



The removal of hydroxonium ions and hypochlorous acid during the reactions above disturbs the equilibrium thereby allowing the hydrolysis reaction of chlorine very much further to the right.

- (b) (i) The boiling points are determined by polarity of the H-X bond and molecular weight and molecular weight. All the hydrides of group (VIIIB) are polar and polarity decreases with decrease in electronegativity down the group. Molecular weight increases from HF to HI and this leads to increased intermolecular forces of attraction. The effect of molecular mass is greater than the effect of polarity and hence the observed boiling point. The boiling point of HF is the highest of the hydrides because HF molecules associate through hydrogen bonding and therefore extra energy is needed. Hence the observed trend in boiling point.

- (ii) The strength of the halogen acids will depend on how easily the hydrogen is lost as a proton and this depends on the strength of the H-X bond. Due to the small size of fluorine forms a strong covalent bond with hydrogen. In aqueous solution HF does not easily ionize to give hydrogen ions. In addition, the fluoride ions produced combine with the undissociated HF molecule. Therefore HF is the weakest of all the halogen acids. Atomic size increases from chlorine to iodine.

- (c) (i) The energy required to break the lattice structure is proportional to the strength of

the electrostatic attraction between sodium ions and halide ions. Hence the melting point decreases in the order $\text{NaCl} > \text{NaBr} > \text{NaI}$

- (iii) The size of the anion increase from F^- to I^- . This causes an increase in internuclear distance and a corresponding decrease in the attractive forces leading to a decrease in lattice energy. The increasing size of the anion also causes decrease in hydration energy. But the lattice energy decreases more rapidly than the hydration energy. This favours solubility in the trend $\text{NaF} < \text{NaCl} < \text{NaBr} < \text{NaI}$.

Question 46

Explain each of the following observation.

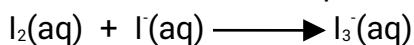
- (a) Potassium chloride is less soluble in concentrated hydrochloric acid than in water.
(b) The acidity of the following oxo acids of chlorine are in the order,
 $\text{HOCl} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$.
(c) Iodine is more soluble in potassium iodide than in water.
(d) When silver nitrate solution is added to aqueous solution containing chloride ions, a white precipitate which dissolved in excess ammonia was formed. But when silver nitrate solution is added to bromide ions, the precipitate does not dissolve in excess ammonia.
(e) Iodine is more soluble in carbon tetrachloride (tetra chloromethane) forming a purple solution than in water.

Solution

- (a) Potassium chloride is an ionic salt and the hydration energy can easily offset the lattice energy therefore potassium chloride dissolves in water.
In concentrated hydrochloric acid, there is a large concentration of chloride ions due to common ion effect and the inability for potassium chloride to form a soluble complex with chloride ions, KCl is less soluble in concentrated hydrochloric acid than in water.
(b) The oxygen atom is more electronegative than the chlorine atom and the hydrogen atom. It tends to draw electrons from the central chlorine atom and the oxygen of the O-H bond. This weakens the O-H bond and as a result hydrogen is easily lost as a proton. The greater the number of oxygen atoms, the greater the tendency and the greater the acidity. Hence the observed trend in the acidity.
(c) Iodine is sparingly soluble in water and the following equilibrium is formed.

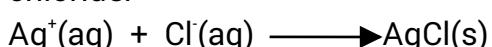


In the presence of potassium iodide, the iodine molecules combine with the iodide ions to form a soluble complex.

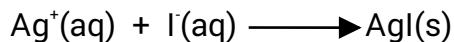


The formation of this complex offsets the equilibrium and causes iodine to dissolve.

- (d) When silver nitrate is added, a white precipitate of silver chloride is formed. This is possible because the ionic product $[\text{Ag}^+][\text{Cl}^-]$ exceeds the solubility product of silver chloride.



Ag^+ ions also combine with iodide ions in a similar way



Both AgCl and AgI are sparingly soluble in water



In the presence of excess ammonia, the silver ions, $\text{Ag}^+(\text{aq})$ combine with aqueous ammonia to form a complex.



The formation of this complex reduces the concentration of Ag^+ ions below the solubility product of AgCl and offsets the equilibrium. Therefore AgCl dissolves.

AgI does not dissolve in excess ammonia. This is because it is the least soluble silver halide and in aqueous solution, provides still enough silver ions to cause the ionic product $[\text{Ag}^+][\text{I}^-]$ to exceed the low solubility product of silver iodide.

- (e) Iodine is not very soluble in water because the intermolecular interaction between iodine-iodine (van der waals forces) and the intermolecular interactions between water-water (hydrogen bond) are incompatible. But the interactions between the molecules of CCl_4 are similar to the interactions between the molecules of iodine. The van der waals forces between the iodine molecules are therefore broken and the molecules are separated in the vapour phase. The solution appears purple.

Question 47

- (a) Explain each of the following observations.

(i) The acidity of the oxo acids of chlorine, bromine and iodine decreases in the order.



(ii) Precipitates of silver halides tend to darken on standing.

(iii) A solution of iodine in ethanol is brown.

(iv) Iodine forms a deep blue solution with starch solution.

- (ii) Describe (observations and equations) how any two of the following can be used to distinguish between chloride ions, bromide ions and iodide ions.

(i) Concentrate sulphuric acid.

(ii) Silver nitrate solution.

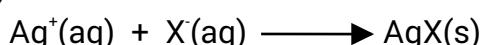
(iii) Bleaching powder and dilute nitric acid.

(iv) Potassium permanganate solution and concentrated sulphuric acid.

Solution

- (a) (i) Electronegativity decreases from chlorine to bromine and iodine is the least electronegative. The chlorine atom has the greatest inductive effect which tends to weaken the O-H bond. This tendency decreases to iodine. Therefore the strength of the O-H bond increases in the order $\text{ClOH} < \text{BrOH} < \text{IOH}$ which favours increasing difficulty of losing hydrogen atom as a proton hence acidity decreases in the order, $\text{ClOH} > \text{BrOH} > \text{IOH}$.

- (ii) Silver ions combine with halide ions to form silver halide



$\text{X}^- = \text{Cl}^-, \text{Br}^- \text{ or } \text{I}^-$

The Ag-X bond is weak and is broken by solar energy. This is an oxidation reaction to silver metal as black deposits.



- (iii) The lone pair of electrons on the oxygen atom in the alcohol molecules interacts through dative covalency with the vacant d-orbital of iodine molecule.



The interaction leads to separation of iodine molecules as in vapour and hence the brown colour of solution.

- (iv) Starch has an open helical structure. The lone pair of electrons on the oxygen atoms in starch molecules interacts with the iodine through dative covalency. This interaction leads to separating the iodine molecules which get absorbed reversibly within the helical (spiral) structure of glucose molecules which make up starch.

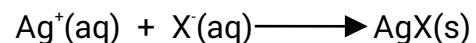
- (b) (i) Concentrated sulphuric acid reacts with ionic halides evolving a sharp smelling gas (halogen hydrides) which fumes in moist air.



Evolution of HCl(g) which forms white fumes with concentrated ammonia solution indicates the presence of chloride ions.

Evolution of HBr(g) with brown $\text{Br}_2(\text{g})$ indicates the presence of bromide ions. This can be confirmed by passing the vapour through potassium iodide solution and the solution turns deep red due to formation iodine solution. Evolution of HI(aq) with purple colour of iodine indicates the presence of iodide ions.

- (ii) Silver nitrate solution is added followed by dilute excess nitric acid precipitates silver halides.



$\text{X}^- = \text{Cl}, \text{Br or I}$

The colour of the halide can be used to distinguish between the silver halide ie AgCl is white, AgBr(s) is pale yellow and AgI is yellow. In addition AgCl and AgBr are soluble in excess ammonia solution whereas AgI is not.

- (iii) Bleaching powder and dilute nitric acid followed by 2-3 drops of carbon tetrachloride, added to the ionic halide leads to the displacement of the halogen. The colour shown by the organic layer (CCl_4) is that of the halogen.

That is if the organic layer is colourless, the chloride ions are confirmed.

A brown colour in organic layer confirms bromide ions.

A purple liquid formed in CCl_4 layer confirms iodide ions.

- (iv) Addition of manganese (IV) oxide and concentrated sulphuric acid to the solid halide and the mixture heated evolves the halogen which can easily be identified by the colour.

Evolution of chlorine confirms chloride ions.

Evolution of bromine gas confirms bromide ions.

Evolution of iodine vapour confirms iodide ions.

Question 48

- (a) (i) Describe briefly the laboratory preparation of hydrogen chloride.

- (ii) Hydrofluoric acid is a weaker acid than hydrochloric acid. Explain.
- (b) A cold solution of sodium chloride is electrolysed using carbon anode and iron cathode. The products are allowed to mix. Describe the changes at each electrode which leads to the formation of the final products.
- (c) Chlorine reacts with both water and cold dilute sodium hydroxide.
- Write equations for the reaction of chlorine with water and cold dilute sodium hydroxide solution.
 - State whether the pH of an aqueous solution of chlorine will be greater than, less than or equal to 7. Give a reason for your answer.
 - The resulting solution in (c) (ii) is exposed to sunlight. State the observation and write equations.
- (d) (i) Sodium chlorate (I) is warmed to 75°C. Write equations.
- Chloric (I) acid, HOCl, reacts with acidified aqueous potassium iodide. Write equation for the reaction.
 - Chloric (V) acid, HOClO_2 is a stronger acid and a weaker oxidizing agent than chloric (I) acid.

Solution

- (a) (i) Common salt (sodium chloride) is placed in flask fitted with a dropping funnel and delivery tube, concentrated sulphuric acid is added from a dropping funnel. Effervescence and misty fumes are observed. The gas HCl(g) is passed through a wash bottle containing concentrated sulphuric acid or U-tube containing anhydrous calcium chloride to dry and is collected by downward delivery.



(ii) Due to its small size, fluorine forms a strong covalent bond with hydrogen. In aqueous solution HF does not easily ionize to give hydrogen ions, H^+ . Chlorine is a bigger atom and less electronegative than fluorine. It therefore forms a weaker covalent bond with hydrogen in HCl. In aqueous solution, HCl easily ionizes to form hydrogen ions, H^+ ions.

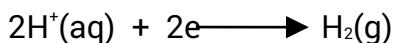


(b) At the cathode

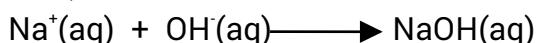
Water and sodium chloride ionizes according to the equation,



The hydrogen ions, H^+ are discharged in preference to Na^+ ions so that hydrogen gas is liberated.



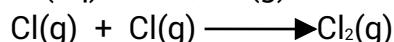
This leaves the solution in excess of the hydroxyl ions, OH^- which combine with sodium ions, Na^+ form sodium chloride to form sodium hydroxide solution.



At the anode

Chloride ions, Cl^- are discharged and the chlorine atoms combine to form molecules of

chlorine.



Then the chlorine gas produced at the anode reacts with the sodium hydroxide produced at the cathode to form NaOCl, NaCl and water.

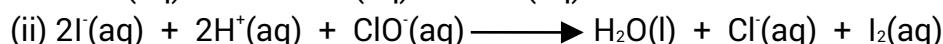
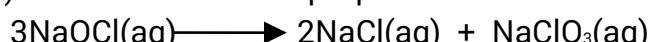


(ii) The pH is less than 7. The hydrolysis gives rise to a higher concentration of hydroxonium ions, H_3O^+ compared to hydroxyl ions, OH^- .

(iii) The solution contains chloric (I) acid, HClO which is a weak acid so oxygen is evolved when exposed to sunlight.



(d) (i) sodium chlorate disproportionate on warming at 75°C



Chloric (V) acid chloric (I) acid

The two oxygen atoms are more electronegative than the central chlorine atom. They have a tendency of drawing electrons from the central atom thereby weakening the H-O bond. Chloric (V) acid is therefore a stronger acid than chloric (I) acid.

Question 49

Explain each of the following observations.

(a) When chlorine is dissolved in cold sodium hydroxide solution and acidified silver nitrate solution added, only half of the chlorine which was dissolved is precipitated as silver chloride. When the sodium hydroxide solution is hot only five - sixth of chlorine gas which has dissolved is precipitated.

(b) A brown solution forms when aqueous solution of sodium hydrogen sulphate and potassium iodate are mixed.

(c) Aqueous copper (II) sulphate solution is blue in colour. When aqueous potassium fluoride is added bright green solution is formed but when aqueous potassium iodide is added, a brown solution is formed.

(d) The thermal stability of the hydrides of chlorine, bromine and iodine decrease in the order.

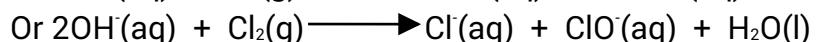


(e) Sulphuric acid is a weaker acid than hydrochloric acid but hydrogen chloride is evolved when concentrated sulphuric acid is added to sodium chloride.

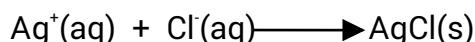
Solution

(a) Chlorine reacts with cold sodium hydroxide to form sodium chloride and sodium

hypochlorite.



For every mole of chlorine that reacts, 2 moles of ions are formed and only one mole of chloride ions react with silver ions to form silver chloride.



Chlorine reacts with hot sodium hydroxide to form sodium chloride and sodium chlorate.

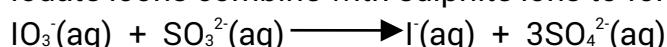


Six moles of ions are formed for three moles of chlorine that reacts. Only five out of the six ions react with silver ions to form a precipitate of silver chloride.

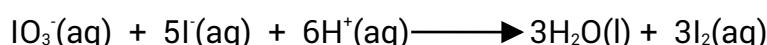
(b) NaHSO_3 ionises in water to form an acidic solution



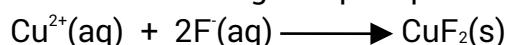
Iodate ions combine with sulphite ions to form iodide ion.



The iodide ions formed reacts with immediately in the acid conditions with remaining iodate ions to liberate iodine.



(c) Copper (II) sulphate is hydrated in water and the blue colour is due to the presence of $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}(\text{aq})$. In the presence of aqueous potassium fluoride, Cu^{2+} ions combine with F^- ions to form a green precipitate of copper (II) fluoride which is insoluble in water.



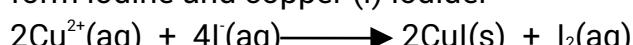
When $\text{KCl}(\text{aq})$ is added, the $\text{Cl}^-(\text{aq})$ ions combine with $\text{Cu}^{2+}(\text{aq})$ ions to form a complex which is soluble i.e. the green solution is due the presence of $[\text{CuCl}_4]^{2-}(\text{aq})$ ions.



Blue

Green

When the blue solution is treated with $\text{KI}(\text{aq})$, the $\text{Cu}^{2+}(\text{aq})$ combine with iodide ions to form iodine and copper (I) iodide.



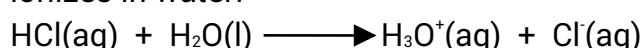
The iodine dissolves in excess potassium iodide solution forming a brown solution.

(d) The anion size increases from chlorine to iodine. Chlorine being smaller forms a stronger covalent bond with hydrogen in HCl than bromine in HBr. Iodine is the biggest forms the weakest bond with hydrogen in HI. The decrease in the strength of the H-X leads to decrease in thermal stability in the order $\text{HCl} > \text{HBr} > \text{HI}$.

(e) Pure sulphuric acid is covalent and the ionization in water takes place in two stages,



An aqueous solution of sulphuric acid therefore contains $\text{H}_3\text{O}^+(\text{aq})$ ions and $\text{SO}_4^{2-}(\text{aq})$ ions. Hence sulphuric acid is a weak acid. Hydrochloric acid completely and easily ionizes in water.



Concentrated sulphuric acid has higher boiling point and more oxidizing than hydrochloric acid. It therefore displaces hydrogen chloride gas from sodium chloride.



Question 50

- (a) (i) Define a transition element.
(ii) State three characteristic properties of transition elements.
- (b) Describe the variation of atomic radii across the transition series from scandium to zinc.
- (c) The melting point and density of some transition elements are given in the table below.
- | Element | Cr | Mn | Fe |
|-------------------|-----|------|------|
| Atomic number | 24 | 25 | 26 |
| Melting point(°C) | 189 | 124 | 153 |
| | 0 | 4 | 5 |
| Density | 7.2 | 7.44 | 7.86 |
- (i) Write the electronic configuration of the atom of each element.
(ii) State and explain the trend in melting point and in density.
- (d) (i) State one ore from which iron can be extracted.
(ii) Describe briefly how iron can be extracted from the ore you have named in (d) (i) above.
(iii) State one use of iron.

Solution

- (a)
- (i) Transition element is an element that has a partially filled d-subshell (ie contains 1-9 electrons)
- (ii) Characteristic properties
- They have variable oxidation states
 - They have paramagnetic properties
 - They form coloured ions
 - They have catalytic activity
 - They have the ability to form interstitial compounds
- (b) Along the series from Sc to Zn, nuclear charge and number of d-electrons increases. Although atomic number is increasing, no new energy level is added. However the d-electrons screen each other from the nuclear attraction poorly and also repel each other rather weakly. The net effect is a slight increase in the effective nuclear charge which leads to a little decrease in atomic radii across the first series of transition elements.
- (c)
- (i) Cr. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2$
Mn. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
Fe. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
- (ii) Melting point indicates the strength of metallic bonding. Atomic number increases from Cr to Fe and therefore melting point increases with increase in atomic number, however the melting point of Mn is lower than expected. This anomaly is

attributed to the stability of half-filled subshell of d⁵ in manganese.

(d)

(i) Ore

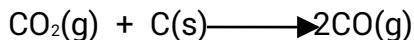
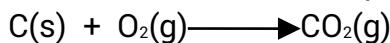
- Haematite, Fe₂O₃
- Limonite, Fe₂O₃·nH₂O
- Iron pyrites, FeS₂
- Siderite, FeCO₃

(ii) The ore is first roasted in air so as to drive off water vapour and carbondioxide and leaves iron (III) oxide.

Coke and limestone are fed in the blast furnace from the top.

Hot air is blown (injected) into the furnace through pipes called tuyeres.

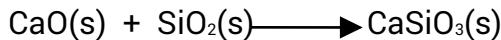
At the base of the furnance where the temperatures are very (1600°C), coke burns in the hot air to from carbondioxide which is then reduced to carbonmonoxide by more carbon as it rises up the furnance.



The carbonmonoxide which rises up the furnance reduces the iron (III) oxide to iron.



The limestone introduced into the furnance decomposes into calcium oxide and carbondioxide. The calcium oxide combines with silica to form slag.



The slag which floats on cast iron are removed separately using a tapping hole.

(iii) Uses of iron

- In the manufacture of alloys which have various uses eg
 - a. stainless steel used as cutlery
 - b. invar used in watches
 - c. permallow used in electromagnets
 - d. tungsten steel inhigh speed cutting tools

Question 51

(a) (i) What is meant by a catalyst.

(ii) Name two transition elements or compounds used as catalysts in industry and in each case give the reaction catalysed and the conditions of the reaction.

(iii) Explain the catalytic acitivity of transition elements.

(b) Manganese (IV) oxide reacts with concentrated hydrochloric acid according to the equation,



Describe briefly how you would determine the percentage by mass of manganese (IV) oxide in an ore of manganese by volumetric analysis.

(c) (i) Oxalic acid was added to manganese (IV) oxide and boiled after adding dilute sulphuric acid. Write the equation for the reaction.

(ii) Aqueous ammonia was added dropwise until inexcess to a solution containing

manganese (II) ions and the mixture allowed to stand for about two minutes. State and explain the observation.

Solution

(a)

(i) Catalyst is a substance that alters the rate of a chemical reaction but remains unchanged chemically.)

(ii)

Catalyst	Reaction catalysed	Conditions
Vanadium (V) oxide	Contact process	450°C
	$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$	
Manganese (IV) oxide	$2\text{KClO}_3(\text{s}) \rightarrow 2\text{KCl}(\text{s}) + \text{O}_2(\text{g})$	300°C
Iron (III) oxide	Haber process	550°C, 200atm
	$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow \text{NH}_3(\text{g})$	
Nickel		
Iron filings		
Manganese (II) ethanoate	$2\text{CH}_3\text{CHO} \xrightarrow{\text{O}_2} 2\text{CH}_3\text{COOH}$	Room temperature

(iii) Transition metals have high catalytic activity both as metals (powdered) in heterogeneous catalysis and also as ions in homogeneous catalysis in solution.

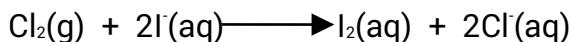
In heterogeneous catalysis, chemical bonds are formed between reactant molecules and the surface catalyst atoms. The transition metals are effective as catalysts because of the presence of d-electrons in addition to s-electrons which can be used in bonding. The weak chemical bonds have the effect of increasing the concentration of the reactants at the catalyst surface and also weakening the bonds in the reactant molecules thereby lowering the activation energy.

In homogeneous catalysis, the variable oxidation state of the transition metal enables the formation of unstable intermediates with lower activation energy.

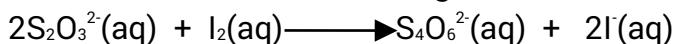


A known mass of manganese (IV) oxide is heated with excess hydrochloric acid.

The liberated chlorine is passed through a solution containing excess potassium iodide. Chlorine reacts with the iodide ions to liberate iodine.



A known volume of the iodine solution is titrated with standard sodium thiosulphate solution from the burette using starch indicator added towards the end.



The amount of iodine liberated can then be calculated and hence the amount of chlorine liberated. Knowing the amount of chlorine liberated, the amount of manganese (IV) oxide can be calculated ie from equations,

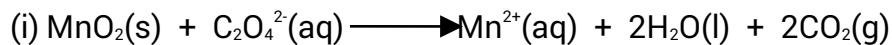
1 mole of MnO_2 liberates 1 mole Cl_2 which liberates 1 mole of iodine from KI solution.

But 1 mole of iodine reacts with 2 moles of $\text{S}_2\text{O}_3^{2-}(\text{aq})$

Therefore 1 mole of MnO₂(s) is equivalent to 2 moles of S₂O₃²⁻(aq)

Since S₂O₃²⁻(aq) is standard and the volume known the mass of MnO₂ in the ore and hence percentage purity can be calculated.

(c)



(ii) White precipitate formed insoluble in excess. The precipitate rapidly turns brown.

The change from white to brown is due to rapid oxidation of the precipitate by air from Mn(OH)₂ to manganese (IV) oxide or manganese (III) oxide.

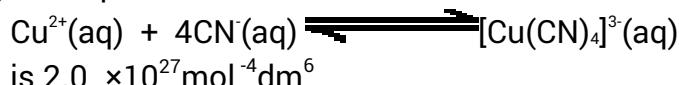
Question 52

(a) Copper (II) ions form complexes with cyanide ions and also with aqueous ammonia as ligands. When aqueous ammonia is added in excess to copper (II) ions a complex is formed. The equilibrium constant for the reaction is $1.4 \times 10^{13} \text{ mol}^4 \text{ dm}^{-6}$

(i) Write an equation for the reaction.

(ii) Write the expression for the stability constant.

(iii) The equilibrium constant for the reaction



Explain what happens if excess potassium cyanide solution is added to the solution formed when excess aqueous ammonia is added to copper (II) ions.

(iv) Calculate the equilibrium constant for the reaction which occurs in (iii) above.

(b) Describe briefly how you would determine the percentage of iron and copper in a double salt containing copper (II) ions and iron (II) ions by volumetric analysis.

(c) In the extraction of copper from its ore, the ores are first concentrated, mixed with silica and heated by hot air in a blast furnace producing copper.

(i) Write the formula of one ore from which copper can be extracted.

(ii) What is meant by concentration of ore. Describe the process by which the ore named in (c) (i) can be concentrated.

(iii) Write equations for the reactions that took place from roasting to the formation of copper in the blast furnace.

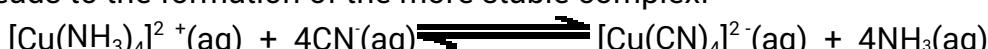
Solution

(a)



(ii) $k_{\text{stab}} = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]^4}$

(iii) The amino ligands in [Cu(NH₃)₄]²⁺ are replaced by the cyano ligands. This reaction leads to the formation of the more stable complex.



(iv) The equilibrium constant k_3 for this reaction is,

$$K_{3\text{eqb}} = \frac{[\text{Cu}(\text{CN})_4]^{2-}}{[\text{Cu}(\text{NH}_3)_4]^{2+}[\text{CN}^-]^4}$$

For the reaction,



$$k_{\text{stab}(2)} = \frac{[\text{Cu}(\text{CN})_4]^{2-}}{[\text{Cu}^{2+}] [\text{CN}^-]^4}$$

$$k_{\text{eqb}} = \frac{k_{\text{stab}(2)}}{k_{\text{stab}(1)}} = \frac{2.0 \times 10^{27}}{1.4 \times 10^{13}} = 1.29 \times 10^{14}$$

(b) Amount of copper

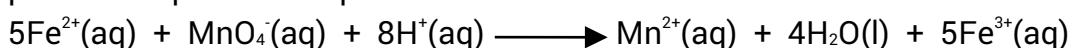
A known volume of the solution containing the double salt is placed in a conical flask. Excess potassium iodide solution is added and the liberated iodine is titrated with standard thiosulphate solution using starch indicator which is added near the end point.



Knowing the amount of iodine liberated, the amount of copper (II) in the double salt can be calculated.

Amount of iron (II)

A known volume of the double salt is placed in a conical flask. The solution is acidified by adding a known volume of dilute sulphuric acid. The mixture is titrated with standard potassium permanganate from the burette. The end point is when a permanent pink colour persists.



(c)

(i) CuFeS_2 , CuCO_3 , Cu(OH)_2 , Cu_2O , Cu_2S

(ii) Concentration is the process (physical or chemical) used to remove unwanted earthy (gangue) material from impure ore.

Concentration of CuFeS_2 by froth floatation

The finely powdered (pulverized) ore is mixed with water in a floatation tank to which one or more 'frothing agents' are added.

Air blown into the mixture and froth is produced. The earthly materials are 'wetted' and sink to the bottom of the tank. The sulphide ore particles, however, rises to the surface (get attached to the bubbles and float on top) in the froth where they can be skimmed off the surface.

(iii) Chemical reactions

e. Roasting of ore



f. Reactions in blast furnace



Question 53

(a) (i) Explain what is meant by a complex ion.

(ii) How would you distinguish between a double salt and complex salt.

(b) Potassium (VII) manganate is a reagent used in volumetric analysis but it is not a

primary standard.

- (i) Explain why nitric acid and hydrochloric acid can not be used to acidify potassium (VII) manganate during volumetric analysis.
 - (ii) Explain why potassium (VII) manganate solution is not a good primary standard. Give one advantage of potassium (VII) manganate as a volumetric reagent.
 - (iii) Describe briefly how you would standardize a solution of potassium permanganate.
 - (iv) Write a half equation for the reduction of managanate (VII) ion in acidic solution and in alkaline solution.
 - (v) Potassium permanganate is strongly heated in air. Write an equation for the reaction.
- (c) Describe briefly a test for managanese (II) ions in solution.
- (d) Describe briefly how potassium permanganate solution can be used to determine the percentage of iron in an ore of iron.

Solution

(a)

(i) Complex ion

Ion having a central metal ion bonded to other atoms, ions or molecules called the ligands through dative covalent bond. Example in $[\text{Cu}(\text{NH}_3)_4]^{2+}$ (aq), the amino ligans are bonded to copper (II) ions through dative covalent bond. This is possible because copper (II) ions have a vacant d-orbital and the ligand ammonia has lone pair of electrons.

(ii) **Double salt** – shows all the reactions of their constituent ions in solution. For example ammonium iron (II) sulphate dissociates in water to give ammonium ions, sulphate ions and iron (II) ions. The aqueous solution will give a white precipitate with acidified barium nitrate solution and a green precipitate insoluble in excess with sodium hydroxide.

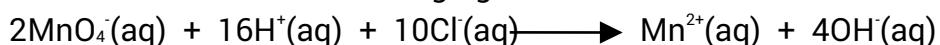
Usually made by mixing hot concentrated solutions of individual salts e.g iron (II) sulphate mixed with ammonium sulphate.

Complex salt – dissolves in water give a complex ion and a simple ion. Eg $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}] \text{Cl}_2 \cdot \text{H}_2\text{O}$ dissolves to give the complex ion $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ (aq) and 2Cl^- (aq)

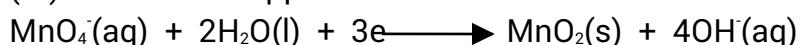
(b)

(i) Potassium permanganate is a stronger oxidizing agent than chlorine. In solution, KMnO_4 (aq) will oxidize chloride ions to chlorine.

Nitric acid is itself an oxidizing agent and would therefore interfere in the reaction.



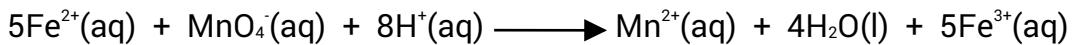
(ii) It is difficult to obtain KMnO_4 (aq) with a high purity. Solutions of MnO_4^- (aq) undergo a slow disproportionation in neutral or slightly acidic solution to give managanese (IV) oxide which appears as a brown solid.



Advantage of KMnO_4

- It doe not require an indicator
- It is stable in water

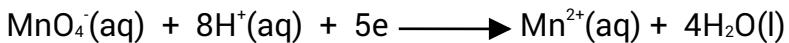
- (iii) A known volume of a solution containing iron (II) ammonium sulphate is placed in a conical flask. It is acidified by adding known volume of dilute sulphuric acid ($2\text{MH}_2\text{SO}_4$). The mixture is titrated with $\text{KMnO}_4(\text{aq})$ from burette until the purple colour is discharged and the end point is when solution turns pink.



Knowing the volume and concentration of iron (II) ions the concentration of MnO_4^- can be calculated.

(iv)

- In acidic solution



- In faintly alkaline solution



- In strongly alkaline solution,



(v) $2\text{KMnO}_4(\text{s}) \longrightarrow \text{K}_2\text{MnO}_4(\text{s}) + \text{MnO}_2(\text{s}) + \text{O}_2(\text{g})$

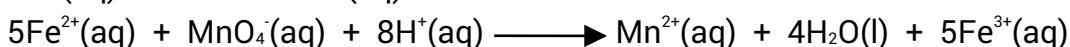
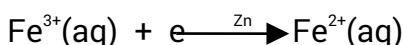
(c) Test for Mn^{2+}

- To the solution add aqueous sodium hydroxide, formation of a white precipitate which darkens on standing going to pink and finally brown indicates the presence of Mn^{2+} .
- To the solution, add solid sodium hydroxide and potassium chlorate (V). The mixture is heated strongly until the solid melts and acid added after cooling. The formation of a green-blue colour which turns into brown solid on cooling and pink solution on adding acid confirms Mn^{2+} .
- To the solution add concentrated nitric acid followed by lead (II) oxide and boil the mixture. The formation of a violet solution indicates Mn^{2+} .

(d) A known mass of the ore is crushed and boiled with excess of dilute sulphuric acid until no further reaction appeared to occur. The solution is cooled and filtered direct into a volumetric flask.

The residue on the filter paper is thoroughly washed and washings also collected in the volumetric flask which is then made to the mark using distilled water.

A known volume of this solution is reduced with zinc and dilute sulphuric acid to give iron (II) ions which is then titrated with standard potassium permanganate from a burette.



The percentage of iron in the ore can be calculated.

Question 54

Chromium is a typical transition element with atomic number 24.

(a) (i) Write the electronic configuration of Cr^{3+} .

(ii) By reference to compounds of chromium, illustrate two characteristic properties of transition elements.

(b) When 0.266g of a sample of chromium (III) chloride hexahydrate, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was

treated with aqueous silver nitrate. 0.286g of silver chloride was precipitated.

(i) Calculate the number of moles of Cl^- ions in one mole of the sample.

(ii) Write the structure of the complex cation contained in the sample.

(iii) Give the oxidation state of chromium in each of the following compounds.



(c) Explain each of the following observations.

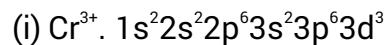
(i) Chromium (III) sulphate dissolves in water to form a solution whose pH is less than seven.

(ii) Chromium (III) oxide is amphoteric.

(iii) When aqueous sodium hydroxide was added to a solution of chromium (III) chloride, a green precipitate was formed and yellow solution formed on adding hydrogen peroxide. A red precipitate was formed when aqueous silver nitrate was added.

Solution

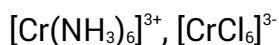
(a)



(ii) Some of the characteristic properties of transition elements are;

- Variable oxidation state
- Complex ion formation
- Formation of coloured compounds (ions)
- Catalytic activity
- Paramagnetism

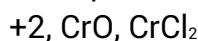
Chromium forms complexes with water, ammonia and chlorine eg $[\text{CrCl}_5\text{H}_2\text{O}]^{3+}$,



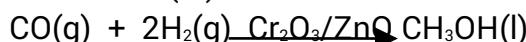
The complex ions formed are coloured eg $[\text{Cr}(\text{NH}_3)_6]^{3+}$ is yellow. Whereas $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ is violet.

The common oxidation states of chromium are +2, +3 and +6.

Examples of compounds in these oxidation states are;



Chromium (III) oxide is used as catalyst in the manufacture of methanol.



400°C, 200atm

Compounds of chromium in the oxidation state of +2 and +3 are paramagnetic because they contain 2 and 3 unpaired electrons respectively.

(b)

(i) 1 mole of $\text{AgNO}_3\text{(aq)}$ reacts with 1 mole of Cl^- ions to form 1 mole of AgCl(s)

$$\text{Rmm of AgCl} = 108 + 35.5 = 143.5$$

$$\text{Moles of silver chloride precipitated} = \frac{0.286}{143.5} = 1.99 \times 10^{-3} \approx 2 \times 10^{-3}$$

$$\text{Molar mass of CrCl}_3\text{.6H}_2\text{O} = 52 + 3(35.5) + 6(18) = 266.5\text{g}$$

$$\text{Moles of } \text{CrCl}_3 \cdot 6\text{H}_2\text{O} = \frac{0.2665}{266.5} = 1 \times 10^{-3}$$

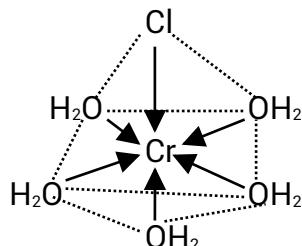
1×10^{-3} Moles of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ precipitated 2×10^{-3} moles of Cl^- ions.

Therefore moles of Cl^- ions in 1 mole of the complex that can be precipitated is given by;

$$= \frac{2 \times 10^{-3}}{1 \times 10^{-3}} = 2.0$$

(ii) Molecular formula of the complex is $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$

(iii) Structure



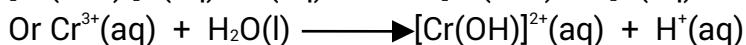
(iv) Oxidation state Cr in

$\text{K}_2\text{Cr}_2\text{O}_7$ is +6

$[\text{CrCl}_6]^{3-}$ is +3

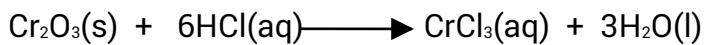
(c)

(i) Chromium (III) sulphate dissolves in water to give hydrated chromium (III) ions, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. This hydrated ion undergoes hydrolysis in aqueous solution to produce an excess of hydrogen ions. Hence the pH is less than seven (ie acidic)

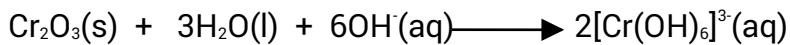


(ii) An oxide which exhibits both acidic and basic properties.

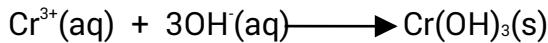
$\text{Cr}_2\text{O}_3(\text{s})$ reacts with hydrochloric acid to form a salt and water thus behaving as a base.



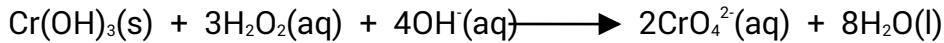
It reacts with sodium hydroxide to give a salt thus behaving as an acid.



(iii) The green precipitate formed is chromium (III) hydroxide which combines with hydrogen peroxide in excess of sodium hydroxide to form yellow solution chromate (VI) ion, $\text{CrO}_4^{2-}(\text{aq})$

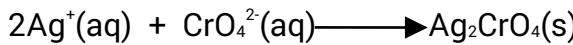


Green precipitate



Yellow solution

Silver ions react with $\text{CrO}_4^{2-}(\text{aq})$ to form a red precipitate of silver chromate.



Red precipitate

Question 55

(a) Explain each of the following.

- (i) When excess hydrochloric acid (or potassium chloride) was added to copper (II) chloride solution a green solution is formed. The green solution changed blue on dilution.
- (ii) A warm pink solution of cobalt (II) ions was treated with just sufficient hydrochloric acid to produce a blue solution. On cooling the pink colour is restored.
- (iii) Copper (I) chloride is insoluble in water but dissolves in both concentrated hydrochloric acid and also in concentrated ammonia.
- (iv) On heating copper (II) sulphate pentahydrate, it readily loses four moles of water but the fifth is only removed with difficulty.
- (v) When ethyne is passed into a solution of copper (I) chloride in aqueous ammonia, a red-brown precipitate is formed.
- (b) A double salt, $\text{Cu}(\text{NH}_4)_x\text{Cl}_y\text{H}_2\text{O}$ was analysed for chloride and ammonium ions. 2.78g of the salt reacted with silver nitrate to precipitate 5.74g of silver chloride. Another 2.78g of the salt boiled with excess sodium hydroxide and the liberated ammonia was neutralized with 40cm³ of 0.5M hydrochloric acid. Determine the molecular formula if the molar mass of the double salt is 277g.

Solution

(a)

- (i) In aqueous solution copper (II) ions exist as hydrated complexes with water molecules. Therefore aqueous copper (II) ions are blue due to the ion, $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$. When excess concentrated hydrochloric solution is added the aqua ligands are displaced and a more stable complex of $[\text{CuCl}_4]^{2-}(\text{aq})$ is formed. This appears as a green solution.



On diluting the green solution the chloro ligands are displaced and a blue solution formed again.

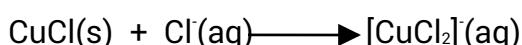
- (ii) Aqueous cobalt (II) ions is pink due to the presence of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion. When the pink solution is treated just sufficient hydrochloric acid a blue solution containing the species $[\text{CrCl}_4]^{2-}(\text{aq})$ is formed. An equilibrium is established between the two ions in solution.

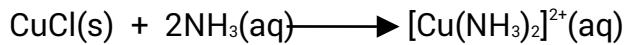


At high temperature (solution warm), and in the presence of excess chloride ions, the equilibrium lies more to the right and the solution appears blue.

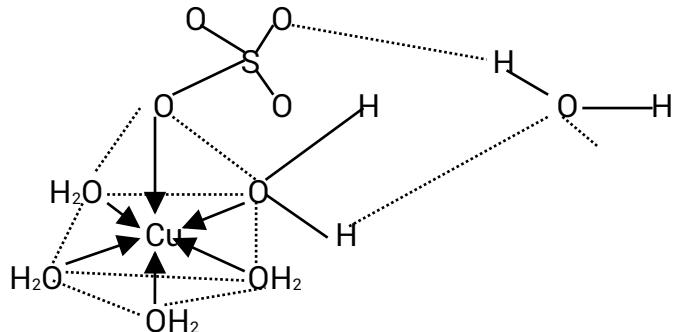
When the solution cools (lower temperature), the equilibrium lies more to the left and therefore the solution appears pink again.

- (iii) Copper (I) chloride is insoluble in water because the hydration energy can not overcome the high lattice energy. Copper (I) chloride forms soluble complexes with concentrated hydrochloric acid and with ammonia. Therefore it dissolves in the two solvents.



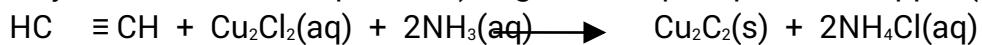


(iv) In the copper (II) sulphate pentahydrate, four water molecules are held together in a square planar position around the copper (II) ion and the fifth water molecule held by hydrogen bond to the oxygen atom of sulphate ion and one of the water molecules in the square planar position. The remaining octahedral positions (5 and 6) are occupied by oxygen atoms of the sulphate ion.

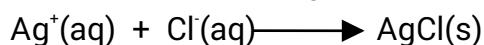


When heated, the four water molecules in the square position are easily lost while the fifth is removed with difficulty.

(v) Copper (I) chloride in the presence of aqueous ammonia reacts with ethyne (an alkyne with terminal triple bond) to give a red precipitate of copper (I) dicarbide.



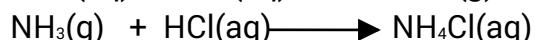
$$(b) \text{ Moles of salt} = \frac{2.78}{277.5} = 0.01$$



$$\text{Molar mass of AgCl} = 108 + 35.5 = 143.5\text{g}$$

$$\text{Moles of chloride ions} = \frac{5.74}{143.5} = 4 \times 10^{-2}$$

When the salt was boiled with excess sodium hydroxide, ammonia was evolved.



1 mole of NH_4^+ ion liberates one mole of ammonia which then reacts with 1 mole of HCl(aq) for reaction.

Moles of NH_4^+ in the salt = moles of HCl in 40cm^3

$$= \frac{0.5 \times 40}{1000} = 2 \times 10^{-3}$$

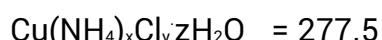
7.01 mole of salt liberated 0.02 moles of NH_3

1 mole of HCl(aq) liberates 2 moles of NH_3

Also 0.01 mole of salt liberated 4×10^{-2} moles of chloride ions.

1 mole salt liberates 4 moles of chloride ions.

Therefore X = 2 and Y = 4



$$64 + 2(18) + 4(35.5) + z(18) = 277.5$$

$$z = \frac{35.5}{18} = 2$$

Therefore the molecular formula of the salt is $\text{Cu}(\text{NH}_4)_2\text{Cl}_4\text{2H}_2\text{O}$

Question 56

One property of chromium as a transition metal is its ability to form complexes, for example $[\text{Cr}(\text{NH}_3)_6]^{3+}$.

- (a) (i) State two other properties of chromium as a transition metal. In each case give two suitable examples.
- (ii) Chromium (III) chloride-6-water, $\text{CrCl}_6 \cdot 6\text{H}_2\text{O}$ is an example of hydrate isomerism. Write the formula of three possible isomers of $\text{CrCl}_6 \cdot 6\text{H}_2\text{O}$.
- (iii) Two of the isomers of $\text{CrCl}_6 \cdot 6\text{H}_2\text{O}$ were analysed for a number of ions present and results shown in the table below.

Test	Result	
	Isomer X	Isomer y
1. Excess Ag^+ (aq) was added to 0.05M aqueous solution of isomer.	0.05 mole of $\text{AgCl}(s)$ was precipitated	0.15 moles of $\text{AgCl}(s)$ was precipitated
2. Conductivity measurements	Two moles of conducting species detected	Four moles of conducting species detected.

Deduce the possible molecular formula of isomers x and y. Explain your answer.

- (b) Explain each of the following.

- (i) When sodium carbonate solution is added to chromium (III) ions a green precipitate and a colourless gas is evolved.
- (ii) When aqueous ammonia is added to chromium (III) ions a green precipitate is formed which dissolves in excess to form a pink solution.
- (iii) When potassium iodide solution is added to a solution of copper (II) salt, the solution turns dark brown and a precipitate was formed. Addition of sodium thiosulphate decolourises the solution leaving a white precipitate.

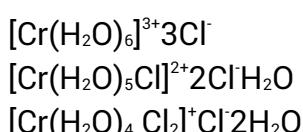
Solution

(a)

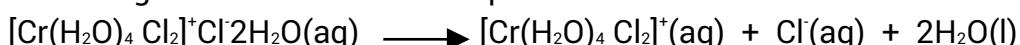
(i)

- Catalytic ability eg Cr_2O_3 during the manufacture of methanol.
 $\text{CO(g)} + 2\text{H}_2\text{O(l)} \xrightarrow{\text{Cr}_2\text{O}_3/\text{ZnO}} \text{CH}_3\text{OH(l)}$
- They have variable oxidation states eg +2 and +3 in CrCl_2 and Cr_2O_3 respectively.
- Ions or compounds are coloured eg $[\text{Cr}(\text{NH}_3)_6]^{3+}$ yellow and Cr_2O_3 is green.

(ii)



- (iii) Isomer X is $[\text{Cr}(\text{H}_2\text{O})_4 \text{Cl}_2]^+ \text{Cl}^- 2\text{H}_2\text{O}$. This because one mole of X would dissolve in water to give two ions ie one complex ion and 1 mole of chloride ions.

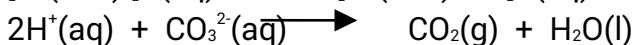
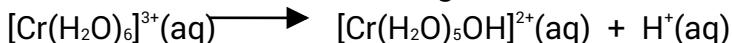


Isomer Y is $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}3\text{Cl}$. This is because 1 mole Y dissolves in water to give four conducting ions. And the mole ration of AgCl precipitated to Ag^+ is 3:1.

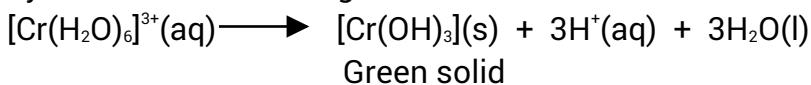


(b)

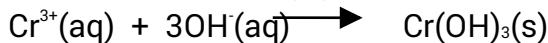
- (i) The hydrated chromium (III) ion undergoes hydrolysis in aqueous solution reducing excess of hydrogen ions. The hydrogen ions react with the carbonate ions to produce carbon dioxide, the colourless gas.



This causes further hydrolysis of the chromium (II) ions to produce chromium (III) hydroxide which is the green solid.



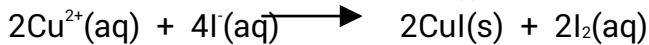
- (ii) In the presence of a few drops of aqueous ammonia, the hydroxide ions combine with the chromium (III) ions to give a green precipitate of chromium (III) hydroxide.



The green precipitate dissolves in excess ammonia to give a complex which is yellow or violet.



- (iii) Copper (II) ions combine with iodide ions to give copper (I) iodide and iodine. The brown mixture contains copper (I) iodide which absorbs iodine and appears brown.



When sodium thiosulphate solution is added, the thiosulphate ions, $\text{S}_2\text{O}_3^{2-}$ react with the dissolved iodine.



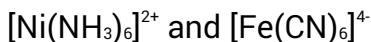
This reaction (removal of iodine) leads to discharge of the brown colour and the white precipitate of copper (I) iodide is left in a clear solution.

Question 57

- (a) One of the distinguishing features of transition elements is the ability to form complex ion. For each of the following complex ions determine

(i) The oxidation state

(ii) The coordination number of the metal ion in each species.



- (b) The stability constant for $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and $[\text{CuCl}_4]^{2-}$ are 1.4×10^{13} and 2.4×10^7 respectively.

y.

(i) What is meant by stability constant?

(ii) Explain what happens if excess aqueous ammonia was added to solution of $[\text{CuCl}_4]^{2-}$.

(iii) For the two complex ions of cobalt,

$[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{NH}_3)_6]^{2+}$ which is more stable. Give a reason.

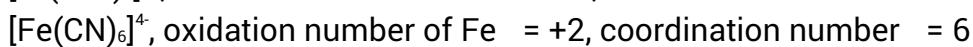
- (c) (i) How do you test for chromium (III) ions.

(ii) How would you use sodium hydroxide to distinguish between Cr^{3+} and $\text{Cu}^{2+}(\text{aq})$.

- (iii) How would you use sodium hydroxide to distinguish between Ni^{2+} and Fe^{2+} (aq).
- (d) A hydrated compound contains copper (II), ammonium ion and chloride ions. 27.75g of the compound was dissolved in water and made to 1 litre of solution with distilled water. 25 cm³ of this solution was boiled with excess sodium hydroxide solution and the liberated ammonia reacted completely with 25cm³ of 0.2M hydrochloric acid. Another 25cm³ reacted aqueous silver nitrate and 1.43g of silver chloride was precipitated. A third sample (25cm³) on treatment with excess potassium iodide liberated iodine which reacted completely with 12.5cm³ of 0.2M sodium thiosulphate. Determine the molecular formula of the compound.

Solution

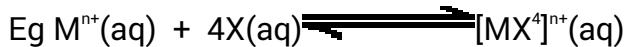
(a)



(b)

(i) Stability constant

This is a special case of an equilibrium constant as applied to the formation of complex ions.



$$K_{\text{stab}} = \frac{[\text{MX}_4]^{n+}}{[\text{M}^{n+}][\text{X}]^4}$$

(ii) The chloro ligands in $[\text{CuCl}_4]^{2-}$ (aq) are displaced and a more stable complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is formed.



(iii) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (aq) is more stable than $[\text{Co}(\text{NH}_3)_6]^{2+}$ (aq). The oxidation number of cobalt in $[\text{Co}(\text{NH}_3)_6]^{3+}$ (aq) is greater and thus greater attraction for electrons than the oxidation number in $[\text{Co}(\text{NH}_3)_6]^{2+}$ (aq).

(c)

(i) Test for Cr^{3+} (aq) ion

- To the solution add dilute hydrochloric acid, then ether and hydrogen peroxide. A blue colouring in the ether indicates Cr^{3+} (aq).
- To the solution add solution of Ba^{2+} or Pb^{2+} (aq) formation of yellow precipitate indicates presence of Cr^{3+} (aq).
- To the solution of potassium dichromate acidified with dilute sulphuric acid is added zinc powder. To the resulting solution is added sodium hydroxide solution dropwise until in excess. The appearance of green solid which dissolves in excess to form a green solution confirms the presence of Cr^{3+} (aq) ions.

(ii) To the solution is added sodium hydroxide dropwise until in excess.

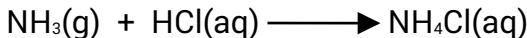
- The appearance of green solid (precipitate) which dissolves in excess to form a green solution confirms the presence of Cr^{3+} (aq).
- The appearance of a blue precipitate which is insoluble in excess but turns black on heating confirms Cu^{2+} (aq) ions.

(iii) To the solution, sodium hydroxide is added dropwise until in excess and then

heated.

- Appearance of a green precipitate insoluble in excess and does not change on heating indicate the presence of $\text{Ni}^{2+}(\text{aq})$.
- Appearance of green precipitate insoluble in excess but turns brown on heating indicates $\text{Fe}^{2+}(\text{aq})$ ions.

(d) When the salt is boiled with sodium hydroxide, ammonia is evolved.

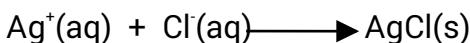


1 mole of $\text{NH}_4^+(\text{aq})$ ion liberates 1 mole of $\text{NH}_3(\text{g})$ which require 1 mole of $\text{HCl}(\text{aq})$ for complete reaction.

Moles of $\text{NH}_4^+(\text{aq})$ in 25cm^3 of solution = moles of HCl in 40cm^3

$$= \frac{0.2 \times 25}{1000}$$

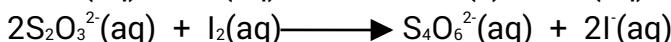
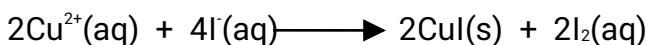
$$\text{Moles of } \text{NH}_4^+(\text{aq}) \text{ in } 1000\text{cm}^3 = \frac{0.2 \times 25 \times 1000 \times 0.2}{1000 \times 25}$$



Rmm of AgCl = 143.5

$$\text{Therefore moles of Cl}^-(\text{aq}) \text{ in } 25\text{cm}^3 = \frac{1.435}{143.5} = 0.01$$

$$\text{Moles of Cl}^-(\text{aq}) \text{ in } 1000\text{cm}^3 = \frac{0.01 \times 1000}{25} = 0.4$$



2 moles of $\text{Cu}^{2+}(\text{aq})$ is equivalent to 2 moles of $\text{S}_2\text{O}_3^{2-}(\text{aq})$

1 mole of $\text{Cu}^{2+}(\text{aq})$ is equivalent to 1 mole of $\text{S}_2\text{O}_3^{2-}(\text{aq})$

$$\text{Moles of S}_2\text{O}_3^{2-}(\text{aq}) \text{ in } 25\text{cm}^3 = \frac{12.5 \times 0.2 \times 1000}{1000 \times 25} = 0.1$$

Mass of Cu = $64 \times 0.1 = 6.4\text{g}$

Mass of NH_4^+ = $18 \times 0.2 = 3.6\text{g}$

Mass of Cl = $35.5 \times 0.4 = 14.2\text{g}$

Total mass = 24.2g

Therefore mass of water in the sample = $(27.75 - 24.2) = 3.55\text{g}$

$$\text{Moles of water} = \frac{3.55}{18} = 0.2$$

Ratio of moles

$$\begin{array}{cccc} \text{Cu} : \text{NH}_4^+ : \text{Cl} : \text{H}_2\text{O} \\ 0.1 & 0.2 & 0.4 & 0.2 \\ 1 & 2 & 4 & 2 \end{array}$$

Therefore the molecular formula of the salt is $\text{Cu}(\text{NH}_4)_2\text{Cl}_2\text{.}2\text{H}_2\text{O}$.

Question 58

- (a) (i) Name one ore of zinc and give its formula.
(ii) Describe briefly how the ore you have named is concentrated.
(iii) What further treatment of the ore is required immediately after concentration?

(iv) Outline the process, giving equations for the production of zinc metal from the treated ore.

(b) Explain each of the following.

(i) Zinc oxide becomes yellow when heated but white when cool.

(ii) Zinc chloride readily dissolves in water to form a solution with pH less than 7.

(iii) Zinc (II) hydroxide is soluble in both aqueous sodium hydroxide and ammonia solution.

(iv) Zinc has a more negative standard electrode potential than copper.

Solution

(a)

(i) Zinc sulphide, ZnS or Zinc blend

Zinc carbonate, ZnCO₃ or calamine

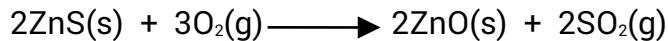
(ii) The ore is concentrated by froth floatation process. Here the ore is first ground to a powder and mixed with water to which has been added a suitable oil (frothing agent)

The oil wets the sulphide particles and the water wets the gangue.

Air is then blown through the mixture. Small air bubbles attach themselves to the oil particles which rise to the surface in the froth and the gangue sinks to the bottom.

The froth is skimmed off and the sulphide recovered.

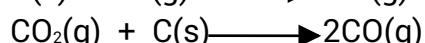
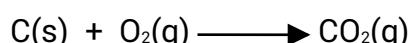
(iii) The ore is roasted in air to produce zinc oxide.



(iv) Thermal reduction

The concentrated zinc oxide, limestone and excess coke is fed into a blast furnace.

Hot air is passed from burning producer gas. The coke combines with oxygen to form carbon dioxide which rises up the furnace and reduced by the unburnt coke to carbon monoxide.



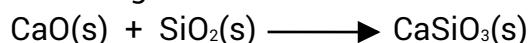
The carbon monoxide reduces zinc oxide to zinc.



The zinc distills off and the vapour is cooled on a spray of molten lead. Calcium carbonate in the blast furnace decomposes to quick lime and carbon dioxide.



The calcium oxide (basic oxide) combines with acidic impurities such as silica to form slag which sinks to the bottom and is removed.



(b)

(i) Zinc oxide, ZnO is a covalent solid with the diamond structure. Each zinc atom is bonded to four oxygen atoms arranged tetrahedrally and each oxygen atom is likewise bonded to four zinc atoms.

This arrangement gives Zinc (II) oxide a 3-dimensional structure and is white when

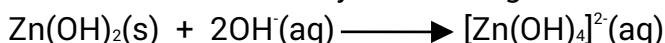
cold. On heating zinc (II) oxide, some oxygen atoms are lost from the lattice structure leaving excess of negative charge resulting in the yellow colour. When it cools, the lost oxygen atoms return and the white colour is restored.

- (ii) In aqueous solution, zinc (II) ions form hydrated complex with water molecules. However the hydrated complex dissociates due to the high charge density on the zinc ion. This leaves excess of hydrogen ions. As a result the pH of the solution is less than seven.



- (iii) Zinc (II) hydroxide is amphoteric thereby reacting with both acids and sodium hydroxide (alkali).

It reacts with sodium hydroxide to give a salt thereby behaving as an acid.



Zn(OH)_2 dissolves in excess ammonia due to the formation of a soluble complex.



- (iv) The factors which determine whether a given metal dissolves are sublimation energy of the metal element, the ionization energy of the gaseous atoms and the hydration energy. The sum of all these energy terms gives the enthalpy of solution.

The large ionization energy of copper and zinc is counterbalanced by the large hydration energies of $\text{Cu}^{2+}(\text{aq})$ and $\text{Zn}^{2+}(\text{aq})$ ions. However zinc has lower sublimation energy than copper (ie low melting point and boiling point due to stability of d-electrons). Therefore the electrode potential of zinc is more negative than that of copper.

Question 59

- (a) Transition elements form a large number of co-ordinated compounds which are coloured.

(i) Explain why the aquo-cations of transition elements are often acidic.

(ii) Explain why aqueous copper (II) ions are blue in colour.

- (b) The compounds $[\text{Co}(\text{NH}_3)_5\text{SO}_4]^+\text{Br}^-$ and $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}\text{SO}_4^{2-}$ are isomers.

(i) What ions will these two isomers yield in solution. How could you confirm which isomer is which?

(ii) What is the oxidation state and coordination number of cobalt in each complex.

(iii) Draw the structure of the $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ complex.

- (c) A pale green chloride of chromium X was analysed and the results presented in the table below.

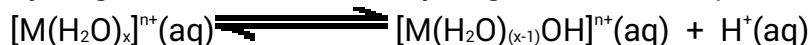
Test	Result
1g of X was heated in air to constant mass	H_2O , HCl was evolved. 0.286 of residue Cr_2O_3 , remained
1g of X was dissolved in water, acidified with dilute nitric acid and silver nitrate solution added. The solution was boiled until no further change	1.077g of silver chloride was precipitated. On boiling the solution 0.538g of $\text{AgCl}(\text{s})$ was precipitated.
1g of X was dried in a desicator over concentrated sulphuric acid.	0.08g of water was lost

- (i) Determine the molecular formula.
 - (ii) Write all possible isomers of X.

Solution

(a)

(i) In aqueous solution transition metal ions exist as hydrated complexex with water molecules. Due to the highy charge density on the metal cation, the hydrated complexes dissociate (ionize) to give solutions in which there is an excess of hydrogen ions. The excess hydrogen ions are responsible for the acidity.



The high charge on the metal cation is able to attract electron in the water molecules thus weakening the O-H bond which loses the hydrogen as a proton.

(ii) The electrons of the d-orbitals are arranged differently in space. The presence of water causes electron repulsion which leads to a break in the degeneracy of the d-electrons. (ie d-electrons are split) into two groups with slightly different energy levels. This process involves absorption of energy from white light. The absorption of red light of appropriate frequency from white light makes hydrated copper (II) sulphate to appear blue.

(b)

(i) $[\text{Co}(\text{NH}_3)_5\text{SO}_4]^+$ Br^- dissociates to give Br^- ion and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]^+$ complex.

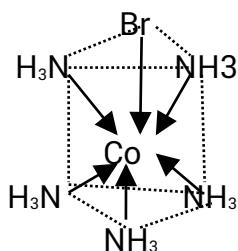
To the aqueous solution add silver nitrate solution, a pale yellow precipitate of AgBr is formed.

$[\text{Co}(\text{NH}_3)_5 \text{Br}]^{2+}$ dissociates in water to give SO_4^{2-} ion and $[\text{Co}(\text{NH}_3)_5 \text{Br}]^{2+}$ ions.

The aqueous solution will give a white precipitate with acidified barium nitrate or lead (II) nitrate solution.

$[\text{Co}(\text{NH}_3)_5 \text{Br}]^{2+}$ SO₄²⁻ Oxidation state = +2
Coordination number = 6

(iii)



(c)



Rmm of AgCl = 143.5

1 mole of silver ions precipitate 1 mole of AgCl

$$\text{Moles of chloride ions in aqueous solution} = \frac{1.077}{14305} = 7.505 \times 10^{-3}$$

$$\text{On boiling, moles of chloride ions} = \frac{0.538}{143.5} = 3.75 \times 10^{-3}$$

Therefore moles of chloride ions in the complex = 3.75×10^{-3}

$$\text{Moles of water} = \frac{0.068}{18} = 3.78 \times 10^{-3}$$

But RMM of Cr_2O_3 = $2(2) + 3(16) = 152$

15.2g of Cr_2O_3 contains 104g of Cr

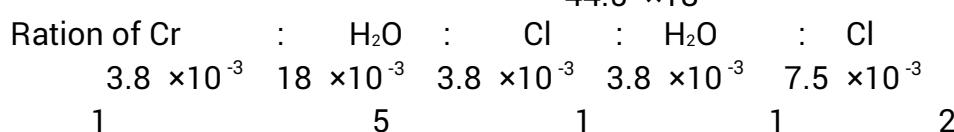
$$0.286\text{g of } \text{Cr}_2\text{O}_3 \text{ contains } \frac{104 \times 0.286}{152} = 0.1956\text{g of Cr}$$

$$\text{Moles of Cr in } 0.196\text{g} = \frac{0.196}{52} = 3.8 \times 10^{-3}$$

Mass of $\text{H}_2\text{O} + \text{HCl}$ = $(1 - 0.286) = 0.714\text{g}$ and RMM of $\text{H}_2\text{O} + \text{HCl}$ = $(18 + 36.5) = 44.5$

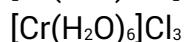
$$\text{Mass of water driven} = \frac{18 \times 0.714}{44.5}$$

$$\text{Moles of water in the complex salt} = \frac{18 \times 0.714}{44.5 \times 18} = 1.8 \times 10^{-2} = 18 \times 10^{-3}$$



Therefore the molecular formula is $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2\text{H}_2\text{O}$

(ii) Isomers



Question 60

(a) Explain why it is a feature of transition element that they

- (i) Show variable oxidation states.
- (ii) Have coloured ions or compounds.

(b) (i) How would you demonstrate the property in (a) (i) above.

(ii) The colour of a transition cation depends on the oxidation state and the type of ligand. Explain.

(c) A green powder was dissolved in dilute hydrochloric acid to form a green solution. The solution was divided into three parts. To the first portion of the solution was added a few drops of potassium hexacyanoferrate (II) solution and a brown precipitate was formed.

(i) Name the cation in the green solid.

(ii) State the observation and write equation when the second part was treated with concentrated hydrochloric acid dropwise until in excess.

(iii) State the observation and write equation when the third part was treated with magnesium powder and the mixture warmed.

(d) 5.85g of ammonium vanadate, NH_4VO_3 was dissolved in dilute sulphuric acid and the solution made to 1 litre with distilled water. 25cm^3 of this solution after boiling with sodium sulphite reacted completely with 12.5cm^3 of potassium permanganate.

Another 25cm^3 of this solution after boiling with zinc metal reacted completely with 37.5cm^3 of the same permanganate solution.

- (i) Deduce the oxidation states of vanadium during both cases.
(ii) Calculate the molarity of manganate (VII) ions in solution.

Solution

(a)

(i) Transition metals have variable number of electrons in the d-subshell depending on the configuration. This means, the metals can utilize the 3d electrons in addition to the 4s electrons in chemical bonding. Therefore transition elements (metals) have variable oxidation state and are able to form ionic and covalent compounds. The successive ionization energies of the transition metals increase gradually (without any distinct break) because electrons are being removed from the same subshell (3d). The greater the number of unpaired electrons in 3d subshell, the greater the range of oxidation states.

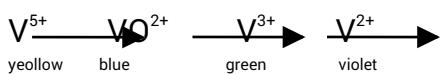
(ii) Colour

The 3d orbitals are not of the same energy level and the electrical field of a ligand around the central metal ion of a transition element affects the energy of the orbitals. The presence of the ligands will lead to the splitting of the 3d orbitals into two groups (ie degeneracy destroyed) this process involves energy and if the energy difference between the two groups is equivalent to an appropriate frequency from white light, then the complex appears coloured.

(b)

(i) Vanadium exists in oxidation state of +5 in a solution of ammoniumvanadate which is yellow.

When a solution of ammoniumvanadate is heated with zinc and hydrochloric acid, (in absence of oxygen) the solution changes progressively to blue, green, green and finally violet.



(ii) The electric field around a ligand varies from one ligand to another. This means the splitting will also vary and therefore colours will vary. Eg $[Cu(NH_3)_4]^{2+}(aq)$ is deep blue whereas $[CuCl_4]^{2-}(aq)$ is green.

(c)

(i) Copper (II) ion

(ii) Solution changesd from green to yellow

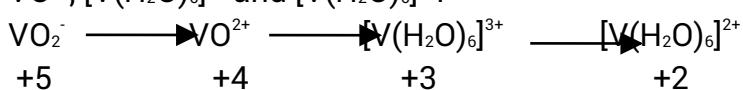


(iii) The solution changes from green to colourless and a reddish brown precipitate is also formed.



(d) Vanadium in ammonium vanadate has oxidation number of +5.

(i) Other oxidation states which can be obtained on reduction are +4, +3 and +2 as in VO^{2+} , $[V(H_2O)_6]^{3+}$ and $[V(H_2O)_6]^{2+}$.



Half equations for zinc and sulphite ions are



When sodium sulphite was used for reduction the volume of MnO_4^- for was 12.5cm^3 .

When zinc metal was used the volume of MnO_4^- was 37.5cm^3 .

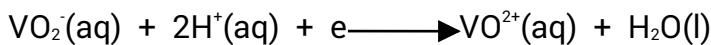
The ratio of volume of MnO_4^- = ratio of change in oxidation state.

Volume of when sodium sulphite is used : volume of when Zn metal is used.

$$12.5\text{cm}^3 : 37\text{cm}^3$$

$$1 \quad 4$$

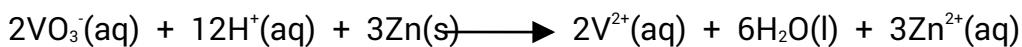
Therefore in the presence of sodium sulphite vanadium in oxidation state of +5 is reduced to oxidation state of +4



General equation



In the presence of zinc, vanadium in oxidation state +5 is reduced to oxidation state of +2.



$$(ii) \text{ Molar mass of } \text{NH}_4\text{VO}_3 = 14 + 4 + 51 + 3(16) = 117$$

$$\text{Moles of } \text{NH}_4\text{VO}_3 \text{ in } 25\text{cm}^3 = \frac{5.85 \times 25}{117 \times 1000} = 1.25 \times 10^{-3}$$

Let the molarity of MnO_4^- = m

From equations moles of MnO_4^- = 2 moles of NH_4VO_3 (in the presence of sodium sulphite)

$$\frac{m \times 125}{1000} = 2(1.25 \times 10^{-3})$$

$$m = \frac{2 \times 1.25 \times 10^{-3}}{12.5 \times 1000} = 0.02$$

Therefore molarity of MnO_4^- = 0.02M

Question 61

(a) In each of the following, state the observation and write equation to explain

- (i) To an aqueous solution of chromium chloride followed by dropwise addition of aqueous ammonia until the solution was in excess.
- (ii) Excess aqueous ammonia and potassium hexacyanoferate (II) solution were separately added to hydrated copper (II) ions.
- (iii) Aqueous sodium hydroxide added to solution of iron (II) sulphate and heated.

(b) Aqueous ammonia was added dropwise until in excess to each of the following ions in solution.

(i) $\text{Ni}^{2+}(\text{aq})$

(ii) $\text{Cr}^{3+}(\text{aq})$

(c) The following tests were carried on solution W, X, Y, Z.

Solution	Test	Observation
----------	------	-------------

n

X Aqueous sodium hydroxide and Green precipitate insoluble in excess.

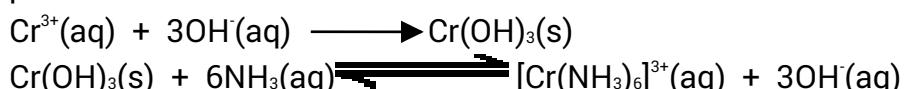
	heated	
Y	Potassium iodide solution followed by sodium thiosulphate	Brown mixture formed. The brown colour decolourises and white precipitate remains on adding $S_2O_3^{2-}$
Z	Sodium hydroxide solution added and allowed to stand	White precipitate formed. The precipitate darkens on standing, going pink then brown
W	Sodium hydroxide added till in excess followed by a solution of hydrogen peroxide and silver nitrate solution	Green precipitate soluble in excess to give a green solution. Yellow solution on adding hydrogen peroxide and red precipitate on adding silver nitrate solution

- (i) What cations are present in solutions X, Y, Z and W.
(ii) Explain the observation with solution Z.

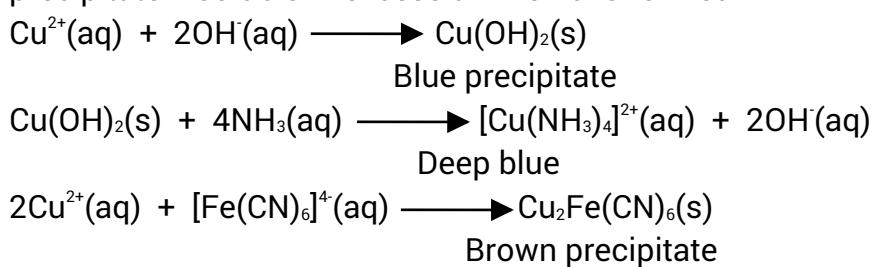
Solution

(a)

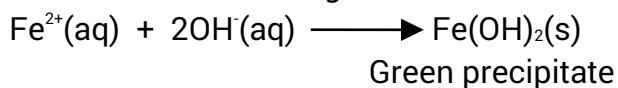
- (i) Grey-green precipitate formed. The precipitate dissolves in excess ammonia to form pink solution.



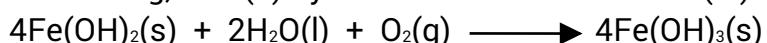
- (ii) Blue precipitate formed. The precipitate dissolves in excess ammonia to give a deep blue solution. Addition of potassium hexacyanoferrate (II) to $\text{Cu}^{2+}(\text{aq})$ forms a brown precipitate insoluble in excess ammonia is formed.



- (iii) A green precipitate insoluble in excess sodium hydroxide is formed. The precipitate turns brown on heating.

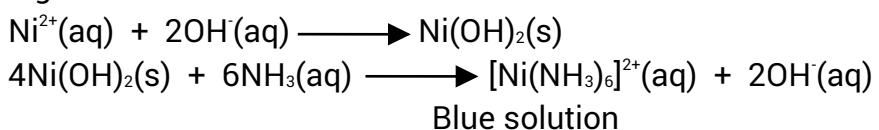


On heating, iron (II) hydroxide is oxidized to iron (III) hydroxide.

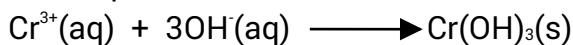


(b)

- (i) Blue-green precipitate formed. The precipitate dissolves in excess ammonia to give a green solution.



- (ii) Grey-green precipitate formed. The precipitate dissolves in excess ammonia to form a pink solution.



(c)

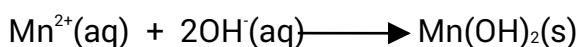
(i) X Ni^{2+}

Y Cu^{2+}

Z Mn^{2+}

W Cr^{3+}

- (ii) The white precipitate formed is manganese (II) hydroxide which undergoes oxidation by atmospheric oxygen to give hydrated manganese (III) oxide which is seen as a brown solid.



Question 62

- (a) Explain why the melting point of magnesium chloride is much higher than the melting point of silicon tetrachloride.
- (b) Suggest why the melting point of magnesium oxide is much higher than the melting point of magnesium chloride.
- (c) Magnesium oxide and sulphur dioxide are added separately to water. In each case describe what happens. Write equations for any reactions which occur and state the approximate pH of any solution formed.
- (d) Write equations for two reactions which together show the amphoteric character of aluminum hydroxide.

Question 63

- (a) At high temperatures, aluminium chloride exists in the vapour phase as the molecule AlCl_3 . On cooling, two molecules of AlCl_3 combine by coordinate bonding to form molecules of Al_2Cl_6 .
- (i) State the shape of the AlCl_3 molecule and give the bond angle.
- (ii) Sketch the structure of Al_2Cl_6 and mark on your sketch the value of one of the bond angles.
- (iii) Explain how two AlCl_3 molecules are able to bond together.
- (b) (i) Describe what is observed when anhydrous AlCl_3 is added to an excess of water. Identify the major aluminium-containing species formed and predict the pH of the final solution.
- (ii) Describe what you would observe when aqueous sodium carbonate is added to aqueous aluminium chloride. Write an equation for the reaction.

Question 64

(a) Write equations for the reactions which occur when the following compounds are added separately to water

(b)

Question 65

(a) In each of the following pairs of compounds, in aqueous solution, can be distinguished by using suitable reagent in test-tube reactions.

For each pair, identify a reagent, describe what you would observe and write equations for any reactions that occur.

(i) Separate solutions of $\text{CuSO}_4(\text{aq})$ and of $\text{Cu}(\text{NO}_3)_2(\text{aq})$

(ii) Separate solutions of $\text{CrCl}_3(\text{aq})$ and of $\text{FeCl}_2(\text{aq})$

(b) Separate aqueous solutions of potassium manganate (VII) and sodium manganate (VII), each contained 1.000g of the compound in 250cm³ of solution.

A 25cm³ of sample of one of these solutions reacted with exactly 17.60cm³ of a 0.100mol dm⁻³ acidified solution of sodium ethanedioate.

(i) Write an equation chm 2008

(c)

Question 66