



# DEMYSTIFYING INORGANIC **CHEMISTRY**

**JOSEPH JOBS KAYIIRA**

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## PREFACE

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

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

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

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

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

Most of the content is presented in a question answer format to enable students to have a clue on question approach. Miscellaneous topical questions are provided at the end of each topic but no answers such that research and consultation is enhanced.

Where C.f is seen, it is an implication that the other elements or compounds listed under go similar reactions or are prepared by similar methods.

Also feel free to contact the author using contacts or his social media platforms for clarity.

*I wish you a safe ride through the book.*

## ACKNOWLEDGEMENTS

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

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**DEMYSTIFYING INORGANIC CHEMISTRY BY Joseph Jobs Kayiira, BScED(Hons. CHEM/MTC)**  
*Email: josephkayirab@gmail.com Call 0782601038 WhatsApp 0753247098*

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# THIRD SHORT PERIOD OF THE PERIODIC TABLE

## BRIEF INTRODUCTION TO THE PERIODIC TABLE

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

## GROUPS AND PERIODS

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

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

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

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

## GROUPS

PERIODS	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII	IB	IIB	IIIB	IVB	VB	VIB	VII B	O		
1	$1^0_1\text{H}$															$1^0_1\text{H}$	$4^0_2\text{He}$	
2	$6^0_3\text{Li}$	$9^0_4\text{Be}$										$10^0_5\text{B}$	$12^0_6\text{C}$	$14^0_7\text{N}$	$16^0_8\text{O}$	$19^0_9\text{F}$	$20^0_{10}\text{Ne}$	
3	$23^{11}_{11}\text{Na}$	$24^{12}_{12}\text{Mg}$										$27^0_{13}\text{Al}$	$28^0_{14}\text{Si}$	$31^0_{15}\text{P}$	$32^0_{16}\text{S}$	$35^0_{17}\text{Cl}$	$40^0_{18}\text{Ar}$	
4	$39^{19}_{19}\text{K}$	$40^{20}_{20}\text{Ca}$	$45^{21}_{21}\text{Sc}$	$47^{22}_{22}\text{Ti}$	$50^{23}_{23}\text{V}$	$52^{24}_{24}\text{Cr}$	$54^{25}_{25}\text{Mn}$	$55^{26}_{26}\text{Fe}$	$58^{27}_{27}\text{Co}$	$58^{28}_{28}\text{Ni}$	$63^{29}_{29}\text{Cu}$	$65^{30}_{30}\text{Zn}$	$69^{31}_{31}\text{Ga}$	$72^{32}_{32}\text{Ge}$	$74^{33}_{33}\text{As}$	$79^{34}_{34}\text{Se}$	$79^{35}_{35}\text{Br}$	$83^{36}_{36}\text{Kr}$
5	$85^{37}_{37}\text{Rb}$	$87^{38}_{38}\text{Sr}$	$88^{39}_{39}\text{Y}$	$91^{40}_{40}\text{Zr}$	$92^{41}_{41}\text{Nb}$	$95^{42}_{42}\text{Mo}$	$98^{43}_{43}\text{Tc}$	$101^{44}_{44}\text{Ru}$	$103^{45}_{45}\text{Rh}$	$106^{46}_{46}\text{Pd}$	$108^{47}_{47}\text{Ag}$	$112^{48}_{48}\text{Cd}$	$115^{49}_{49}\text{In}$	$119^{50}_{50}\text{Sn}$	$122^{51}_{51}\text{Sb}$	$128^{52}_{52}\text{Te}$	$127^{53}_{53}\text{I}$	$131^{54}_{54}\text{Xe}$
6	$133^{55}_{55}\text{Cs}$	$137^{56}_{56}\text{Ba}$	$139^{57}_{57}\text{La}$	$178^{72}_{72}\text{Hf}$	$181^{73}_{73}\text{Ta}$	$184^{74}_{74}\text{W}$	$186^{75}_{75}\text{Re}$	$190^{76}_{76}\text{Os}$	$192^{77}_{77}\text{Ir}$	$195^{78}_{78}\text{Pt}$	$197^{79}_{79}\text{Au}$	$201^{80}_{80}\text{Hg}$	$204^{81}_{81}\text{Tl}$	$207^{82}_{82}\text{Pb}$	$209^{83}_{83}\text{Bi}$	$210^{84}_{84}\text{Po}$	$210^{85}_{85}\text{At}$	$222^{86}_{86}\text{Rn}$
7	$223^{87}_{87}\text{Fr}$	$226^{88}_{88}\text{Ra}$	$227^{89}_{89}\text{Ac}$	$261^{104}_{104}\text{Rf}$	$262^{105}_{105}\text{Db}$	$266^{106}_{106}\text{Sg}$	$264^{107}_{107}\text{Bh}$	$277^{108}_{108}\text{Hs}$	$278^{109}_{109}\text{Mt}$	$281^{110}_{110}\text{Ds}$	$280^{111}_{111}\text{Rg}$	$285^{112}_{112}\text{Cn}$	$286^{113}_{113}\text{Nh}$	$289^{114}_{114}\text{Fl}$	$289^{115}_{115}\text{Mc}$	$293^{116}_{116}\text{Lv}$	$294^{117}_{117}\text{Ts}$	$294^{118}_{118}\text{Og}$

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

## PERIODIC BLOCKS

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

### s-block elements

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

IA whose electronic configuration ends with  $ns^1$ ,

IIA whose electronic configuration ends with  $ns^2$ .

### p-block elements

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

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

### **d-block elements**

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

**1. The first transition series:**

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

**2. The second transition series:**

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

**3. The third transition series:**

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

### **f-block elements**

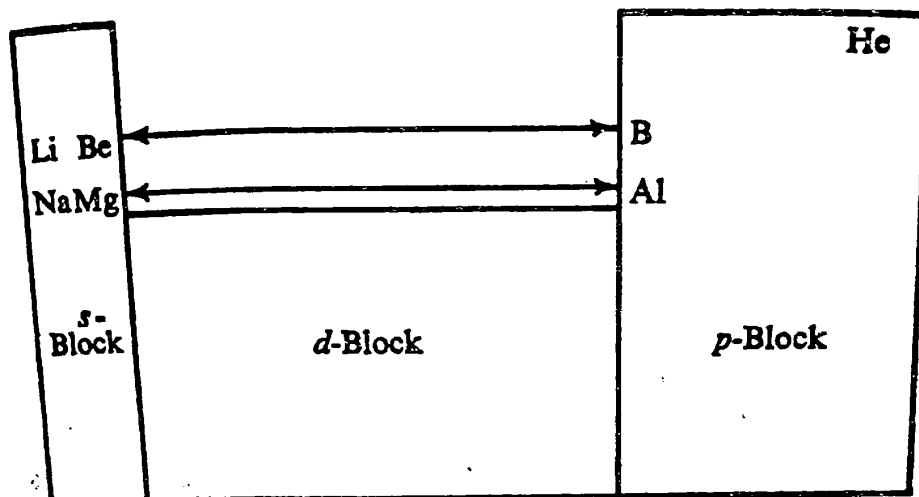
They are separated down the Periodic table, to avoid being a very wide table, in which the f sub-energy level is filled successively. The f-block is divided into 2 series, each with 14 elements. These are:

**1. The lanthanides**

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

**2. The actinides**

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



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

Element	Atomic number	Electronic configuration	Group	Period	Periodic Block
H	1				
He	2				
Li	3				
Be	4				
B	5				
C	6				
N	7				
O	8				
F	9				
Ne	10				
Na	11				
Mg	12				
Al	13				

<i>Si</i>	14				
<i>P</i>	15				
<i>S</i>	16				
<i>Cl</i>	17				
<i>Ar</i>	18				
<i>K</i>	19				
<i>Ca</i>	20				
<i>Sc</i>	21				
<i>Ti</i>	22				
<i>V</i>	23				
<i>Cr</i>	24				
<i>Mn</i>	25				
<i>Fe</i>	26				
<i>Co</i>	27				
<i>Ni</i>	28				
<i>Cu</i>	29				
<i>Zn</i>	30				
<i>Ge</i>	32				
<i>Sr</i>	38				
<i>Sn</i>	50				
<i>I</i>	53				
<i>Ba</i>	56				
<i>Pb</i>	82				

## Classification into metals, metalloids and non-metals

	<b>Metals</b>
	<b>Metalloids</b>
	<b>Non-metals</b>

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

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

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

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

### Periodicity of atomic properties in the Periodic Table

The common atomic properties include

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

The factors affecting atomic properties of elements include;

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

#### 1. *Nuclear charge (Z)*

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

#### 2. *Shielding effect/ screening effect(S)*

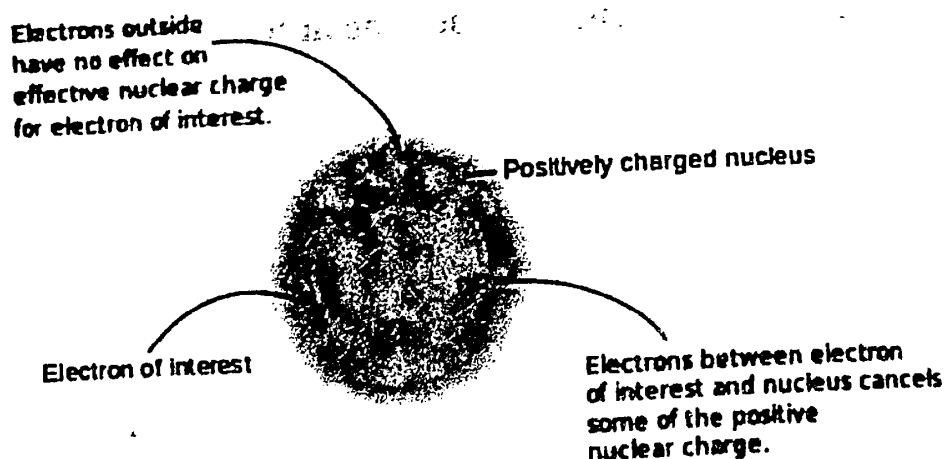
This is the repulsion of the outermost electrons by those in the innermost sub energy levels from nuclear attraction. Electrons in an atom shield each other from the pull of the nucleus. Shielding effect describes the decrease in attraction between an electron and the nucleus in any atom with more than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

#### 3. *Effective nuclear charge ( $Z_{eff}$ )*

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

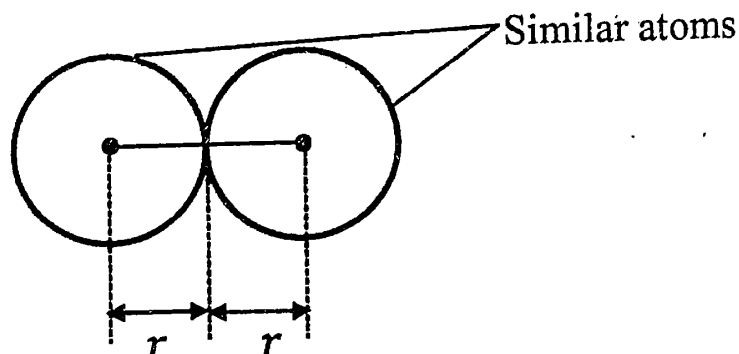
$$Z_{eff} = Z - S$$

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



### Atomic radius and Ionic radius

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



where  $r$  is atomic radius

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

#### 1. Nuclear charge

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

## 2. Screening effect.

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

### Variation in atomic radius and ionic radius in Periods and groups

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

Element	Na	Mg	Al	Si	P	S	Cl
Atomic radius(nm)	0.156	0.136	0.125	0.117	0.110	0.104	0.099
Ionic radius(nm)	0.095	0.065	0.054	0.040	0.212	0.184	0.181

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

*Atomic radius decreases from sodium to chlorine.*

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

(b) Explain why:

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

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

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

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

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

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

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

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

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

*Atomic radius increases from Beryllium to Barium.*

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

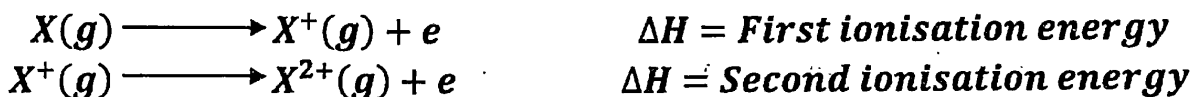
- (a) Explain why the ionic radius is smaller than the atomic radius of corresponding neutral atom for each element.

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

### Ionisation energy

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

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



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

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

#### 1. Nuclear charge

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

#### 2. Screening effect

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

#### 3. Atomic radius

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

#### 4. Electronic configuration/ electronic structure

Atoms with outermost sub energy levels half-filled or completely filled with electrons are thermodynamically stable and require abnormally higher amount of energy to remove an electron. Atoms whose outermost sub energy levels are

neither half-filled nor completely filled with electrons are unstable and require a low amount of energy to remove an electron.

### 5. Penetrating power of valence electrons

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

### Variation in ionisation energy in Periods and groups

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

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

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

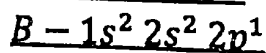
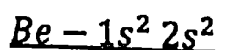
(b) Briefly explain why;

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

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

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

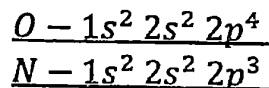
(b)(i)



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

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

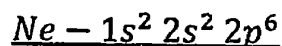
(ii)



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

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

(iii)



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

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

Element	F	Cl	Br	I
First ionisation energy (kJmol <sup>-1</sup> )	1681	1255	1142	1007

State and explain the trend in ionization energy of the elements

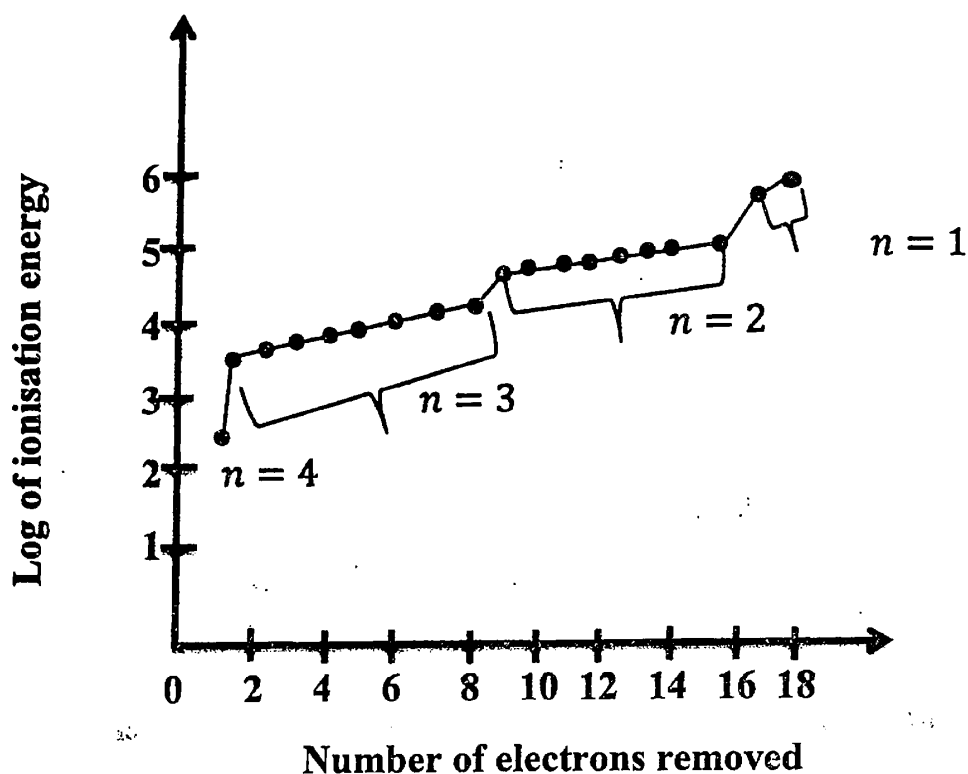
First ionization energy decreases from fluorine to iodine.

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

### Successive ionisation energies

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

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



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

(i) *The atomic number*

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

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

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

(iii) *Valency*

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

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

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

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

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

(v) *Period in the Periodic Table*

Q is in Period 4 since it has four energy levels

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

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

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

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

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

(a) Explain the trend in the ;

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

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

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

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

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

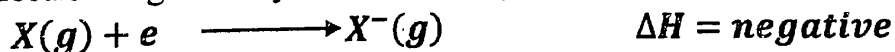
**B belongs to group II.** This is because the difference between second and third ionisation energies is very big compared to the difference between first and second, third and fourth ionisation energies. This implies that the third electron is removed from an inner energy level, completely filled with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

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

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

#### Electron affinity

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



This energy is called first electron affinity.

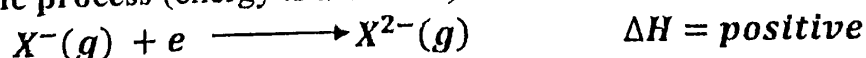
**First electron affinity** is the energy given out when one mole of electrons combines with one mole of gaseous atoms to form one mole of uninegatively charged gaseous ions

or

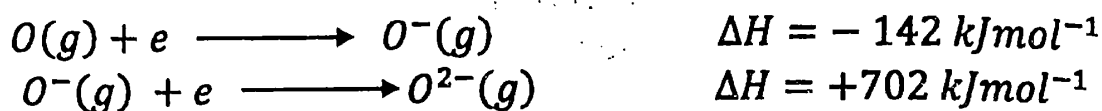
The energy given out when an electron is added to a gaseous atom to form a uninegatively charged gaseous ion

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

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



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



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

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

### 1. Nuclear charge

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

### 2. Screening effect

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

### 3. Atomic radius

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

#### 4. Electronic configuration

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

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

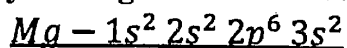
Element	Na	Mg	Al	Si	P	S	Cl	Ar
First electron affinity ( $\text{kJmol}^{-1}$ )	-21	+67	-44	-135	-72	-200	-364	0

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

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

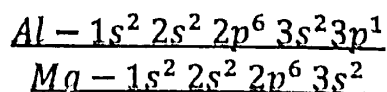
*From sodium to argon, nuclear charge increases because a proton is added to nucleus from element to element. Screening effect almost remains constant, because electrons are added to the same energy level. Effective nuclear charge increases, atomic radius reduces. The attraction for the incoming electron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

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



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

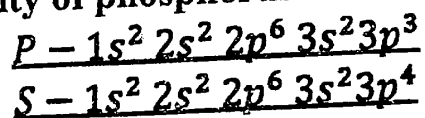
(ii) the first electron affinity of aluminium is higher than that of magnesium



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

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

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



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

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

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

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

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

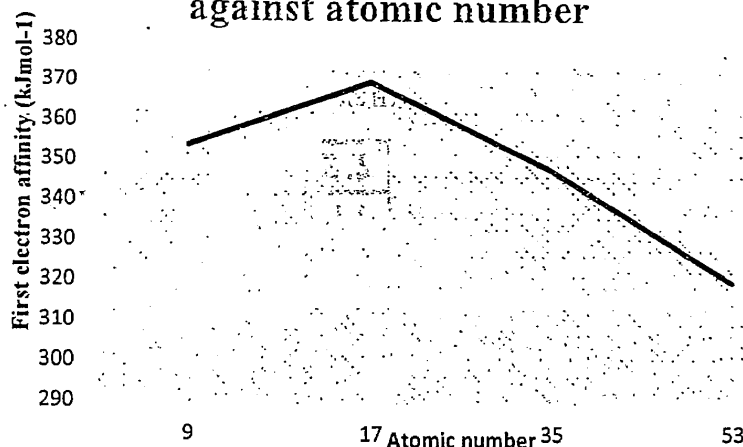
(b) Plot a graph of first electron affinity against atomic number of the elements.

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

(c) (i) Explain the general trend in variation of the first electron affinities

(ii) Explain why fluorine has an abnormal value

A graph of first electron affinity against atomic number



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

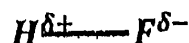
This is because from fluorine to iodine, nuclear charge increases, screening effect also increases, because an extra energy level completely filled with electrons is added from element to element. Increase in screening effect outweighs increase in nuclear charge. Effective nuclear charge decreases, atomic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

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

### Electronegativity

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

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



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

The table below shows some common elements and their electronegativity values

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

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

### 1. Nuclear charge

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

### 2. Screening effect

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

### 3. Atomic radius

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

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

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

State and explain the trend in electronegativity values of the elements

*Electronegativity increases from sodium to chlorine.*

*This is because from sodium to chlorine, nuclear charge increases because a proton is added to nucleus from element to element. Screening effect almost remains constant, because electrons are added to the same energy level. Effective nuclear charge increases, atomic radius reduces and the bonding electrons experience a greater nuclear attraction.*

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

Element	Be	Mg	Ca	Sr	Ba
Electronegativity	1.57	1.31	1.00	0.95	0.89

State and explain the trend in electronegativity values of the elements

*Electronegativity decreases from Beryllium to Barium.*

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

### Electropositivity

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

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

#### 1. Nuclear charge

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

#### 2. Screening effect

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

### 3. Atomic radius

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

### 4. Electronic configuration

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

#### Variation of electropositivity across period 3

*Electropositivity decreases from sodium to chlorine.*

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

#### Variation of electropositivity across group II

*Electropositivity increases from beryllium to Barium.*

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

#### Metallic character

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

For variation in Standard electrode potential and for variation in melting and boiling points in groups and periods, check under further topics in this same book but you can also refer to Demystifying Physical chemistry by the same author.

### Miscellaneous Questions

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

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

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

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

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

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

- (a) Define the term first ionisation energy.  
 (b) State and explain the trend in ionization energy of the elements
4. The table below shows the results obtained for the ionisation energies of element X.

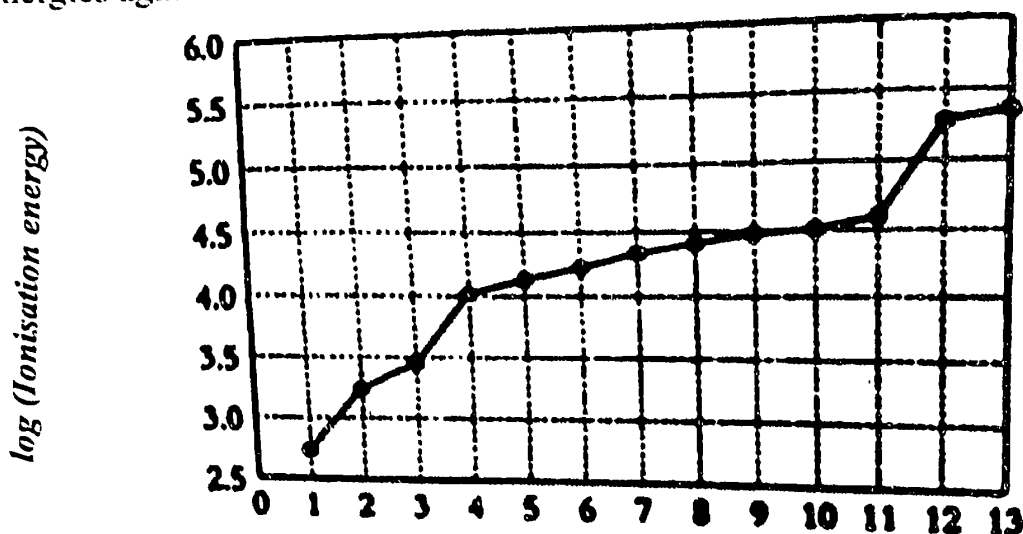
Electron number	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	5 <sup>th</sup>
Ionisation energy (kJmol <sup>-1</sup> )	800	2400	3700	25000	32800

(a) Plot a graph of  $\log_{10}$  (ionisation energy) against number of electron removed.

(b) Explain the shape of your graph

(c) Write the formula of the chloride of X.

5. The graph below shows a plot of the logarithm of all the successive ionisation energies against number of electrons removed for element Y.



*Number of electrons removed.*

(a) Explain the shape of the graph

(b) State the electronic configuration of element Y.

6. Successive ionisation energies ( $\text{kJmol}^{-1}$ ) for some elements in Period 3 of the periodic Table are shown in the table below.

Element	Ionisation energy				
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	5 <sup>th</sup>
Silicon	787	1577	3230	4355	16090
Phosphorus	1060	1896	2908	4954	6272
Sulphur	1000	2258	3381	4565	6995

(a) State and explain the trend in successive ionisation energies.

(b) Explain why the;

- First ionisation energy of sulphur is less than that of phosphorus
- third ionisation energy of phosphorus is less than that of silicon.
- the first ionisation energy of aluminium is less than that of magnesium.

7. The table below shows the first three successive ionisation energies of elements A, B, C, D, E and F.

Ionisation energy(kJmol <sup>-1</sup> )	Element					
	A	B	C	D	E	F
1 <sup>st</sup>	1013	1000	1255	1519	418	590
2 <sup>nd</sup>	1904	2255	2297	2665	3067	1146
3 <sup>rd</sup>	2916	3389	3853	3933	4393	4916

With a reason in each case; state which element;

- is a noble gas
  - belongs to group I
  - belongs to group II
8. The table below shows the first five ionisation energies of elements W, X, Y and Z.

Element	Ionisation energy(kJmol <sup>-1</sup> )				
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	5 <sup>th</sup>
W	577	1816	2745	11575	13251
X	738	1450	7730	10550	12756
Y	495	4563	6912	9540	11936
Z	1255	2297	3849	5163	13989

- Identify the group to which each of the elements belongs and give a reason for your answer.
  - Give a pair of elements which;
    - forms an ionic bond between them
    - forms an ionic compound.
9. Explain what is meant by the term first electron affinity.
- State three factors that can affect electron affinity.
  - The first electron affinities of some elements in Period 3 are given in the table below.

Element	Al	Si	P	S
First electron affinity	-44	-134	-71.7	-200

- State the trend in variation in electron affinities
- Explain your answer in c (i) above.

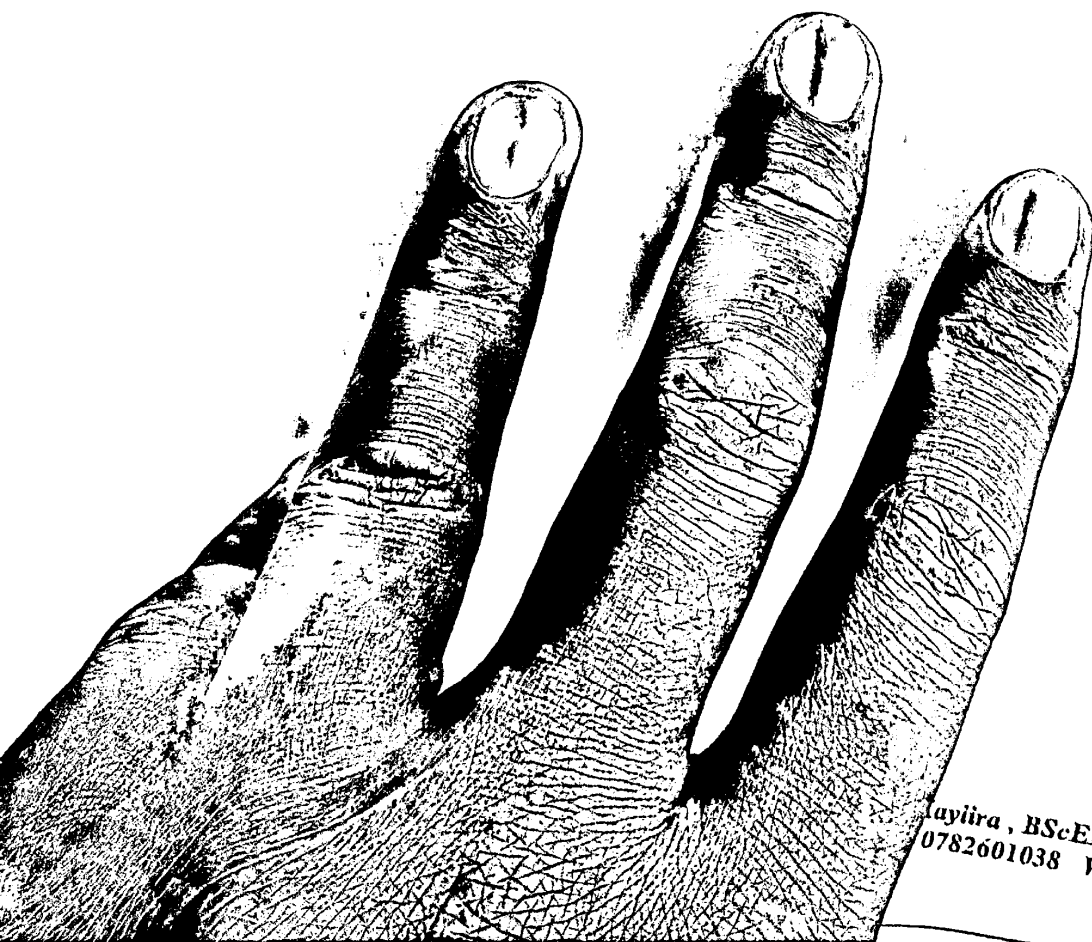
10. The table below shows the electronegativity values of the elements in Group VII of the Periodic Table.

Element	<i>F</i>	<i>Cl</i>	<i>Br</i>	<i>I</i>
Electronegativity	4.10	2.83	2.74	2.21

State and explain the trend in electronegativity values of the elements.

11. Explain the following observations;

- The potassium ion and the calcium ion have the same electronic configurations, yet the potassium ion is larger than the calcium ion.
- The ions  $Na^+$  and  $Mg^{2+}$  have the same electronic configuration but the ionic radius of  $Mg^{2+}$  is lower than that of  $Na^+$
- The first electron affinities of the halogens generally decrease down the group. However, the first electron affinity of fluorine is abnormally high.
- There are no compounds containing the  $O^-$  or  $S^-$  ions although the first electron affinities of oxygen and Sulphur are  $-142 \text{ kJmol}^{-1}$  and  $-200 \text{ kJmol}^{-1}$  respectively.
- Oxygen is more electronegative than Sulphur although more energy is released when a Sulphur atom accepts an electron than when an oxygen atom accepts an electron.



## ELEMENTS IN THE THIRD SHORT PERIOD

### Electronic structures/ configurations

Element	Atomic number	Configuration
<i>Na</i>	11	$1s^2 2s^2 2p^6 3s^1$
<i>Mg</i>	12	$1s^2 2s^2 2p^6 3s^2$
<i>Al</i>	13	$1s^2 2s^2 2p^6 3s^2 3p^1$
<i>Si</i>	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
<i>P</i>	15	$1s^2 2s^2 2p^6 3s^2 3p^3$
<i>S</i>	16	$1s^2 2s^2 2p^6 3s^2 3p^4$
<i>Cl</i>	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
<i>Ar</i>	18	$1s^2 2s^2 2p^6 3s^2 3p^6$

### Bonding and structure

Element	Sodium	Magnesium	Aluminium	Silicon	Phosphorus	Sulphur	Chlorine	Argon
Symbol	<i>Na</i>	<i>Mg</i>	<i>Al</i>	<i>Si</i>	<i>P</i>	<i>S</i>	<i>Cl</i>	<i>Ar</i>
Bonding	Metallic			Covalent				
Structure	Giant metallic			Giant covalent	Simple molecular			

## VARIATION IN ATOMIC AND PHYSICAL PROPERTIES OF THE ELEMENTS

### 1. Melting points/ boiling points

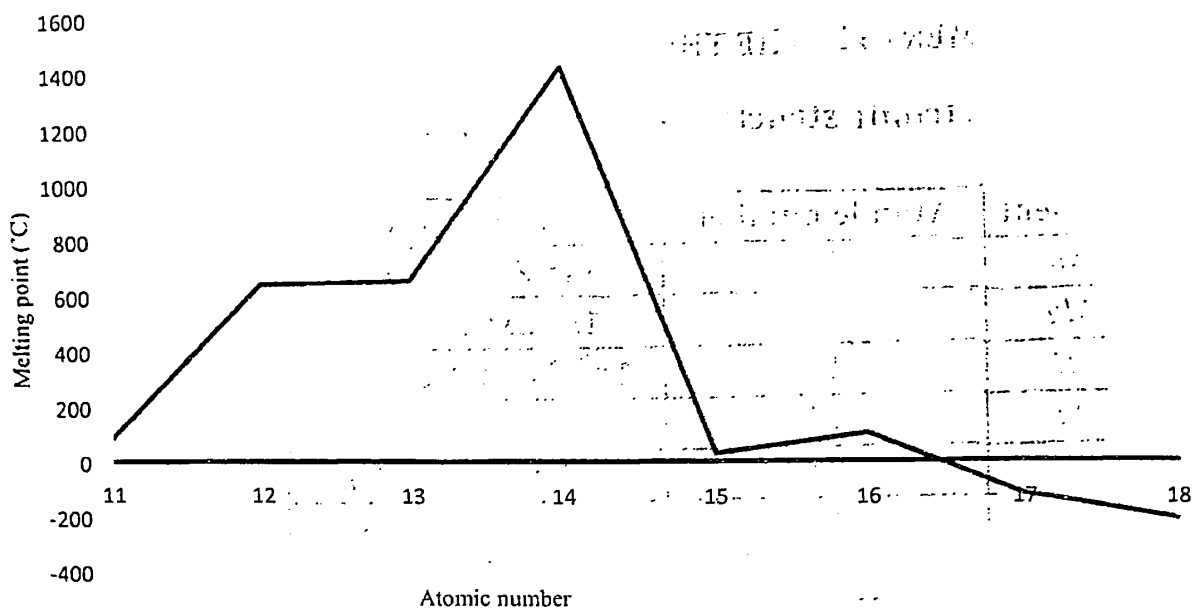
The table below shows the melting points of the elements in Period 3 of the Periodic Table.

Element	<i>Na</i>	<i>Mg</i>	<i>Al</i>	<i>Si</i>	<i>P</i>	<i>S</i>	<i>Cl</i>	<i>Ar</i>
Atomic number	11	12	13	14	15	16	17	18
Melting point(°C)	97.8	650	660.3	1414	44.2	115.2	-101.5	-189.4

(a) Plot a graph of melting point against atomic number of the elements

(You are advised to make an own plot of the graph for practice)

(b) Explain the shape of the graph



(b) Generally, melting point increases from sodium to silicon followed by a general decrease from silicon to argon, with Sulphur having a higher melting point than phosphorus.

Sodium, magnesium and aluminium have a giant metallic structures held by metallic bonds whose strength increases with increase in number of electrons contributed per atom to the metallic bond. Sodium contributes one electron per atom, magnesium contributes two electrons per atom. Therefore, magnesium forms stronger metallic bonds than sodium. However, due to its smaller atomic radius, Aluminium forms shorter and stronger metallic bonds than magnesium resulting into a slightly higher melting point than magnesium.

Silicon has a giant molecular structure, in which each silicon atom is bonded to four other silicon atoms, forming very many strong covalent bonds that require a high amount of energy to break, thus a very high melting point.

Phosphorus, Sulphur, chlorine and argon have simple molecular structures with weak Van-der-Waal's forces of attraction whose magnitude increase in strength with increase in molecular weight. Sulphur is octatomic ( $S_8$ ) with a higher molecular weight hence stronger Van der Waal's forces of attraction than Phosphorus which is tetratomic ( $P_4$ ). Chlorine is diatomic ( $Cl_2$ ), with a higher molecular weight and stronger van der Waal's forces than argon which is monoatomic. The energy required to break the Van-der-Waal's forces therefore decreases from phosphorus to argon.

## 2. Atomic and ionic radius

The table below shows the atomic radii and ionic radii of the elements in Period 3 of the Periodic Table. *The ionic radius of silicon is missing because it does not form a simple ion.*

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

(a) Define the term atomic radius

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

(c) Explain why:

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

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

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

(e) Which of the metal ions  $Na^+$ ,  $Mg^{2+}$  and  $Al^{3+}$  is likely to have the highest hydration energy? Give a reason.

*The aluminium ion has the highest hydration energy because it has the highest ionic charge, smallest ionic radius, highest charge density and highest polarizing power. The ion is easily hydrated and therefore strongly attracts very many water molecules hence giving off the highest amount of energy.*

## 3. First ionization energy

The table below shows the first ionization energies of the elements in Period 3 of the Periodic Table.

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

(a) Plot a graph of ionization energy against atomic number of the elements

*(To be done by student)*

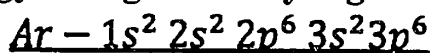
(b) State and explain the trend in ionization energy of the elements

First ionization energy generally increases from sodium to argon.

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

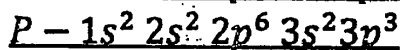
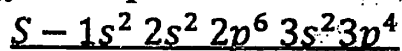
(c) Explain why the;

(i) first ionization energy of argon is very high



For argon, an electron is removed from a completely filled 3p-sub energy level which is thermodynamically stable. High amount of energy is required to remove the electron

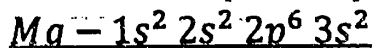
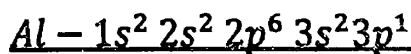
(ii) first ionization energy of Sulphur is less than that of phosphorus



For Sulphur, an electron is removed from a 3p-sub energy level which has four electrons hence thermodynamically unstable. Lower amount of energy is required to remove the electron.

For phosphorus, an electron is removed from a half filled 3p-sub energy level which is thermodynamically stable. Higher amount of energy is required to remove the electron

(iii) first ionization energy of aluminium is less than that of magnesium



For aluminium, the electron is removed from a 3p-sub energy level which has only one electron hence thermodynamically unstable. Lower amount of energy is required to remove the electron.

For magnesium, an electron is removed from a completely filled 3s-sub energy level which is thermodynamically stable. Higher amount of energy is required to remove the electron

#### 4. Electron affinity

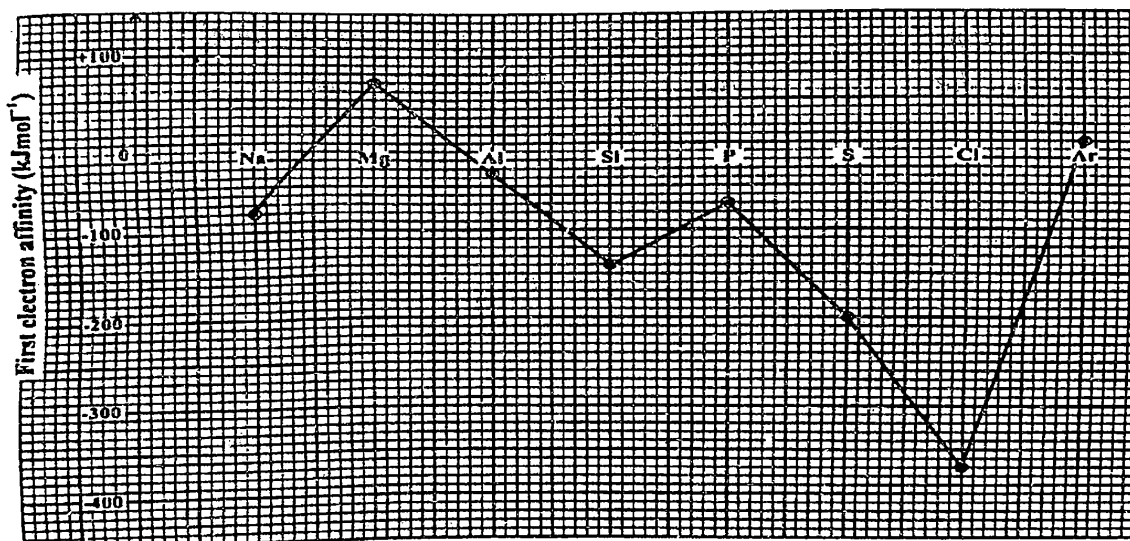
##### (a) Define the term first electron affinity

*This is the energy given out when one mole of electrons combines with one mole of gaseous atoms to form one mole of uninegatively charged gaseous ions.*

*or*

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

##### (b) The graph below shows the variation in the first electron affinity of the elements in Period 3 of the Periodic Table.

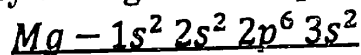


Explain why;

- (i) there is a general increase in first electron affinity from sodium to argon

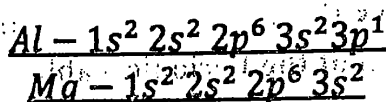
*From sodium to argon, nuclear charge increases because a proton is added to nucleus from element to element. Screening effect almost remains constant, because electrons are added to the same energy level. Effective nuclear charge increases, atomic radius reduces. The attraction for the incoming electron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

- (ii) the first electron affinity of magnesium is positive.



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

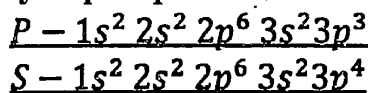
- (iii) the first electron affinity of aluminium is higher than that of magnesium



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

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

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



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

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

## 5. Electronegativity

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

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

State and explain the trend in electronegativity values of the elements

## 6. Electropositivity

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

*Electropositivity decreases from sodium to chlorine.*

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

## 7. Electrode potential

The table below shows the standard electrode potential values of some of the elements in Period 3 of the Periodic Table.

Element	Na	Mg	Al	Cl
Standard electrode potential( $E^\theta$ ) (Volts) for $M^{n+}/M(s/g)$	-2.71	-2.37	-1.66	+1.36

(a) Define the term standard electrode potential

*This is the potential difference or reduction potential established when a metal electrode is dipped in a 1 molar solution of its ions measured relative to the standard hydrogen electrode at 25 °C and 1 atmosphere.*

(a) State;

- (i) the factors that affect the magnitude of standard electrode potential
- ionization energy
  - atomization energy
  - hydration energy

(ii) with a reason, name the strongest reducing agent

*Sodium; because it has the most negative standard electrode potential*

(iii) with a reason, name the strongest oxidizing agent

*Chlorine; because it has a positive standard electrode potential*

(b) Explain the trend in standard electrode potential of the metallic elements

*Standard electrode potential becomes less negative (decreases) from sodium to aluminium because ionic radius decreases, ionization energy increases, atomization energy increases and hydration energy also increases. However, the increase in ionization energy and atomization energy is more rapid than increase in hydration energy.*

## 8. Electrical Conductivity

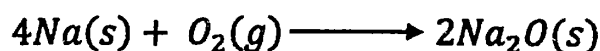
*Electrical conductivity decreases from sodium to argon*

*Sodium, magnesium and aluminium are all good conductors of electricity because of delocalized electrons which are free to move throughout the solid or liquid metal. Silicon is a semi-conductor. The rest are non-conductors because they are simple molecular substances. There are no free mobile electrons.*

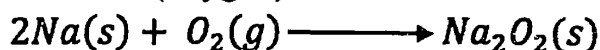
## CHEMICAL PROPERTIES OF THE ELEMENTS

### 1. Describe the reactions of Period 3 elements with air.

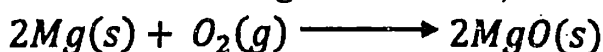
Sodium reacts with oxygen of the air to form sodium oxide



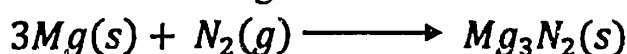
Heated sodium burns in excess air (oxygen) with to form sodium peroxide



Heated magnesium burns in air to form magnesium oxide; a white solid

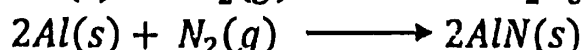
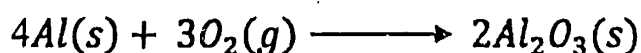


Heated magnesium also reacts with nitrogen in the air to form magnesium nitride.

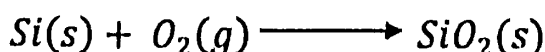


Aluminium is stable in air at ordinary temperatures due to formation of a thin layer of aluminium oxide which resists further action

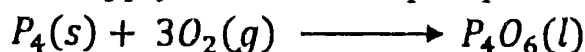
However, when the layer is removed, heated aluminium reacts with air at 800 °C, to form aluminium oxide and aluminium nitride.



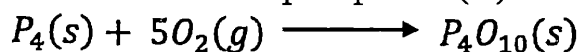
Strongly heated Silicon reacts with air to form silicon dioxide



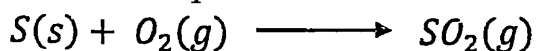
Phosphorus burns in a limited supply of air to form phosphorus(III) oxide.



Phosphorus also burns in excess air to form phosphorus(V) oxide; a white solid



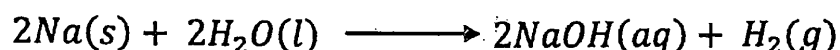
Heated Sulphur burns in air to form Sulphur dioxide



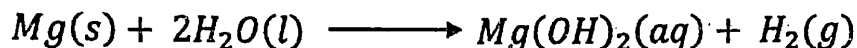
Chlorine does not react with air/oxygen under any condition.

## 2. Describe the reactions of Period 3 elements with water

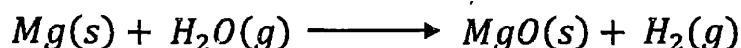
Sodium reacts vigorously with cold water to form sodium hydroxide and hydrogen gas.



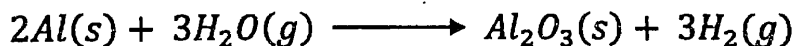
Magnesium reacts slowly with cold water to form magnesium hydroxide and hydrogen.



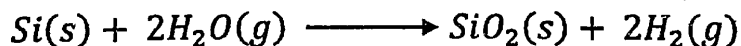
Heated magnesium reacts rapidly with steam to form magnesium oxide and hydrogen.



Aluminium does not react with water because of the protective layer of aluminium oxide. However, when the layer is removed, heated aluminium reacts with steam to form aluminium oxide and hydrogen.

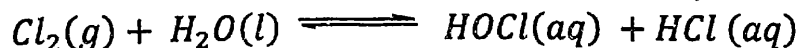


Red hot silicon reacts with steam forming silicon(IV) oxide and hydrogen



Phosphorus and Sulphur do not react with water.

Chlorine disproportionates in water to form chloric(I) acid and hydrochloric acid.



## 3. Describe how Period 3 elements react with;

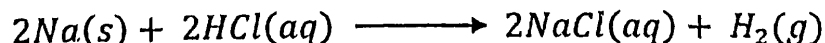
(a) dilute acids

(b) concentrated acids

(a) dilute acids

(i) Dilute hydrochloric acid.

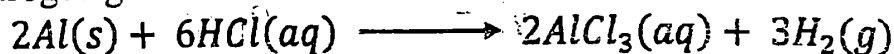
Sodium reacts with cold dilute hydrochloric acid to form sodium chloride and hydrogen gas



Magnesium reacts with cold dilute hydrochloric acid to form magnesium chloride and hydrogen gas



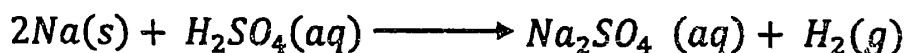
Aluminium reacts slowly with **cold dilute hydrochloric acid** to form aluminium chloride and hydrogen gas



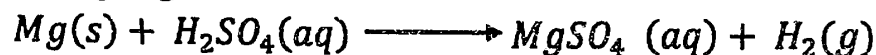
Silicon, phosphorus, Sulphur and chlorine do not react with **dilute hydrochloric acid**.

**(ii) Dilute sulphuric acid**

Sodium reacts with **cold dilute sulphuric acid** to form sodium sulphate and hydrogen gas



Magnesium also reacts with **cold dilute sulphuric acid** to form magnesium sulphate and hydrogen gas

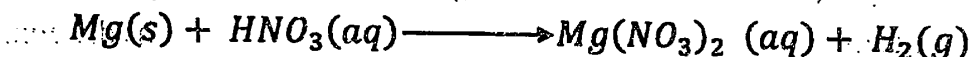


Aluminium does not react with **dilute sulphuric acid**

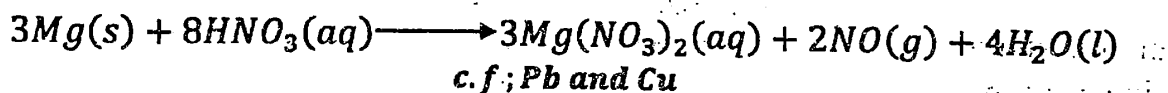
Silicon, phosphorus, Sulphur and chlorine do not react with **dilute sulphuric acid**.

**(iii) Dilute nitric acid.**

**Very dilute cold nitric acid (1%)** reacts with magnesium to form magnesium nitrate and hydrogen.

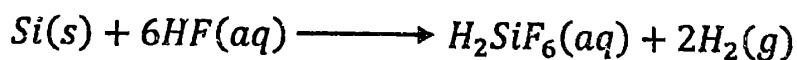


**Dilute/ half concentrated/ moderately concentrated nitric acid** oxidises magnesium to magnesium nitrate and itself reduced to nitrogen monoxide and water.



**(iv) Dilute hydrofluoric acid**

Only silicon reacts with **dilute hydrofluoric acid** to form hexafluorosilicic acid and hydrogen

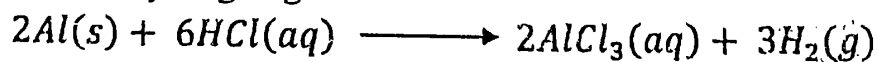


**(b) concentrated acids**

**(i) concentrated hydrochloric acid.**

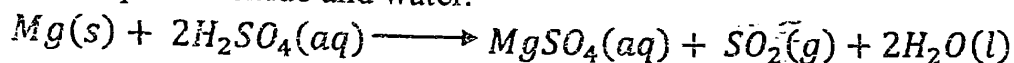
Sodium, magnesium, silicon, phosphorus, Sulphur and chlorine do not react with **concentrated hydrochloric acid**

Aluminium reacts rapidly with **hot concentrated hydrochloric acid** to form aluminium chloride and hydrogen gas.



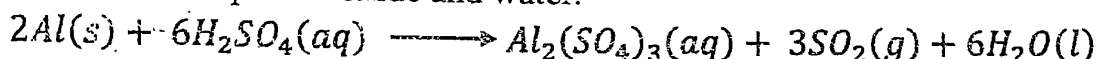
**(ii) concentrated sulphuric acid**

Hot concentrated sulphuric acid oxidises magnesium to magnesium sulphate and itself reduced to Sulphur dioxide and water.



*c. f ; Pb, Cu, Be and Co*

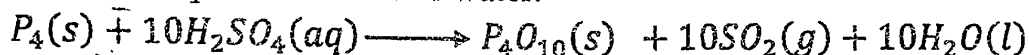
Hot concentrated sulphuric acid also oxidises aluminium to aluminium sulphate and itself reduced to Sulphur dioxide and water.



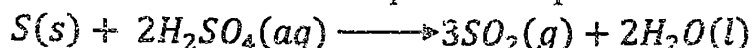
*c. f ; Cr and Fe*

Silicon does not react with concentrated sulphuric acid

Hot concentrated sulphuric acid oxidises phosphorus to phosphorus(V) oxide and itself reduced to Sulphur dioxide and water.



Hot concentrated sulphuric acid oxidises Sulphur to Sulphur dioxide and water.



Chlorine does not react with concentrated sulphuric acid.

**(iii) concentrated nitric acid**

Cold concentrated nitric acid oxidises magnesium to magnesium nitrate and itself reduced to nitrogen dioxide and water.

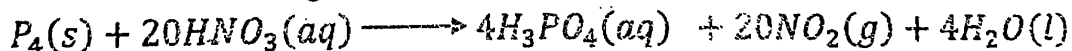


*c. f ; Pb and Cu*

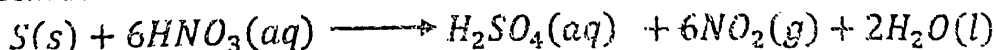
Aluminium is rendered passive by concentrated nitric acid due to the impenetrable layer of the oxide on its surface.

*c. f ; Be, Cr, Fe, Co and Ni*

Fairly/moderately concentrated nitric acid oxidises phosphorus to phosphoric acid and itself reduced to nitrogen dioxide and water.



Hot concentrated nitric acid oxidises Sulphur to Sulphuric acid and itself reduced to nitrogen dioxide and water

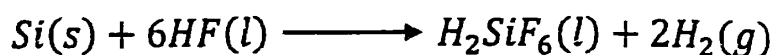


Silicon is resistant to attack by concentrated nitric acid.

Chlorine does not react with concentrated nitric acid.

**(iv) Hydrofluoric acid.**

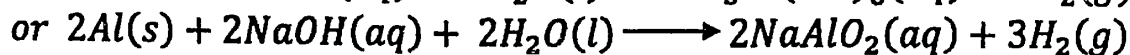
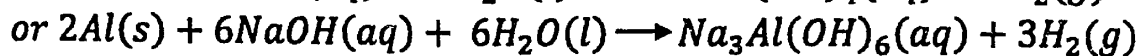
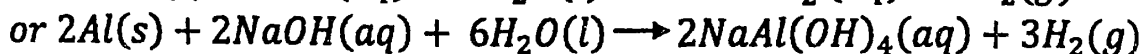
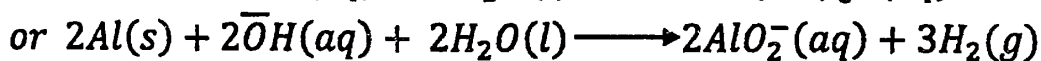
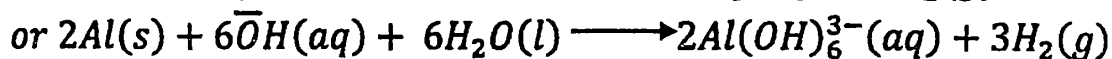
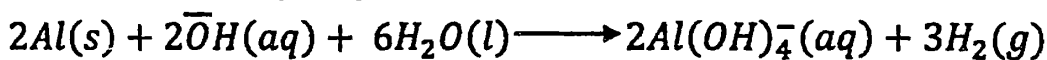
Only silicon reacts with concentrated hydrofluoric acid to form hexafluorosilicic acid and hydrogen



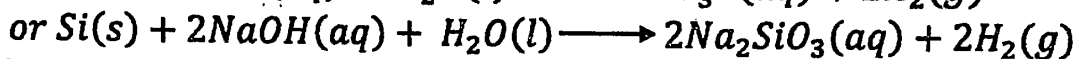
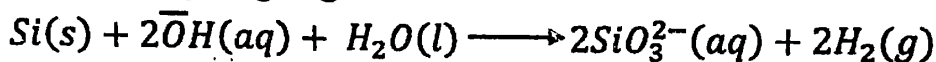
**4. Discuss, stating the conditions under which each of the elements reacts with sodium hydroxide.**

Sodium and magnesium **do not** react with sodium hydroxide.

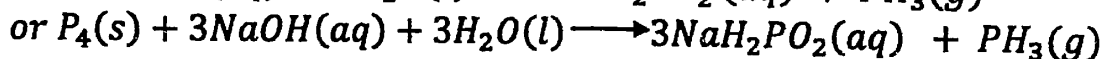
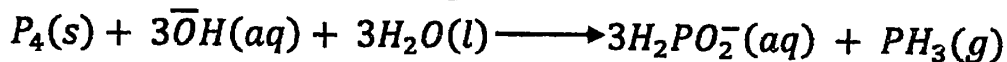
Aluminium reacts with **hot concentrated sodium hydroxide** to aluminate ions/ sodium aluminate and hydrogen.



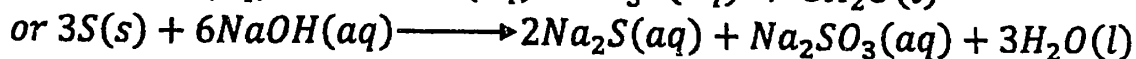
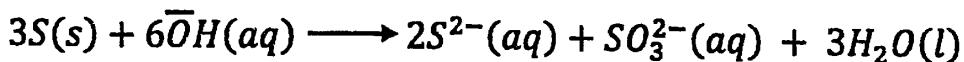
Silicon reacts with **both dilute and hot concentrated** sodium hydroxide to form sodium silicate and hydrogen gas



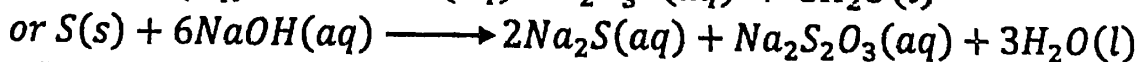
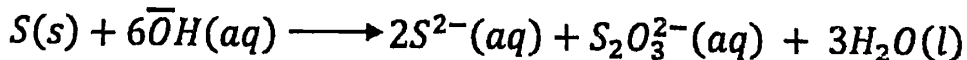
Phosphorus reacts with **hot concentrated sodium hydroxide** to form phosphine and phosphinate ions/ sodium phosphinate



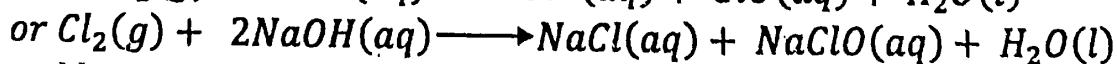
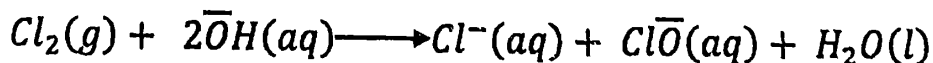
Sulphur reacts with **hot concentrated sodium hydroxide** forming sodium sulphide and sodium sulphite.



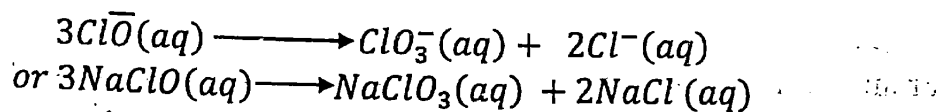
If the **Sulphur is in excess**, thiosulphate ions are formed instead of sulphite ions



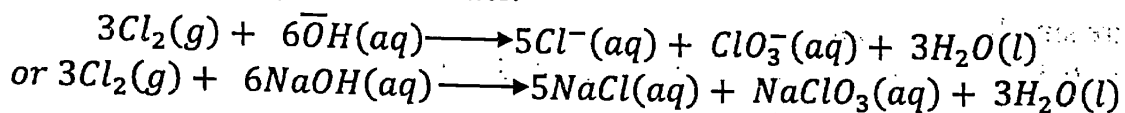
Chlorine **disproportionates in cold dilute sodium hydroxide** to form chloride ions, chlorate(I) ions and water



*N.B; The chlorate(I) ions /sodium chlorate(I) formed by the above reaction undergo further disproportionation if heated/ warmed to form chlorate(V) ions and chloride ions. The yellow solution turns colourless during this reaction*



Chlorine also disproportionates in hot concentrated sodium hydroxide to form chloride ions, chlorate(V) ions and water.

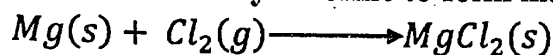


**5. State the conditions and write the equations under which the elements react with chlorine**

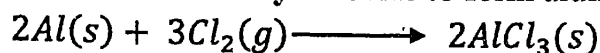
**Burning sodium** reacts with dry chlorine to form sodium chloride



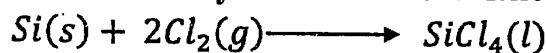
**Heated magnesium** reacts with dry chlorine to form magnesium chloride



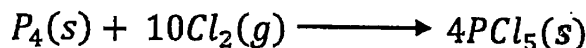
**Heated aluminium** reacts with dry chlorine to form aluminium chloride



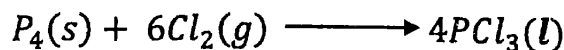
**Heated silicon** reacts with dry chlorine to form silicon tetrachloride



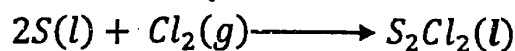
**Heated phosphorus** reacts with excess dry chlorine to form phosphorus(V) chloride.



**Heated phosphorus** reacts with limited dry chlorine to form phosphorus(III) chloride.



**Molten Sulphur** reacts with dry chlorine to form disulphur dichloride



**COMPOUNDS OF THE ELEMENTS**

**THE OXIDES**

Formula of the oxide	$\text{Na}_2\text{O}$	$\text{MgO}$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{P}_4\text{O}_{10}$ – solid $\text{P}_4\text{O}_6$ – liquid	$\text{SO}_2$ $\text{SO}_3$	$\text{Cl}_2\text{O}_7$ $\text{Cl}_2\text{O}_5$
Physical state	Solid					Gas	
Character	Basic		Amphoteric	mainly acidic but with some amphoteric character		Acidic	
Bonding	Ionic			Covalent			
Structure	Giant ionic			Giant molecular	Simple molecular		

### (a) Structure and bonding

From sodium oxide to aluminium oxide, cationic radius decreases and ionic charge increases. This increases the charge density of the cations, hence reducing the ionic character. Silicon(V) oxide forms a giant covalent structure. The rest of the oxides are simple molecular.

N.B; Sodium oxide, magnesium oxide and aluminium oxide show characteristics of ionic compounds such as;

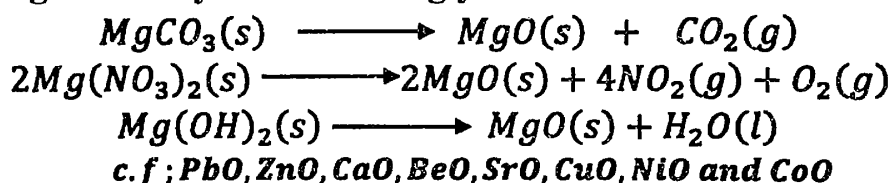
- high melting and boiling points
- conduct electricity in molten state
- sodium oxide and magnesium oxide dissolve in water though aluminium oxide is insoluble.

### (a) With relevant equations, describe how the oxides of Period 3 elements can be formed.

Sodium oxide is formed by heating sodium in a limited supply of oxygen

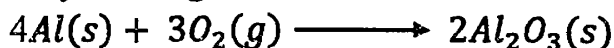


Magnesium oxide is formed by heating either magnesium nitrate, magnesium carbonate or magnesium hydroxide strongly.

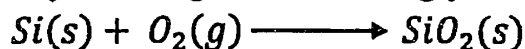


*c. f ; PbO, ZnO, CaO, BeO, SrO, CuO, NiO and CoO*

Aluminium oxide is formed by heating cleaned aluminium in air at 800 °C.



Silicon dioxide is formed by heating Silicon strongly in oxygen.



Phosphorus(V) oxide is formed by heating phosphorus burns in excess air.



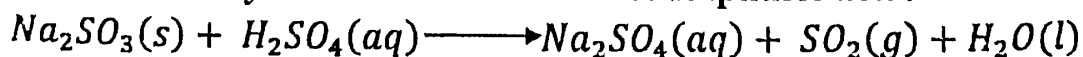
Sulphur dioxide is formed by heating Sulphur in air.

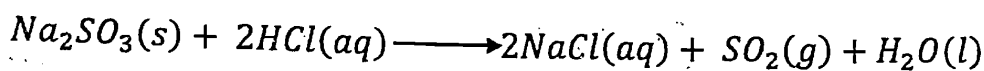


Sulphur dioxide can also be formed by the reaction between hot concentrated sulphuric acid and copper



Sulphur dioxide can as well be prepared by heating sodium sulphite or potassium sulphite with dilute hydrochloric acid or dilute sulphuric acid.

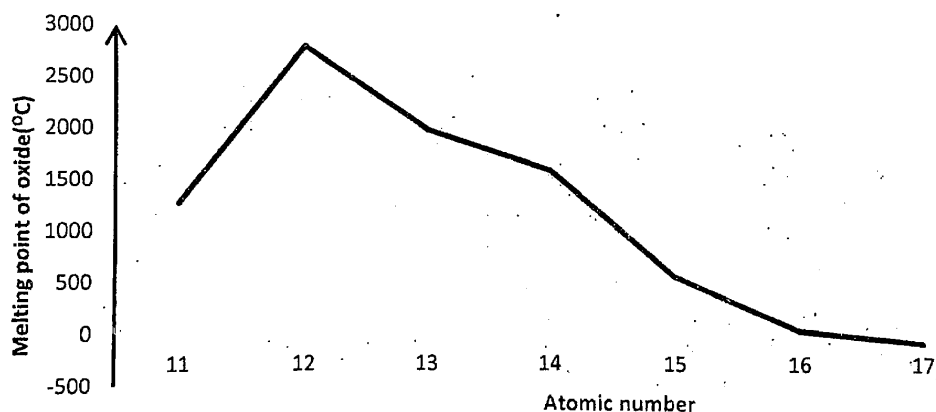




(b) The table below shows the atomic numbers of Period 3 elements and the melting points of their oxides.

Element	<i>Na</i>	<i>Mg</i>	<i>Al</i>	<i>Si</i>	<i>P</i>	<i>S</i>	<i>Cl</i>
Atomic number	11	12	13	14	15	16	17
Oxide	<i>Na<sub>2</sub>O</i>	<i>MgO</i>	<i>Al<sub>2</sub>O<sub>3</sub></i>	<i>SiO<sub>2</sub></i>	<i>P<sub>2</sub>O<sub>5</sub></i>	<i>SO<sub>3</sub></i>	<i>Cl<sub>2</sub>O<sub>7</sub></i>
Melting point of oxide(°C)	1275	2827	2007	1607	560	30	-91

(i) Plot a graph of melting points of the oxides against atomic numbers of the elements (*To be done by student, the graph below is just a sketch and not on scale*)



(i) Explain the shape of the graph

Generally, melting point increases from sodium oxide to magnesium oxide and then reduces to Chlorine (VII) oxide because;

Sodium oxide, magnesium oxide and aluminium oxide have giant ionic structures whose ions are held by strong ionic bonds. Melting point increases from sodium oxide to magnesium oxide because magnesium oxide has a higher product of charges than sodium oxide. Melting point decreases from magnesium oxide to aluminium oxide because the aluminium ion has a small ionic radius, very high charge density and high polarising power, making aluminium oxide less ionic. Silicon(IV) oxide has a giant covalent structure in which each silicon atom is bonded to four oxygen atoms making very many strong covalent bonds that

require a high amount of energy to break. Phosphorus pentoxide, sulphur trioxide and Chlorine(VII) oxide have simple molecular structures whose molecules are held by weak van der waal's forces of attraction whose strength decreases with decrease in polarity of the molecules as a result of increase in electronegativities of the atoms bonded to oxygen.

(c) Discuss the reactions of the above oxides with

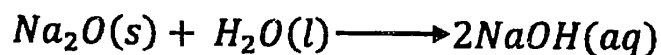
(i) Water (Indicating the pH of the resultant solutions)

(ii) Acids

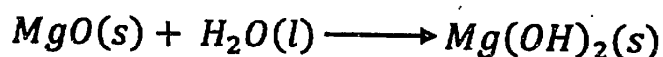
(iii) Sodium hydroxide

(i) reaction with water

Sodium oxide reacts with water to form sodium hydroxide. *Resultant solution is alkaline.*

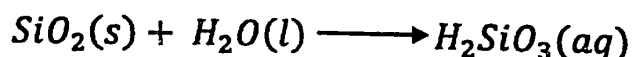


Magnesium oxide reacts with water to form magnesium hydroxide. *Resultant solution is alkaline.*

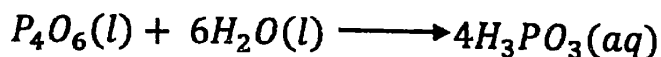


Aluminium oxide is insoluble in water hence no reaction occurs

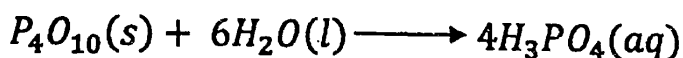
Silicon(IV) oxide reacts with water only when heated and under high pressure to form silicic acid. *Resultant solution is acidic.*



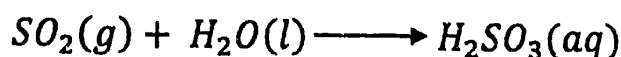
Phosphorus(III) oxide reacts with water to form phosphoric(III) acid. *Resultant solution is acidic.*



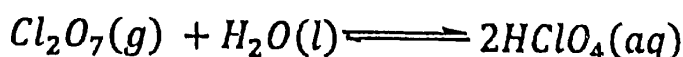
Phosphorus(V) oxide reacts with water to form phosphoric(V) acid. *Resultant solution is acidic.*



Sulphur dioxide reacts with water to form sulphurous acid. *Resultant solution is acidic.*

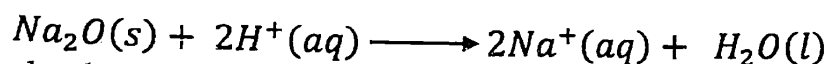


Chlorine(VII) oxide reacts with water to form chloric(VII) acid. *Resultant solution is acidic.*

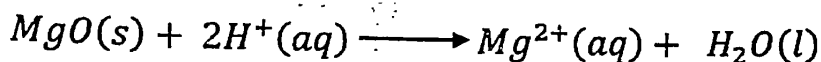


(ii) reaction with acids.

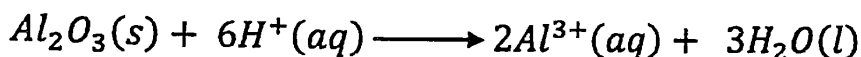
Sodium oxide is basic, hence reacts with dilute hydrochloric acid/dilute sulphuric acid or dilute nitric acid to form corresponding sodium salts and water.



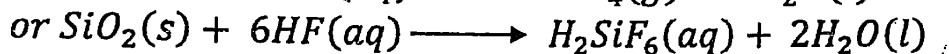
Magnesium oxide is also basic hence reacts with **dilute hydrochloric acid/dilute sulphuric acid or dilute nitric acid** to form corresponding magnesium salts and water.



Aluminium oxide is amphoteric hence reacts with **dilute hydrochloric acid/dilute sulphuric acid or dilute nitric acid** to form corresponding aluminium salts and water.



Silicon(IV) oxide does not react with any other acid but **only reacts with hydrofluoric acid** to form silicon tetrafluoride and water (*or hexafluorosilicic acid and water*)

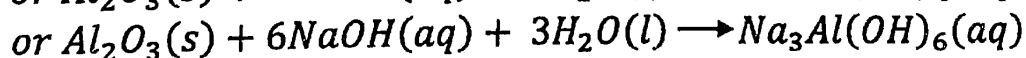
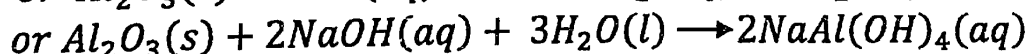
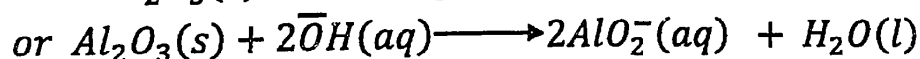
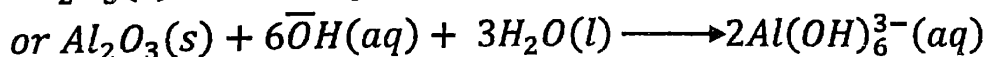
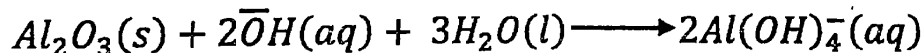


The oxides of phosphorus, sulphur and chlorine are acidic hence **do not react** with acids

### (iii) reaction with sodium hydroxide

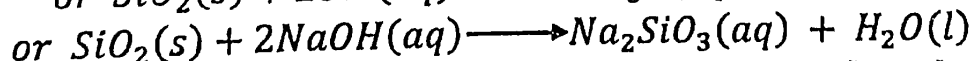
Sodium oxide and magnesium oxide are basic hence **do not react** with sodium hydroxide.

Aluminium oxide is amphoteric hence reacts with **hot concentrated sodium hydroxide** to form **sodium aluminate**.

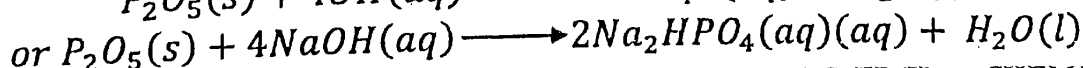


*cf. Cr<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>*

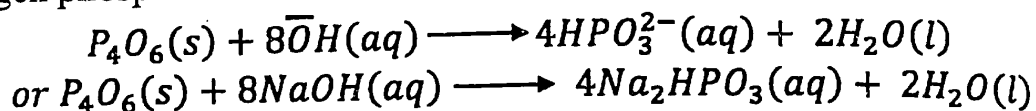
Silicon(IV) oxide reacts with **hot concentrated sodium hydroxide** to form **sodium silicate**.



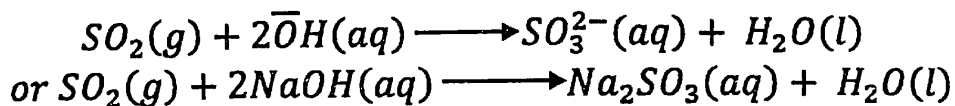
Phosphorus(V) oxide is acidic hence reacts with **cold dilute sodium hydroxide** to form hydrogen phosphate ions /**disodium hydrogen phosphate**.



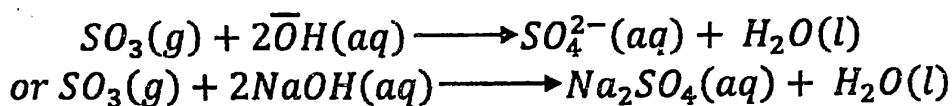
Phosphorus(III) oxide is acidic hence reacts with cold dilute sodium hydroxide to form hydrogen phosphite ions /disodium hydrogen phosphite.



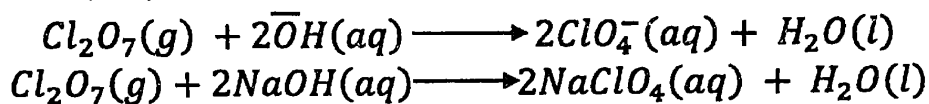
Sulphur dioxide reacts with cold dilute sodium hydroxide to form sodium sulphite and water.



Sulphur dioxide reacts with cold dilute sodium hydroxide to form sodium sulphate and water.



Chlorine(VII) oxide reacts with cold dilute sodium hydroxide to form sodium chlorate(VII)/ chlorate(VII) ions and water.



#### OXO-ACIDS OF SULPHUR, PHOSPHORUS AND CHLORINE

Where you have a challenge coming up with the structures and naming the shapes, refer to **DEMYSTIFYING PHYSICAL CHEMISTRY** by the same author.

- The table below shows the name of the oxoacids of sulphur. Complete it to show the; formula, structure, shapes of the different oxoacids and the oxidation state of sulphur in each.

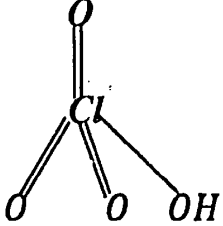
Oxo-acid	Formula	Structure	Shape	Oxidation state of sulphur
Sulphuric acid	$H_2SO_4$		Tetrahedral	+6
Sulphurous acid	$H_2SO_3$		Trigonal pyramidal	+4

2. The table below shows the name of the oxoacids of phosphorus. Complete it to show the; formula, structure and shapes of the different oxoacids.

Oxo-acid	Formula	Structure	Shape	Oxidation state of phosphorus
phosphoric acid (phosphoric(v) acid)	$H_3PO_4$		<i>Tetrahedral</i>	+5
phosphorous acid (phosphoric(III) acid)	$H_3PO_3$		<i>Trigonal pyramidal</i>	+3

3. (a) The table below shows the name of the oxoacids of chlorine. Complete it to show the; formula, structure and shapes of the different oxoacids.

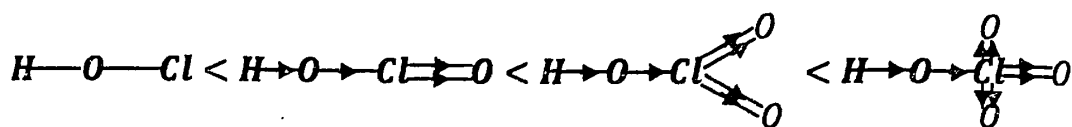
Oxo-acid	Formula	Structure	Shape	Oxidation state of chlorine
chloric (I) acid (Hypochlorous acid)	$HOCl$		<i>Linear</i>	+1
Chloric(III) acid	$HClO_2$		<i>Bent</i>	+3
Chloric(V) acid	$HClO_3$		<i>Trigonal pyramidal</i>	+5

Chloric(VII) acid	$HClO_4$		Tetrahedral	+7
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(b) Arrange the Oxo-acids in 3(a) above in order of increasing acid strength.

Acid strength increases in the order;  $HOCl < HClO_2 < HClO_3 < HClO_4$

(c) Explain your answer in 3(b) above.



The strength of an acid depends on how easily it releases protons. The acid strength increases depending on the number of oxygen atoms that exert a negative inductive effect in each molecule of the acid, increasing the polarity of the oxygen-hydrogen bond. This is because oxygen is more electronegative than chlorine. In chloric(VII) acid, 3 oxygen atoms exert a negative inductive effect on the O-H bond making it very weak and breaks to release very many hydrogen ions making it stronger than chloric(V) acid in which two oxygen atoms exert a negative inductive effect making the O-H bond weaker than in chloric(III) acid in which only one oxygen atom has a negative inductive effect. Chloric(I) acid has the strongest oxygen-hydrogen bond because no oxygen atom has a negative inductive effect in it.

### THE CHLORIDES

Element	Na	Mg	Al	Si	P	S
Formula of the chloride	$NaCl$	$MgCl_2$	$AlCl_3$	$SiCl_4$	$PCl_5$ – solid $PCl_3$ – liquid	$S_2Cl_2$ $SCl_2$
Physical state	Solids			Liquid		Liquids
Nature/pH in solution	Neutral		Acidic			
Bonding	Ionic		Mainly covalent	Covalent		
Structure	Giant ionic		Layered molecular	Layered Molecular	Simple molecular	

**(a) Structure and bonding**

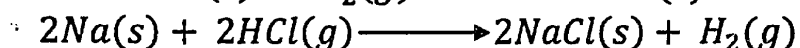
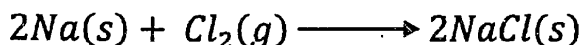
From sodium chloride to disulphur dichloride, ionic character decreases as electropositivity decreases. Sodium chloride and magnesium chloride are purely ionic. Aluminium chloride is mainly covalent. The chlorides of silicon, phosphorus and sulphur are purely covalent. This variation in structure and bonding in turn affects the variation in melting point among the chlorides.

**(b) With relevant equations, describe how the chlorides of Period 3 elements can be formed.**

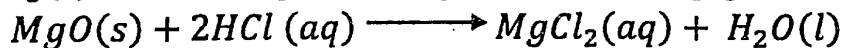
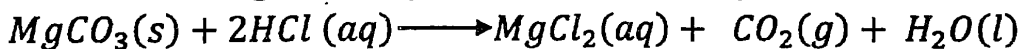
Sodium chloride is formed by a neutralisation reaction between sodium hydroxide and dilute hydrochloric acid



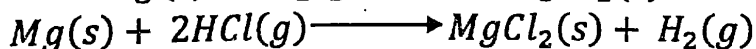
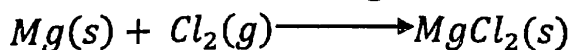
*N.B. If anhydrous sodium chloride is required, burning sodium reacted with dry chlorine or dry hydrogen chloride.*



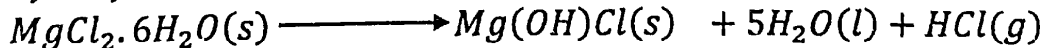
Magnesium chloride is formed by the reaction between magnesium carbonate, magnesium oxide or magnesium hydroxide with dilute hydrochloric acid



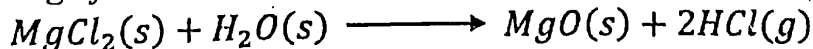
*N.B. If anhydrous magnesium chloride is required; it is formed by passing dry chlorine or dry hydrogen chloride over heated magnesium.*



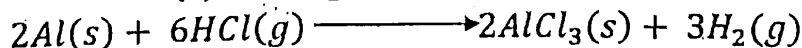
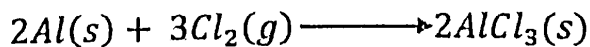
*Anhydrous magnesium chloride cannot be prepared by heating hydrated magnesium chloride or by evaporation of its aqueous solution because it undergoes hydrolysis to form a basic chloride, magnesium hydroxychloride.*



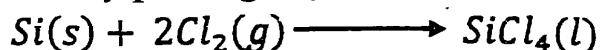
*Further heating of the chloride yields magnesium oxide and hydrogen chloride.*



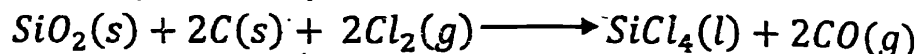
Aluminium chloride is formed by passing dry chlorine or dry hydrogen chloride over heated aluminium.



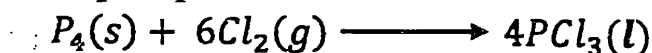
Silicon tetrachloride is formed by passing dry chlorine over heated silicon.



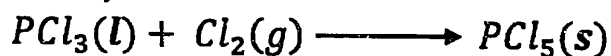
*N.B Silicon(IV) chloride can also be prepared by heating a mixture of silicon(IV) oxide and carbon in a dry current of chlorine.*



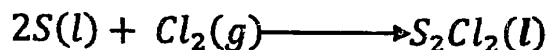
Phosphorus(III) chloride, a colourless liquid is formed by passing limited dry chlorine over heated white phosphorus.



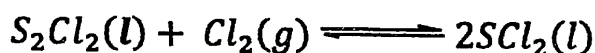
Phosphorus(V) chloride, a white solid is formed by passing dry chlorine over heated phosphorus(III) chloride. It is not a convenient method to prepare it from phosphorus and chlorine directly.



Disulphur dichloride, a red liquid is formed by passing dry chlorine over molten sulphur.

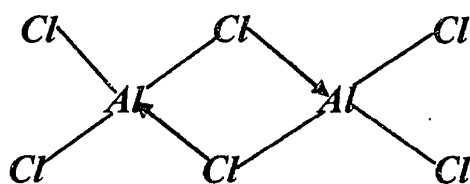
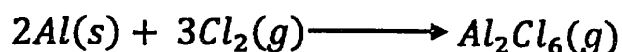


Sulphur dichloride is a red liquid prepared by reacting chlorine with disulphur dichloride at 0 °C.



**Qn. Aluminium chloride dimerises vapour phase. State the conditions under which the dimerised form can be formed and write an equation. Draw the structure of aluminium chloride in vapour phase.**

*By passing dry chlorine over heated aluminium at a temperature of 183 °C*



*N.B. Chlorides of beryllium and iron also dimerise in vapour phase.*

**(c) The table below shows the melting points of the chlorides of Period 3 elements.**

Chloride	NaCl	MgCl <sub>2</sub>	AlCl <sub>3</sub>	SiCl <sub>4</sub>	PCl <sub>3</sub>	PCl <sub>5</sub>	S <sub>2</sub> Cl <sub>2</sub>	SCl <sub>2</sub>
Melting point (°C)	808	714	192	-68	-92	160	-76	-80

DEMYSTIFYING INORGANIC CHEMISTRY BY Joseph Jobs Kayiira, BScED(Hons.CHEM/MTC)  
Email:josephkayirab@gmail.com Call 0782601038 WhatsApp 0753247098

Explain the trend in variation of the melting points of the chlorides.

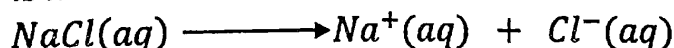
Melting points of the chlorides generally decrease from sodium chloride to sulphur dichloride.

Sodium chloride and magnesium chloride have giant ionic structures held by strong ionic bonds which require a high amount of energy to break. The decrease in melting point from sodium chloride to magnesium chloride is because magnesium ion has a smaller ionic radius, higher charge density and higher polarising power than sodium ion making magnesium chloride less ionic than sodium chloride. Aluminium chloride has a lower melting point than magnesium chloride because among the cations, the aluminium ion has the smallest ionic radius, a very high charge density and high polarising power. Aluminium chloride is therefore predominantly covalent. Silicon tetrachloride is covalent and its molecules are held by weak Van der Waals' forces of attraction that require a low amount of energy to break hence a low melting point. Phosphorus trichloride has a simple molecular structure thus a low melting point. Phosphorus pentachloride has an abnormally high melting point because at ordinary temperatures it consists of  $\text{PCl}_4^+$  and  $\text{PCl}_6^-$  ions hence exhibiting ionic character. Disulphur dichloride and sulphur dichloride form simple molecular structures held by weak Van der Waals' forces of attraction.

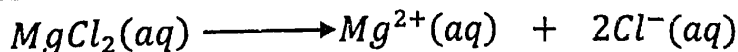
(d) Discuss the reactions of chlorides of Period 3 elements with water. In each case indicate the pH of the resultant solution.

Sodium chloride dissolves in water to form sodium ions and chloride ions.

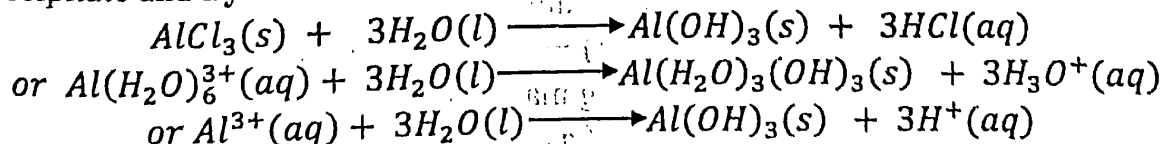
Resultant solution is neutral



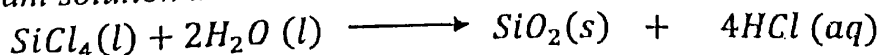
Magnesium chloride dissolves in water to form magnesium ions and chloride ions. Resultant solution is neutral



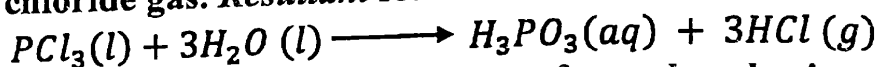
Aluminium chloride hydrolyses in water to form aluminium hydroxide; a white precipitate and hydrochloric acid. Resultant solution is acidic.



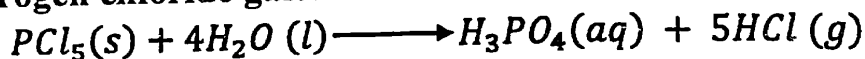
Silicon tetrachloride reacts with water to form silicon(IV) oxide and hydrochloric acid. Resultant solution is acidic.



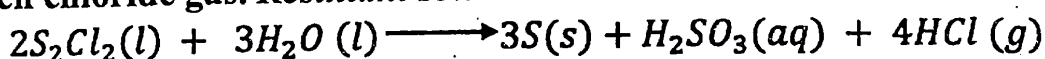
Phosphorus trichloride reacts with water to form **phosphonic acid** and white fumes of **hydrogen chloride gas**. *Resultant solution is acidic.*



Phosphorus pentachloride reacts with water to form **phosphoric acid** and white fumes of **hydrogen chloride gas**. *Resultant solution is acidic.*



Disulphur dichloride hydrolyses in water forming **sulphurous acid**, **sulphur** and **hydrogen chloride gas**. *Resultant solution is acidic.*



### THE HYDRIDES

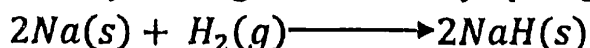
Formula of the hydride	NaH	MgH <sub>2</sub>	AlH <sub>3</sub>	SiH <sub>4</sub>	PH <sub>3</sub>	H <sub>2</sub> S	HCl
Physical state	Solids			Gases			
Bonding	Ionic		Mainly covalent	Covalent			Covalent though polar
Structure	Giant ionic		polymeric	Simple molecular			

#### (a) Structure and bonding

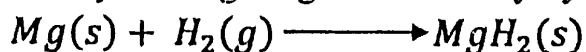
From sodium hydride to hydrogen chloride, ionic character decreases as electropositivity decreases for the metallic elements, electronegativity increasing for the non-metallic elements. Sodium hydride and magnesium hydride are ionic. Aluminium hydride is mainly covalent due to the small ionic radius of the aluminium ion, high charge density and high polarising power. The hydrides of silicon, phosphorus and sulphur and chlorine purely covalent. This variation in structure and bonding in turn affects the variation in melting point among the chlorides.

#### (b) With relevant equations, describe how the hydrides of Period 3 elements can be formed.

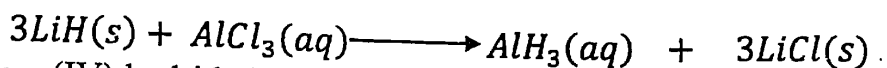
Sodium hydride is prepared by heating sodium in dry hydrogen gas



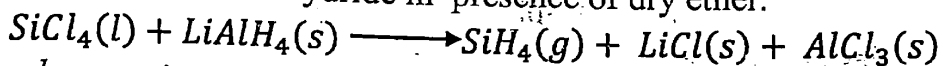
Magnesium hydride is formed by heating magnesium in dry hydrogen gas.



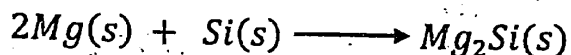
Aluminium hydride is formed by the reaction between lithium hydride and excess aluminium chloride in a solution of ether.



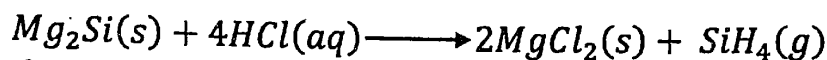
Silane / Silicon(IV) hydride is formed by the reaction between silicon tetrachloride and lithium Aluminium tetrahydride in presence of dry ether.



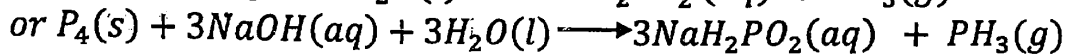
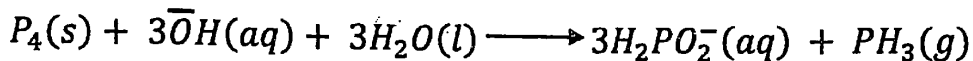
*N.B.* Also when a mixture of magnesium and silicon is heated, magnesium silicide is formed.



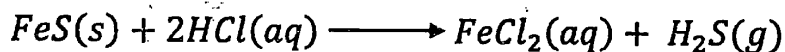
When magnesium silicide is warmed with dilute hydrochloric acid, silane is formed.



Phosphine is formed by heating concentrated sodium hydroxide with white phosphorus.



Hydrogen sulphide is formed by the reaction between warm dilute hydrochloric acid or warm dilute sulphuric acid and iron(II) sulphide.



Hydrogen chloride is prepared by reacting concentrated sulphuric acid and either solid potassium chloride or solid sodium chloride.

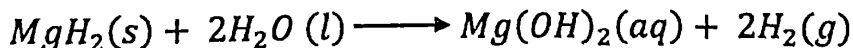


**(c) Discuss the reactions of hydrides of Period 3 elements with water.**

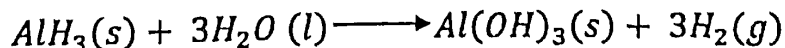
Sodium hydride reacts with water to form sodium hydroxide and hydrogen gas



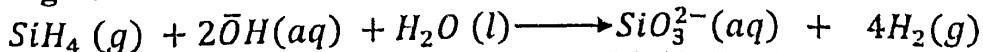
Magnesium hydride reacts with water to form magnesium hydroxide and hydrogen gas.



Aluminium hydride reacts with water to form aluminium hydroxide and hydrogen.



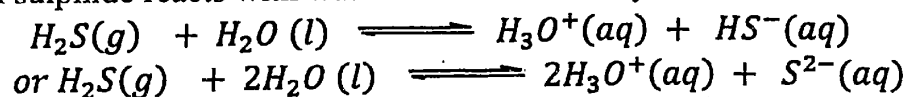
Silane is hydrolysed by water in alkaline medium to form silicate ions and hydrogen gas.



N.B. An alkaline catalyst required because the Si-H bond is less polar since silicon and hydrogen have almost similar electronegativities.

Phosphine is non-polar since phosphorus and hydrogen have almost equal electronegativities hence **does not react with water**.

Hydrogen sulphide reacts with water to form a weakly acidic solution



Hydrogen chloride hence reacts with water to form a strongly acidic solution.



### QUALITATIVE ANALYSIS FOR

### $Mg^{2+}$ , $Al^{3+}$ , $NO_3^-$ , $SO_4^{2-}$ , $SO_3^{2-}$ , $Cl^-$ AND $PO_4^{3-}$ IONS

In each case, the test in bold is the confirmatory test for each cation/ anion. The deductions given are general and do not depend on any previous tests that could have been done

ION	TEST	OBSERVATION	DEDUCTION	EXPLANATION
$Mg^{2+}$	Add sodium hydroxide drop wise until in excess	White precipitate insoluble in excess	$Mg^{2+}$ , $Ca^{2+}$ , $Ba^{2+}$ Probably present	Magnesium ions react with hydroxyl ions to form insoluble magnesium hydroxide. Magnesium hydroxide is basic hence cannot react with excess sodium hydroxide $Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$
	Add ammonia solution drop wise until in excess	White precipitate insoluble in excess	$Al^{3+}$ , $Pb^{2+}$ , $Mg^{2+}$ Probably present	Magnesium ions react with hydroxyl ions to form insoluble magnesium hydroxide. $Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$
	Add sodium carbonate solution drop wise until in excess	White precipitate	$Mg^{2+}$ , $Ca^{2+}$ , $Ba^{2+}$ $Zn^{2+}$ , $Pb^{2+}$ Probably present	Magnesium ions react with carbonate ions to form insoluble magnesium carbonate. $Mg^{2+}(aq) + CO_3^{2-}(aq) \rightarrow MgCO_3(s)$
	Add dilute sulphuric acid	No observable change	$Mg^{2+}$ , $Zn^{2+}$ , $Pb^{2+}$ Probably present	Magnesium ions react with sulphate ions to form magnesium sulphate which is a soluble compound $Mg^{2+}(aq) + SO_4^{2-}(aq) \rightarrow MgSO_4(aq)$

	<i>Add solid ammonium chloride and disodium hydrogenphosphate and then dilute ammonia solution drop wise until in excess</i>	<i>White precipitate <u>insoluble</u> in excess ammonia</i>	<i>Mg<sup>2+</sup> Confirmed present</i>	<i>Not required</i>
<i>Al<sup>3+</sup></i>	<i>Add sodium hydroxide drop wise until in excess</i>	<i>White precipitate soluble in excess to form a colourless solution</i>	<i>Zn<sup>2+</sup>, Pb<sup>2+</sup>, Al<sup>3+</sup> Probably present</i>	<i>Aluminium ions react with hydroxyl ions to form insoluble aluminium hydroxide. Aluminium hydroxide is amphoteric hence reacts with excess sodium hydroxide to form a soluble complex of aluminate ions.</i> $Al^{3+}(aq) + 3\bar{O}H(aq) \rightarrow Al(OH)_3(s)$ $Al(OH)_3(s) + \bar{O}H(aq) \rightarrow Al(OH)_4^{-}(aq)$
<i>Al<sup>3+</sup></i>	<i>Add ammonia solution drop wise until in excess</i>	<i>White precipitate insoluble in excess</i>	<i>Al<sup>3+</sup>, Pb<sup>2+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup> Probably present</i>	<i>Aluminium ions react with hydroxyl ions to form insoluble aluminium hydroxide.</i> $Al^{3+}(aq) + 3\bar{O}H(aq) \rightarrow Al(OH)_3(s)$
<i>Al<sup>3+</sup></i>	<i>Add potassium iodide</i>	<i>No observable change</i>	<i>Pb<sup>2+</sup> absent Al<sup>3+</sup> probably present</i>	
	<i>Add 2-3 drops of litmus solution followed by ammonia solution drop wise until in excess</i>	<i>Blue- lake solution</i>	<i>Al<sup>3+</sup> confirmed present</i>	<i>Not required</i>

$\text{NO}_3^-$	Heat a spatula end-ful of the solid sample	Brown fumes turn blue litmus paper red and relight a glowing splint	$\text{NO}_2$ gas evolved $\text{NO}_3^-$ present	All nitrates except potassium nitrate, sodium nitrate, ammonium nitrate, silver nitrate, manganese(II) nitrate and mercury nitrate decompose to form nitrogen dioxide and oxygen, leaving residue. $2\text{X}(\text{NO}_3)_2(\text{s}) \rightarrow 2\text{XO}(\text{s}) + 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ $\text{X} = \text{Ca, Mg, Al, Zn, Pb, Cu, Co or Ni}$
	To a spatula end-ful of the solid sample, add 5 drops of concentrated sulphuric acid and heat	Pale brown fumes, pungent, turn blue litmus red	$\text{NO}_2$ gas evolved $\text{NO}_3^-$ present	Concentrated sulphuric acid reacts with nitrate ions to form nitric acid vapour. $\text{NO}_3^-(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{HNO}_3(\text{g}) + \text{HSO}_4^-(\text{aq})$ When heated, nitric acid decomposes to form nitrogen dioxide. $4\text{HNO}_3(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$
	To the solution, add half a spatula of copper turnings followed by 5 drops of concentrated sulphuric acid and heat	Brown fumes evolved  Blue solution	$\text{NO}_2$ gas evolved $\text{NO}_3^-$ present	Concentrated sulphuric acid reacts with nitrate ions to form nitric acid. $\text{NO}_3^-(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{HNO}_3(\text{aq}) + \text{HSO}_4^-(\text{aq})$ Nitric acid oxidises copper to form copper (II) nitrate, itself reduced to nitrogen dioxide. $\text{Cu}(\text{s}) + 4\text{HNO}_3(\text{aq}) \rightarrow \text{Cu}(\text{NO}_3)_2(\text{aq}) + 2\text{NO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
$\text{NO}_3^-$	(Brown ring test) To the solution, add an equal volume of freshly prepared iron(II) sulphate. Then hold the test tube in a slanting position and carefully add concentrated sulphuric acid.	A brown ring is formed.	$\text{NO}_3^-$ confirmed	Concentrated sulphuric acid reacts with nitrate ions to form nitric acid. $\text{NO}_3^-(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{HNO}_3(\text{aq}) + \text{HSO}_4^-(\text{aq})$ The nitric acid oxidises some of the iron(II) sulphate to iron(III) sulphate, itself reduced to nitrogen monoxide and water. $3\text{Fe}^{2+}(\text{aq}) + 4\text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \rightarrow 3\text{Fe}^{3+}(\text{aq}) + \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ The nitrogen monoxide formed reacts with more iron(II) sulphate to form a complex which appears as the brown ring. $2\text{FeSO}_4(\text{aq}) + \text{NO}(\text{g}) \rightarrow (\text{FeSO}_4)_2 \cdot \text{NO}(\text{aq})$

	<p>To the solution, add dilute sodium hydroxide solution followed by zinc powder or aluminium powder and heat</p>	<p>Colourless gas with a pungent choking smell that turns red litmus blue and forms dense white fumes with concentrated hydrogen chloride</p>	<p><math>\text{NH}_3</math> evolved <math>\text{NO}_3^-</math> confirmed</p> <p>In alkaline medium, Zinc reduces nitrate ions to ammonia and itself oxidised to zincate ions or in alkaline medium, Aluminium reduces nitrate ions to ammonia and itself oxidised to aluminate ions.</p> <div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 10px auto;"> <p>Practice on how to derive the equations from the half-cell reactions</p> </div>
$4\text{Zn}(s) + 7\text{OH}^-(aq) + 6\text{H}_2\text{O}(l) + \text{NO}_3^-(aq) \longrightarrow 4\text{Zn}(\text{OH})_4^{2-}(aq) + \text{NH}_3(g)$ $8\text{Al}(s) + 5\text{OH}^-(aq) + 18\text{H}_2\text{O}(l) + 3\text{NO}_3^-(aq) \longrightarrow 8\text{Al}(\text{OH})_4^-(aq) + 3\text{NH}_3(g)$			
$\text{SO}_4^{2-}$	<p>To the solution, add dilute nitric acid followed lead(II) nitrate solution</p>	<p>White precipitate</p>	<p><math>\text{C}_2\text{O}_4^{2-}</math>, <math>\text{SO}_3^{2-}</math>, <math>\text{SO}_4^{2-}</math>, <math>\text{Cl}^-</math> probably present</p> <p>Lead(II) ions react with sulphate ions to form insoluble lead(II) sulphate <math>\text{Pb}^{2+}(aq) + \text{SO}_4^{2-}(aq) \longrightarrow \text{PbSO}_4(s)</math></p>
	<p>Add lead(II) nitrate followed by dilute nitric acid</p>	<p>White precipitate insoluble in acid</p>	<p><math>\text{SO}_4^{2-}</math>, <math>\text{Cl}^-</math> probably present</p> <p>Lead(II) ions react with sulphate ions to form insoluble lead(II) sulphate <math>\text{Pb}^{2+}(aq) + \text{SO}_4^{2-}(aq) \longrightarrow \text{PbSO}_4(s)</math></p>
	<p>To the acidified solution, lead(II) nitrate solution and heat/boil/ Warm</p>	<p>White precipitate insoluble on heating/boiling/warming</p>	<p><math>\text{SO}_4^{2-}</math> present</p> <p>Lead(II) ions react with sulphate ions to form insoluble lead(II) sulphate <math>\text{Pb}^{2+}(aq) + \text{SO}_4^{2-}(aq) \longrightarrow \text{PbSO}_4(s)</math> Lead(II) sulphate is insoluble on heating/boiling/warming</p>
	<p>Add dilute nitric acid followed by barium nitrate solution</p>	<p>White precipitate</p>	<p><math>\text{C}_2\text{O}_4^{2-}</math>, <math>\text{SO}_3^{2-}</math>, <math>\text{SO}_4^{2-}</math> probably present</p> <p>Barium ions react with sulphate ions to form insoluble barium sulphate <math>\text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \longrightarrow \text{BaSO}_4(s)</math></p>

	Add barium nitrate solution followed by dilute nitric acid	White precipitate insoluble in acid	$SO_4^{2-}$ confirmed present	Barium ions react with sulphate ions to form insoluble barium sulphate $Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$ Barium sulphate is insoluble in dilute nitric acid.
$SO_3^{2-}$	To the solution, add dilute nitric acid followed lead(II) nitrate solution	White precipitate	$C_2O_4^{2-}$ , $SO_3^{2-}$ , $SO_4^{2-}$ , $Cl^-$ probably present	Lead(II) ions react with sulphite ions to form insoluble lead(II) sulphite $Pb^{2+}(aq) + SO_3^{2-}(aq) \longrightarrow PbSO_3(s)$
	Add dilute nitric acid followed by barium nitrate solution	White precipitate	$C_2O_4^{2-}$ , $SO_3^{2-}$ , $SO_4^{2-}$ probably present	Barium ions react with sulphite ions to form insoluble barium sulphite $Ba^{2+}(aq) + SO_3^{2-}(aq) \longrightarrow BaSO_3(s)$
	Add barium nitrate solution followed by dilute nitric acid (distinguishing test from a sulphate)	White precipitate soluble in acid to form a colourless solution	$SO_3^{2-}$ present	Barium ions react with sulphite ions to form insoluble barium sulphite $Ba^{2+}(aq) + SO_3^{2-}(aq) \longrightarrow BaSO_3(s)$ Barium sulphite is soluble in dilute nitric acid.
	Add acidified potassium permanganate solution.	Purple solution turns colourless	$SO_3^{2-}$ confirmed	Manganate(VII) ions in an acidic medium oxidise sulphite ions to sulphate ions and itself reduced to manganese(II) ions. This reaction can occur without heating unlike for oxidation of oxalate ions where heating is a must.
	$2MnO_4^-(aq) + 6H^+(aq) + 5SO_3^{2-}(aq) \longrightarrow 2Mn^{2+}(aq) + 5SO_4^{2-}(aq) + 3H_2O(l)$			
	To a spatula endful of the solid, add 2-3 drops of concentrated sulphuric acid and heat	White fumes turn blue litmus red and form dense white fumes with concentrated ammonia	HCl gas evolved Cl <sup>-</sup> present	Concentrated sulphuric acid reacts with chloride ions to form hydrogen chloride gas. $Cl^-(s) + H_2SO_4(l) \longrightarrow HCl(g) + HSO_4^-(aq)$ Hydrogen chloride gas reacts with concentrated ammonia to form ammonium chloride $HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$

<b>Cl<sup>-</sup></b>	To the solution, add dilute nitric acid followed lead(II) nitrate solution	White precipitate	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> , SO <sub>3</sub> <sup>2-</sup> , SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> probably present	Lead(II) ions react with chloride ions to form insoluble lead(II) chloride $Pb^{2+}(aq) + 2Cl^{-}(aq) \longrightarrow PbCl_2(s)$
	Add lead(II) nitrate followed by dilute nitric acid	White precipitate insoluble in acid	SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> probably present	Lead(II) ions react with chloride ions to form insoluble lead(II) chloride $Pb^{2+}(aq) + 2Cl^{-}(aq) \longrightarrow PbCl_2(s)$
	To the acidified solution, lead(II) nitrate solution and heat/boil/warm	White precipitate soluble on heating/boiling/warming and reprecipitates on cooling	Cl <sup>-</sup> present	Lead(II) ions react with chloride ions to form insoluble lead(II) chloride $Pb^{2+}(aq) + 2Cl^{-}(aq) \longrightarrow PbCl_2(s)$
	Add dilute nitric acid followed by silver nitrate solution	White precipitate	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> , SO <sub>3</sub> <sup>2-</sup> , Cl <sup>-</sup> probably present	Silver ions react with chloride ions to form insoluble silver chloride $Ag^{+}(aq) + Cl^{-}(aq) \longrightarrow AgCl(s)$
	Add dilute nitric acid followed by silver nitrate solution. Then add aqueous ammonia drop wise until in excess.	White precipitate soluble in excess ammonia to form a colourless solution	Cl <sup>-</sup> confirmed	Silver ions react with chloride ions to form insoluble silver chloride $Ag^{+}(aq) + Cl^{-}(aq) \longrightarrow AgCl(s)$ Silver chloride reacts with excess ammonia to form a soluble complex of diamminesilver(I) ion. $AgCl(s) + 2NH_3(aq) \longrightarrow Ag(NH_3)_2^{+}(aq) + Cl^{-}(aq)$

$\text{Cl}^-$	To the solution, add bleaching powder then dilute nitric acid (or add chlorine water) followed by tetrachloromethane and shake. Allow to stand	Tetrachloromethane layer remains colourless	$\text{Cl}^-$ present	The acidified bleaching powder or chlorine water produces Chlorine. The chlorine cannot oxidise chloride ions hence the tetrachloromethane layer remains colourless
	To the solid, add magnesium powder and heat in an ignition tube. Allow to cool and add cold water	A colourless gas with a smell of rotten fish is formed	$\text{PO}_4^{3-}$ present	Not required
$\text{PO}_4^{3-}$	Add dilute nitric acid followed by barium nitrate solution	White precipitate	$\text{C}_2\text{O}_4^{2-}$ , $\text{SO}_3^{2-}$ , $\text{SO}_4^{2-}$ or $\text{PO}_4^{3-}$ probably present	Barium ions react with phosphate ions to form insoluble barium phosphate $3\text{Ba}^{2+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Ba}_3(\text{PO}_4)_2(\text{s})$
	Add dilute nitric acid followed by silver nitrate solution	Yellow precipitate	$\text{PO}_4^{3-}$ or $\text{I}^-$ probably present	Silver ions react with phosphate ions to form insoluble silver phosphate $3\text{Ag}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Ag}_3\text{PO}_4(\text{s})$
	Add silver nitrate solution followed by dilute nitric acid	Yellow precipitate soluble in dilute nitric acid	$\text{PO}_4^{3-}$ present	Silver ions react with phosphate ions to form insoluble silver phosphate $3\text{Ag}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Ag}_3\text{PO}_4(\text{s})$

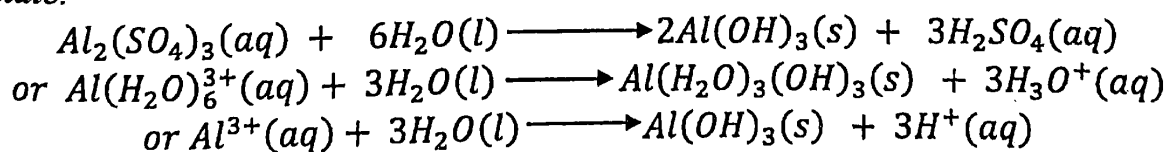
	Add dilute nitric acid followed by silver nitrate solution. Then add aqueous ammonia drop wise until in excess.	Yellow precipitate soluble in excess ammonia to form a yellow solution	$PO_4^{3-}$ present	Silver ions react with phosphate ions to form insoluble silver phosphate $3Ag^+(aq) + PO_4^{3-}(aq) \longrightarrow Ag_3PO_4(s)$
$PO_4^{3-}$	Add dilute nitric acid followed by ammonium molybdate solution and warm. Then add aqueous ammonia or sodium hydroxide solution.	Yellow precipitate soluble in aqueous ammonia or sodium hydroxide solution.	$PO_4^{3-}$ confirmed present	Not required

### HYDROLYSIS OF SALTS OF HIGHLY CHARGED CATIONS

**Qn.** Explain why an aqueous solution of aluminium sulphate turns blue litmus paper red/ has a pH below 7?

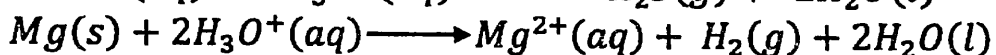
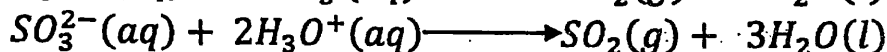
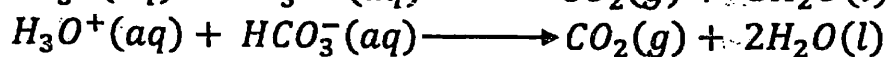
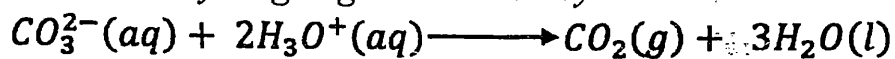
*The aluminium ion in aluminium sulphate has a high charge and a small ionic radius.*

*It has a high charge density and high polarising power, exists as hexaaquaaluminium(III) ion in solution. Aluminium ion therefore undergoes cationic hydrolysis forming hydrogen ions hence making the resultant solution acidic.*



N.B;

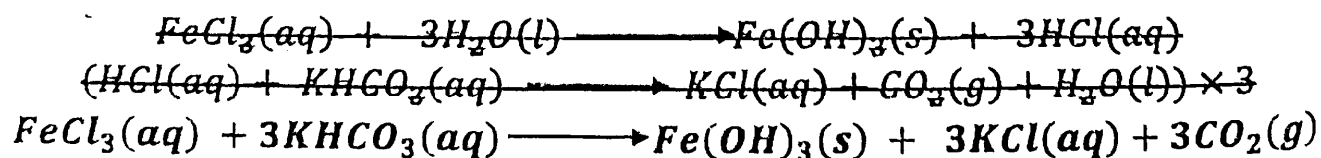
- Not only solutions of aluminium are acidic due to hydrolysis, but also chromium(III) salts and iron(III) salts.
- They precipitate as hydroxides in water on addition of a basic substance. The basic substances include; sodium carbonate or potassium carbonate, sodium hydrogen carbonate or potassium hydrogen carbonates, sodium sulphite or potassium sulphite, sodium sulphide/ ammonium sulphide, magnesium powder, or an alkali.
- The carbonates or hydrogen carbonates evolve carbon dioxide, the sulphites produce sulphur dioxide, sulphides liberate hydrogen sulphide gas and magnesium liberates hydrogen gas as shown by the reactions below;

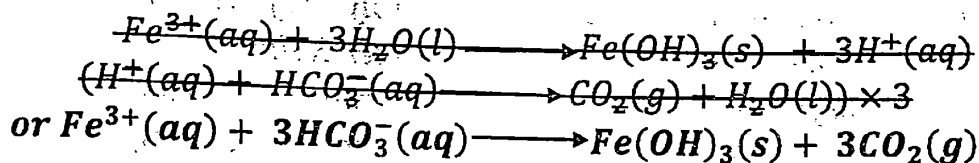
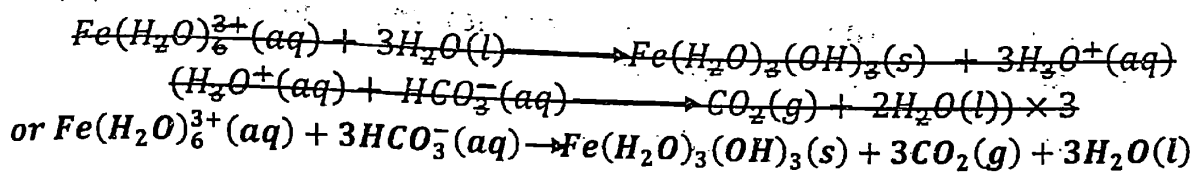


- When writing the overall equation, one of the above equations is combined with the equation for the hydrolysis of the salts in (a) by eliminating the acid ( $\text{H}_3\text{O}^+$  or  $\text{H}^+$ ) in the half cell reaction equations. A well balanced molecular equation can as well be written.

Qn. When potassium hydrogen carbonate is added to a solution of iron(III) chloride, a brown precipitate and bubbles of a colourless gas are observed. Explain this observation.

The iron(III) ion in iron(III) chloride has a high charge and a small ionic radius. It has a high charge density and high polarising power, exists as hexaqua iron (III) ion in solution. The ion therefore undergoes cationic hydrolysis forming insoluble iron(III) hydroxide and hydrogen ions making the resultant solution acidic. The hydrogen ions react with hydrogen carbonate ions forming carbon dioxide gas.

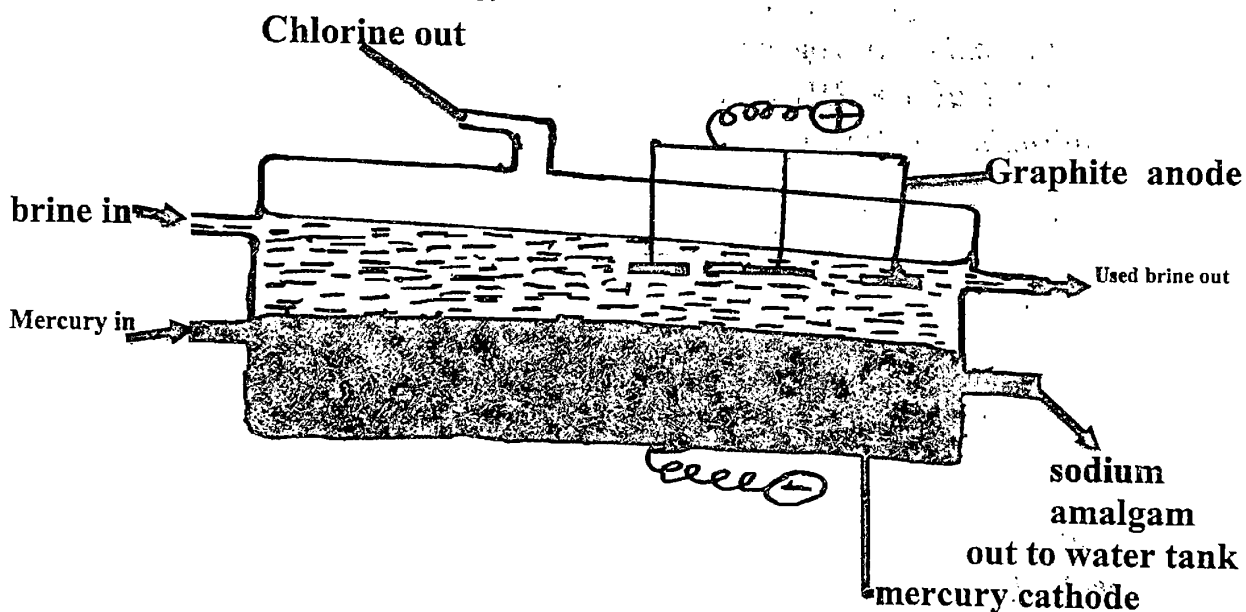




Check for more questions about this in the miscellaneous topical questions

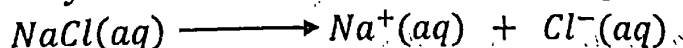
### INDUSTRIAL PROCESSES

Qn. Describe; using a well labelled diagram, the industrial process for the manufacture of chlorine.

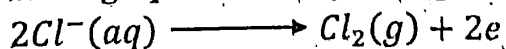


Chlorine is manufactured by electrolysis of brine using a graphite anode and a flowing mercury cathode.

Brine is decomposed by electric current according to the equation;



Chloride ions discharge at the graphite anode forming chlorine gas.

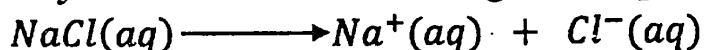


**Qn. (a) Describe the industrial process for the manufacture of sodium hydroxide. (No diagram required)**

**(b) State the uses of sodium hydroxide**

*Sodium hydroxide is manufactured by electrolysis of brine using a graphite anode and a flowing mercury cathode using a Castner-Kellner cell.*

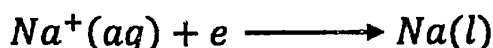
*Brine is decomposed by electric current according to the equation;*



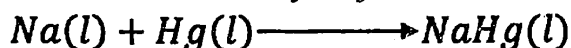
*Chloride ions discharge at the graphite anode forming chlorine gas.*



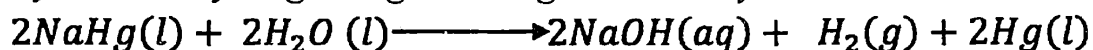
*Sodium ions are discharged at the cathode to obtain sodium.*



*The sodium formed combines with mercury to form sodium amalgam.*



*The sodium amalgam moves to the water tank where it reacts with water to form sodium hydroxide, hydrogen regenerating the mercury.*



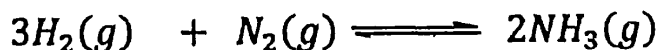
*Uses of sodium hydroxide*

- *Manufacture of soap*
- *Manufacture of rayon and paper*
- *Purification of Bauxite in Aluminium extraction*

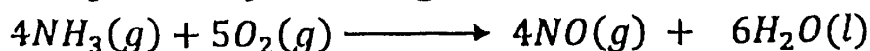
**Qn. Describe how nitric acid is manufactured using hydrogen and nitrogen as raw materials.**

*Dry hydrogen obtained from natural gas and dry nitrogen obtained from fractional distillation of liquid air are mixed in a 3:1 proportion by volume respectively.*

*The mixture is then heated at temperature of about 450-550 ° C and pressure between 200-500 atmospheres in presence of finely divided iron catalyst to form ammonia*

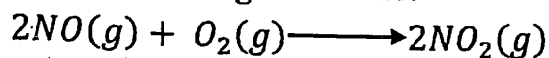


*The ammonia is dried and mixed with excess dust free air and passed over Platinum-Rhodium catalyst at red heat at a temperature of about 900 ° C and a pressure of 8 atmospheres to form nitrogen monoxide and water.*

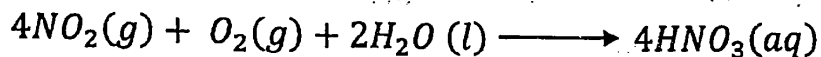


DEMYSTIFYING INORGANIC CHEMISTRY BY Joseph Jobs Kayiira, BScED(Hons. CHEM/MTC)  
Email: josephkayiira@gmail.com Call 0782601038 WhatsApp 0753247098

The nitrogen monoxide formed is rapidly cooled and further oxidised by oxygen from an excess of the air to form nitrogen dioxide.



The nitrogen dioxide, in presence of more air, is then absorbed in hot water to form nitric acid.



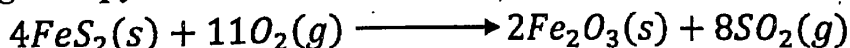
**Qn. Sulphur dioxide is a raw material used in manufacture of sulphuric acid by the contact process.**

- With relevant equations, describe the various ways how sulphur dioxide used in this process may be obtained on a large scale.
- Describe how sulphuric acid can be manufactured using one of the sources above.
- Describe the reactions of sulphuric acid with hydrohalic acids of group(VII) elements. State any observations made.
- Briefly describe how the sulphuric acid can be converted to superphosphate fertiliser.

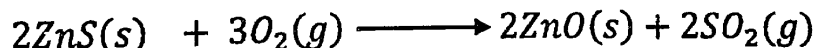
(a) Sulphur dioxide can be obtained by burning sulphur in air



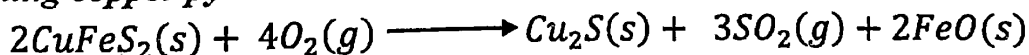
or by roasting iron pyrites in air



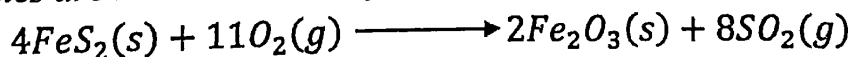
or roasting zinc blende in air



or roasting copper pyrites

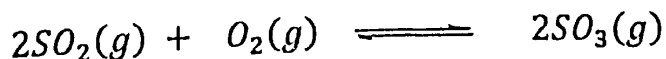


(b) Iron pyrites are roasted in air to form iron(III) oxide and sulphur dioxide.

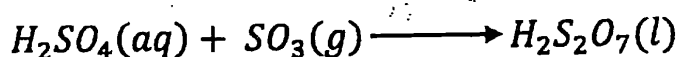


The sulphur dioxide obtained above and oxygen obtained by fractional distillation of liquid air are purified to clear them off any dust that may poison the catalyst and dried.

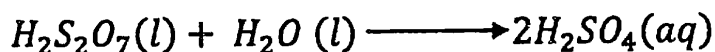
The purified and dried gases are passed over Vanadium(V) oxide catalyst at temperatures about 450-500 °C and pressures between 1-3 atmospheres to form sulphur trioxide.



The sulphur trioxide is dissolved in concentrated sulphuric acid to form a fuming liquid called oleum.



The oleum is carefully diluted with a correct amount of water to form 98% concentrated sulphuric acid.



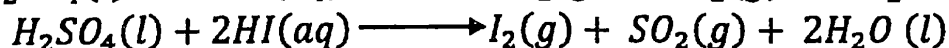
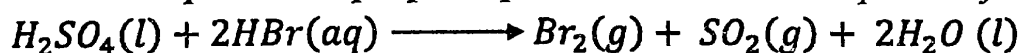
N.B. 1. Vanadium pentoxide is preferred over Platinum as catalyst because it is cheaper and not commonly poisoned by impurities

2. The sulphur trioxide is not dissolved in water because its reaction with water is highly exothermic and it leads to formation of sulphuric acid sprays that damage plants and animals

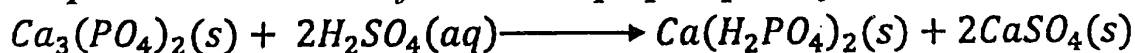
(c) Sulphuric acid does not react with hydrofluoric acid and hydrochloric acid because the fluoride ion and chloride ion have small ionic radii hence making the hydrides have a weak reducing action.

Hydrobromic acid and hydroiodic acid are strongly reducing due to large ionic radius of bromide ions and iodide ions. They reduce hot concentrated sulphuric acid to sulphur dioxide as they are oxidised to bromine and iodine respectively.

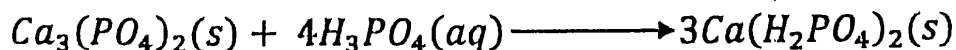
Reddish brown vapours and purple vapours are observed respectively



(d) Calcium phosphate is dissolved and stirred in about 65% sulphuric acid to form a mixture calcium sulphate and calcium dihydrogenphosphate. The product is dried and forms the superphosphate fertiliser.



N.B; The Single Superphosphate(SSP) fertiliser made above is less efficient because it is contaminated with Calcium sulphate. A more efficient fertiliser called Triple Superphosphate fertiliser is formed by using concentrated phosphoric acid instead.



Qn. (a) Write the name and formula of the chief ore from which aluminium is extracted.

(b) Name the common impurities present in the ore in (a) above

(c) Describe how the ore is;

(i) concentration

(ii) pure aluminium is obtained from the concentrated ore.

(No diagram is required)

(d) Explain why in the extraction process;

(i) a low voltage is used

(ii) anodes have to be replaced after some time.

(iii) iron cannot be obtained by the same process as aluminium is obtained in (c) (ii) above.

(e) State the uses of aluminium in relation to its properties.

(f) Explain why aluminium utensils should not be washed using soap.

(a) Bauxite  $Al_2O_3 \cdot 2H_2O$

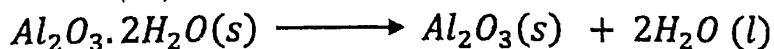
(b) Silicon(IV) oxide

Iron(III) oxide

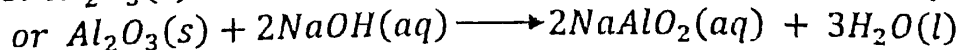
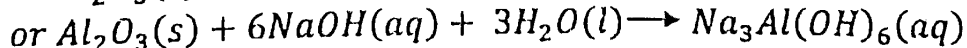
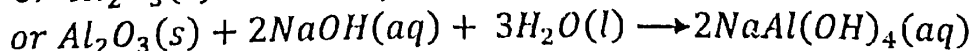
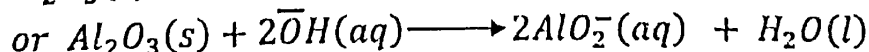
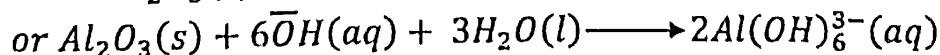
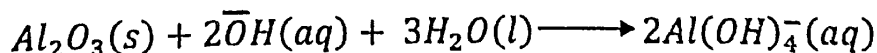
Titanium(IV) oxide

### Purification

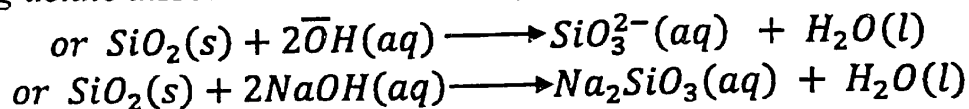
(c) (i) The ore is heated in presence of oxygen to drive off water of crystallisation, to obtain anhydrous aluminium oxide and also convert iron(II) ions to iron(III) oxide.



The roasted product is crushed/ pulverised into fine powder and digested with hot concentrated sodium hydroxide under pressure to dissolve amphoteric aluminium oxide that forms aluminate ions.

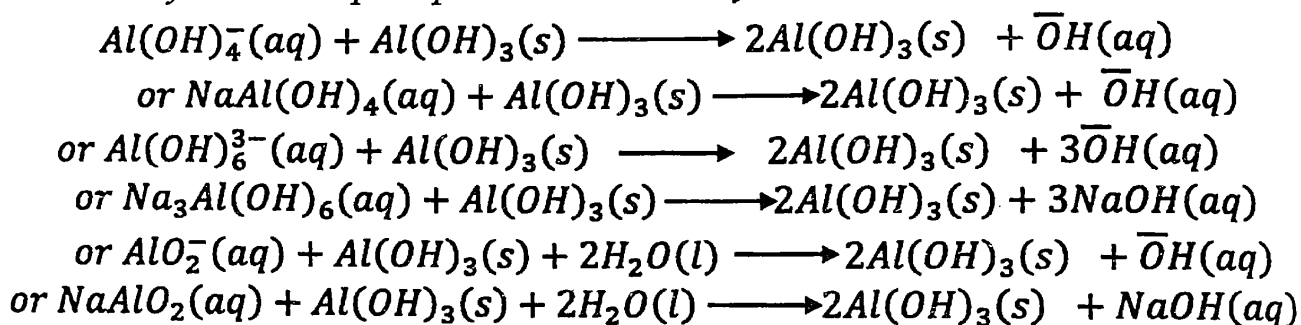


Silica being acidic dissolves in the sodium hydroxide to form sodium silicate

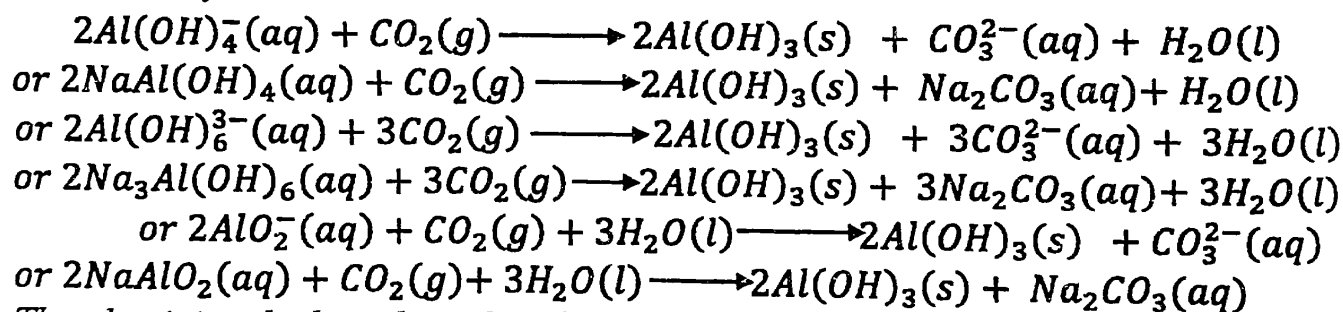


The basic iron(III) oxide and titanium(IV) oxide do not dissolve in the sodium hydroxide hence filtered off, forming a residue. The aluminate and silicate form the filtrate.

The filtrate is cooled, diluted with water, and seeded with freshly precipitated aluminium hydroxide to precipitate aluminium hydroxide.



Alternatively, carbon dioxide is bubbled through the filtrate to precipitate out aluminium hydroxide.

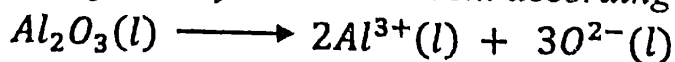


The aluminium hydroxide is then filtered off, washed, dried and heated strongly to form pure anhydrous aluminium oxide.

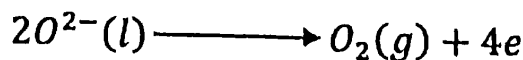


(ii) Pure aluminium is obtained from aluminium oxide by electrolysis using graphite electrodes in presence of molten cryolite that lowers the melting point of aluminium oxide at a low voltage and a high current density.

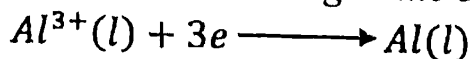
Aluminium oxide is decomposed by electric current according to the equation



Oxygen is given off at the anode.



Aluminium is obtained at the cathode according to the equation

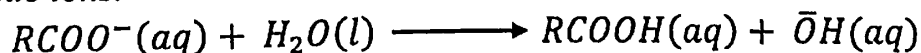


- (d) (i) A low voltage is used to avoid decomposition of the cryolite  
 (ii) Anodes have to be replaced because oxygen liberated there attacks them to form gaseous oxides of carbon. This makes them wear out after some time.  
 (This effect can be overcome by using a special self-baking Söderberg type of anode.)  
 (iii) Iron cannot be extracted by electrolysis but by reduction because iron is less reactive than carbon hence forms a less stable oxide, easily reduced by carbon. Aluminium is more reactive than carbon hence its oxide is stable and cannot be reduced by carbon. Therefore, aluminium is extracted by electrolysis.

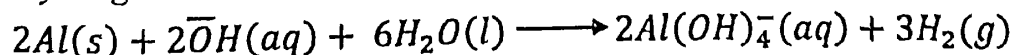
(e) Uses of aluminium in relation to its properties

Property	Related use
Lightness and a high tensile strength	Used to make alloys like Duralumin for air craft construction, aluminium bronze and magnalium
Light, good appearance, good heat conductivity	Making cooking utensils
Light	Making overhead electric cables
Resistant to corrosion	Construction of windows and doors
Malleable (easily shaped or bent), ductile and light	Making aluminium foil used in packaging industry
Reducing property	In Thermite welding and extraction of manganese and chromium

- (f) Soap is an organic salt of an organic acid and sodium hydroxide. Soap undergoes hydrolysis in solution to form a weak organic acid and hydroxide ions.



The hydroxide ions react with aluminium to form aluminate ions and hydrogen. This causes wearing off/ tarnishing of the aluminium utensils.



## MISCELLANEOUS TOPICAL QUESTIONS

### Short answer type questions

1. Successive ionisation energies ( $\text{kJmol}^{-1}$ ) for some elements in Period 3 of the periodic Table are shown in the table below.

Element	Ionisation energy				
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	5 <sup>th</sup>
Silicon	787	1577	3230	4355	16090
Phosphorus	1060	1896	2908	4954	6272
Sulphur	1000	2258	3381	4565	6995

- (a) State and explain the trend in successive ionisation energies. (03 marks)
- (b) Explain why the;
- (i) First ionisation energy of sulphur is less than that of phosphorus (03 marks)
  - (ii) third ionisation energy of phosphorus is less than that of silicon. (03 marks)
2. (a) Explain what is meant by the term first electron affinity. (01 mark)
- (b) State three factors that can affect electron affinity. (1 ½ marks)
- (c) The first electron affinities of some elements in Period 3 are given in the table below.

Element	Al	Si	P	S
First electron affinity	-44	-134	-71.7	-200

- (i) State the trend in variation in electron affinities (½ mark)
  - (ii) Explain your answer in c (i) above. (02 marks)
3. Both aluminium and phosphorus form compounds in the oxidation state of +3.
- (a) Briefly explain in terms of electronic configuration why aluminium conducts electricity but common allotropes of phosphorus do not. (03 marks)
- (b) Write an equation for the reaction between each element with sodium hydroxide solution. (03 marks)
4. Describe and explain how the oxides of magnesium, aluminium and silicon react with;(your answer should include conditions and equations for the reactions if any)
- (i) Sodium hydroxide (4 ½ marks)
  - (ii) Hydrochloric acid (4 ½ marks)

5. (a) Write an ionic equation for the reaction between concentrated sodium hydroxide solution and;

(i) Phosphorus(V) oxide

(ii) Chlorine

(iii) Aluminium oxide

(03 marks)

(c) State what was observed and write an ionic equation when sulphur dioxide was bubbled through acidified potassium dichromate solution. (2 ½ mark)

6. (a) The melting points of magnesium and sulphur are 660 °C and 119 °C respectively. Explain the difference in the melting points. (2 ½ marks)

(b) (i) Write the formulae of the oxides formed by magnesium and sulphur. State the types of bond in each oxide.

Element	Formula of oxide	Type of bond
Magnesium		
Sulphur		

(ii) Write an equation for the reaction between each oxide in (b) (i) above with sodium hydroxide solution. (02 marks)

(c) Both magnesium and sulphur react with silicon to form corresponding silicides. Write an equation for the reaction between;

(i) The silicide of magnesium and dilute hydrochloric acid. (01 mark)

(ii) The silicide of sulphur and cold water. (01 mark)

7. (a) Draw the structures and name the shapes of the following species. In each case, state the oxidation state of the central atom in the species.

Species	Structure	Shape	Oxidation state
$SO_3^{2-}$			
$SO_4^{2-}$			
$S_2O_3^{2-}$			

$SO_2$			
$ClO_2^-$			
$ClO^-$			
$ClO_4^-$			
$HCCl_3$			

(b) Explain why the sulphite ion adopts the shape you have named in (a).  
(02 marks)

(c) Name a reagent(s) which can be used to distinguish between the sulphite ion and sulphate ion. State what would be observed in each and write equation for the reaction(s) that occurs in each case.  
(3½ marks)

8. (a) The elements Aluminium, silicon and phosphorus belong to Period 3 of the Periodic Table.

(i) Write the formulae of the chlorides of the elements. (1 ½ marks)

Element	Formula of chloride
Aluminium	
Silicon	
Phosphorus	

(ii) State the conditions and write equations for the reactions that take place between each element and water. (4 ½ marks)

(b) sodium hydrogen carbonate solution was added to a solution of aluminium chloride in water.

(i) State what was observed (01 mark)

(ii) Write equation for the reaction. (1 ½ marks)

9. (a) Write an equation between water and the chloride of;
- Aluminium
  - Sulphur
  - Phosphorus
- (b) Write an equation for the reaction between hot concentrated sodium hydroxide solution and;
- aluminium
  - silicon
  - chlorine
- 10.(a) When 0.1g of aluminium was vapourised at 350 °C and a pressure of 1 atmosphere, 19.2 cm<sup>3</sup> of vapour was formed.
- Calculate the relative molecular mass of aluminium chloride. (02 marks)
  - Write the structural formula and molecular formula of aluminium chloride in the gaseous state at 350 °C. (02 marks)
- (b) Aluminium chloride is normally contaminated with traces of iron(III) chloride.
- Name one reagent that can be used to detect the presence of iron(III) ion in a contaminated solution of aluminium chloride. (01 mark)
  - State what would be observed if the contaminated aluminium chloride solution was treated with the reagent you have named in (b) (i) (½ mark)
  - Write equation for the reaction leading to the observation you have stated in (b)(ii)
- (c) Water was added drop wise to aluminium chloride.
- State what was observed. (01 mark)
  - Write equation for the reaction that took place. (1 ½ marks)
- (d) State one use of aluminium chloride in organic synthesis. (½ mark)
11. When 0.13g of a chloride of iron was vapourised at 600K and 1 atmosphere, 20 cm<sup>3</sup> of a vapour was formed.
- Calculate the relative molecular mass of the chloride of iron. (02 marks)
  - Determine the;
    - Molecular formula of the chloride of iron,
    - Structural formula of the chloride of iron in vapour phase. (02 marks)

12. Sodium, magnesium, silicon and sulphur are some of the elements in the Periodic Table.

(a) For each element, write the formulae and name the structure of the hydride.

Element	Formula of hydride	Structure

(b) Write equation for the reaction between water and

(i) Magnesium hydride. (01 mark)

(ii) Sulphur hydride. (01 mark)

(c) Silicon hydride is hydrolysed by water whereas carbon hydride is not.

(i) Write the equation of hydrolysis of silicon hydride (1 ½ mark)

(ii) Give a reason for the difference in reactivity of the two hydrides. (1 ½ marks)

13. Explain the following observations:

(a) Silicon(IV) chloride is hydrolysed by water whereas carbon tetrachloride is not. (3 ½ marks)

(b) When magnesium ribbon was added to a solution of chromium(III) sulphate, a green precipitate and bubbles of a colourless gas were evolved. (3 ½ marks)

(c) Chloric(I) acid and chloric(VII) acid are both oxoacids of chlorine. However, chloric (VII) acid is a stronger acid than chloric(I) acid. (02 marks)

(d) Sodium chloride melts at 800 °C whereas aluminium chloride sublimes at 180 °C (02 marks)

(e) When hydrogen iodide is treated with concentrated sulphuric acid, iodine is liberated, whereas when hydrogen chloride is similarly treated, chlorine is not evolved. (03 marks)

(f) Anhydrous magnesium chloride is commonly contaminated with magnesium oxide. (03 marks)

14. Chlorine is manufactured by electrolysis of a saturated solution of sodium chloride.

(a) Name;

(i) the cathode used (½ mark)

(ii) the anode used (½ mark)

(b) Write equation for the reaction at the anode. (01 mark)

(c) Write equation for the reaction that takes place if chlorine is bubbled through

(i) cold dilute sodium hydroxide solution (1 ½ marks)

(ii) hot concentrated sodium hydroxide solution (1 ½ marks)

(d) Explain what would happen if the resultant mixture in (c) (i) is heated. (1 ½ marks)

(e) Chlorine can be prepared by reacting lead(IV) oxide and hydrochloric acid.

(i) State the conditions for the reaction. (01 mark)

(ii) Write equation for the reaction. (1 ½ mark)

15.(a) In the manufacture of sulphuric acid, sulphur trioxide is not dissolved in water, but another solvent.

(i) State why water is not used as solvent. (01 mark)

(ii) Write equation(s) to show the formation of sulphuric acid from sulphur trioxide. (03 marks)

(b) State what would be observed and write equation for the reaction between concentrated sulphuric acid and;

(i) solid potassium bromide. (02 marks)

(ii) solid sodium iodide (2 ½ marks)

16. During the manufacture of sulphuric acid by the contact process, sulphur dioxide is catalytically oxidised to sulphur trioxide. The sulphur trioxide formed is then absorbed in 98% sulphuric acid to form compound Q.

(a) Name one source of sulphur dioxide and one source of oxygen used in the contact process. (01 mark)

(b) State the industrial conditions used to obtain a maximum yield of sulphur dioxide. (1 ½ marks)

(c) Write equation to show how compound Q is converted into sulphuric acid

(d) State the conditions under which sulphuric acid reacts with each of the following and in each case write an equation for the reaction that takes place.

- Tin
- Copper
- Carbon

(06 marks)

(e) Concentrated sulphuric acid is 98% w/w and has a density of  $1.84\text{gcm}^{-3}$ . Calculate the molarity of the concentrated sulphuric acid. (2 ½ marks)

17.(a) Name and write the formula of the major ore used in the extraction of aluminium. (01 mark)

(b) Using equations only, state how the named ore in (a) is converted to pure aluminium oxide. (06 marks)

(c) The aluminium oxide obtained in (b) is mixed with molten cryolite and electrolysed between carbon electrodes. State;

(i) why the carbon anodes have to be replaced from time to time. (½ mark)

(ii) the role of cryolite (½ mark)

(d) Explain one use of aluminium. (01 mark)

(e) Ammonium sulphide was added to an aqueous solution of aluminium chloride.

(i) State what was observed (01 mark)

(ii) Write an equation for the reaction that took place. (01 mark)

18. Bauxite is the principal ore used for the extraction of aluminium.

(a)(i) Write the formula of Bauxite. (½ mark)

(ii) Write the chemical formulae of two impurities present in Bauxite. (01 mark)

(b) Briefly describe how pure aluminium can be obtained from bauxite. (include appropriate equations where necessary) (05 marks)

(c) Describe the reaction of aluminium with acids. (04 marks)

(d) Sodium carbonate solution was added to an aqueous solution of aluminium chloride.

(i) State what was observed. (01 mark)

(ii) Write equation for the reaction that took place. (1 ½ marks)

19. Name a reagent that can be used to distinguish each of the following pairs of ions. In each case state what is observed and write an equation if each reagent is separately treated with the reagent.

- (i)  $Mg^{2+}$  and  $Ca^{2+}$  (3½ marks)
- (ii)  $Mg^{2+}$  and  $Al^{3+}$  (3½ marks)
- (iii)  $SO_4^{2-}$  and  $S_2O_3^{2-}$  (3½ marks)
- (iv)  $SO_4^{2-}$  and  $Cl^-$  (3½ marks)
- (v)  $CO_3^{2-}$  and  $HCO_3^-$  (3½ marks)
- (vi)  $NO_2^-$  and  $NO_3^-$  (3½ marks)

20. Aluminum ammonium sulphate (also called ammonium alum),  $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ , is a double salt formed by Aluminium. Crystals of the salt were dissolved in water and the solution formed divided into three portions.

(i) to the first portion was added sodium hydroxide solution drop wise until in excess and the mixture warmed. Explain the reactions that took place and state any observations made. (6½ marks)

(ii) to the second portion was added some drops of litmus solution followed by ammonia solution drop wise until in excess. State what was observed. (01 mark)

(iii) to the third part was added ammonia solution drop wise until in excess. State what was observed and write equation(s) to illustrate your answer. (2½ marks)

**Long answer type questions.**

21. Magnesium, Aluminium, Phosphorus and chlorine are elements of Period 3 of the Periodic Table. Their atomic numbers and melting points are given below.

Element	Atomic number	Melting point(°C)
Magnesium	12	649
Aluminium	13	661
Phosphorus	15	44
Chlorine	17	-101

(a) Explain the trend in melting point of the elements (06 marks)

(b) Discuss the reactivity of the elements with;

(i) Water (08 marks)

(ii) Sodium hydroxide (06 marks)

22.(a) Write the formulae of the anhydrous chlorides of sodium, magnesium, aluminium and silicon.

(02 marks)

(b) (i) Write equations for the changes that take place when each of the chlorides in (a) is added to water.

(04 marks)

(ii) Interpret the changes in the type bonding for each of the chlorides in (a) above.

(02 marks)

(iii) Explain why the chloride of carbon does not react with water but that of silicon does so.

(04 marks)

(c) Aluminium hydroxide is amphoteric. Write ionic equations to show the meaning of this statement.

(02 marks)

(d) The table below shows the ionic radii of sodium, magnesium and aluminium ions and the melting points of the chlorides formed by the three cations.

Ion	$Na^+$	$Mg^{2+}$	$Al^{3+}$
Ionic radius(nm)	0.095	0.065	0.050
Melting point of the chloride( $^{\circ}C$ )	801	712	180

(i) Calculate the charge-radius ratio for each cation. (1 ½ marks)

(ii) State and explain the trend in melting points of the chlorides of the three metals. (4 ½ marks)

23. The table below shows the melting points of both Period 3 elements of the Periodic Table and their oxides

Element	<i>Na</i>	<i>Mg</i>	<i>Al</i>	<i>Si</i>	<i>P</i>	<i>S</i>	<i>Cl</i>
Melting point(K)	370.8	923	933.3	1687	317.2	388.2	171.5
Oxide	$Na_2O$	$MgO$	$Al_2O_3$	$SiO_2$	$P_2O_5$	$SO_3$	$Cl_2O_7$
Melting point(K)	1548	3100	2280	1880	833	303	182

(a) Explain the differences in melting points of the;

(i) Elements

(ii) Oxides

(b) Describe the reactions of:

(i) Aluminium, silicon and phosphorus with sodium hydroxide

(ii) the hydrides of sodium, silicon and sulphur with water

(iii) the chlorides aluminium, silicon and phosphorus with water

24. The elements sodium, aluminium, phosphorus, silicon and chlorine all belong to Period 3 in the Periodic Table.

(a) Write the formulae of the hydride formed by each element and in each case state the type of bonding in the hydride. (05 marks)

(b) Using equations only, illustrate how each of the hydrides can be prepared in the laboratory. (05 marks)

(c) Explain what happens when each of the hydrides in (a) above is added to water and state whether the resultant solution is acidic, alkaline or neutral. Write equations in each case. (10 marks)

25.(a) The melting points of magnesium, silicon and sulphur are  $650^{\circ}\text{C}$ ,  $1423^{\circ}\text{C}$  and  $120^{\circ}\text{C}$  respectively. Explain the difference in the melting point of the elements. (06 marks)

(b)(i) Name the type of bond that exists in the hydride of magnesium, silicon and sulphur. (1 ½ marks)

(ii) Write the equation to show the reaction of each of the hydrides in (b)(i) above with water. (4 ½ marks)

(c) Describe the reaction of the oxide of silicon with:

(i) hydrofluoric acid

(ii) sodium hydroxide

(iii) water (08 marks)

26.(a) Describe the manufacture of sulphuric acid starting from zinc blende. (06 marks)

(b) Describe the reactions of sulphuric acid with;

(i) iron

(ii) copper

(iii) benzene (9 ½ marks)

(c) concentrated sulphuric acid is 98% w/w and has a density of  $1.84\text{ g cm}^{-3}$ . Determine the volume of the acid that must be dissolved in  $200\text{ cm}^3$  of water to make a solution that will completely neutralise 16.8g of sodium carbonate. (4 ½ marks)

27.(a) Write the formula and name the main ore of Aluminium (01 mark)

(b) Describe how;

(i) the ore is concentrated. (08 marks)

(ii) pure aluminium is obtained from the concentrated ore. (03 marks)

(c) describe the reaction of aluminium with;

- (i) sulphuric acid (04 marks)  
(ii) sodium hydroxide. (2 ½ marks)
- (d) Write the equation for the reaction between aluminium and trimanganese tetraoxide. (1 ½ marks)

28. Explain the following observations;

- (a) The pH of aluminium(III) sulphate in water is less than 7. (3 ½ marks)  
(b) The first ionisation energy of aluminium is less than that of magnesium. (03 marks)  
(c) When sodium hydroxide solution was added to aluminium sulphate solution, a white precipitate was formed which dissolved to form a colourless solution. (05 marks)  
(d) Aluminium chloride dissolves in methylbenzene but sodium chloride does not. (03 marks)  
(e) The melting points of  $P_4O_{10}$  and  $SO_2$  are much lower than that of  $SiO_2$ . (03 marks)  
(f) Sodium melts at  $97.8^\circ C$  whereas magnesium melts at  $665^\circ C$ . (02 marks)  
(g) Ionic radius of potassium ion is smaller than that of potassium atom yet ionic radius of chloride ion is larger than that of chloride ion. (03 marks)

# THE CHEMISTRY OF GROUP II ELEMENTS

## Electronic structures/ configurations

Element	Atomic number	Configuration
<i>Be</i>	4	$1s^2 2s^2$
<i>Mg</i>	12	$1s^2 2s^2 2p^6 3s^2$
<i>Ca</i>	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
<i>Sr</i>	38	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$
<i>Ba</i>	56	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$

From the above electronic configurations, it can be concluded that the outermost electronic configuration of group II elements is  $ns^2$ .

They have two electrons in their outermost sub-energy level and it is these electrons that they use in chemical reaction.

### Bonding and structure

**Qn. Explain why group II elements form metals with higher melting and boiling points than group I elements**

*Both group I and group II elements form metallic bonds whose strength depend on the number of electrons contributed per atom to the formation of the metallic bonds. Group II elements contribute two electrons per atom forming stronger metallic bonds that require a higher amount of energy to break than Group I elements which only contribute one electron per atom towards forming weaker metallic bonds that require a lower amount of energy to break.*

### VARIATION IN ATOMIC AND PHYSICAL PROPERTIES OF THE ELEMENTS

#### 1. Melting points

The table below shows the melting points of group II elements

Element	<i>Be</i>	<i>Mg</i>	<i>Ca</i>	<i>Sr</i>	<i>Ba</i>
Melting points( $^{\circ}\text{C}$ )	1280	650	850	770	720

Explain the trend in melting points of the elements

Melting point generally decreases from Beryllium to Barium with magnesium having an abnormally lower melting than calcium.

From Beryllium to Barium, atomic radius increases, bond length increases and bond strength decreases reducing the amount of energy required to break the metallic bonds.

Magnesium has an abnormally lower melting than calcium because magnesium has a hexagonal close packed structure compared to calcium with a packed structure.

## 2. Atomic and ionic radius

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

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

- (a) State and explain the trend in atomic radius of the elements  
(b) Explain why the ionic radius is smaller than the atomic radius of corresponding neutral atom for each element.

## 3. First ionization energy

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

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

- (c) Define the term first ionisation energy.

*The minimum amount of energy required to remove an electron from a gaseous atom to form a unipositively charged gaseous ion.*

or

*The minimum amount of energy required to remove one mole of electrons from one mole of gaseous atoms to form one mole of unipositively charged gaseous ions.*

- (d) State and explain the trend in ionization energy of the elements

*First ionization energy decreases from Beryllium to Barium.*

*This is because from Beryllium to Barium, nuclear charge increases, screening effect also increases, because an extra energy level completely filled with electrons is added from element to element. Increase in screening effect outweighs increase in nuclear charge. Effective nuclear charge decreases, atomic radius increases*

and outer most electron is far and weakly attracted by the nucleus requiring a low amount of energy to be removed.

#### 4. Electronegativity

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

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

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

State and explain the trend in electronegativity values of the elements

#### 5. Electropositivity

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

Electropositivity increases from beryllium to Barium.

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

#### 6. Electrode potential

The table below shows the standard electrode potential values of Group II elements.

Element	<i>Be</i>	<i>Mg</i>	<i>Ca</i>	<i>Sr</i>	<i>Ba</i>
Standard electrode potential( $E^\theta$ ) (Volts) for $M^{2+}/M$	-1.70	-2.37	-2.87	-2.89	-2.90

(a) Name with reasons;

- (i) the strongest reducing agent
- (ii) the weakest reducing agent

(b) Explain the trend in standard electrode potential of the elements

(a) (i) *Barium (but not Ba) because it has the most negative standard electrode potential*

(ii) *Beryllium (but not Be) because it has the least negative standard electrode potential*

(b) *Standard electrode potential generally becomes more negative from beryllium to barium because ionic radius increases, ionisation energy decreases, atomisation energy decreases and hydration energy also decreases. However, the decrease in ionisation energy and atomisation energy is more rapid than decrease in hydration energy.*

*Beryllium has an abnormally less negative value because the beryllium ion has the smallest ionic radius, highest charge density and highest polarising power, thus attracting many water molecules, giving off highest amount of energy.*

## 7. Electrical Conductivity

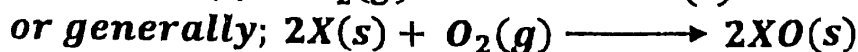
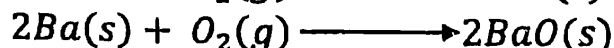
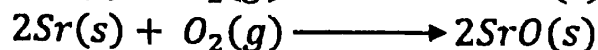
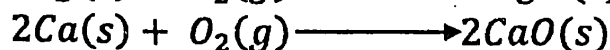
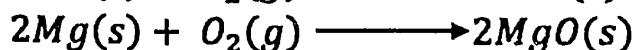
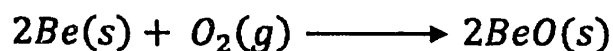
*Electrical conductivity increases from Beryllium to Barium*

*This is because from beryllium to barium, atomic radius increases, ionisation energy decreases, valence electrons become easily delocalised hence more available for electrical conductivity.*

## CHEMICAL PROPERTIES OF THE ELEMENTS

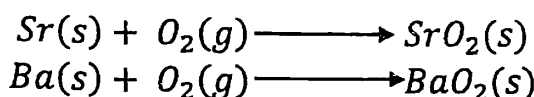
### 1. Discuss the reactions of group II elements with air.

Beryllium, magnesium, calcium, strontium and barium react with oxygen when heated to form beryllium oxide, magnesium oxide, calcium oxide, strontium oxide and barium oxide respectively

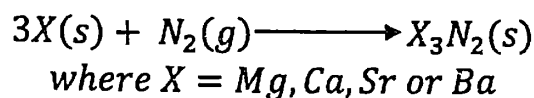


*where X = Be, Mg, Ca, Sr or Ba*

Heated Strontium and heated barium react with excess air to form strontium peroxide and barium peroxide.



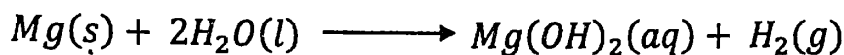
Apart from beryllium, other group II elements when heated also react with dry nitrogen to form corresponding nitrides.



## 2. Describe the reactions of group II elements with water

Beryllium does not react with water under any condition due to the insolubility of beryllium hydroxide.

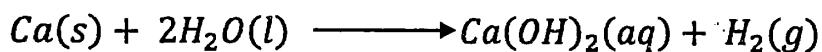
Magnesium reacts slowly with cold water to form magnesium hydroxide and hydrogen.



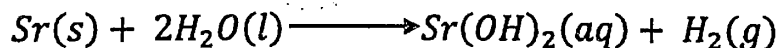
Heated magnesium reacts rapidly with steam to form magnesium oxide and hydrogen.



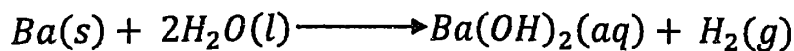
Calcium reacts moderately with cold water to form calcium hydroxide and hydrogen gas.



Strontium reacts quickly with water to form strontium hydroxide and hydrogen gas.



Barium reacts vigorously with water to form barium hydroxide and hydrogen gas



## 3. Describe how group II elements react with;

(a) dilute acids

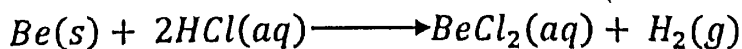
(b) concentrated acids

(c)

(a) dilute acids

(i) Dilute hydrochloric acid.

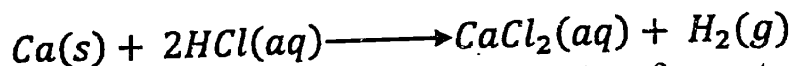
Beryllium reacts with warm dilute hydrochloric acid to form beryllium chloride and hydrogen.



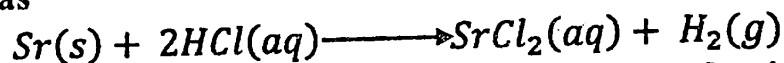
Magnesium reacts with cold dilute hydrochloric acid to form magnesium chloride and hydrogen gas



Calcium reacts with cold dilute hydrochloric acid to form calcium chloride and hydrogen gas.



Strontium reacts with cold dilute hydrochloric acid to form strontium chloride and hydrogen gas

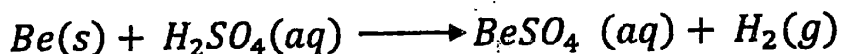


Barium reacts with cold dilute hydrochloric acid to form barium chloride and hydrogen gas



(ii) *Dilute sulphuric acid*

Beryllium reacts with warm dilute sulphuric acid to form beryllium sulphate and hydrogen.



Magnesium reacts with cold dilute sulphuric acid to form magnesium sulphate and hydrogen gas.

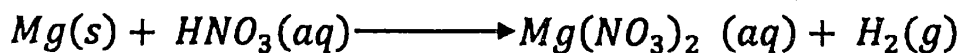


Calcium, barium and strontium react slowly with cold dilute sulphuric acid forming insoluble calcium sulphate, barium sulphate and strontium sulphate respectively which stop the reaction.

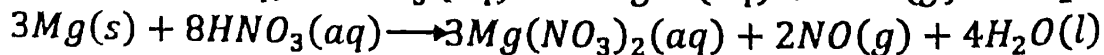
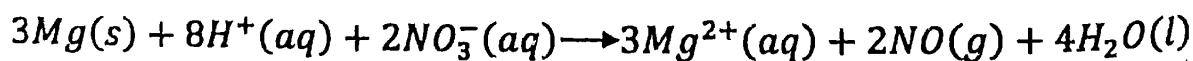
(iii) *Dilute nitric acid*

Beryllium does not react with dilute nitric acid

Very dilute cold nitric acid (1%) reacts with magnesium to form magnesium nitrate and hydrogen.



Dilute/ moderately concentrated/ half concentrated nitric acid oxidises magnesium to magnesium nitrate, itself reduced to nitrogen monoxide and water.



c.f Cu and Pb

Calcium, strontium and barium do not react with dilute nitric acid.

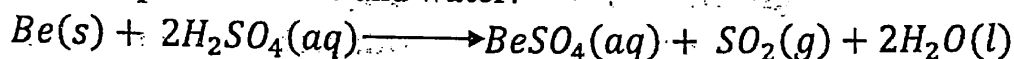
**(b) concentrated acids**

**(i) concentrated hydrochloric acid.**

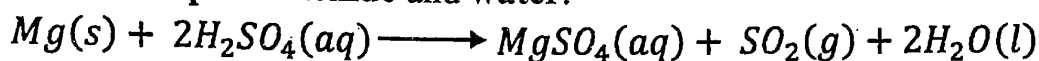
The metals do not react with concentrated hydrochloric acid because it is a reducing agent and they are also reducing.

**(ii) concentrated sulphuric acid**

Hot concentrated sulphuric acid oxidises beryllium to beryllium sulphate and itself reduced to Sulphur dioxide and water.



Hot concentrated sulphuric acid oxidises magnesium to magnesium sulphate and itself reduced to Sulphur dioxide and water.



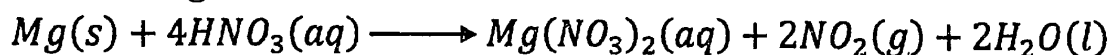
*c. f ; Pb, Cu and Co*

Calcium, barium and strontium react slowly with concentrated sulphuric acid forming insoluble calcium sulphate, barium sulphate and strontium sulphate respectively which stop the reaction.

**(iii) concentrated nitric acid**

Beryllium is rendered passive by concentrated nitric acid

Cold concentrated nitric acid oxidises magnesium to magnesium nitrate and itself reduced to nitrogen dioxide and water

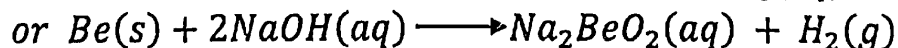
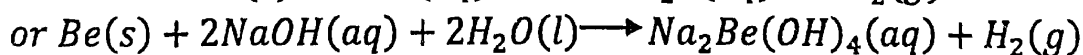
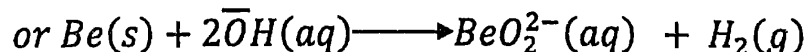
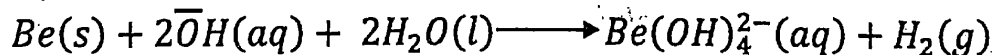


*c. f ; Pb and Cu*

Calcium, strontium and barium do not react with concentrated nitric acid

**4. Describe the reaction of group II elements with sodium hydroxide.**

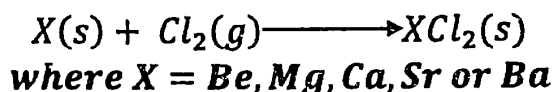
Beryllium reacts with hot concentrated sodium hydroxide to form sodium beryllate and hydrogen gas.



Magnesium, calcium, strontium and barium do not react with sodium hydroxide.

5. State the conditions and write the equations under which the elements react with chlorine

All the metals when heated react with dry chlorine to form corresponding chlorides



6. Beryllium, magnesium and calcium are group II elements.

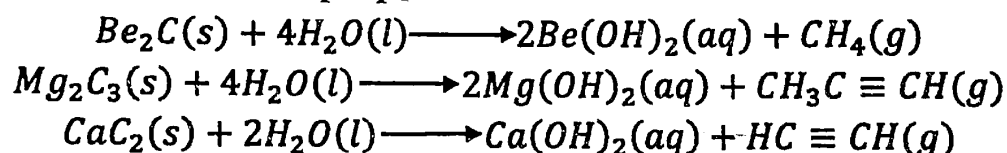
(a) Each of the above elements reacts with carbon to form carbides. Write the equation for the reaction that occurs when each carbide reacts with water.

(b) Show how the following conversions can be effected

(i) 2,2-dichloropropane from magnesium carbide

(ii) Calcium carbide to benzoic acid

(iii) Calcium carbide to propanoic acid



## COMPOUNDS OF GROUP II ELEMENTS

### THE OXIDES

Formula of the oxide	<i>BeO</i>	<i>MgO</i>	<i>CaO</i>	<i>SrO</i>	<i>BaO</i>
Physical state	<i>White solids</i>				
Character	<i>Amphoteric</i>		<i>Basic</i>		
Bonding	<i>Partly covalent</i>		<i>Ionic</i>		
Solubility in water	<i>Insoluble</i>		<i>Solubility increases</i> $\longrightarrow$		

(a) Structure and bonding

From Beryllium oxide to Barium oxide, cationic radius increases. This decreases the charge density of the cations, hence increasing the ionic character. Beryllium oxide is partly covalent. The rest of the oxides are ionic.

N.B; Beryllium oxide shows characteristics of covalent compounds such as;

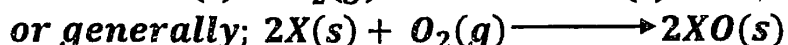
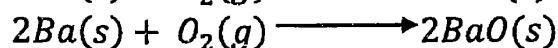
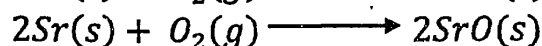
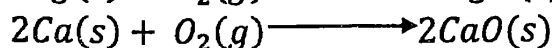
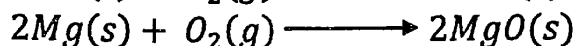
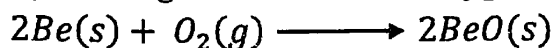
- Lower melting point than expected among the oxides
- Soluble in non-polar solvents but insoluble in water.

**Qn.** The melting point of calcium oxide is 2580 °C whereas that of beryllium oxide is 2530 °C. Explain.

*The beryllium ion has a smaller ionic radius than the calcium ion. The beryllium ion therefore has a higher charge density and higher polarising power than the calcium ion. This makes beryllium oxide predominantly covalent whereas calcium oxide is purely ionic. The covalent bonds in beryllium oxide require a lower amount of energy to break than the ionic bonds in calcium oxide. Calcium oxide therefore has a higher melting point than beryllium oxide.*

**(b)** With relevant equations, describe how the oxides of Group II elements can be formed.

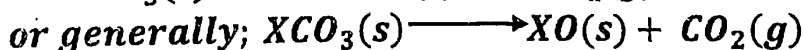
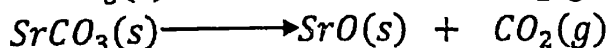
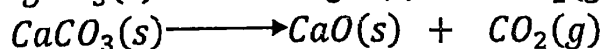
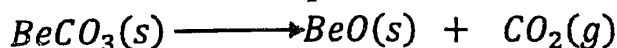
The oxides can be formed by heating the elements in oxygen



where X = Be, Mg, Ca, Sr or Ba

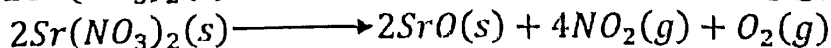
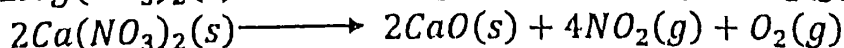
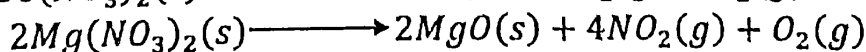
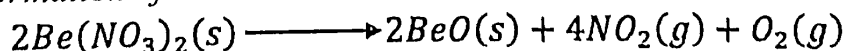
Beryllium oxide, magnesium oxide, calcium oxide and strontium oxide can also be formed by **thermal decomposition of the carbonates.**

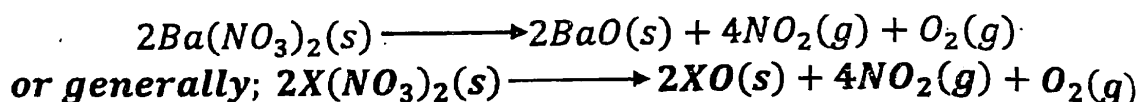
*This method is not convenient for formation of barium oxide because requires a temperature of about 1500 °C before the pressure of its carbon dioxide reaches 1 atmosphere.*



where X = Be, Mg, Ca or Sr

The oxides can also be formed by heating the nitrates. *This is the easiest method for formation of barium oxide.*





where X = Be, Mg, Ca, Sr or Ba

(c) The table below shows the melting points of the oxides of group II elements.

Oxide	BeO	MgO	CaO	SrO	BaO
Melting point of oxide(°C)	2530	2800	2580	2430	1928

Explain the trend in melting points of the oxides

Melting point increases from beryllium oxide to magnesium oxide and then decreases from magnesium oxide to barium oxide.

The decrease from magnesium oxide to barium oxide is because cationic radius increases, bond length increases, bond strength decreases reducing the amount of energy required to break the ionic bonds.

Beryllium oxide has a lower melting point than expected because the beryllium ion has a very small ionic radius, high polarising power and high charge density making beryllium oxide predominantly covalent. A low amount of energy is required to break the covalent bonds.

(d) Discuss the reactivity of the above oxides with

- (i) Water
- (ii) dilute sulphuric acid and dilute hydrochloric acids
- (iii) Sodium hydroxide

(i) reaction with water

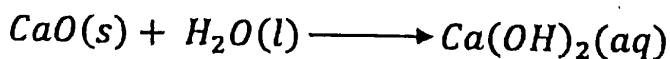
Reactivity of the oxides with water increases from beryllium oxide to barium oxide.

Beryllium oxide does not react or dissolve in water

Magnesium oxide slowly reacts with water to form magnesium hydroxide.



Calcium oxide, strontium oxide and barium oxide react vigorously with water to form calcium hydroxide, strontium hydroxide and barium hydroxide respectively, with evolution of heat.

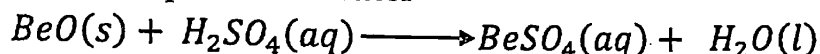


(ii) *reaction with dilute acids.*

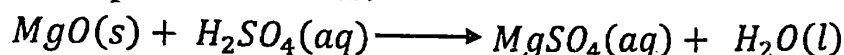
**Dilute sulphuric acid**

Reaction of the oxides with dilute sulphuric acid decreases from beryllium oxide to barium oxide due to decrease in solubility of the sulphates formed.

Beryllium oxide is amphoteric, hence reacts with warm dilute sulphuric acid to form beryllium sulphate and water



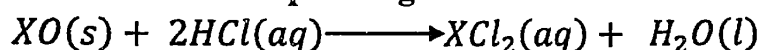
Magnesium oxide is basic hence reacts with warm dilute sulphuric acid to form magnesium sulphate and water.



Calcium oxide, strontium oxide and barium oxide react slowly with dilute sulphuric acid and the reaction stops due to formation of insoluble sulphates.

**Dilute hydrochloric acid**

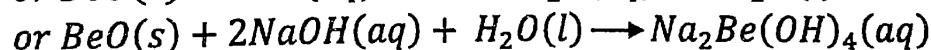
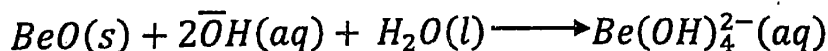
Beryllium oxide being amphoteric and the other oxides basic, all react with dilute hydrochloric acid to form corresponding chlorides and water.



where X = Be, Mg, Ca, Sr or Ba

(iii) *reaction with sodium hydroxide*

Beryllium oxide is amphoteric hence reacts with hot concentrated sodium hydroxide to form sodium beryllate.



Magnesium oxide, calcium oxide, strontium oxide and barium oxide are basic hence do not react with sodium hydroxide.

**THE HYDROXIDES**

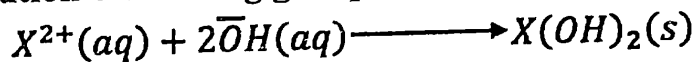
Formula	$\text{Be}(\text{OH})_2$	$\text{Mg}(\text{OH})_2$	$\text{Ca}(\text{OH})_2$	$\text{Sr}(\text{OH})_2$	$\text{Ba}(\text{OH})_2$
Physical state	White solids				
Character	Amphoteric	Basic			
Bonding	Covalent	Ionic			
Solubility in water	Insoluble	Slightly soluble	Solubility increases $\longrightarrow$		

**(a) Structure and bonding**

From Beryllium hydroxide to Barium hydroxide, cationic radius increases. This decreases the charge density of the cations, hence increasing the ionic character. Beryllium hydroxide is essentially covalent. The rest of the oxides are ionic.

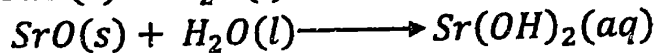
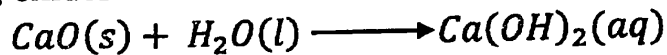
**(b) With an equation(s), state how the hydroxides of group II elements can be formed.**

The hydroxides are formed as white precipitates by adding aqueous sodium hydroxide to a solution containing group II ions.



where X = Be, Mg, Ca, Sr or Ba

The hydroxides apart from beryllium hydroxide, which is insoluble in water, and magnesium oxide, which is very slightly soluble, can also be formed by dissolving their corresponding oxides in water



**THERMOSTABILITY**

**(c) Explain the trend in thermo stability of the hydroxides.**

*Thermo stability increases from beryllium hydroxide to barium hydroxide. This is because as cationic radius increases, charge density and polarising power decreases, and ionic character increases leading to an increase in the decomposition temperature.*

**SOLUBILITY OF THE HYDROXIDES**

**(d) The table below shows the solubility of group II hydroxides in water at 20°C.**

Explain the trend in solubility of the hydroxides.

Hydroxide	Be(OH) <sub>2</sub>	Mg(OH) <sub>2</sub>	Ca(OH) <sub>2</sub>	Sr(OH) <sub>2</sub>	Ba(OH) <sub>2</sub>
Solubility(g/100g at 20°C)	Insoluble	0.002	0.15	0.9	4.0

*Solubility increases from magnesium hydroxide to barium hydroxide. Beryllium hydroxide is insoluble.*

*The increase in solubility is because cationic radius increases, both lattice energy and hydration energy of the cations decrease from magnesium ion to barium ion. However, due to low product of charges, the lattice energy decreases more rapidly than hydration energy.*

*Beryllium hydroxide is insoluble because of the high polarising power of the small beryllium ion making beryllium hydroxide covalent.*

(e) Discuss the reactivity of the above hydroxides with

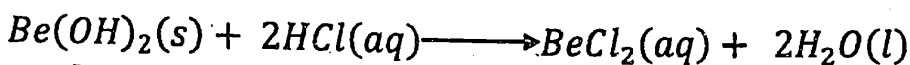
(i) Dilute hydrochloric acid and dilute sulphuric acid

(ii) Sodium hydroxide

(i) *reaction with acids.*

*Dilute hydrochloric acid*

Beryllium hydroxide is amphoteric, hence reacts with dilute hydrochloric acid to form beryllium chloride and water.



Magnesium hydroxide, calcium hydroxide, strontium hydroxide and barium hydroxide are basic hence reacts with dilute hydrochloric acid to form corresponding chlorides and water.



where X = Mg, Ca, Sr or Ba

*Dilute sulphuric acid*

Reactivity of the hydroxides with dilute sulphuric acid decreases from beryllium sulphate to barium sulphate due to decrease in solubility of the sulphates formed.

Beryllium hydroxide is amphoteric, hence reacts with dilute sulphuric acid to form beryllium sulphate and water.



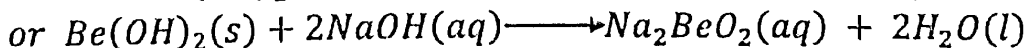
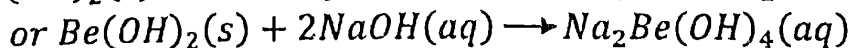
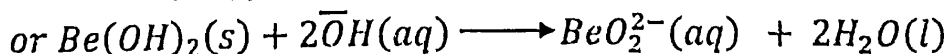
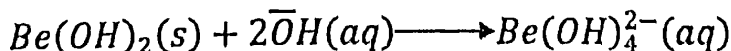
Magnesium hydroxide is basic hence reacts with dilute sulphuric acid to form magnesium sulphate and water.



Calcium hydroxide, strontium hydroxide and barium hydroxide react slowly with dilute sulphuric acid and the reaction stops due to formation of insoluble sulphates.

(ii) *reaction with sodium hydroxide*

Beryllium hydroxide is amphoteric hence reacts with hot concentrated sodium hydroxide to form sodium beryllate.



Magnesium hydroxide, calcium hydroxide, strontium hydroxide and barium hydroxide are basic hence do not react with sodium hydroxide.

### THE CHLORIDES

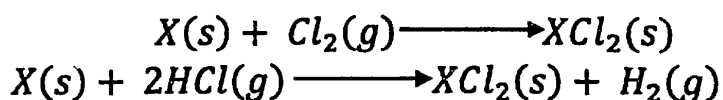
Formula of the chloride	$BeCl_2$	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$
Physical state	White solids				
Bonding	Mainly covalent	Ionic	Ionic	Ionic	Ionic
Solubility in water	All very soluble				
Solubility in ethanol	Very soluble	Moderately soluble	Moderately soluble	Slightly soluble	Almost soluble

#### (a) Structure and bonding

From beryllium chloride to barium chloride, ionic character increases as cationic radius increases, polarising power and charge density decreasing. Beryllium chloride is mainly covalent. The chlorides of magnesium, calcium, strontium and barium are essentially ionic. This variation in structure and bonding in turn affects the variation in melting point among the chlorides.

#### (b) With relevant equations, describe how the anhydrous chlorides of group II elements can be formed.

The anhydrous chlorides are formed by passing dry chlorine or dry hydrogen chloride over the heated metals.

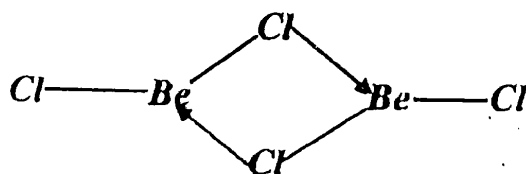


where  $X = Be, Mg, Ca, Sr$  or  $Ba$

N.B.

The aqueous solutions of the chlorides can be formed by reacting respective metal carbonates, oxides or hydroxides with dilute hydrochloric acid.

Like Aluminium chloride and iron(III) chloride, beryllium chloride dimerises vapour phase,  $Be_2Cl_4$ .



(c) The table below shows the melting points of the chlorides of Group II elements.

Explain the trend in variation of the melting points of the chlorides.

Chloride	$BeCl_2$	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$
Melting point ( $^{\circ}C$ )	405	714	782	875	962

Melting point increases from beryllium chloride to barium chloride because cationic radius increases, charge density and polarising power of the cations decrease, and ionic character increases, requiring an increasing amount of energy to break the increasingly strong ionic bonds.

The melting point of beryllium chloride is very low compared to other chlorides because the beryllium ion has a very small ionic radius, high polarising power and high charge density making beryllium chloride predominantly covalent. A low amount of energy is required to break the covalent bond.

#### THE HYDRIDES

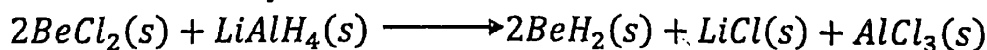
Formula of the hydride	$BeH_2$	$MgH_2$	$CaH_2$	$SrH_2$	$BaH_2$
Physical state	White crystalline solids				
Bonding and structure	Polymeric		Ionic character increases $\longrightarrow$		

#### (a) Structure and bonding

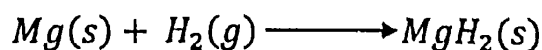
The metals mainly form ionic hydrides. Calcium hydride, strontium hydride and barium hydride are purely ionic.

#### (b) With relevant equations, describe how the hydrides of group II elements can be formed.

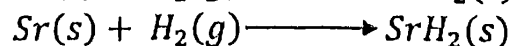
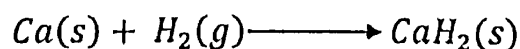
Beryllium hydride is formed by the reaction between beryllium chloride and lithium Aluminium tetrahydride

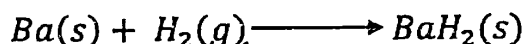


Magnesium hydride is formed by heating magnesium with dry hydrogen gas under high pressure.



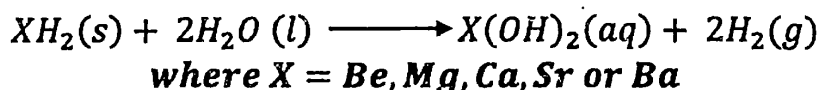
Calcium hydride, strontium hydride and barium hydride are formed by heating the metals with dry hydrogen.





(c) Discuss the reactions of hydrides of group II elements with water.

All hydrides of group II elements react with water to form corresponding hydroxides and hydrogen gas. Reactivity of the hydrides with water increases as the solubility of the hydroxides increases from beryllium hydroxide to barium hydroxide.



### THE SULPHATES

#### Solubility of the sulphates

The table below shows the solubility of group II hydroxides in water at 25°C.

Sulphates	$\text{BeSO}_4$	$\text{MgSO}_4$	$\text{CaSO}_4$	$\text{SrSO}_4$	$\text{BaSO}_4$
Solubility(g/100g at 25°C)	43	36	0.20	0.011	0.0024

Explain the trend in solubility of the sulphates.

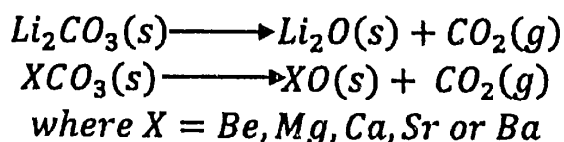
*Solubility decreases from beryllium sulphate to barium sulphate.*

*This is because cationic radius increases, both lattice energy and hydration energy of the cations decrease from beryllium ion to barium ion. However, due to a high product of charges, the hydration energy decreases more rapidly than lattice energy.*

### THE CARBONATES

The carbonates of group II elements are insoluble in water unlike group I carbonates which are soluble in water.

Carbonates of group I elements do not decompose (apart from Lithium carbonate) on heating whereas those of group II elements decompose to form respective oxides and carbon dioxide.

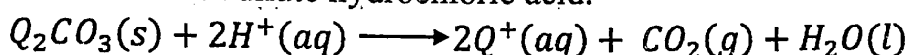


Therefore, group I carbonates are generally thermally more stable than group II carbonates.

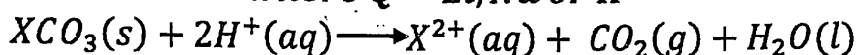
The thermal stability of group II carbonates however increases down the group.

For example, sodium carbonate does not decompose on heating but magnesium decomposes on heating. This is because the sodium ion has a larger ionic radius and a smaller charge than magnesium ion. The sodium ion therefore has a lower charge density, lower polarising power than the magnesium ion. Therefore, sodium carbonate is more strongly ionic than magnesium carbonate.

However, all carbonates whether group I or group II carbonates evolve carbon dioxide on treatment with dilute hydrochloric acid.



where  $Q = Li, Na$  or  $K$



where  $X = Be, Mg, Ca, Sr$  or  $Ba$

### 1. Thermo stability

The table below shows the temperatures for complete decomposition of group II metal carbonates to the metal oxides at 1 atmosphere.

Carbonate	$BeCO_3$	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
Decomposition temperature ( $^{\circ}C$ )	25	540	900	1290	1360

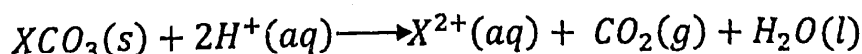
Explain the trend in thermo stability of the carbonates

Since decomposition temperature increases from beryllium carbonate to barium carbonate, thermo stability increases in the same order. This is because as cationic radius increases, charge density and polarising power decreases, and ionic character increases and the ions become strongly held leading to an increase in the decomposition temperature.

### 2. Describe the reactions of group II carbonates with dilute hydrochloric acid and dilute sulphuric acid

#### Dilute hydrochloric acid

All the carbonates react with dilute hydrochloric acid to form corresponding chlorides, carbon dioxide and water.

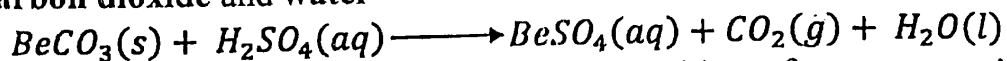


where  $X = Be, Mg, Ca, Sr$  or  $Ba$

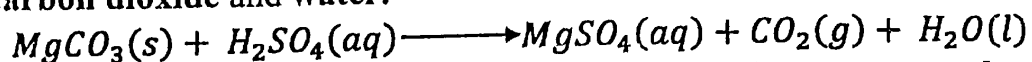
#### Dilute sulphuric acid

Reactivity of the carbonates with dilute sulphuric acid decreases from beryllium carbonate to barium carbonate due to decrease in solubility of the sulphates formed.

Beryllium carbonate reacts with dilute sulphuric acid to form beryllium sulphate, carbon dioxide and water



Magnesium carbonate reacts with dilute sulphuric acid to form magnesium sulphate, carbon dioxide and water.



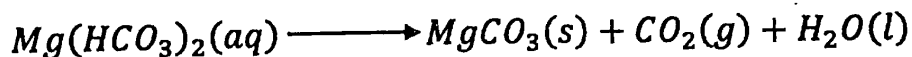
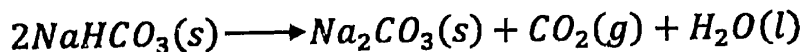
Calcium carbonate, strontium carbonate and barium carbonate react slowly with dilute sulphuric acid and the reaction stops due to formation of insoluble sulphates.

### THE HYDROGEN CARBONATES

Magnesium hydrogen carbonate and calcium hydrogen carbonate are very unstable to exist in solid state and known only to exist in solution. They are very soluble in water.

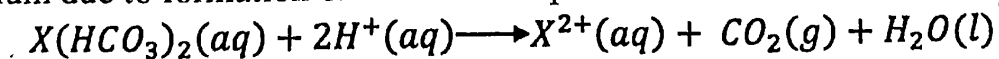
On the other hand, sodium hydrogencarbonate and potassium hydrogencarbonate exist as solids, although Lithium hydrogen carbonate exists only in solution.

Group II hydrogencarbonates easily decompose compared to group I hydrogen carbonates. All of them form respective carbonates, carbon dioxide and water.



However, all hydrogencarbonates whether group I or group II evolve carbon dioxide on treatment with dilute acids where no insoluble salts are formed.

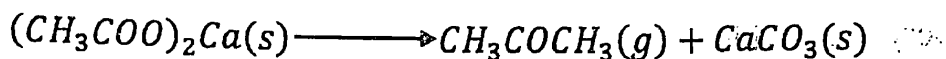
Reactivity of group II hydrogencarbonates with dilute sulphuric acid decreases down the group due to decrease in solubility of the sulphates formed. The reaction is very slow and eventually stops for hydrogen carbonates of calcium, strontium and barium due to formation of insoluble sulphates.



where  $X = \text{Be or Mg}$

### ETHANOATES (ACETATES)

These are group II salts formed from ethanoic acid. They decompose on heating to form carbonates and propanone, which can be tested using Brady's reagent (2,4-dinitrophenylhydrazine). A yellow precipitate is formed with Brady's reagent. They are used in organic synthesis of ketones.



They do not decompose to form carbon dioxide under normal conditions very high temperatures are needed to effect that reaction.

However ethanoates of copper, nickel and other elements can decompose to form the oxide, carbon dioxide and propanone.

### ANOMALOUS BEHAVIOUR OF BERYLLIUM AND ITS COMPOUNDS

In some of its properties, beryllium and its compounds behave differently from the other elements.

(d) State the reasons for this anomalous behaviour.

- Beryllium atom has the smallest atomic radius among the elements
- Beryllium atom has the highest electronegativity
- Beryllium ion has the highest polarising power
- Beryllium ion has the least negative standard electrode potential

(e) State the properties in which;

(i) beryllium behaves differently from other elements

(ii) beryllium compounds behave differently from other group II compounds

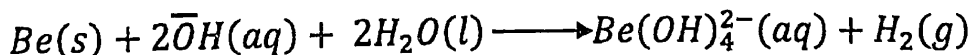
*(Equations may be included where necessary)*

(i)

- Beryllium does not react with water under any condition where as other elements react with water.
- Beryllium reacts with warm dilute hydrochloric acid. Other elements react with the cold dilute acid.



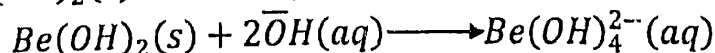
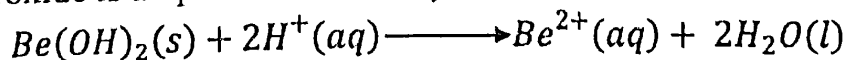
- Beryllium reacts with hot concentrated sodium hydroxide to form sodium beryllate and hydrogen gas. Other elements do not react with sodium hydroxide.



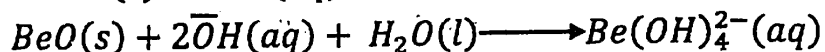
- Beryllium does not combine directly with hydrogen

(ii)

- Beryllium hydroxide is completely insoluble in water. Other hydroxides have some degree of solubility in water.
- Beryllium hydroxide is amphoteric. Other hydroxides are basic



- Beryllium oxide is partly covalent. Other oxides are ionic
- Beryllium oxide is amphoteric. Other oxides are basic.



- Beryllium chloride is covalent. Other chlorides are ionic
- Beryllium chloride dimerises in vapour phase. Other chlorides do not dimerise.

### QUALITATIVE ANALYSIS FOR $\text{Mg}^{2+}$ , $\text{Ca}^{2+}$ AND $\text{Ba}^{2+}$ IONS

In each case, the test in **BOLD** is the confirmatory test for each cation. The deductions given are general and **DO NOT** depend on any previous tests that could have been done

ION	TEST	OBSERVATION	DEDUCTION	EXPLANATION
$\text{Mg}^{2+}$	Add sodium hydroxide drop wise until in excess	White precipitate insoluble in excess	$\text{Mg}^{2+}$ , $\text{Ca}^{2+}$ , $\text{Ba}^{2+}$ Probably present	Magnesium ions react with hydroxyl ions to form insoluble magnesium hydroxide. Magnesium hydroxide is <u>basic</u> hence cannot react with excess sodium hydroxide $\text{Mg}^{2+}(aq) + 2\overline{\text{O}}\text{H}(aq) \longrightarrow \text{Mg}(\text{OH})_2(s)$
	Add ammonia solution drop wise until in excess	White precipitate insoluble in excess	$\text{Al}^{3+}$ , $\text{Pb}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Ba}^{2+}$ Probably present	Magnesium ions react with hydroxyl ions to form insoluble magnesium hydroxide. $\text{Mg}^{2+}(aq) + 2\overline{\text{O}}\text{H}(aq) \longrightarrow \text{Mg}(\text{OH})_2(s)$
	Add sodium carbonate solution drop wise until in excess	White precipitate Insoluble in excess	$\text{Mg}^{2+}$ , $\text{Ca}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Pb}^{2+}$ Probably present	Magnesium ions react with carbonate ions to form insoluble magnesium carbonate. $\text{Mg}^{2+}(aq) + \text{CO}_3^{2-}(aq) \longrightarrow \text{MgCO}_3(s)$
	Add dilute sulphuric acid	No observable change	$\text{Mg}^{2+}$ , $\text{Zn}^{2+}$ Probably present	Magnesium ions react with sulphate ions to form magnesium sulphate which is a soluble compound $\text{Mg}^{2+}(aq) + \text{SO}_4^{2-}(aq) \longrightarrow \text{MgSO}_4(aq)$
	Add ammonium oxalate solution	No observable change	$\text{Mg}^{2+}$ present	Magnesium ions react with oxalate ions to form soluble magnesium oxalate. $\text{Mg}^{2+}(aq) + \text{C}_2\text{O}_4^{2-}(aq) \longrightarrow \text{MgC}_2\text{O}_4(aq)$ A white precipitate can only be formed when ethanoic acid is added.

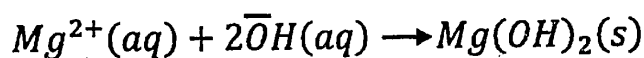
$Mg^{2+}$	Add solid ammonium chloride and disodium hydrogenphosphate and then dilute ammonia solution drop wise until in excess	White precipitate <u>insoluble</u> in excess ammonia	$Mg^{2+}$ Confirmed present	Not required
$Ca^{2+}$	Add sodium hydroxide drop wise until in excess	White precipitate insoluble in excess	$Mg^{2+}, Ca^{2+}, Ba^{2+}$ Probably present	Calcium ions react with hydroxyl ions to form insoluble calcium hydroxide. calcium hydroxide is basic hence cannot react with excess sodium hydroxide $Ca^{2+}(aq) + 2\bar{O}H(aq) \rightarrow Ca(OH)_2(s)$
	Add ammonia solution drop wise until in excess	No observable change	$Ca^{2+}$ Present	Ammonia is a weak base which partially ionises to form few hydroxyl ions $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$ The concentration of the hydroxyl ions formed from the weak ammonia base is low for the solubility product of calcium hydroxide to be exceeded. Therefore no precipitation occurs.
	Add sodium carbonate solution drop wise until in excess	White precipitate insoluble in excess	$Mg^{2+}, Ca^{2+}, Ba^{2+}$ $Zn^{2+}, Pb^{2+}$ Probably present	Calcium ions react with carbonate ions to form insoluble calcium carbonate. $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$
	Add dilute sulphuric acid	White precipitate	$Ba^{2+}$ or $Ca^{2+}$ Probably present	Calcium ions react with sulphate ions to form insoluble calcium sulphate. $Ca^{2+}(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4(s)$
	Add potassium chromate(VI) solution followed by ethanoic acid/ sodium hydroxide solution	Yellow precipitate soluble in ethanoic acid/sodium hydroxide.	$Ca^{2+}$ present	Calcium ions react with chromate ions to form insoluble calcium chromate. $Ca^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow CaCrO_4(s)$

$\text{Ca}^{2+}$	Add ammonium oxalate solution followed by dilute ethanoic acid	White precipitate insoluble in ethanoic acid	$\text{Ca}^{2+}$ confirmed present	Calcium ions react with oxalate ions to form insoluble calcium oxalate. $\text{Ca}^{2+}(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}) \rightarrow \text{CaC}_2\text{O}_4(\text{s})$
$\text{Ba}^{2+}$	Add sodium hydroxide drop wise until in excess	White precipitate insoluble in excess	$\text{Mg}^{2+}, \text{Ca}^{2+}, \text{Ba}^{2+}$ Probably present	Barium ions react with hydroxyl ions to form insoluble barium hydroxide. Barium hydroxide is basic hence cannot react with excess sodium hydroxide $\text{Ba}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Ba}(\text{OH})_2(\text{s})$
	Add ammonia solution drop wise until in excess	White precipitate insoluble in excess	$\text{Mg}^{2+}, \text{Ba}^{2+}$ Probably present	Barium ions react with hydroxyl ions to form insoluble barium hydroxide. Barium hydroxide is basic hence cannot react with excess sodium hydroxide $\text{Ba}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Ba}(\text{OH})_2(\text{s})$
	Add sodium carbonate solution drop wise until in excess	White precipitate insoluble in excess	$\text{Mg}^{2+}, \text{Ca}^{2+}, \text{Ba}^{2+}, \text{Zn}^{2+}, \text{Pb}^{2+}$ Probably present	Barium ions react with carbonate ions to form insoluble barium carbonate. $\text{Ba}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{BaCO}_3(\text{s})$
	Add dilute sulphuric acid	White precipitate	$\text{Ba}^{2+}$ or $\text{Ca}^{2+}$ Probably present	Barium ions react with sulphate ions to form insoluble barium sulphate. $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$
	Add ammonium oxalate solution followed by dilute ethanoic acid	White precipitate soluble in ethanoic acid	$\text{Ba}^{2+}$ present	Barium ions react with oxalate ions to form insoluble barium oxalate. $\text{Ba}^{2+}(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}) \rightarrow \text{BaC}_2\text{O}_4(\text{s})$ Barium oxalate is soluble in ethanoic acid.

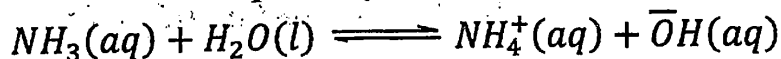
$Ba^{2+}$	Add potassium chromate(VI) solution followed by sodium hydroxide solution/ethanoic acid	Yellow precipitate insoluble in sodium hydroxide/ethanoic acid.	$Ba^{2+}$ confirmed present	Barium ions react with chromate ions to form insoluble barium chromate. $Ba^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow BaCrO_4(s)$ Note; Barium chromate is however soluble in nitric acid to form a yellow solution of chromic acid and barium nitrate
	$BaCrO_4(s) + 2HNO_3(aq) \rightarrow H_2CrO_4(aq) + Ba(NO_3)_2(aq)$			

**Qn.** When ammonia solution is added to magnesium chloride solution, a white precipitate insoluble in excess is formed but when the same solution is added to calcium chloride solution, there is no observable change.

Magnesium ions react with hydroxyl ions to form insoluble magnesium hydroxide. This is because the solubility product of magnesium hydroxide is exceeded.



Ammonia is a weak base which partially ionises to form few hydroxyl ions



The concentration of the hydroxyl ions formed from the weak ammonia base is low for the ionic product of calcium hydroxide to exceed its solubility product. Therefore, no precipitation occurs.

Name a reagent that can be used to distinguish between the following pairs of ions;

- (i)  $Mg^{2+}$  and  $Ca^{2+}$
- (ii)  $Ca^{2+}$  and  $Ba^{2+}$
- (iii)  $Mg^{2+}$  and  $Ba^{2+}$

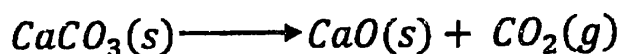
## MANUFACTURE OF CEMENT

### Raw materials

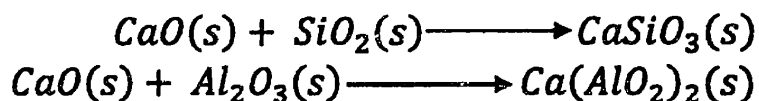
Name	Formula
Limestone	$CaCO_3$
Clay	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$
Gypsum	$CaSO_4 \cdot 2H_2O$

Portland cement is a mixture of calcium silicates and calcium aluminates. Limestone and clay containing aluminosilicates is crushed into fine powder. The fine powder is then mixed with water and allowed to flow down a rotating cylinder in which it is strongly heated.

The limestone is decomposed by the heat to form calcium oxide and carbon dioxide.



The calcium oxide then reacts with aluminium oxide and silicon(IV) oxide in the clay to form lumps which are a mixture calcium aluminates and calcium silicates respectively

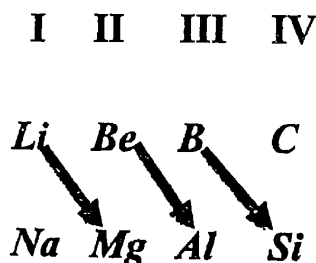


The product is then crushed to form cement as a fine powder

Gypsum is then added to slow the reaction between cement and water.

### DIAGONAL RELATIONSHIP

There is a marked resemblance between the following pairs of elements in the Periodic Table



This relationship is called the diagonal relationship and it occurs for the pairs of elements

- Lithium and magnesium
- Beryllium and aluminium
- Boron and silicon

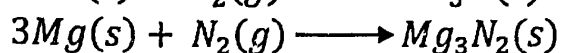
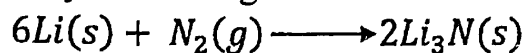
A diagonal relationship is the similarity in properties of elements in Period 2 and their adjacent diagonally opposite neighbours in Period 3 of the Periodic Table.

The reasons as to why lithium resembles magnesium are because;

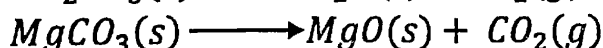
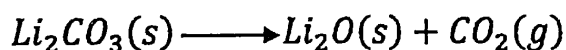
- Both lithium and magnesium have almost similar atomic radii
- Both lithium and magnesium have similar electronegativity
- Both lithium ion and magnesium ion have similar polarising power
- Both lithium ion and magnesium ion have almost similar standard electrode potential

*Lithium resembles magnesium in the following properties;*

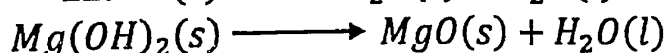
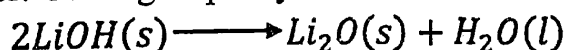
1. They both combine directly with nitrogen to form nitrides



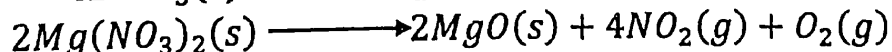
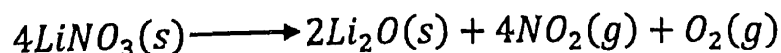
2. Both react with oxygen to form normal oxides only. Other group I elements can form peroxides.
3. Both lithium carbonate and magnesium carbonate decompose on heating to form oxides and carbon dioxide. Other group I carbonates do not decompose on heating



4. Both lithium hydroxide and magnesium hydroxide decompose on heating to form oxides and water. Other group I hydroxides do not decompose on heating.



5. Both lithium nitrate and magnesium nitrate decompose on heating to form oxides, nitrogen dioxide and oxygen. Other group I nitrates form nitrites and oxygen on decomposition.



6. Both lithium and magnesium react with carbon to form ionic carbides
7. Both lithium hydroxide and magnesium hydroxide are weak bases.
8. All phosphates, carbonates and fluorides of both lithium and magnesium are insoluble in water

The reasons as to why beryllium resembles aluminium are because;

- Both beryllium and aluminium have almost the same atomic radius
- Both beryllium and aluminium have the same electronegativity
- Both beryllium ion and aluminium ion have almost similar polarising power
- Both beryllium and aluminium have almost similar standard electrode potentials (i.e. -1.7V and -1.66V respectively)

*Beryllium resembles aluminium in the following properties;*

1. Both beryllium and aluminium react with hot concentrated sodium hydroxide to form beryllate and aluminate respectively. Other group II elements do not react with sodium hydroxide
2. Both beryllium oxide and aluminium oxide are amphoteric. Other group II oxides are basic
3. Both beryllium hydroxide and aluminium hydroxide are amphoteric. Other group II hydroxides are basic
4. Both beryllium chloride and aluminium chloride are covalent. Other group II chlorides are ionic
5. Both beryllium chloride and aluminium chloride dimerise in vapour phase
6. Both beryllium and aluminium are rendered passive by concentrated nitric acid
7. Both form polymerised covalent hydrides
8. Both beryllium carbide and aluminium carbide form methane on hydrolysis

Boron resembles silicon because;

- both boron and silicon have the same electronegativity
- both boron and silicon have almost similar atomic radii.

*Boron resembles silicon in the following properties;*

1. Both boron and silicon form acidic oxides
2. Both boron and silicon form covalent compounds
3. Both silicon tetrahydride and boron trihydride are hydrolysed to form acidic solutions
4. Both silicon tetrachloride and boron trichloride are hydrolysed to form hydrogen chloride/ hydrochloric acid
5. Both silicon and boron react with hot concentrated sodium hydroxide to form silicate and metaborate ion respectively and hydrogen
6. Both silicon tetrafluoride and boron trifluoride are hydrolysed to form acidic solutions.

## USES OF GROUP II COMPOUNDS

1. A suspension of magnesium hydroxide in water is used in medicine as an antacid.
2. Calcium hydroxide is used in the Solvay process for making sodium carbonate, making builders' mortar, making white wash, bleaching powder, neutralising acidic soil, sugar refining and for softening hard water
3. Strontium hydroxide may be used instead of calcium hydroxide in sugar refining; it is more efficient
4. Anhydrous Calcium chloride is used in the laboratory as a drying agent
5. Barium chloride is used in detection of sulphates
6. Limestone (a natural form of calcium carbonate) is used in making quick lime, cement, glass, and sodium carbonate, in iron extraction and as building stones.
7. Purified calcium carbonate is used in tooth pastes and metal polishes
8. Barium carbonate is added in making the glass of television tubes to prevent exposure to X-rays.
9. Calcium nitrate is used as a fertiliser
10. Strontium nitrate is used in fireworks to give a crimson flame and barium nitrate to give a green one.
11. Magnesium sulphate is used as a purgative drug, filler in making glazed paper, as a mordant in dyeing textiles.
12. Gypsum is used in manufacture of cement.

## MISCELLANEOUS TOPICAL QUESTIONS

### *Short answer type questions*

1. The table below shows the atomic radii and ionic radii of alkaline earth metals.

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

- (a) Explain what is meant by the term atomic radius. (02 marks)
- (b) The ionic radius in each case is smaller than the atomic radius. Explain (02 marks)
- (c) Explain why atomic radius increases from Beryllium to Barium (02 marks)
- (d) The potassium ion and the calcium ion have the same electronic configurations, yet the potassium ion is larger than the calcium ion. (02 marks)

2. The table below shows the standard electrode potentials of some elements in group II of the Periodic Table.

Element	Mg	Ca	Sr	Ba
Standard electrode potential( $E^\theta$ ) (Volts)	-2.34	-2.87	-2.89	-2.91

- (a) (i) Identify the element which is the most powerful reducing agent. (½ mark)
- (ii) Give a reason for your answer in (a)(i) (01 mark)
- (b)(i) State the trend in the standard electrode potential of the elements. (01 mark)
- (ii) Explain your answer in b (i) above. (2 ½ marks)
3. (a) Beryllium, magnesium, calcium and barium are some of the elements that belong to Group II of the Periodic Table.  
State how the elements react with sulphuric acid and give the conditions for the reactions. (03 marks)
- (b)(i) State how the solubilities of the sulphates of Group II elements vary down the group. (01 mark)
- (ii) Explain your answer in (b) (i) (02 marks)
- (f) Write equation for the reaction of;
- (iii) Beryllium with sodium hydroxide solution. (1 ½ marks)
- (iv) Calcium carbide with water. (1 ½ marks)
4. Write equation(s) for the reaction between each of the following and sodium hydroxide. (06 marks)
- (i) Beryllium
- (ii) Aluminium
- (iii) Beryllium oxide
- (iv) Aluminium oxide
5. The elements beryllium, magnesium, calcium, strontium and barium belong to group II of the Periodic Table.
- (a) Write the general outermost electronic configuration of group II elements in the Periodic Table. (01 mark)
- (b) Explain why;
- (i) the second and the third ionisation energies of magnesium are  $1450 \text{ kJmol}^{-1}$  and  $7730 \text{ kJmol}^{-1}$  respectively. (03 marks)
- (ii) the melting points of chlorides of the elements generally increase from beryllium chloride to barium chloride. (03 marks)

- (c) (i) State one use of barium chloride in the laboratory. (½ mark)  
 (ii) Write an ionic equation to support your answer in (i) (01 mark)
6. The first ionisation energies of some group II elements of the Periodic Table and the melting points of their chlorides are given below.

Element	<i>Mg</i>	<i>Ca</i>	<i>Sr</i>	<i>Ba</i>
First ionisation energy (kJmol <sup>-1</sup> )	738	590	549	505
Melting point of chloride(°C)	708	772	873	967

Explain;

- (i) Why ionisation energy decreases with increasing atomic number. (02 marks)
- (ii) Why melting points of the chlorides of these metals increase with increase in atomic number. (02 marks)
7. State what is observed and write equation for the reaction between the following and water (08 marks)
- (i) Aluminium chloride  
 (ii) magnesium chloride  
 (iii) aluminium hydride  
 (iv) magnesium hydride
8. (a) State three reasons why lithium and magnesium resemble. (1 ½ marks)  
 (b) Mention three properties to show the relationship between lithium and magnesium. (03 marks)
9. (a) What is meant by the term diagonal relationship? (02 marks)  
 (b) State three properties in which Beryllium resembles Aluminium. (03 marks)
- (c) State four properties in which Beryllium behaves differently from other group II elements. (04 marks)
10. The chemical properties of beryllium differ from those of other group II elements but resemble those of Aluminium.
- (a) State the term used to describe the similarities in chemical properties between beryllium and aluminium. (½ mark)
- (b) State three reasons why the properties of beryllium;  
 (i) differ from those of other group II elements. (1 ½ marks)  
 (ii) resemble those of aluminium. (1 ½ marks)

- (c) (i) State what will be observed and write equation for the reaction that takes place when a piece of beryllium metal is dropped into concentrated sodium hydroxide solution. (01 mark)
- (ii) Write equation for the reaction (01 mark)
11. Although Boron is in group (III) of the Periodic Table, it resembles silicon which is in group (IV) in some of its properties.
- (a) State four properties in which Boron resembles silicon. (04 marks)
- (b) Give two reasons why boron resembles silicon. (02 marks)
- 12.(a) Outline a method of preparing each of the following from the stated reagent.
- (i) calcium hydroxide from calcium carbonate. (02 marks)
- (ii) ethyne from calcium carbide (02 marks)
- (b) Explain each of the following statements.
- (i) anhydrous calcium chloride is commonly contaminated with calcium oxide. (03 marks)
- (ii) beryllium carbonate has a lower decomposition temperature calcium carbonate. (02 marks)
- 13.(a) Beryllium, Magnesium, Calcium and Barium are elements in group II of the Periodic Table. Briefly describe how the hydroxides of the elements above react with ;
- (i) sodium hydroxide solution (02 marks)
- (ii) hydrochloric acid (02 marks)
- (b) The table below shows the solubility of group II hydroxides in water at 20°C.

Hydroxide	$Be(OH)_2$	$Mg(OH)_2$	$Ca(OH)_2$	$Sr(OH)_2$	$Ba(OH)_2$
Solubility(g/100g at 20°C)	Insoluble	0.002	0.15	0.9	4.0

- (i) State and explain the trend in solubility of the hydroxides. (3 ½ marks)
- (ii) Different masses of solid calcium hydroxide and barium hydroxide containing the same number of moles were separately shaken with the same volume of water at 25°C. Identify the solution with higher pH value. Give a reason for your answer. (1 ½ marks)

14. Explain each of the following observations.

- (b) The ions  $Na^+$  and  $Mg^{2+}$  have the same electronic configuration, yet the ionic radius of  $Mg^{2+}$  is lower than that of  $Na^+$  (02 marks)
- (c) Although standard electrode potentials of alkali metals and alkaline earth metals become more negative down the groups, the standard electrode potentials of Lithium and beryllium are most negative in the respective groups. (04 marks)
- (d) The melting points of group II elements are higher than the melting points of corresponding group I elements. (03 marks)
- (e) Second ionisation energies of group I elements are higher than second ionisation energies of group II elements. (02 marks)
- (f) Decomposition temperatures of group II carbonates increase from beryllium carbonate to barium carbonate. (02 marks)

*Long answer type questions*

15. Beryllium, magnesium, calcium, strontium and barium belong to group II of the Periodic Table

- (a) Explain the trend in
- (i) electropositivity of the elements (03 marks)
- (ii) melting points (03 marks)
- (b) Describe the reaction of the elements with;
- (i) water (4 ½ marks)
- (ii) sulphuric acid (04 marks)
- (c) Beryllium hydroxide is soluble in aqueous sodium hydroxide whereas magnesium hydroxide does not dissolve. Explain. (04 marks)
- (d) Write equation for the hydrolysis of magnesium carbide. (1 ½ marks)

16. Beryllium is a group II element but behaves differently from other elements.

- (a) State the reasons why beryllium behaves differently from other elements (03 marks)
- (b) The table below shows the temperatures for complete decomposition of group II metal carbonates to the metal oxides at 1 atmosphere.

Carbonate	$BeCO_3$	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
Decomposition temperature ( $^{\circ}C$ )	25	540	900	1290	1360

Explain the trend in thermo stability of the carbonates (2 ½ marks)

- (c) Compare the thermo stability of group II carbonates and carbonates of group II carbonates (02 marks)
- (d) Write a general equation for the reaction of carbonates of group II carbonates with hydrochloric acid. (1 ½ marks)
- (e) Cement, a mixture of calcium silicates and calcium aluminates is a useful substance in the construction industry.
- (i) State the main raw materials used in the manufacture of cement. (03 marks)
- (ii) Describe how cement is made from the raw materials above. (08 marks)
17. (a) Write the outermost electronic configuration of group II elements. (01 mark)
- (b) Describe the reactions of group II elements with:
- (i) water (5 ½ marks)
- (ii) sulphuric acid (7 ½ marks)
- (iii) sodium hydroxide (02 marks)
- (c) Potassium chromate solution was added to barium chloride solution followed by dilute nitric acid drop wise until in excess.
- (i) State what was observed. (02 marks)
- (ii) Write equation(s) for the reaction(s) that took place. (02 marks)
18. A compound Z, whose molecular mass is 142, contains 16.9% magnesium, 33.8% carbon, 45.1% oxygen, and the rest being hydrogen.
- (a) (i) Determine the empirical formula of Z. (02 marks)
- (ii) Work out the molecular formula of Z. (02 marks)
- (b) On heating, Z decomposes to form a white residue, X and a gas Y that forms a yellow precipitate with 2,4-dinitrophenylhydrazine in acidic medium.
- (i) Deduce the chemical formula of Z. (01 mark)
- (ii) Identify X and Y. (02 marks)
- (c) Write equation for the reaction that;
- (i) takes place when Z is heated. (1 ½ marks)
- (ii) leads to formation of the yellow precipitate. (01 mark)
- (d) (i) State what will be observed when dilute sulphuric acid is added to X. (02 marks)

(ii) Write equation for the reaction between dilute sulphuric acid and X. (1 ½ marks)

(e) Write;

(i) the mechanism for the reaction in (c)(ii) (04 marks)

(ii) equation(s) for conversion of Y to ethene. (03 marks)

19. Briefly explain the following observations.

(a) The melting points of group II elements decrease down the group whereas that of group VII elements increase down the group. (06 marks)

(b) Beryllium chloride is more soluble in ethanol than in water whereas barium chloride is more soluble in water than in ethanol. (04 marks)

(c) When both sodium and magnesium were burnt in excess air and the products treated with water, there was effervescence of a gas in each case. (05 marks)

(d) Calcium phosphate is sparingly soluble in water. It is less soluble in calcium nitrate solution but more soluble in dilute hydrochloric acid. (04 marks)

(e) When ammonia solution is added to a solution of magnesium sulphate, a white precipitate is formed. However, when ammonia solution is added to the same solution in the presence of ammonium chloride solution, no precipitate is formed. (05 marks)

(f) The atomic radius of group IIA metals increases down the group. (03 marks)

(g) Beryllium hydroxide dissolves in excess sodium hydroxide solution whereas magnesium hydroxide is insoluble in the alkali. (04 marks)

(h) The melting points of group IIA metal chlorides are in the order  $MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2$  whereas the melting points of the oxides are in the reverse order. (05 marks)

# THE CHEMISTRY OF GROUP IV ELEMENTS

## Electronic structures/ configurations

Element	Atomic number	Configuration
C	6	$1s^2 2s^2 2p^2$
Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Ge	32	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
Sn	50	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$
Pb	82	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^2$

From the above electronic configurations, it can be concluded that the outermost electronic configuration of group IV elements is  $ns^2 np^2$ .

### The concept of inert pair effect

The general outermost configuration of group IV elements is  $ns^2 np^2$ .

As atomic radius increases from carbon to lead, the *two outermost ns-electrons* experience increased nuclear attraction due to poor screening by the electrons in the *d* and *f*-orbitals. This makes the *ns*-electrons less available for bonding.

Inert pair effect is therefore the inability of the two outermost *s*-electrons of group IV atoms to participate in bonding.

### Metallic character

Element	Character
Carbon	Non metal
Silicon	Metalloids
Germanium	
Tin	Metals
Lead	

Metallic character increases from carbon to lead. Carbon is a non-metal; silicon and germanium are semi-metals but silicon being more of a non-metal than a metal and germanium being more of a metal than a non-metal. Tin and lead are weakly electropositive metals.

### Bonding and structure

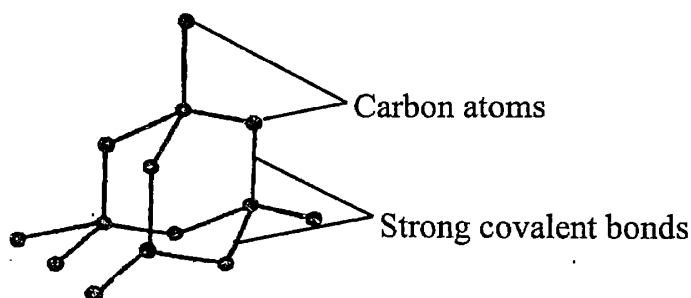
In diamond, each carbon atom is covalently bonded to four other carbon atoms to form a tetrahedral structure which is continuous to form a giant molecular structure.

In graphite, each carbon atom is covalently bonded to three other carbon atoms to form hexagonal layers of carbon atoms held together by weak Van-der-Waals' forces of attraction.

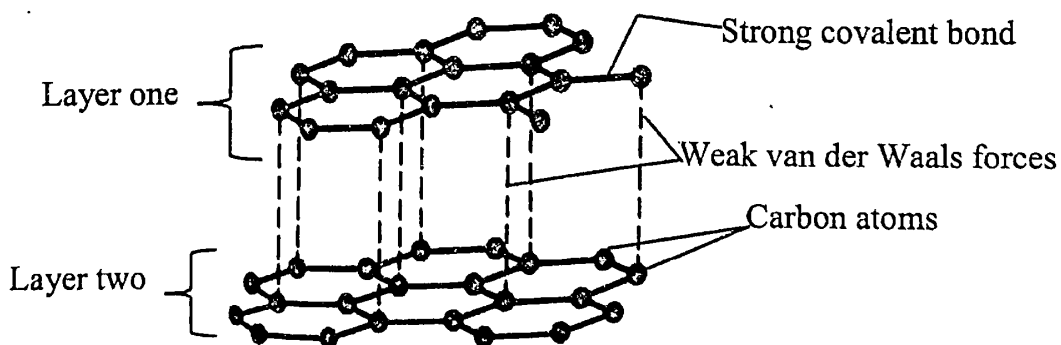
Silicon and germanium have a giant molecular diamond like structure. Each silicon or germanium atom is covalently bonded to four other atoms to form a tetrahedral structure which is continuous to form a giant molecular structure.

Tin and lead have a giant metallic structure in which the atoms are held by strong metallic bonds. However, the metallic bonds in lead are stronger than tin.

*Diamond*



*Graphite*



## VARIATION IN ATOMIC AND PHYSICAL PROPERTIES OF THE ELEMENTS

### 1. Melting point

The table below shows the melting points of group II elements

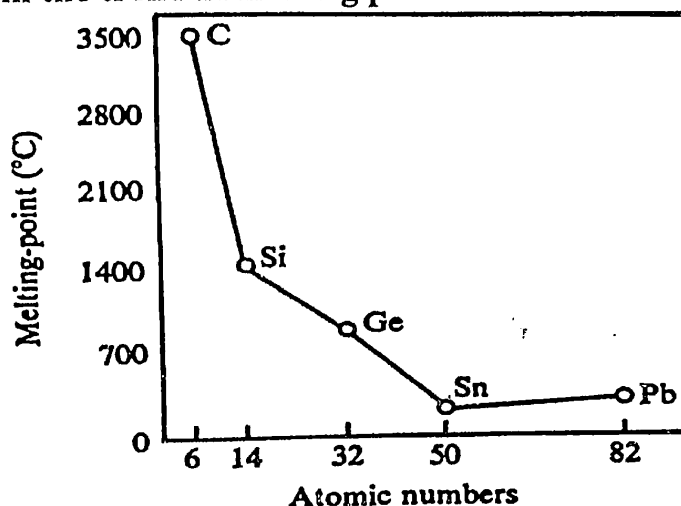
Element	C(diamond)	Si	Ge	Sn	Pb
Atomic number	6	14	32	50	82
Melting points( $^{\circ}\text{C}$ )	3550	1410	937	232	327

(a) Plot a graph of melting point against atomic number

(You are advised to plot own graph. The graph below is just a sketch and not on scale)

(b) Explain the trend in melting points of the elements

(a)



(b) Melting point decreases from carbon to tin and then increases slightly from tin to lead.

Carbon has the highest melting point because it has a large number of short and strong covalent bonds which require high amount of energy to break before it melts.

From carbon to germanium, atomic radius increases, bond length increases, bond strength decreases, and lower amount of energy is required to break the covalent bonds.

The further decrease in melting point from germanium to tin is because of weaker metallic bonds in tin.

Melting point increases slightly from tin to lead due to increase in metallic bond strength as a result of inert pair effect.

## 2. Ionization energy

None of the group IV elements forms ions in the +1 oxidation state. This means that first ionisation energy alone is not helpful. However, some of the elements form ions in the +2 and +4 oxidation state.

Therefore total of first and second ionisation energies can be considered or the total of the first four ionisation energies which both a general trend.

### State and explain the trend in ionization energy of the elements

*Ionization energy generally decreases from carbon to lead.*

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

## 3. Electropositivity

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

*Electropositivity generally increases from carbon to lead because metallic character increases, atomic radius increases and the valence electrons experience a lower nuclear attraction than repulsion hence easily lost.*

## 4. Electrical Conductivity

*Electrical conductivity increases from carbon to lead.*

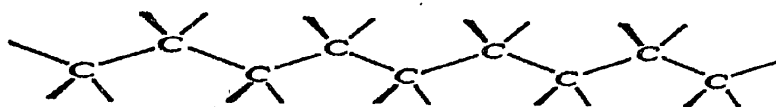
*Graphite is a conductor of electricity although diamond is a non-conductor. Silicon and germanium are semi-conductors. The electrical conductivity of graphite, silicon and germanium increases on heating.*

*Tin and lead are good conductors. The electrical conductivity of tin and lead decreases on heating.*

### The catenation of carbon

Catenation is the ability of an atom to form long chains of identical atoms. Carbon is one of the few elements which can catenate. Carbon atoms are able to link covalently to form stable chains which may contain from two up to very large numbers of carbon atoms. In these chains, only two valencies of carbon are used, leaving other two free to link with other elements or other carbon atoms (forming branched chains). The chains act as a backbone or skeleton on which an enormous number of organic compounds can be formed. For an element to be able to catenate, it must have a valency of at least two and be able to form relatively strong covalent bonds with itself.

Briefly, carbon is able to catenate due to its small atomic radius that enables it to form stable and strong carbon-carbon bonds



### OXIDATION STATES

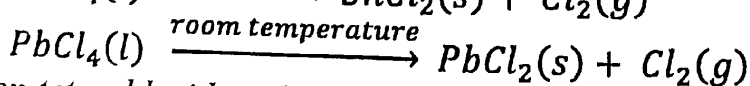
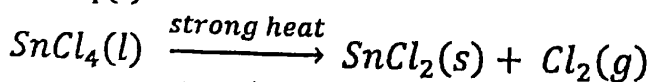
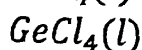
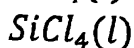
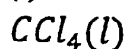
**Qn. (a) State the common oxidation states exhibited by elements in group IV of the Periodic Table.**

**(b) Discuss the stability of the oxidation states in (a) from carbon to lead using the;**

- (i) Chlorides
- (ii) Oxides

*(a) Group IV elements exhibit the +2 and +4 oxidation states*

**(b) (i) Considering the tetrachlorides;**

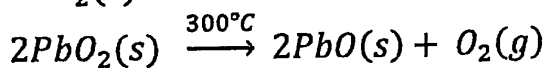
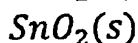
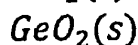
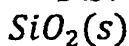
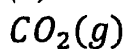


*Carbon tetrachloride, silicon tetrachloride and germanium tetrachloride exist and are stable to heat.*

*Tin(IV) chloride on strong heating decomposes to form tin(II) chloride and chlorine.*

*Lead(IV) chloride is unstable. It decomposes on simple warming or even at room temperature to form lead(II) chloride and chlorine. This means that the +2 oxidation state is more stable than the +4 oxidation state for compounds of lead. Carbon(II) chloride and silicon(II) chloride do not exist but tin(II) chloride and lead(II) chloride exist with increasing stability down the group. Therefore stability of +2 oxidation state increases from carbon to lead whereas stability of +4 oxidation state decreases from carbon to lead.*

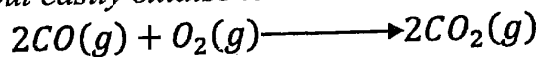
(ii) Considering the dioxides.



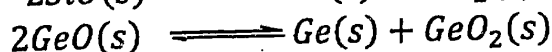
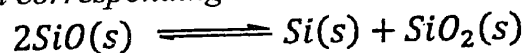
*Carbon dioxide, silicon(IV) oxide, Germanium(IV) oxide and tin(IV) oxide exist and are stable to heat.*

*Lead(IV) oxide exists but decomposes on heating to form lead(II) oxide and oxygen implying that the +2 oxidation state is more stable in lead.*

*Carbon monoxide exists but easily oxidise to more stable carbon dioxide*



*Silicon(II) oxide and germanium(II) oxide are unstable and undergo disproportionation to form corresponding stable dioxides and the elements.*



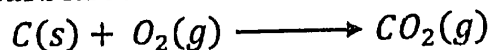
*Therefore stability of +2 oxidation state increases from carbon to lead whereas stability of +4 oxidation state decreases from carbon to lead*

*This variation in stability of the two oxidation states is due to inert pair effect.*

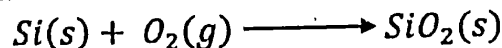
### CHEMICAL PROPERTIES OF THE ELEMENTS

2. Describe the reactions of group IV elements with air.

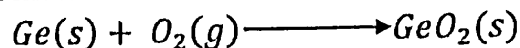
Strongly heated carbon reacts with air to form carbon dioxide.



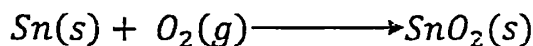
Strongly heated silicon reacts with air to form silicon(IV) oxide.



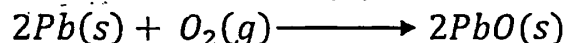
Strongly heated germanium reacts with air to form germanium(IV) oxide.



Strongly heated tin reacts with air to form tin(IV) oxide.

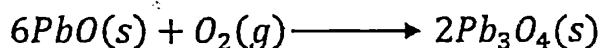


Heated lead burns in air to form lead(II) oxide



*Note:* Lead does not form lead(IV) oxide because its compounds are more stable in the +2 oxidation state.

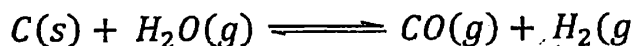
However when heated up to 470°C, the lead(II) oxide is oxidised further to dilead(II) lead(IV) oxide.



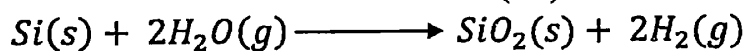
### 3. Describe the reactions and conditions under which group IV elements react with water

Carbon, silicon, germanium and tin do not react with cold water

Red hot carbon reacts slowly and reversibly with steam to form carbon monoxide and hydrogen. The gaseous mixture of carbon monoxide and hydrogen is called water gas

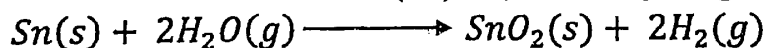


Red hot silicon reacts with steam to form silicon(IV) oxide and hydrogen.

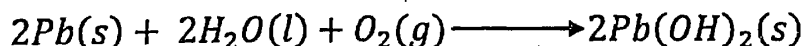


Germanium does not react with water under any condition.

Red hot tin reacts with steam to form tin(IV) oxide and hydrogen.



Lead reacts with soft water containing dissolved oxygen to form lead(II) hydroxide.



### 4. Describe how group IV elements react with;

(a) dilute acids

(b) concentrated acids

(a) dilute acids

(i) *Dilute hydrochloric acid.*

Carbon, silicon and germanium do not react with dilute hydrochloric acid.

Tin reacts with cold dilute hydrochloric acid to form tin(II) chloride and hydrogen gas.



Lead also reacts slowly with dilute hydrochloric acid and the reaction stops due to formation of insoluble lead(II) chloride.

**(ii) Dilute sulphuric acid**

Carbon, silicon and germanium **do not react** with dilute sulphuric acid.

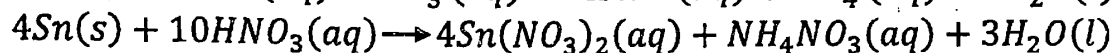
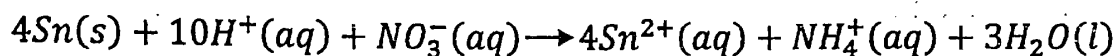
Tin **does not react** with sulphuric acid.

Lead reacts **slowly** with **dilute sulphuric acid** and the reaction stops due to formation of insoluble lead(II) sulphate.

**(iii) Dilute nitric acid**

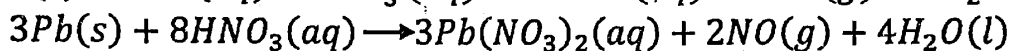
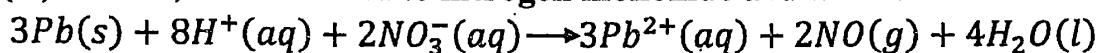
Carbon, silicon and germanium **do not react** with dilute nitric acid

Cold dilute nitric acid oxidises tin to tin(II) nitrate, itself reduced to ammonium nitrate and water.



*C.f Fe and Zn*

Dilute/ moderately concentrated/ half concentrated nitric acid oxidises lead to lead(II) nitrate, itself reduced to nitrogen monoxide and water.

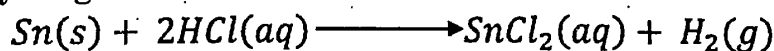


**(b) concentrated acids**

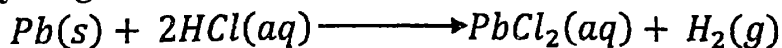
**(i) concentrated hydrochloric acid.**

Carbon, silicon and germanium **do not react** with concentrated hydrochloric acid.

Tin reacts vigorously with **hot concentrated hydrochloric acid** to form tin(II) chloride and hydrogen.

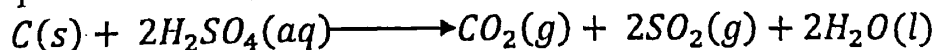


Lead also reacts with **boiling concentrated hydrochloric acid** to form lead(II) chloride and hydrogen.



**(ii) concentrated sulphuric acid**

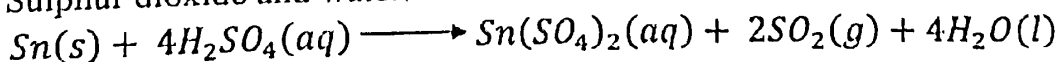
Hot concentrated sulphuric acid oxidises carbon to carbon dioxide and itself reduced to Sulphur dioxide and water.



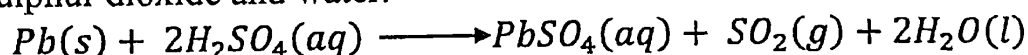
Silicon **does not react** with concentrated sulphuric acid

Germanium **does not react** with concentrated sulphuric acid.

Hot concentrated sulphuric acid oxidises tin to tin(IV) sulphate and itself reduced to Sulphur dioxide and water.

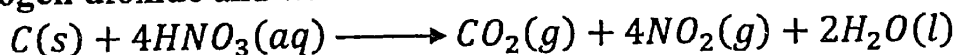


Hot concentrated sulphuric acid oxidises lead to lead(II) sulphate and itself reduced to Sulphur dioxide and water.



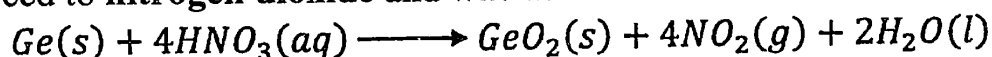
(iii) *concentrated nitric acid*

Hot concentrated nitric acid oxidises carbon to carbon dioxide and itself reduced to nitrogen dioxide and water

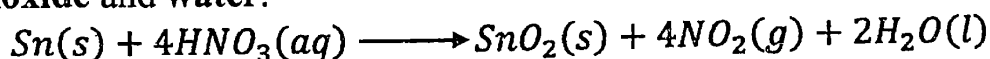


Silicon does not react with concentrated nitric acid

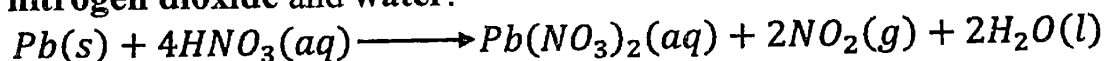
Germanium is oxidised by hot concentrated nitric acid to germanium(IV) oxide and itself reduced to nitrogen dioxide and water.



Tin is oxidised by hot concentrated nitric acid to tin(IV) oxide and itself reduced to nitrogen dioxide and water.



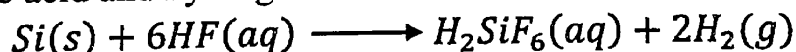
Lead is oxidised by hot concentrated nitric acid to lead(II) nitrate and itself reduced to nitrogen dioxide and water.



**Other acids.**

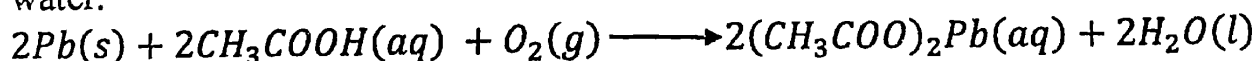
(i) *hydrofluoric acid*

Silicon is the only element that reacts with hydrofluoric acid to form hexafluorosilicic acid and hydrogen.



(ii) *ethanoic acid*

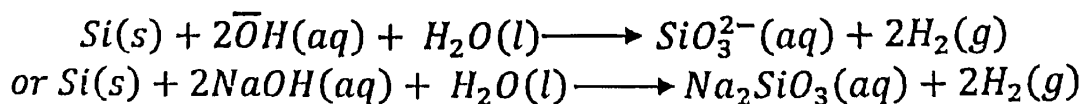
Lead reacts with ethanoic acid in presence of air to form lead(II) ethanoate and water.



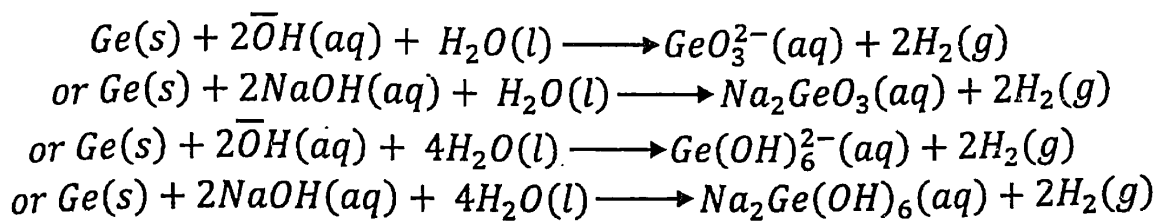
**5. Describe the reaction of group IV elements with dilute and concentrated sodium hydroxide.**

Carbon does not react with dilute or concentrated sodium hydroxide solution.

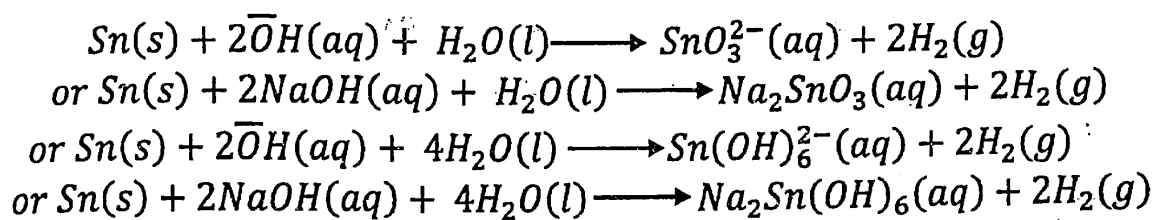
Silicon reacts with both dilute and hot concentrated sodium hydroxide to form sodium silicate and hydrogen gas



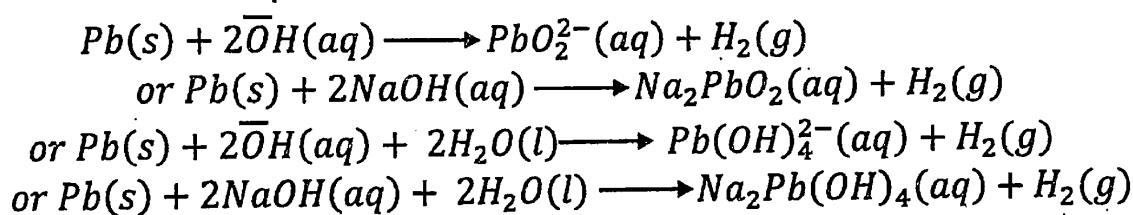
Germanium reacts with hot concentrated sodium hydroxide to form sodium germate(IV) and hydrogen gas



Tin reacts with hot concentrated sodium hydroxide to form sodium stannate(IV) and hydrogen gas



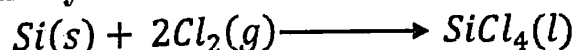
Lead reacts with hot concentrated sodium hydroxide to form sodium plumbate(II) and hydrogen gas



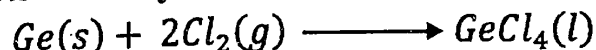
## 6. Describe the reactions of group IV elements with chlorine

Carbon does not react with chlorine.

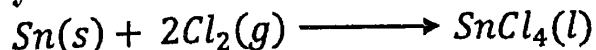
Heated silicon reacts with dry chlorine to form silicon tetrachloride.



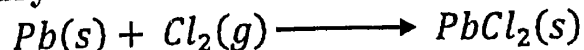
Heated germanium reacts with dry chlorine to form germanium(IV) chloride.



Heated tin reacts with dry chlorine to form tin(IV) chloride.

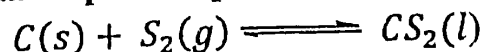


Heated lead reacts with dry chlorine to form lead(II) chloride.

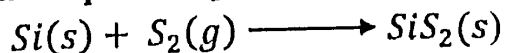


## 7. Discuss the reactions of group IV elements with sulphur

Heated carbon reacts with sulphur vapour to form carbon disulphide

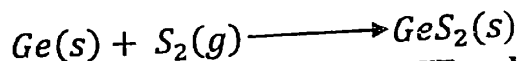


Heated silicon reacts with sulphur vapour to form silicon(IV) sulphide

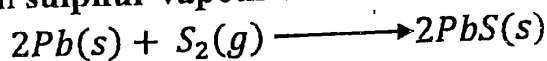
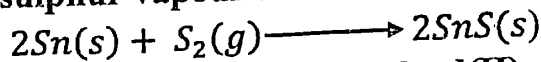


Heated germanium reacts with sulphur vapour to form germanium(IV) sulphide

Heated tin reacts with sulphur vapour to form tin(II) sulphide



Heated lead reacts with sulphur vapour to form lead(II) sulphide



### COMPOUNDS OF GROUP IV ELEMENTS THE DIOXIDES

Formula of the oxide	$\text{CO}_2$	$\text{SiO}_2$	$\text{GeO}_2$	$\text{SnO}_2$	$\text{PbO}_2$
Physical state	Gas	Solids			
Bonding and structure	Simple molecular	Giant covalent	Giant covalent	Giant ionic	Giant ionic

#### (a) Structure and bonding

Carbon dioxide has a simple molecular structure with discrete molecules held by weak Van der Waals' forces.

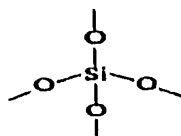
Silicon dioxide and germanium dioxide have giant covalent structures with a 3-dimensional network of strong covalent bonds.

Tin(IV) oxide and lead(IV) oxide have giant ionic structures held by strong ionic bonds.

**Qn.** Briefly explain why carbon dioxide is a gas whereas silicon(IV) oxide is a solid at room temperature.

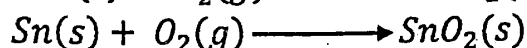
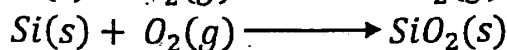
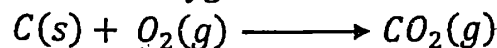
*Carbon dioxide is non-polar. It has discrete molecules with a simple molecular structure held by weak van der Waals forces of attraction which are easily overcome at room temperature keeping them far apart from each other.*

*However, in silicon(IV) oxide, each silicon atom is covalently bonded to four oxygen atoms to form a tetrahedral structure which is continuous to form a giant molecular structure with very many strong covalent bonds that keep its molecules very close to each other.*

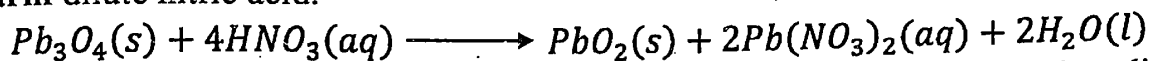


(b) With relevant equations, describe how the dioxides of Group IV elements can be formed.

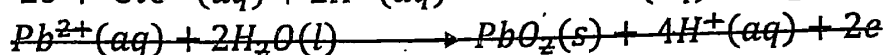
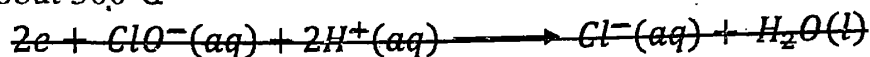
Carbon(IV) oxide, silicon(IV) oxide, germanium(IV) oxide and tin(IV) oxide can be formed by heating the elements in oxygen



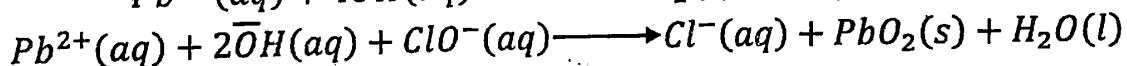
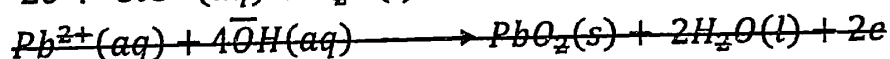
Lead(IV) oxide is formed by the reaction between dilead(II) lead(IV) oxide with warm dilute nitric acid.



It can also be prepared by heating a mixture of lead(II) nitrate and sodium chlorate(I) at about 300°C



Lead(IV) oxide can also be prepared by heating a mixture of lead(II) nitrate, calcium chlorate(I) and calcium hydroxide.



(c) The table below shows the melting points of group IV dioxides.

Explain the trend in melting points of the oxides

Oxide	CO <sub>2</sub>	SiO <sub>2</sub>	GeO <sub>2</sub>	SnO <sub>2</sub>	PbO <sub>2</sub>
Melting point of oxide(°C)	-56.5	1700	1116	1827	752

Carbon dioxide has the lowest melting point because it has a simple molecular structure with discrete molecules held by weak Van der Waals forces.

Silicon dioxide and germanium dioxide have giant covalent structures with a 3-dimensional network of strong covalent bonds. However, germanium dioxide has a lower melting point than silicon dioxide because germanium has a bigger atomic radius making the covalent bonds in germanium(IV) oxide longer and weaker than those in silicon(IV) oxide.

*Tin(IV) oxide and lead(IV) oxide have giant ionic structures held by strong ionic bonds. However, lead(IV) oxide has a lower melting point than tin(IV) oxide because the lead(IV) ion has a bigger ionic radius than the tin(IV) ion hence weaker ionic bonds than those in tin(IV) oxide.*

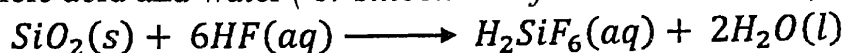
**(d) Discuss the reactivity of the above oxides with**

- (i) dilute and concentrated acids**
- (ii) dilute and concentrated alkalis**

**(i) reaction with dilute acids.**

**Carbon dioxide, germanium(IV) oxide, tin(IV) oxide and lead(IV) oxide do not react with dilute acids.**

Only silicon (IV) oxide reacts with dilute hydrofluoric acid to form hexafluorosilicic acid and water (*or silicon tetrafluoride and water*)

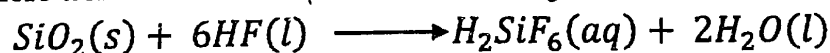


*N.B Silicon dioxide is an acidic oxide hence does not react with other dilute strong acids. However, it reacts with hydrofluoric acid because it is a weak acid the fluorine atom has a very small atomic radius and highly electronegative.*

**reaction with concentrated acids**

**Carbon dioxide, germanium(IV) oxide and tin(IV) oxide do not react with concentrated acids.**

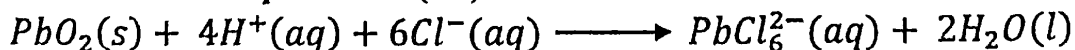
Silicon (IV) oxide reacts with **concentrated hydrofluoric acid** only to form hexafluorosilicic acid and water (*or silicon tetrafluoride and water*)



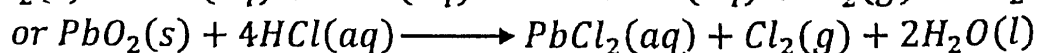
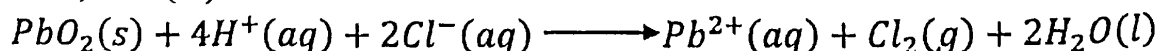
Lead(IV) oxide reacts with **cold concentrated hydrochloric acid** to form lead(IV) chloride, a yellow liquid and water.



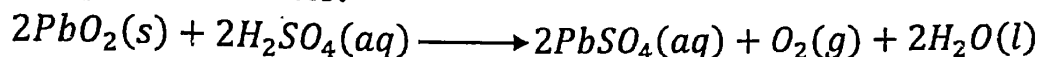
Lead(IV) oxide reacts with **excess cold concentrated hydrochloric acid** to form complex of hexachloroplumbate(IV) ions and water.



Lead(IV) oxide reacts with **hot concentrated hydrochloric acid** to form chlorine, lead(II) chloride and water.

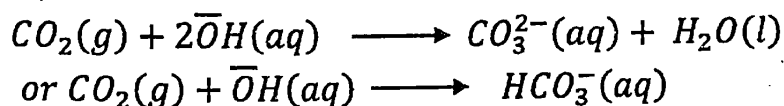


Lead(IV) oxide reacts with **hot concentrated sulphuric acid** to form oxygen, **lead(II) sulphate** and water.



(ii) *reaction with dilute alkalis*

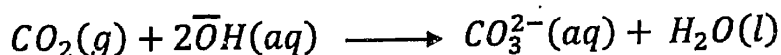
Carbon dioxide reacts with **cold dilute alkalis** to form a **carbonate** and water (or a **hydrogencarbonate**)



Silicon dioxide, germanium(IV) oxide, tin(IV) oxide and lead(IV) oxide **do not react with dilute alkalis**.

*reaction with concentrated alkalis*

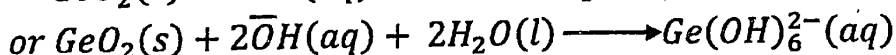
Carbon dioxide reacts with **hot concentrated alkalis** to form a **carbonate** and water



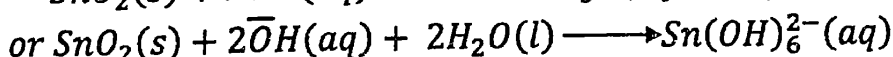
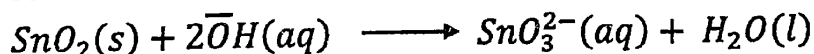
Silicon dioxide reacts with **hot concentrated alkalis** to form a **silicate** and water.



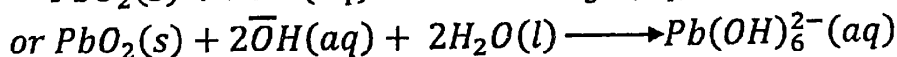
Germanium(IV) oxide reacts with **hot concentrated alkalis** to form a **germate(IV)**.



Tin(IV) oxide reacts with **hot concentrated alkalis** to form a **stannate(IV)**



Lead(IV) oxide reacts with **hot concentrated alkalis** to form a **plumbate(IV)**



### Redox properties of the dioxides

Group IV dioxides are strong oxidising agents. Lead(IV) oxide is the most powerful oxidising agent among them.

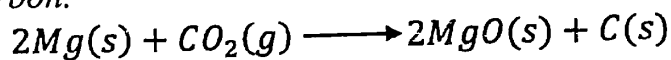
Qn. State what would be observed and explain your observation in each case when;

- (a) A piece of burning magnesium is lowered into a gas jar of dry carbon dioxide.

**Observation;** magnesium continues to burn with a bright white flame forming a white ash and black specks.

**Explanation;**

Magnesium is oxidised by carbon dioxide to magnesium oxide, the carbon dioxide being reduced to carbon.

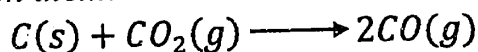


(b) dry carbon dioxide is passed over red hot charcoal

**Observation;** A colourless gas is formed.

**Explanation;**

Carbon is oxidised by carbon dioxide to carbon monoxide

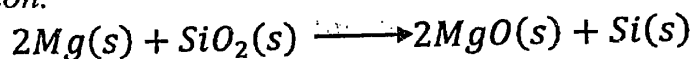


(c) silicon(IV) oxide is heated with magnesium powder

**Observation;** The grey and white solid mixture formed a white ash and grey solid.

**Explanation;**

Magnesium is oxidised by silicon dioxide to magnesium oxide, the silicon dioxide being reduced to silicon.

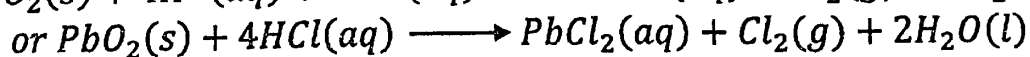


(d) concentrated hydrochloric acid is added to lead(IV) oxide and the mixture heated.

**Observation;** The dark brown solid dissolves forming a colourless solution and bubbles of a greenish yellow gas

**Explanation;**

Lead(IV) oxide oxidises concentrated hydrochloric acid to chlorine and itself reduced to lead(II) ions

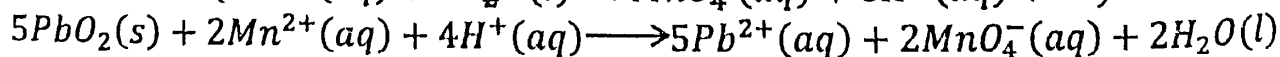
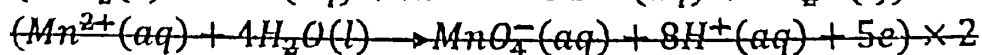
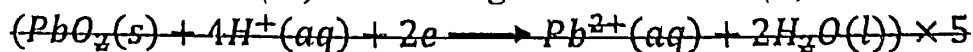


(e) Lead (IV) oxide is added to a solution containing manganese (II) sulphate and concentrated nitric acid and the mixture boiled.

**Observation;** Dark brown solid dissolves and the pale pink solution turns purple.

**Explanation;**

Manganese(II) ions are oxidised by lead(IV) oxide to manganate(VII) ions in acidic medium, the lead(IV) oxide being reduced to lead(II) ions.



DEMYSTIFYING INORGANIC CHEMISTRY BY Joseph Jobs Kayiira, BScED(Hons.CHEM/MTC)

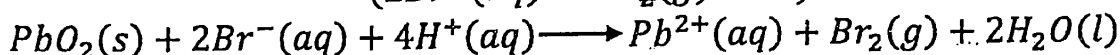
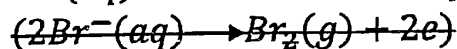
Email;josephkayirab@gmail.com Call 0782601038 WhatsApp 0753247098

(f) Lead (IV) oxide is added to sodium bromide solution followed by dilute nitric acid and the mixture heated.

*Observation; Dark brown solid dissolves to form a colourless solution and reddish brown vapours.*

*Explanation;*

*Bromide ions are oxidised by lead(IV) oxide to bromine, the lead(IV) oxide being reduced to lead(II) ions.*

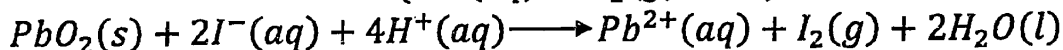
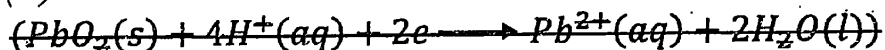


(g) Lead (IV) oxide is added to potassium iodide solution followed by dilute nitric acid and the mixture heated.

*Observation; Dark brown solid dissolves to form a colourless solution and purple vapours.*

*Explanation;*

*Iodide ions are oxidised by lead(IV) oxide to iodine, the lead(IV) oxide being reduced to lead(II) ions.*

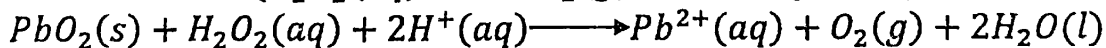
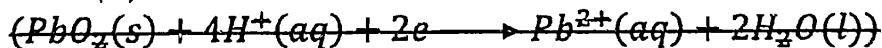


(h) Dilute nitric acid is added to lead(IV) oxide followed by hydrogen peroxide

*Observation; Dark brown solid dissolves forming a colourless solution and bubbles of a colourless gas.*

*Explanation;*

*Hydrogen peroxide is oxidised by lead(IV) oxide to oxygen and the lead(IV) oxide being reduced to lead(II) ions.*

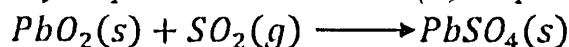


(i) Sulphur dioxide is passed over heated lead(IV) oxide.

*Observation; Dark brown solid forms a white solid*

*Explanation;*

*Lead(IV) oxide is reduced by sulphur dioxide to lead(II) sulphate .*



### THE MONOXIDES

Formula of the oxide	<i>CO</i>	<i>SiO</i>	<i>GeO</i>	<i>SnO</i>	<i>PbO</i>
Physical state	<i>Colourless gas</i>	Brown powder but unstable, readily disproportionates and known only to exist as a gas at 2300°C	A yellow solid but unstable, readily disproportionates	<i>Bluish-black solid</i>	<i>Yellow/orange powder</i>
Nature	<i>Neutral, but slightly acidic</i>	Neutral		<i>Amphoteric</i>	
Bonding and structure	<i>Simple molecular</i>	<i>Simple molecular</i>	<i>Covalent</i>	<i>Giant ionic</i>	<i>Giant ionic</i>

#### (a) Structure and bonding

Carbon monoxide has a **simple molecular structure** with **discrete molecules** held by **weak Van der Waals' forces**.

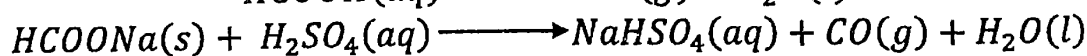
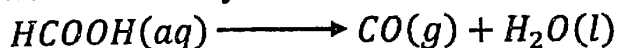
Silicon monoxide also has a **simple molecular structure** with **discrete molecules** held by **weak Van der Waals' forces**.

Germanium(II) oxide is held by **covalent bonds**

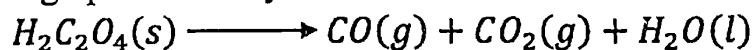
Tin(II) oxide and lead(II) oxide have **giant ionic structures** held by **strong ionic bonds**.

#### (b) With relevant equations, describe how the monoxides of Group IV elements can be formed.

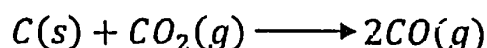
Carbon monoxide is formed by dehydration of methanoic acid with concentrated sulphuric acid. Sodium methanoate may be used instead of methanoic acid.



or carbon monoxide can also be formed by dehydration of oxalic acid with concentrated sulphuric acid and removing the carbon dioxide by passing the gaseous mixture through potassium hydroxide solution.

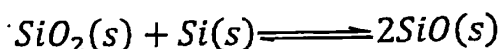


or carbon monoxide can be formed by passing a stream of carbon dioxide over red hot charcoal

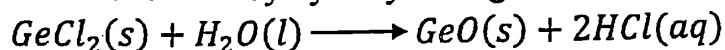


Silicon monoxide is formed when silicon(IV) oxide and silicon are heated in a vacuum at 1527°C. Silicon monoxide vapour is formed and forms a brown powder

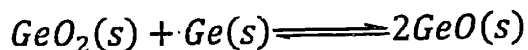
on cooling. However, the brown powder rapidly disproportionates into the dioxide and the metal.



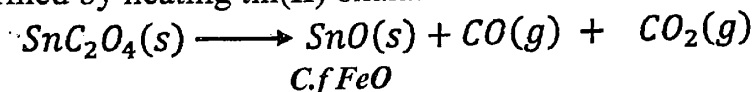
Germanium monoxide is formed by hydrolysis of germanium(II) chloride



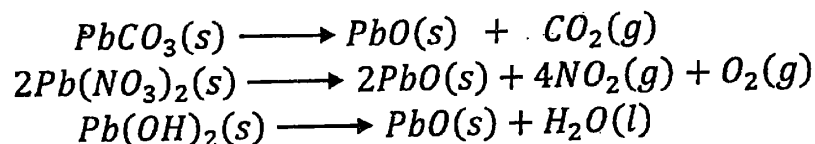
Germanium monoxide can also be formed reduction of germanium(IV) oxide with germanium.



Tin(II) oxide is formed by heating tin(II) oxalate in absence of air.



Lead(II) oxide is formed by heating lead(II) carbonate or lead(II) nitrate or lead(II) hydroxide.



**(c) Discuss the reactivity of the above oxides with**

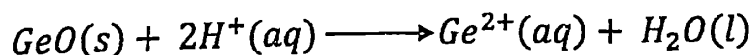
- (i) dilute and concentrated acids**
- (ii) dilute and concentrated alkalis**

**(i) reaction with dilute acids.**

Carbon monoxide is neutral hence **does not react** with dilute acids.

Silicon monoxide is neutral hence **does not react** with dilute acids.

Germanium monoxide reacts with dilute acids to form germanium(II) salts and water.

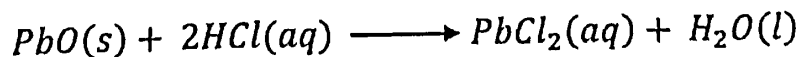


Tin(II) oxide reacts with dilute acid to form tin(II) salts and water.

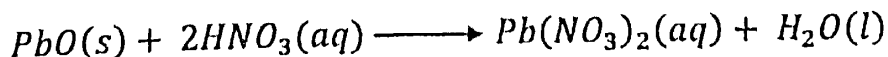


Lead(II) oxide reacts slowly with **cold dilute hydrochloric acid** and **dilute sulphuric acid** and the reactions stop due to formation of **insoluble lead(II) chloride** and **insoluble lead(II) sulphate** respectively.

Lead(II) oxide reacts with **hot dilute hydrochloric acid** to form lead(II) chloride and water.



However, lead(II) oxide reacts with dilute nitric acid to form lead(II) nitrate and water.

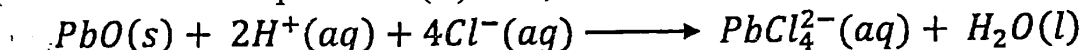


**reaction with concentrated acids**

Carbon monoxide **does not** react with concentrated acids.

Silicon monoxide **does not** react with concentrated acids

Lead(II) oxide reacts with **excess concentrated hydrochloric acid** to form complex of tetrachloroplumbate(II) ions; a colourless solution and water.

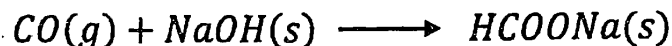


**(ii) reaction with dilute alkalis**

The monoxides **do not** react with dilute alkalis.

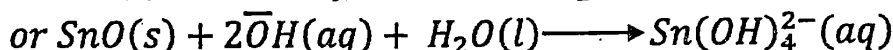
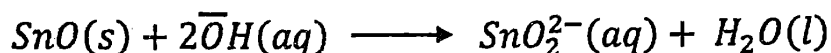
**reaction with concentrated alkalis**

Carbon monoxide reacts with fused sodium hydroxide to form sodium methanoate

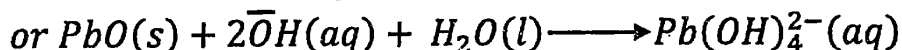
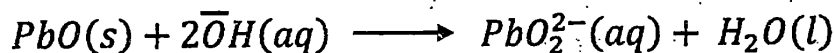


Silicon(II) oxide **does not** react with concentrated alkalis

Tin(II) oxide reacts with **hot concentrated alkalis** to form stannate(II) ions



Lead(II) oxide reacts with **hot concentrated alkalis** to form a plumbate(II)



**Redox properties of the monoxides**

Carbon monoxide is a reducing agent. It is oxidised in most of its reactions to carbon dioxide.

Tin(II) oxide and lead(II) oxide can be reduced by carbon, carbon monoxide or hydrogen.

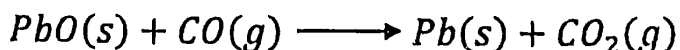
**Qn. State what would be observed and explain your observation in each case when;**

(a) carbon monoxide is passed over heated lead(II) oxide.

*Observation; reddish brown hot solid formed a grey residue.*

*Explanation;*

*Carbon monoxide reduces lead(II) oxide to lead, itself oxidised to carbon dioxide*



(b) carbon monoxide is passed over heated copper(II) oxide.

(c) carbon monoxide is passed over heated iron(III) oxide.

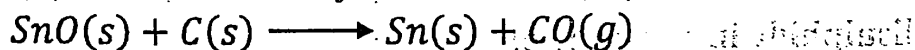
(d) A mixture of carbon and lead(II) oxide is heated.

(e) A mixture of carbon and tin(II) oxide is heated.

**Observation;** the black solid mixture formed a silvery white solid.

**Explanation;**

Carbon reduces tin(II) oxide to tin, itself oxidised to carbon monoxide.

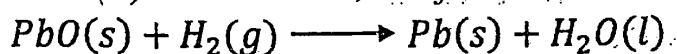


(f) dry hydrogen is passed over heated lead(II) oxide.

**Observation;** the reddish brown hot solid formed a grey solid and a colourless condensate.

**Explanation;**

Hydrogen reduces lead(II) oxide to lead, itself oxidised to water.



(g) dry hydrogen is passed over heated tin(II) oxide.

### THE TETRACHLORIDES

Formula of the chloride	$\text{CCl}_4$	$\text{SiCl}_4$	$\text{GeCl}_4$	$\text{SnCl}_4$	$\text{PbCl}_4$
Physical state	Colourless liquids				Yellow liquid
Bonding	All covalent				
Volatility	All non-volatile				
Shape	All tetrahedral				

#### (a) Structure and bonding

All the molecules are tetrahedral, covalent and liquids at room temperature. Although their bonds are polar, the molecules as a whole are non-polar due to their symmetry.

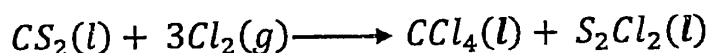
**Qn.** Carbon tetrachloride is non-polar yet the carbon-chlorine bond is polar. Explain this observation.

*Chlorine is more electronegative than carbon. The chlorine atom therefore tends to attract the bonding electrons towards itself hence acquires a partial negative charge ( $\delta^-$ ) and the carbon atom gains a partial positive charge ( $\delta^+$ ). This makes the carbon-chlorine bond polar.*

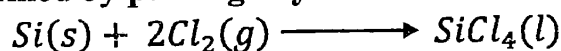
*However, the whole molecule is non-polar because it has a tetrahedral structure in which the chlorine atoms are symmetrically distributed about the carbon atom. This creates equal and opposite dipole moments in all directions that cancel out making the resultant dipole moment zero.*

(b) With relevant equations, describe how each of the above tetrachlorides is formed.

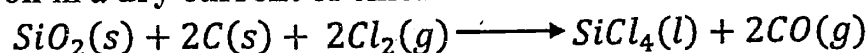
Carbon tetrachloride is formed by the reaction between chlorine and carbon disulphide in presence of iron(III) chloride or aluminium(III) chloride catalyst at 30°C



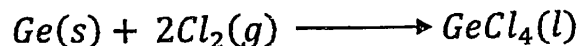
Silicon tetrachloride is formed by passing dry chlorine over heated silicon.



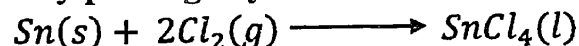
Silicon(IV) chloride can also be prepared by heating a mixture of silicon(IV) oxide and carbon in a dry current of chlorine.



Germanium tetrachloride is formed by passing dry chlorine over heated germanium.



Tin tetrachloride is formed by passing dry chlorine over heated tin.



Heated lead however reacts with dry chlorine to form a more stable lead(II) chloride but not lead(IV) chloride. Therefore this method cannot be used to form lead(IV) chloride.

Lead(IV) chloride is therefore formed by the reaction between lead(IV) oxide and cold concentrated hydrochloric acid.



(c) The table below shows the boiling points of the tetrachlorides of group IV elements.

Tetrachloride	$CCl_4$	$SiCl_4$	$GeCl_4$	$SnCl_4$	$PbCl_4$
Boiling point(°C)	77	58	83	114	Decomposes

Explain the trend in variation of the melting points of the chlorides.

Boiling point decreases from carbon tetrachloride to silicon tetrachloride and then increases to tin tetrachloride.

Lead tetrachloride decomposes even at room temperature.

The liquids are held by van der Waals' forces of attraction whose strength increases with increase in molecular size and increase in the total number of electrons in the molecules that can be polarised. Silicon tetrachloride has a lower boiling point than carbon tetrachloride because Silicon is much less

*electronegative than carbon and the silicon tetrachloride molecules have greater repulsive forces than those of carbon tetrachloride.*

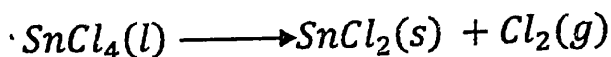
*Lead(IV) chloride is unstable. It decomposes even at room temperature to form more stable lead(II) chloride and chlorine because lead compounds are more stable in +2 oxidation state than the +4 oxidation state due to increase in inert pair effect.*

**(d) Discuss the trend in thermal stability of the tetrachlorides**

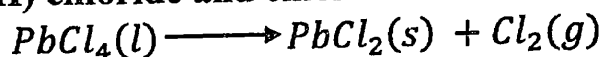
Thermal stability decreases from carbon tetrachloride to lead tetrachloride.

Carbon tetrachloride, silicon tetrachloride and Germanium tetrachloride are thermally stable hence do not decompose.

Tin tetrachloride decomposes on strong heating to form tin(II) chloride and chlorine.



Lead tetrachloride decomposes slowly at room temperature and rapidly when heated to form lead(II) chloride and chlorine.



This decrease in thermal stability is because atomic radius increases from the carbon atom to lead atom, element-chlorine bond length increases and bond strength decreases. Hence a decreasing amount of energy is required to break the increasingly weakening bonds.

**Hydrolysis of the tetrachlorides**

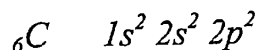
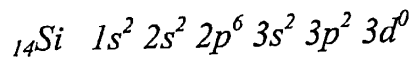
Apart from tetrachloromethane, other tetrachlorides are easily hydrolysed (*react with water*) to form dioxides (white solids) apart from lead(IV) oxide which forms a brown solid. This is the same reason why the tetrachlorides fume in moist air.

This is due to presence of empty d- orbitals that accommodate lone pairs of electrons from the oxygen atom in water.

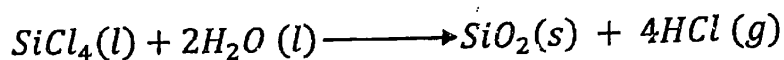
Note; From the electronic configurations;

$_{14}\text{Si}$ -  $1s^2 2s^2 2p^6 3s^2 3p^2$ ,  
 $_{32}\text{Ge}$ -  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$   
 $_{50}\text{Sn}$ -  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$  and  
 $_{82}\text{Pb}$ -  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5d^{10} 6s^2 6p^2$ : Silicon, germanium, tin and lead have empty 3d orbitals, 4d orbitals, 5d orbitals, and 6d orbitals responsible for hydrolysis respectively.

Explain why silicon (IV) chloride fumes in moist air and also forms a white solid but carbon(IV) chloride does not.

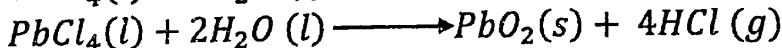
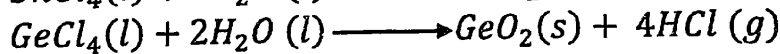
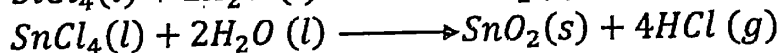
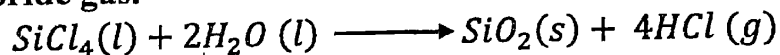


The silicon atom in silicon tetrachloride has an empty 3d-orbital to accommodate lone pairs of electrons from the oxygen atom in water hence silicon tetrachloride easily undergoes hydrolysis to form silicon(IV) oxide and hydrogen chloride. However, the carbon atom in carbon tetrachloride lacks an empty d-orbital hence does not undergo hydrolysis.



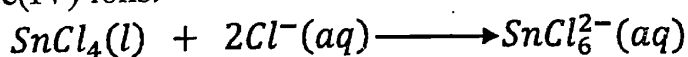
(a) Discuss the reactions of tetrachlorides of group IV elements with water. Carbon tetrachloride does not react with water.

Other tetrachloride reacts with water to form corresponding dioxides and hydrogen chloride gas.

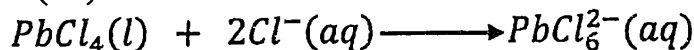


### (b) reaction with acids

Tin(IV) chloride reacts with cold concentrated hydrochloric acid to form hexachlorostannate(IV) ions.



Lead(IV) chloride reacts with cold concentrated hydrochloric acid to form hexachloroplumbate(IV) ions



Qn. When cold concentrated hydrochloric acid was added to lead(IV) oxide, a yellow liquid was formed. On addition of excess hydrochloric acid, a yellow solution was formed. Explain this observation.

## THE DICHLORIDES

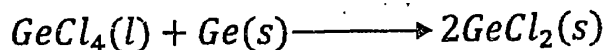
The dichlorides of carbon and silicon do not exist due to decrease in stability of the +2 oxidation state on ascending the group.

Only germanium(II) chloride, tin(II) chloride and lead(II) chloride exist

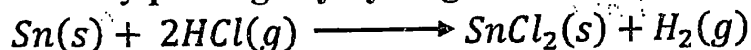
Formula of the chloride	<i>GeCl<sub>2</sub></i>	<i>SnCl<sub>2</sub></i>	<i>PbCl<sub>2</sub></i>
Physical state	<i>All solids</i>		
Bonding	<i>Mainly covalent</i>	<i>Mainly covalent</i>	<i>Mainly Ionic</i>
Shape	<i>V-shaped in vapour phase</i>		

(a) With relevant equations, describe how each of the above dichlorides is formed.

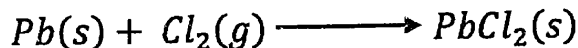
Germanium(II) chloride is formed by passing germanium(IV) chloride vapour over heated germanium.



Tin(II) chloride is formed by passing dry hydrogen chloride over heated tin.



Lead(II) chloride is formed by passing dry chlorine or dry hydrogen chloride over heated lead.

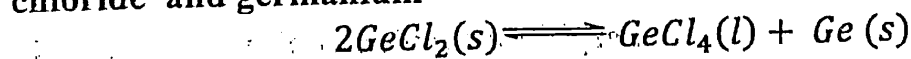


(b) The melting point of lead(II) chloride is 500°C whereas that of tin(II) chloride is 247°C. Explain this observation.

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

(c) Discuss the thermal stability of the dichlorides

Germanium(II) chloride decomposes on heating to form germanium(IV) chloride and germanium



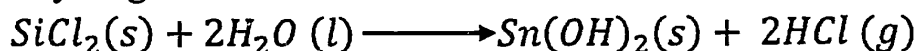
Tin(II) chloride and lead(II) chloride are stable to heat hence do not decompose.

**(d) Discuss the difference in solubility of tin(II) chloride and lead(II) chloride in;**

**(i) water**

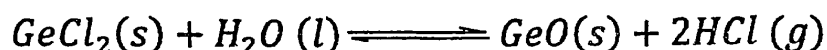
**(ii) concentrated hydrochloric acid**

(i) Tin(II) chloride is **very soluble in cold water** due to hydrolysis to form tin(II) hydroxide and hydrogen chloride.

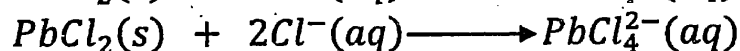
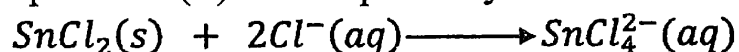


Lead(II) chloride is **sparingly soluble in cold water** because it does not undergo hydrolysis. However, lead(II) chloride is more soluble in hot water.

*Germanium(II) chloride is also hydrolysed by water to form germanium(II) oxide and hydrogen chloride*



(ii) Both tin(II) chloride and lead(II) chloride are soluble in concentrated hydrochloric acid due to formation of soluble complexes of tetrachlorostannate(II) ions and tetrachloroplumbate(II) ions respectively.



### THE HYDRIDES

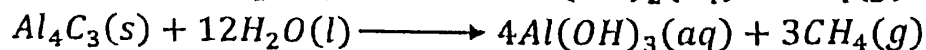
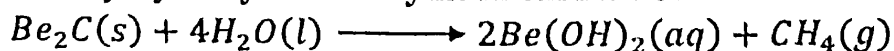
Formula of the hydride	$\text{CH}_4$	$\text{SiH}_4$	$\text{GeH}_4$	$\text{SnH}_4$	$\text{PbH}_4$
Name	<i>Methane</i>	<i>Silane</i>	<i>Germane</i>	<i>Stannane</i>	<i>Plumbane</i>
Physical state	<i>All colourless gases</i>				
Bonding	<i>All covalent</i>				
Structure	<i>All simple molecular</i>				
Shape	<i>All tetrahedral</i>				

**(a) Structure and bonding**

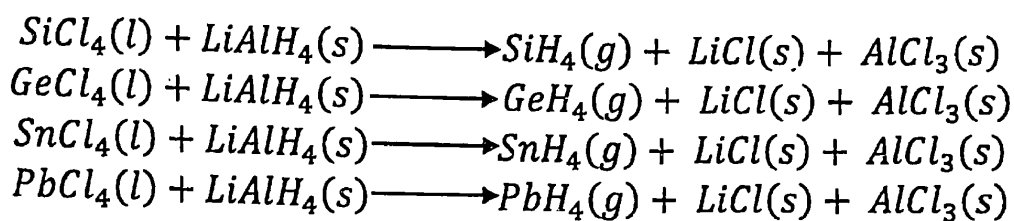
The metals form covalent hydrides with a simple molecular structure, tetrahedral in shape. They are all colourless gases.

**(b) With relevant equations, describe how the hydrides of group IV elements can be formed.**

Methane is formed by hydrolysis of beryllium carbide or aluminium carbide



Silane, Germane, Stannane and Plumbane are formed by reduction of their corresponding tetrachlorides by Lithium aluminium tetrahydride in presence of dry ether at 0 °C



(c) The table below shows the boiling points of the hydrides of group IV elements.

Hydride	$\text{CH}_4$	$\text{SiH}_4$	$\text{GeH}_4$	$\text{SnH}_4$	$\text{PbH}_4$
Boiling point(°C)	-161.5	-111.9	-88	-52	-13

Explain the trend in variation of the melting points of the hydrides.

*Boiling point increases from methane to plumbane.*

*This is because molecules of the hydrides are covalent and held by weak van der Waals' forces of attraction whose strength increases with increase in molecular weight and molecular size.*

(d) The table below shows the decomposition temperatures of the hydrides of group IV hydrides. Explain the trend in thermo stability of the hydrides.

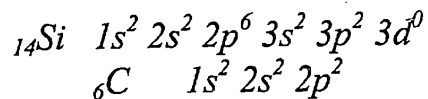
Hydride	$\text{CH}_4$	$\text{SiH}_4$	$\text{GeH}_4$	$\text{SnH}_4$	$\text{PbH}_4$
Decomposition temperature(°C)	800	450	285	150	0

*Since decomposition temperature decreases from methane to Plumbane, thermo stability decreases in the same order. This is because atomic radius increases from the carbon atom to lead atom, effective overlap of orbitals decreases, bond length increases, bond strength decreases from one hydride to the next. Therefore the amount of energy required to break the bonds decreases.*

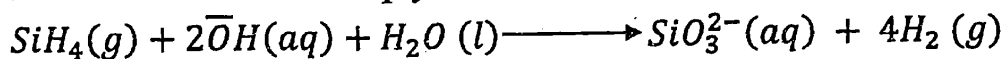
### Hydrolysis of the hydrides

Only silane is immediately hydrolysed by water containing a trace of alkali, but methane and other hydrides are unexpectedly not hydrolysed.

Qn. Explain why methane does not react with water but silane does.



The silicon atom in silicon(IV) hydride has an empty 3d-orbital to accommodate lone pairs of electrons from the oxygen atom in water hence easily undergoes hydrolysis to form silicate ions and hydrogen gas. However, the carbon atom in carbon tetrachloride lacks an empty d-orbital hence does not undergo hydrolysis.

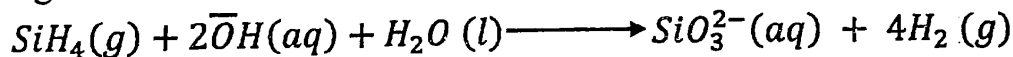


N.B. An alkaline catalyst is required because the Si—H bond is less polar since hydrogen and silicon have almost equal electronegativity.

(a) Discuss the reactions of hydrides of group IV elements with water.

Methane, germane, stannane and plumbane do not react with water

Only silane reacts with water in presence of an alkali to form silicate ions and hydrogen gas



(b) Discuss the reactivity of the above hydrides with

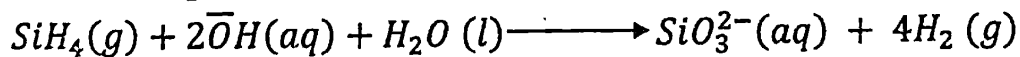
(i) acids

(ii) alkalis

(i) The hydrides do not react with acids

(ii) Methane does not react with alkalis

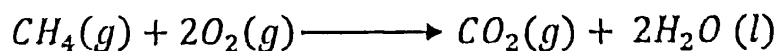
Silane reacts with aqueous alkalis to form silicate ions and hydrogen gas



Germane, stannane and plumbane do not react with alkalis

(c) Describe the combustion of group IV hydrides.

Methane burns in air at temperatures above 500 °C to form carbon dioxide and water.



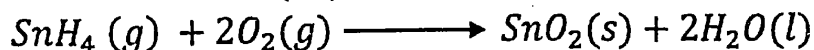
Silane burns spontaneously in air to form silicon dioxide and water.



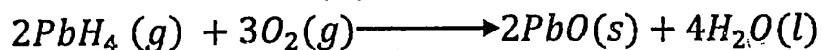
Germane burns in air at an intermediate temperature to form Germanium(IV) oxide and water



Stannane burns in air to form tin(IV) oxide and water



Plumbane burns in air to form lead(II) oxide and water



### RED LEAD

Formular:  $\text{Pb}_3\text{O}_4$

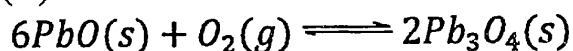
IUPAC name: Dilead(II) lead(IV) oxide

Other names: trilead tetraoxide, lead(II,II, IV) oxide

The red solid is a mixed oxide of lead(II) oxide and lead(IV) oxide in a ratio of 2:1 respectively

#### Preparation

It is prepared by heating lead(II) oxide in air at about  $470^\circ\text{C}$  for several hours.



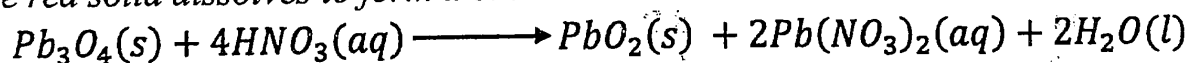
#### Reaction of the mixed oxide with acids

##### (i) Nitric acid

The dilead(II) lead(IV) oxide reacts with warm dilute nitric acid to form lead(IV) oxide, lead(II) nitrate and water. *This reaction is used to prepare lead(IV) oxide.*

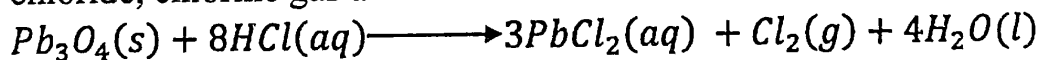
##### Observation:

*The red solid dissolves to form a brown solid and a colourless solution.*



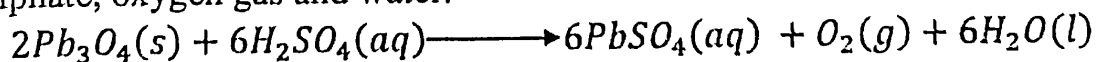
##### (ii) Hydrochloric acid

Dilead(II) lead(IV) oxide reacts with hot concentrated hydrochloric acid to form lead(II) chloride, chlorine gas and water.



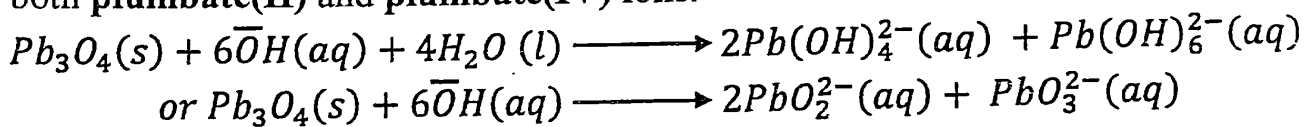
##### (iii) Sulphuric acid

Dilead(II) lead(IV) oxide reacts with hot concentrated sulphuric acid to form lead(II) sulphate, oxygen gas and water.



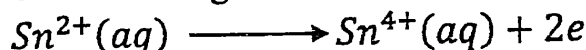
### Reaction with sodium hydroxide.

Dilead(II) lead(IV) oxide reacts with hot concentrated sodium hydroxide to form both plumbate(II) and plumbate(IV) ions.



### Reducing reactions of tin(II) ions

Solutions of tin(II) ions are good reducing agents. During the redox reactions, they are oxidised to tin(IV) ions according to the half-cell reaction below;



However, solutions of tin(II) ions can be reduced by zinc which has a greater negative standard electrode potential than tin

Tin(II) ions reduce each of the following;

- Iron(III) ions to iron(II) ions
- Acidified potassium permanganate solution to manganese(II) ions
- Acidified potassium dichromate solution to chromium(III) ions
- Iodine solution to iodide ions

**Qn. State what would be observed and write equations when tin(II) chloride solution was added to**

- (i) acidified potassium dichromate solution
- (ii) acidified potassium manganate(VII) solution
- (iii) iron(III) chloride solution

### QUALITATIVE ANALYSIS FOR $Pb^{2+}$ AND $Sn^{2+}$ IONS

The deductions given are general and DO NOT depend on any previous tests that could have been done. The tests for tin(II) ions are only required for theory purposes.

ION	TEST	OBSERVATION	DEDUCTION	EXPLANATION
$Pb^{2+}$	Add sodium hydroxide drop wise until in excess	White precipitate soluble in excess to form a colourless solution	$Zn^{2+}, Al^{3+}, Pb^{2+}$ probably present	Lead(II) ions react with hydroxyl ions to form insoluble lead(II) hydroxide. $Pb^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Pb(OH)_2(s)$ lead(II) hydroxide is amphoteric hence reacts with excess hydroxide ions to form a soluble complex of plumbate ions. $Pb(OH)_2(s) + 2\bar{O}H(aq) \longrightarrow Pb(OH)_4^{2-}$
	Add ammonia solution drop wise until in excess	White precipitate insoluble in excess	$Al^{3+}, Pb^{2+}, Mg^{2+}, Ba^{2+}$ Probably present	Lead(II) ions react with hydroxyl ions to form insoluble lead(II) hydroxide. $Pb^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Pb(OH)_2(s)$

<b>Pb<sup>2+</sup></b>	Add sodium carbonate solution drop wise until in excess	White precipitate Insoluble in excess	Mg <sup>2+</sup> , Ca <sup>2+</sup> , Ba <sup>2+</sup> Zn <sup>2+</sup> , Pb <sup>2+</sup> Probably present	lead(II) ions react with carbonate ions to form insoluble Lead(II) carbonate. $Pb^{2+}(aq) + CO_3^{2-}(aq) \rightarrow PbCO_3(s)$
	Add dilute sulphuric acid	White precipitate	Pb <sup>2+</sup> , Ba <sup>2+</sup> or Ca <sup>2+</sup> Probably present	lead(II) ions react with sulphate ions to form insoluble lead(II) sulphate. $Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$
	Add dilute sulphuric acid and heat	White precipitate insoluble on heating	Pb <sup>2+</sup> Present	lead(II) ions react with sulphate ions to form insoluble lead(II) sulphate. $Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$ Lead(II) sulphate is insoluble on heating
	Add dilute hydrochloric acid	White precipitate	Pb <sup>2+</sup> Present	lead(II) ions react with chloride ions to form insoluble lead(II) chloride. $Pb^{2+}(aq) + 2Cl^{-}(aq) \rightarrow PbCl_2(s)$
	Add dilute hydrochloric acid and heat/warm/ Boil	White precipitate soluble on heating and reprecipitates on cooling	Pb <sup>2+</sup> Present	lead(II) ions react with chloride ions to form insoluble lead(II) chloride. $Pb^{2+}(aq) + 2Cl^{-}(aq) \rightarrow PbCl_2(s)$ Lead(II) chloride is soluble in hot water but insoluble in cold water
	Add potassium iodide solution	Yellow precipitate	Pb <sup>2+</sup> Present	lead(II) ions react with iodide ions to form insoluble lead(II) iodide. $Pb^{2+}(aq) + 2I^{-}(aq) \rightarrow PbI_2(s)$
	Add potassium iodide solution followed by dilute sodium hydroxide solution	Yellow precipitate soluble in sodium hydroxide solution	Pb <sup>2+</sup> Present	lead(II) ions react with iodide ions to form insoluble lead(II) iodide. $Pb^{2+}(aq) + 2I^{-}(aq) \rightarrow PbI_2(s)$
	Add potassium chromate(VI) solution followed by sodium hydroxide solution.	Yellow precipitate soluble in sodium hydroxide solution to form a yellow solution.	Pb <sup>2+</sup> confirmed present	lead(II) ions react with chromate ions to form insoluble Lead(II) chromate. $Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(s)$  Note; Lead(II) chromate is soluble in dilute nitric acid to form a yellow solution. Its however insoluble in ethanoic acid.

<b>Sn<sup>2+</sup></b>	Add sodium hydroxide solution drop wise until in excess	White precipitate soluble in excess to form a colourless solution	Zn <sup>2+</sup> , Al <sup>3+</sup> , Pb <sup>2+</sup> , Sn <sup>2+</sup> probably present	Tin(II) ions react with hydroxyl ions to form insoluble tin(II) hydroxide. $\text{Sn}^{2+}(\text{aq}) + 2\bar{\text{O}}\text{H}(\text{aq}) \longrightarrow \text{Sn}(\text{OH})_2(\text{s})$ Tin(II) hydroxide is amphoteric hence reacts with excess hydroxide ions to form a soluble complex of Stannate ions. $\text{Sn}(\text{OH})_2(\text{s}) + 2\bar{\text{O}}\text{H}(\text{aq}) \longrightarrow \text{Sn}(\text{OH})_4^{2-}$
	Add ammonia solution drop wise until in excess	White precipitate insoluble in excess	Al <sup>3+</sup> , Pb <sup>2+</sup> , Mg <sup>2+</sup> , Ba <sup>2+</sup> , Sn <sup>2+</sup> probably present	Tin(II) ions react with hydroxyl ions to form insoluble tin(II) hydroxide. $\text{Sn}^{2+}(\text{aq}) + 2\bar{\text{O}}\text{H}(\text{aq}) \longrightarrow \text{Sn}(\text{OH})_2(\text{s})$
	Add acidified potassium permanganate solution	The purple solution turns colourless	Sn <sup>2+</sup> present	Tin(II) ions reduce manganate(VII) ions in acidic medium to manganese(II) ions, as they are oxidised to tin(IV) ions. $\text{MnO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+} (\text{aq}) + 4\text{H}_2\text{O} (\text{l}) \times 2$ $\text{Sn}^{2+} (\text{aq}) \longrightarrow \text{Sn}^{4+} (\text{aq}) + 2\text{e}^- \times 5$ $2\text{MnO}_4^- (\text{aq}) + 16\text{H}^+ (\text{aq}) + 5\text{Sn}^{2+} (\text{aq}) \longrightarrow 2\text{Mn}^{2+} (\text{aq}) + 5\text{Sn}^{4+} (\text{aq}) + 8\text{H}_2\text{O} (\text{l})$
	Add acidified potassium permanganate solution until no further decolourisation. Then sodium sulphide solution	Dirty yellow precipitate	Sn <sup>2+</sup> present	Tin(II) ions reduce manganate(VII) ions in acidic medium to manganese(II) ions, as they are oxidised to tin(IV) ions. The tin(IV) ions formed reacts with sulphide ions to form insoluble tin(IV) sulphide. $2\text{MnO}_4^- (\text{aq}) + 16\text{H}^+ (\text{aq}) + 5\text{Sn}^{2+} (\text{aq}) \longrightarrow 2\text{Mn}^{2+} (\text{aq}) + 5\text{Sn}^{4+} (\text{aq}) + 8\text{H}_2\text{O} (\text{l})$ $\text{Sn}^{4+} (\text{aq}) + 2\text{S}^{2-} (\text{aq}) \longrightarrow \text{SnS}_2 (\text{s})$
	Add iron(III) chloride solution	Brown solution turns green	Sn <sup>2+</sup> present	Tin(II) ions reduce iron(III) ions to iron(II) ions, as the tin(II) ions are oxidised to tin(IV) ions $2\text{Sn}^{2+} (\text{aq}) + 2\text{Fe}^{3+} (\text{aq}) \longrightarrow \text{Sn}^{4+} (\text{aq}) + 2\text{Fe}^{2+} (\text{aq})$
	Add acidified potassium dichromate solution	Orange solution turns green	Sn <sup>2+</sup> present	Tin(II) ions reduce dichromate(VI) ions in acidic medium to chromium(III) ions, as they are oxidised to tin(IV) ions. $\text{Cr}_2\text{O}_7^{2-} (\text{aq}) + 3\text{Sn}^{2+} (\text{aq}) + 14\text{H}^+ (\text{aq}) \longrightarrow 2\text{Cr}^{3+} (\text{aq}) + 3\text{Sn}^{4+} (\text{aq}) + 7\text{H}_2\text{O} (\text{l})$
	Add mercury(II) chloride solution	A white precipitate which slowly turns grey	Sn <sup>2+</sup> present	Tin(II) ions reduce mercury(II) chloride to mercury(I) chloride as they are oxidised to tin(IV) ions $\text{Sn}^{2+} (\text{aq}) + 2\text{HgCl}_2 (\text{aq}) \longrightarrow \text{Hg}_2\text{Cl}_2 (\text{s}) + \text{Sn}^{4+} (\text{aq}) + 2\text{Cl}^- (\text{aq})$

$\text{Sn}^{2+}$	Add ammonium molybdate solution followed by dilute sulphuric acid	A blue colouration	$\text{Sn}^{2+}$ present	Not required
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### UNIQUENESS OF CARBON

In some of its properties, carbon behaves uniquely from the other elements.

**1. State the reasons for this unique behaviour.**

- Carbon has the smallest atomic radius among the elements
- Carbon has the greatest electronegativity compared to other elements
- Carbon has a maximum covalency of 4
- Carbon can form very stable multiple covalent bonds with itself and many other elements
- Carbon does not show inert pair effect

**2. State the properties in which carbon behaves uniquely from other elements**

- Carbon (diamond) has an abnormally high melting point than other elements
- Carbon has the ability to form long chains of carbon atoms. Other elements do not catenate
- Carbon reacts with air to form gaseous oxides. Other elements form solid oxides.
- Carbon does react with chlorine. Other elements react with chlorine to form tetrachlorides. Lead forms lead(II) chloride
- Carbon reacts with sulphur to form a liquid, carbon disulphide. Other elements form solid sulphides.

*Note; The chemistry of carbon compounds is not included here since question is specific to carbon*

## THE GREEN HOUSE EFFECT

The level of Carbon dioxide in the atmosphere has shown an increase since industrial revolution. This is due to the extensive combustion of fossil fuels and the production of the gas from car exhausts, and the destruction of large areas of rainforest to burn the trees as a source of fuel. The carbon dioxide is slowly building up in the atmosphere, which results into an overall increase in the temperature of the atmosphere (greenhouse effect).

## USES OF GROUP IV ELEMENTS

1. A number of carbon allotropes have different uses;
  - Diamond, the hardest naturally occurring substance known, is used for making jewellery and, industrially, for cutting and drilling equipment.
  - Graphite is used in making lead pencils and as electrodes in electrolysis
  - Wood charcoal is used in drawing and as a fuel
  - Animal charcoal is used to remove brown colour from sugar
  - Lamp black is used in making shoe polish and printer's ink
  - Coke in extraction of iron as a reducing agent and manufacture of producer gas and water gas
2. Silicon and germanium are used as semiconductors in transistors.
3. Tin is used in making alloys like bronze, solder and type metal (Sn, Pb and Sb)
4. Lead is used in making alloys like solder.

## MISCELLANEOUS TOPICAL QUESTIONS

### *Short answer type questions*

1. Carbon, silicon, germanium, tin and lead are group IV elements in increasing atomic number.
  - (a) (i) Write the general outermost configuration of the elements. (01 mark)
  - (ii) Tin and lead show *inert pair effect*. Briefly explain what is meant by the term *inert pair effect* and give an example to illustrate your answer. (3 ½ marks)
  - (b) State the reason why carbon has a very high melting point compared to other elements. (1 ½ marks)
  - (c) (i) Write the formulae of the hydrides formed by the elements. (2 ½ marks)
  - (ii) Identify the thermally most stable hydride in c (i) above. (½ mark)

2. The elements tin and lead belong to group IV of the Periodic Table. Describe the reactions of the elements with:
- (a) Water (03 marks)
  - (b) Concentrated sulphuric acid. (03 marks)
  - (c) Alkalis (03 marks)
3. (a) State the conditions and write equations for the reaction between carbon and;
- (i) water (2 ½ marks)
  - (ii) sulphuric acid. (2 ½ marks)
- (b) Compare the reactions of carbon and silicon with:
- (i) concentrated nitric(V) acid. (2 ½ marks)
  - (ii) concentrated sodium hydroxide. (2 ½ marks)
4. (a) Draw the structures and name the shapes of the following species. (09 marks)

Species	Structure	Shape
$CO_2$		
$SiO_2$		
$CCl_4$		
$CH_4$		
$CS_2$		
$SnO_3^{2-}$		

- (b) Briefly explain why  $CO_2$  adopts the shape you have named in (a) above. (02 marks)
- (c) Compare the bond angle of  $CS_2$  and  $SnO_3^{2-}$ . Give a reason for your answer. (03 marks)

5. (a) Carbon, silicon, germanium and tin belong to group IV of the Periodic Table and their respective bond energies are given below.

Bond	C—C	Si—Si	Ge—Ge	Sn—Sn
Bond energy(kJmol <sup>-1</sup> )	346	175	168	156

- (i) State the trend in bond energy. Give a reason for your answer. (1 ½ marks)
- (ii) How does bond energy affect the tendency of the above elements to catenate? (01 mark)
- (b) Describe the reactions of the elements in (a) above with concentrated hydrochloric acid. (02 marks)
- (c) Write equation for the formation of silane. (1 ½ marks)
6. (a) Lead(IV) oxide reacts with hydrochloric acid by redox reaction. (01 mark)
- (i) State the conditions for the reaction. (01 mark)
- (ii) Write the reduction and oxidation half reactions for the redox reaction that occurs above. (02 marks)
- (b) Lead(IV) oxide was added to a solution of manganese(II) sulphate in the presence of concentrated nitric acid.
- (i) State what was observed. (½ mark)
- (ii) Write the equation for the reaction that took place. (1 ½ marks)
7. (a) State how the following anhydrous chlorides can be prepared. (01 mark)
- (i) tin(II) chloride (01 mark)
- (ii) tin(IV) chloride (01 mark)
- (b) State the reasons why tin(IV) chloride exists but tin(IV) bromide does not. (02 marks)
- (c) Write equations for the reaction of each of the chlorides in (a) (i) with water. (02 marks)
- (d) (i) State what would be observed when sodium hydroxide solution was added drop wise until in excess to a solution of tin(IV) ions. (1 ½ marks)
- (ii) Write equations for the reaction(s) in d(i) above. (02 marks)
- (e) (i) State what would be observed and write equation for the reaction that would take place when tin(II) chloride is added to an acidified solution of sodium dichromate(VI) (2 ½ marks)
- (ii) Give a reason for your answer in (e)(i) (01 mark)
8. Carbon, silicon, germanium, tin and lead are in group IV of the Periodic Table.
- (a) State
- (i) the common oxidation states exhibited by the elements in their ions or compounds. (01 mark)

- (ii) how the stability of the oxidation states of the elements in (a) (i) vary down the group. (01 mark)
- (b) Give a reason for your answer in (a)(ii) (01 mark)
- (c) Compare the thermal stabilities of carbon tetrachloride and lead tetrachloride. (*Include equations of reactions if any*) (2 ½ marks)
- (d) Describe the reaction if any between each of the carbon tetrachloride and lead tetrachloride with water. (3 ½ marks)
9. (a) Compare the thermal stabilities of silicon(IV) chloride and tin(IV) chloride. (*Include the equations of reactions if any*) (2 ½ marks)
- (b) (i) Write equation for the reaction between tin and chlorine. (1 ½ marks)  
(ii) State the conditions for the reaction. (01 mark)
- (c) State what would be observed and write equation for the reaction that would take place if the product in (b) (i) was exposed to moist air. (2 ½ marks)
- (d) State why silicon(IV) chloride readily undergoes hydrolysis whereas carbon tetrachloride does not. (02 marks)
10. (a) (i) Write the electronic configuration of tin (Atomic number is 50)  
(ii) State the common oxidation states exhibited by tin in its compounds. (01 mark)
- (b) (i) State how anhydrous tin(II) chloride can be prepared. (01 mark)  
(ii) Draw the structure and name the shape of tin(II) chloride. (01 mark)  
(c) Write equation for the reaction between tin(II) chloride and water. (1 ½ marks)
11. (a) (i) Draw the structure and name the shape of tin(IV) chloride. (01 mark)  
(ii) State how anhydrous tin(IV) chloride can be prepared. (01 mark)  
(iii) Write equation for the reaction leading to formation of tin(IV) chloride. (1 ½ marks)
- (b) State what would be observed and write equation for the reaction that would take place if tin(IV) chloride is treated with water. (02 marks)
12. The atomic number of element Q is 32.
- (a) Write the electronic configuration of Q. (01 mark)
- (b) Write the formula of the;  
(i) hydride of Q. (½ mark)  
(ii) chloride of Q. (½ mark)
- (c) Water was added to the chloride of Q. State whether the resultant solution was neutral, acidic or alkaline. Explain your answer giving an equation for the reaction. (03 marks)

13. The elements tin and lead belong to group IV of the Periodic Table.

(a) Write equation for the formation of the tetrachlorides of the elements.

(02 marks)

(b) Tin(IV) chloride fumes in moist air. Explain this observation.

(03 marks)

14. (a) Lead is an element in group IV of the Periodic Table.

Write the general electronic configuration of group IV elements. (0½ mark)

(b) State what would be observed and write an equation when lead(IV) oxide was heated on a deflagrating spoon and quickly plunged in gas jar of sulphur dioxide.

(2 ½ marks)

(c) When red lead (trilead tetroxide) was heated with nitric acid, a solid was formed. Write the equation for the reaction.

(1 ½ marks)

(d) The mixture in (c) was filtered and the residue warmed with concentrated hydrochloric acid.

(i) What was observed? Explain your answer.

(2 ½ marks)

(ii) Write the equation for the reaction.

(1 ½ marks)

(e) The filtrate from (d) was divided into three parts.

(i) to the first part was added aqueous potassium iodide. State what was observed and write equation for the reaction.

(02 marks)

(ii) aqueous sodium chromate solution was added to the second portion.

State what was observed and write equation for the reaction.

(02 marks)

(iii) the third part was evaporated to dryness and then heated strongly.

Explain what was observed and write equations for the reaction that took place.

(3 ½ marks)

15. (a) Write:

(i) the formulae of the possible oxides of lead.

(1 ½ marks)

(ii) equation to show how each of the oxides in (a)(i) can be prepared.

(1 ½ marks)

(b) Describe how the oxides in (a) react with dilute nitric acid.

(04 marks)

(c) When one of the oxides in (a) was added to a mixture of a manganese(II) salt and concentrated nitric acid, a purple solution was formed.

(i) Identify the oxide

(½ mark)

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

(1 ½ mark)

16. Trilead tetraoxide (red lead oxide),  $Pb_3O_4$  can be prepared when lead(II) oxide is heated in excess oxygen.

(a) Write equation for formation of  $Pb_3O_4$ .

(1 ½ marks)

(b) Write equation for the reaction of  $Pb_3O_4$  with;

(i) hot concentrated sodium hydroxide solution.

(1 ½ marks)

(ii) hot concentrated hydrochloric acid. (1 ½ marks)

(c) Lead(II) oxide is almost insoluble in dilute hydrochloric acid, but readily dissolves in concentrated hydrochloric acid. Explain this observation.

(4 ½ marks)

17. Lead and iron form mixed oxides of the formulae  $Pb_3O_4$  and  $Fe_3O_4$  respectively.

(a) Write the:

(i) IUPAC name of the mixed oxide of lead that represents the ratio in which the oxides mix. (01 mark)

(ii) equation to show that is  $Pb_3O_4$  a mixed oxide. (1 ½ marks)

(b)  $Pb_3O_4$  oxidises hot concentrated hydrochloric acid to a pale green gas and itself reduced to a colourless solution which forms a white precipitate on cooling.

(i) Identify the pale green gas and the white precipitate. (01 mark)

(ii) Write the equation for the reaction between  $Pb_3O_4$  and hot concentrated hydrochloric acid. (01 mark)

(c) State any two other chemical properties to show the similarity between iron and lead. (01 mark)

18. Write equation for the reaction between sodium hydroxide and; (09 marks)

(i) lead(II) oxide

(ii) lead(IV) oxide

(iii) Tin(IV) oxide

(iv) Tin(II) oxide

(v) Carbon(II) oxide

(vi) tin

19.(a) A compound Q contains 63.7% lead, 14.8% carbon, 1.8% hydrogen and the rest being oxygen. When vapourised, 0.225g of Q occupies  $15.5 \text{ cm}^3$  at standard temperature and pressure.

(i) Calculate the empirical formula of Q. (02 marks)

(ii) Deduce the molecular formula of Q. (03 marks)

(b) Compound Q decomposed on heating to form a yellow residue on cooling and a colourless vapour that turned limewater milky and formed a yellow precipitate with 2,4-dinitrophenyl hydrazine in presence of sulphuric acid.

(i) Write the name and formula of Q. (01 mark)

(ii) Write equation leading to formation of the yellow precipitate.

(1 ½ marks)

20. D is a dark-brown solid which on heating loses mass to form a yellow compound E, D reacts with cold concentrated hydrochloric acid to form a colourless liquid F of formula mass 349. On warming, F decomposes to form a white solid G. G dissolves in both concentrated sodium hydroxide and concentrated hydrochloric acid.

- (a) Identify D, E, F and G. (04 marks)  
(b) Write equations for all the five reactions that take place. (05 marks)

21. Explain each of the following observations.

- (a) Carbon tetrachloride is stable to water but other group(IV) tetrachlorides are readily hydrolysed. (03 marks)  
(b) Carbon atoms are able to form long chains to a greater extent than other group IV elements. (03 marks)  
(c) Although both silicon dioxide and carbon dioxide are covalent, carbon dioxide is a gas whereas silicon dioxide is solid of high melting point. (04 marks)  
(d) Iron(III) chloride and tin(II) chloride cannot exist together in solution. (2 ½ marks)  
(e) The carbon- oxygen bond is polar but carbon dioxide is non-polar. (03 marks)  
(f) The bonds in carbon tetrachloride are polar yet the carbon tetrachloride molecule is not polar. (03 marks)  
(g) Silicon(IV) chloride is hydrolysed by water whereas carbon tetrachloride is not. (1 ½ marks)  
(h) Lead(IV) chloride exists but lead(IV) bromide does not. (02 marks)  
(i) Both graphite and copper conduct electricity. (02 marks)  
(j) Silicon(IV) oxide is a solid of very high melting point. However, lead(IV) oxide easily decomposes when heated. (2 ½ marks)  
(k) Lead(II) chloride is insoluble in ethanol whereas lead(IV) chloride readily dissolves in ethanol. (03 marks)  
(l) When an aqueous solution of sodium chlorate(I) was and lead(II) nitrate was warmed, a brown precipitate was formed: (2 ½ marks)

**Long answer type questions**

22. The elements carbon, silicon, tin and lead are in group IV of the Periodic Table. Carbon differs in some properties from other members of the group.

(a) (i) Give two reasons why carbon differs from other members of the group. (02 marks)

(ii) State two properties that distinguish carbon from other members of the group. (02 marks)

(b) Describe the reactions of the dioxides of these elements with sodium hydroxide. (06 marks)

(c) Describe the reactions of the chlorides of group IV elements with water. (04 marks)

(d) Write an equation for the reaction to show how you would prepare:

(i) lead(II) oxide. (01 mark)

(ii) lead(IV) oxide. (01 mark)

(e) Describe the reactions of lead(IV) oxide with hydrochloric acid. (04 marks)

23. Carbon, Silicon, germanium and tin are some of the elements in group IV of the Periodic Table.

(a) Describe the trend among the elements in;

(i) metallic character (02 marks)

(ii) electropositivity (3 ½ marks)

(b) Describe the reactions of the elements with:

(i) air (04 marks)

(ii) nitric acid (05 marks)

(iii) Chlorine (03 marks)

(c) Excess tin(II) chloride solution was added to iodine solution.

(i) State what was observed. (01 mark)

(ii) Write equation for the reaction that took place. (1 ½ marks)

24. Both tin and lead are group IV elements.

(a) State the oxidation states exhibited by tin and lead in most of their compounds. (02 marks)

(b) Write equations to show how the chlorides and the oxides of tin and lead in the +4 oxidation state can be formed. (06 marks)

(c) Compare the thermo stability of the following compounds of tin and lead

(i) the tetrachlorides

(ii) the dioxides (06 marks)

(d) State two similarities in the chemistry of the following compounds of tin and lead. (Illustrate your answers with equations)

- (i) oxides (06 marks)  
(ii) chlorides
- 25.(a) Compare the thermo stability of the monoxides and dioxides of group IV elements. (04 marks)
- (b) Describe the reactions of the oxides of:  
(i) carbon and tin with sodium hydroxide. (5 ½ marks)  
(ii) lead with hydrochloric acid. (04 marks)
- (f) Explain the following observations.  
(i) carbon(IV) oxide is a gas whereas silicon(IV) oxide is a solid. (04 marks)  
(ii) silicon(IV) oxide reacts with hydrofluoric acid but does not react with hydrofluoric acid. (2 ½ marks)
26. The elements Carbon, silicon, tin and lead belong to group IV of the Periodic Table.
- (a) State the oxidation states of the elements. (01 mark)  
(b) Explain the trend in the stability of the oxidation states. (03 marks)  
(c) (i) State the type of bonding that is in the chlorides of lead. (01 mark)  
(ii) State two physical properties of each chloride that shows the type of bonding you have mentioned above. (04 marks)  
(d) Describe the reactions of the chlorides of the elements above with water. Write equations for the reactions that take place. (04 marks)  
(e) Describe the reaction of the oxides of these elements with sodium hydroxide. Write equations for the reactions that take place. (07 marks)
- 27.(a) Carbon, silicon, tin and lead belong to group IV of the Periodic Table.
- (i) State the two oxidation states exhibited by these elements. (01 mark)  
(ii) Explain how the stability of the two oxidation states varies from carbon to lead. (03 marks)
- (b) Describe the reactions between:  
(i) the elements in (a) above with sulphuric acid. (06 marks)  
(ii) silicon(IV) chloride with water (02 marks)  
(iv) Lead(IV) oxide and hydrochloric acid. (04 marks)
- (c) State two chemical properties in which carbon differs from the rest of the group IV elements. (02 marks)  
(d) Give reasons why carbon differs from the rest of the group IV elements. (02 marks)

28. The elements carbon, silicon, germanium, tin and lead belong to group IV of the Periodic Table.

(a) Describe the reactions of the elements with;

(i) water (05 marks)

(ii) sodium hydroxide solution (04 marks)

(iii) Sulphuric acid (04 marks)

(b) Below are the boiling points of the tetrachlorides of group IV elements.

Tetrachloride	$CCl_4$	$SiCl_4$	$GeCl_4$	$SnCl_4$	$PbCl_4$
Boiling point( $^{\circ}C$ )	76.4	57.0	86.0	118	Decomposes

State and explain the trend in the boiling points of the tetrachlorides.

(04 marks)

(c) State what would be observed and write equation for the reaction that would take place if excess concentrated hydrochloric acid was mixed with lead(IV) oxide and heated. (03 marks)

29. Explain each of the following observations.

(a) Solid lead(II) chloride can be prepared in the laboratory by heating lead(II) oxide with dilute hydrochloric acid and cooling. When lead(II) oxide is treated with concentrated hydrochloric acid under the same conditions, no solid is formed. (04 marks)

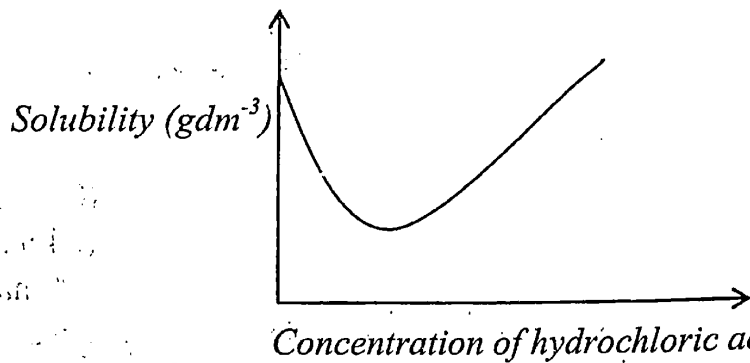
(b) When concentrated hydrochloric acid is added to lead(II) ethanoate solution, a white precipitate is formed which dissolves in excess acid. (05 marks)

(c) When lead(IV) chloride is added to water, white fumes and a brown precipitate are observed. (03 marks)

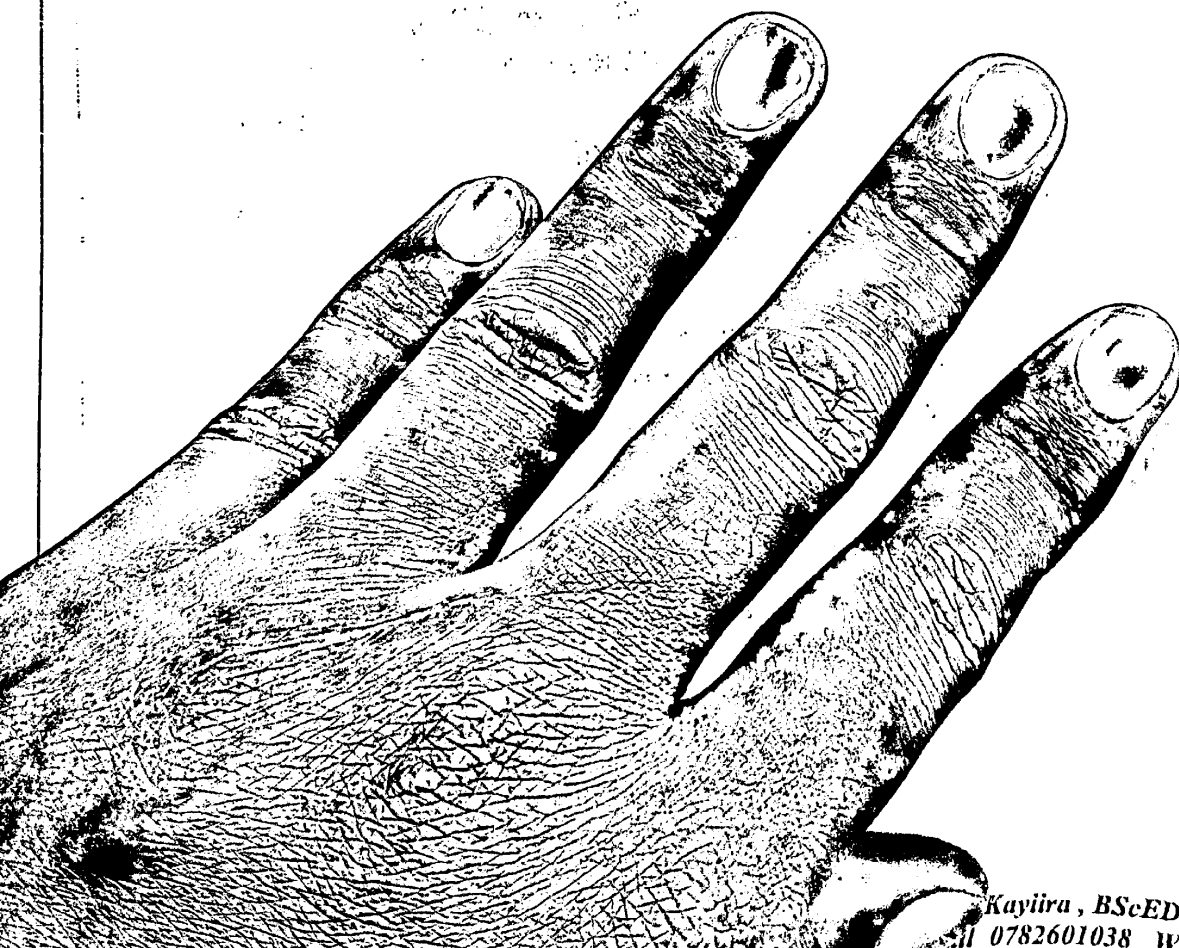
(d) When lead(IV) oxide was added to a solution containing manganese(II) sulphate and concentrated nitric acid and the mixture boiled, the colour of the solution changed from pale pink to purple. (04 marks)

(e) Diamond melts at  $4827^{\circ}C$  and silicon melts at  $2355^{\circ}C$  although both have similar structures. (04 marks)

(f) When concentrated hydrochloric acid is added to lead(II) nitrate solution drop wise until in excess, the curve below is obtained. Explain the shape of the graph. (04 marks)



- (g) The bond dissociation energy of the hydrides of group IVB are in the order  $CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$ . However, the boiling points are in the reverse order. (05 marks)
- (h) The boiling points of the hydrides of group IV elements are in the order  $CH_4 < SiH_4 < GeH_4 < SnH_4 < PbH_4$  whereas the boiling points of the hydrides of group VII elements are in the order  $HCl < HBr < HI < HF$  (05 marks)



# THE CHEMISTRY OF GROUP VII ELEMENTS

## Electronic structures/ configurations

Element	Atomic number	Configuration
F	9	$1s^2 2s^2 2p^5$
Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Br	35	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$
I	53	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$

From the above electronic configurations, it can be concluded that the outermost electronic configuration of group VII elements is  $ns^2 np^5$

## Bonding and structure

Element	Bonding	Structure	Physical state and colour at room temperature
Fluorine	All covalent	All simple molecular	Pale yellow gas
Chlorine			Greenish yellow gas
Bromine			Red liquid
Iodine			Grey/ black solid

**Qn.** Explain why fluorine and chlorine exist as gases whereas bromine and iodine exist as liquid and solid respectively at room temperature

*From fluorine to iodine, atomic radius increases, molecular size and molecular mass increases, hence magnitude of Van der Waals' forces of attraction holding the molecules increases in the order;  $F_2 < Cl_2 < Br_2 < I_2$ . The Van der Waals' forces in bromine and iodine are strong enough to hold the molecules closer to each other existing as liquid and solid respectively. Fluorine and chlorine have weaker Van der Waals' forces due to their small size and low molecular masses. Their molecules are therefore far apart.*

## VARIATION IN ATOMIC AND PHYSICAL PROPERTIES OF THE ELEMENTS

### 1. Melting points/ boiling points

The table below shows the boiling points/melting points of halogens

Element	<i>F</i>	<i>Cl</i>	<i>Br</i>	<i>I</i>
Boiling point( $^{\circ}\text{C}$ )	-187.9	-34.0	58.2	+184.5
Melting points( $^{\circ}\text{C}$ )	-219.6	-102.4	-7.2	+113.6

Explain the trend in boiling points/ melting points of the halogens

*Boiling point/melting point increases from fluorine to iodine because atomic radius increases, molecular size and molecular mass increases, hence magnitude of Van der Waals' forces of attraction holding the molecules increases in the order  $\text{F}_2 < \text{Cl}_2 < \text{Br}_2 < \text{I}_2$ . The energy required to break the forces therefore increase from fluorine to iodine.*

### 2. Atomic and ionic radius

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

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

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

*Atomic radius increases from fluorine to iodine.*

*This is because from fluorine to iodine, nuclear charge increases because a proton is added to nucleus from element to element. Screening effect also increases, because an extra energy level completely filled with electrons is added. Increase in screening effect outweighs increase in nuclear charge. Effective nuclear charge decreases, and outer most electrons are far and weakly attracted by the nucleus.*

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

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

### 3. First ionization energy

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

Element	<i>F</i>	<i>Cl</i>	<i>Br</i>	<i>I</i>
First ionisation energy (kJmol <sup>-1</sup> )	1681	1255	1142	1007

(a) Define the term first ionisation energy.

(b) State and explain the trend in ionization energy of the elements

### 4. Electron affinity

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

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

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

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

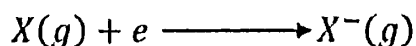
*(To be done by student. When plotting the graph, the negative sign may be eliminated since it's on all values and it just indicates that the process is exothermic. The graph below is just a sketch and not on scale)*

(c) (i) Explain the general trend in variation of the first electron affinities

(iii) Explain why fluorine has an abnormal value

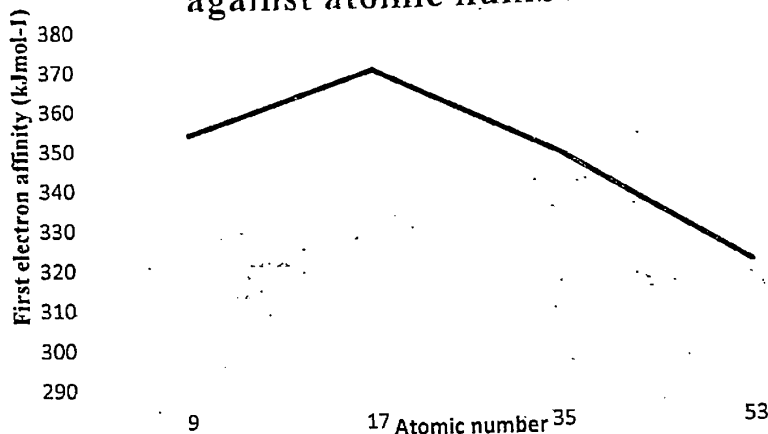
*(a) This is the energy given out when one mole of electrons combines with one mole of gaseous atoms to form one mole of uninegatively charged gaseous ions*

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



(b)

A graph of first electron affinity against atomic number



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

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

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

## 5. Electronegativity

The tendency of an atom in a molecule to attract bonding electrons towards itself

The table below shows the electronegativity values of the elements in Group VII of the Periodic Table.

Element	F	Cl	Br	I
Electronegativity	4.10	2.83	2.74	2.21

State and explain the trend in electronegativity values of the elements

Electronegativity decreases from fluorine to iodine.

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

DEMYSTIFYING INORGANIC CHEMISTRY BY Joseph Jobs Kayiira, BScED(Hons.CHEM/MTC)  
Email:josephkayirab@gmail.com Call 0782601038 WhatsApp 0753247098

## 6. Bond dissociation energy

The table below shows the values of Bond dissociation energy of halogens.

Element	$F_2$	$Cl_2$	$Br_2$	$I_2$
Bond dissociation energy( $\text{kJmol}^{-1}$ )	158.1	242.2	193	151

- (a) State the difference between bond dissociation energy and bond energy.  
(b) Explain the trend, stating any anomalies in the bond dissociation energy of the halogens.

- (a) *Bond dissociation energy is the heat absorbed to break one mole of a covalent bond into its constituent gaseous atoms whereas bond energy is the heat given out that when one mole of a covalent bond is formed from its constituent gaseous atoms.*  
(b) *Bond dissociation energy decreases from chlorine to iodine but with fluorine having an abnormally low value of bond dissociation energy.*

*This is because from chlorine to iodine, atomic radius increases, bond length increases and bond strength decreases, resulting into weaker attraction between the atoms in the molecule, requiring a reducing amount of energy to break the increasingly weakening bonds.*

*Fluorine has an abnormally low value of bond dissociation energy because fluorine has the smallest atomic radius, and the non-bonding electrons in the molecule repel each other strongly. This strong repulsion tends to force the fluorine atoms far apart thus weakening the F-F bond, requiring low amount of energy to break it.*

## 7. Electrode potential

The table below shows the standard electrode potential values of Group VII elements.

Element	$F$	$Cl$	$Br$	$I$
Standard electrode potential( $E^\theta$ ) (Volts) for $\frac{1}{2}X_2/X^-(aq)$	+2.80	+1.36	+1.07	+0.54

- (a) State;
- (i) the strongest oxidising agent
  - (ii) order of oxidising strength of the halogens
- (b) Explain the trend in standard electrode potential of the elements
- (c) State what would be observed when;
- (i) Chlorine is bubbled through potassium bromide solution
  - (ii) Chlorine is bubbled through potassium iodide solution
- (d) Explain your observations in c(i) and (ii) basing on the table above
- (e) Explain why tin(IV) chloride exists but tin(IV) bromide and tin(IV) iodide do not exist.

(a) (i) Fluorine or  $F_2$  (but not F)

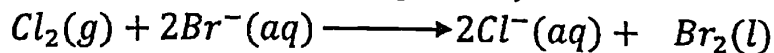
(ii)  $F_2 \gg Cl_2 > Br_2 > I_2$

(b) Standard electrode potential becomes less positive (increases) from fluorine to iodine because atomic radius increases, electron affinity decreases, bond dissociation energy generally decreases and hydration energy also decreases. However, the decrease in electron affinity and bond dissociation energy is more rapid than decrease in hydration energy.

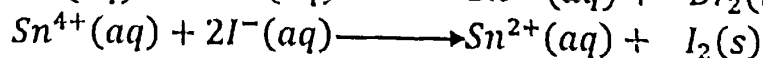
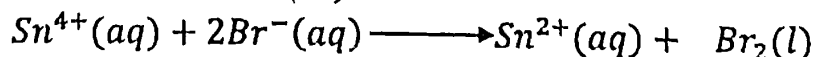
(c) (i) The greenish-yellow gas dissolves and the colourless solution forms a red liquid.

(ii) The greenish-yellow gas dissolves and the colourless solution turns dark brown finally forming a black solid deposit.

(d) The standard electrode potential for  $Cl_2/Cl^-(aq)$  is more positive than that of  $Br_2/Br^-(aq)$  or  $I_2/I^-(aq)$  and the chloride ion has a smaller ionic radius than bromide and iodide ions respectively. Chlorine therefore a stronger oxidising agent than bromine or iodine. Chlorine oxidises bromide and iodide ions to bromine and iodine respectively.



(e) Bromide ions and iodide ions have a larger ionic radius than the chloride ion. The ions are therefore strongly reducing. They reduce tin(IV) ions to tin(II) ions, as they are oxidised to bromine and iodine respectively. Chloride ions cannot reduce tin(IV) ions.

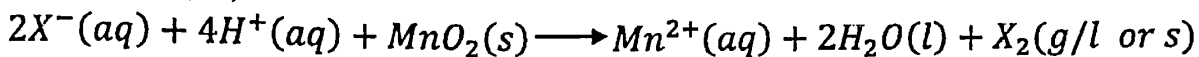


## METHODS OF PREPARATION OF HALOGENS

**Qn. Describe the general method of preparing halogens except fluorine**

All halogens apart from fluorine are prepared by;

Heating a solid halide salt with concentrated sulphuric acid in presence of manganese(IV) oxide.



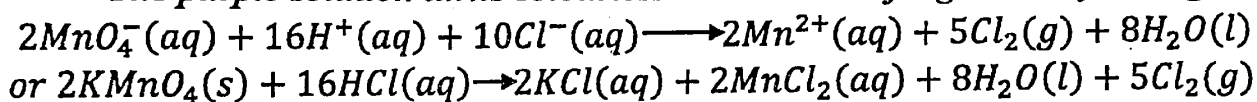
Where  $X = Cl, Br \text{ or } I$

*N.B. The Chemistry in action here is that concentrated sulphuric acid acts upon the halide salt (KCl/KBr/KI or NaCl/NaBr /NaI) to form a hydrogen halide (HCl or HBr or HI) which is then oxidised to the halogen by manganese(IV) oxide.*

**Qn. Describe the reactions, stating the conditions and under which chlorine can be prepared in the laboratory. State any observations made.**

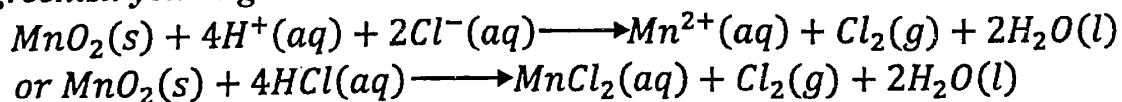
1. Chlorine can be prepared by the reaction between **cold concentrated hydrochloric acid and potassium manganate(VII)**.

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



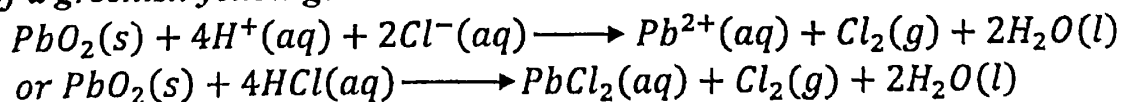
2. Chlorine can also be prepared by **heating concentrated hydrochloric acid with manganese(IV) oxide**.

*The black solid dissolves forming a colourless solution and bubbles of a greenish yellow gas.*



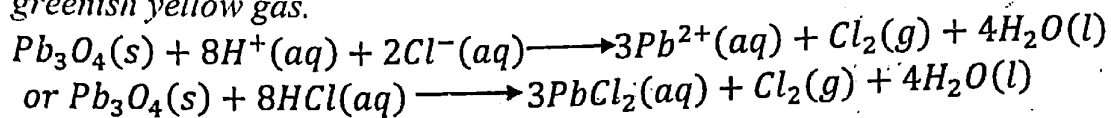
3. Chlorine can also be prepared by **heating concentrated hydrochloric acid with lead(IV) oxide**.

*The dark brown solid dissolves forming a colourless solution and bubbles of a greenish yellow gas.*

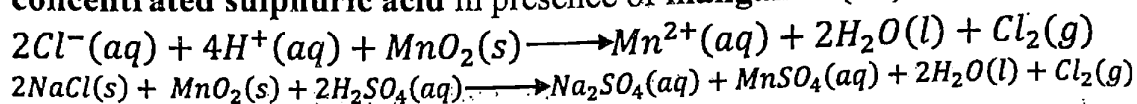


4. Chlorine can as well be prepared by **heating concentrated hydrochloric acid with Dilead(II) lead(IV) oxide**.

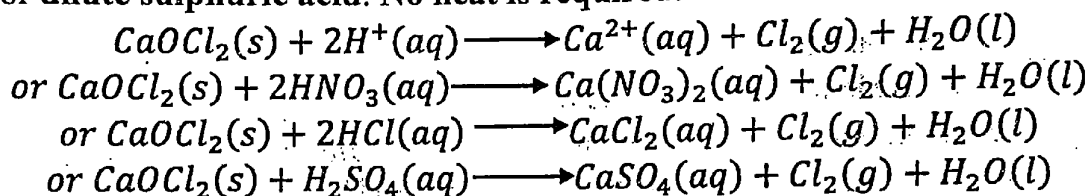
The red solid dissolves forming a colourless solution and bubbles of a greenish yellow gas.



5. Chlorine can be prepared by heating solid sodium chloride with concentrated sulphuric acid in presence of manganese(IV) oxide.



6. Chlorine is also prepared by the reaction between bleaching powder (Calcium hypochlorite) with dilute nitric acid or dilute hydrochloric acid or dilute sulphuric acid. No heat is required.

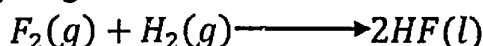


### CHEMICAL PROPERTIES OF THE ELEMENTS

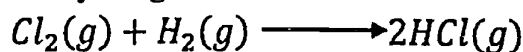
1. Describe the reactions of Group VII elements react with hydrogen.

State the conditions for the reactions.

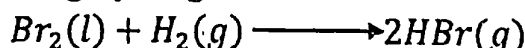
Fluorine explodes in hydrogen even in darkness forming hydrogen fluoride.



Chlorine explodes with hydrogen on heating or presence of sunlight or ultraviolet light to form hydrogen chloride.



Bromine reacts with hydrogen on heating or in the presence of platinum catalyst at 300 °C forming hydrogen bromide

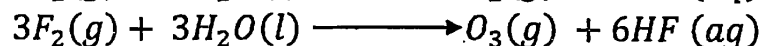


Iodine reacts with hydrogen in the presence of platinum catalyst at 400 °C forming hydrogen iodide.



2. (a) Describe the reactions of halogens with water.

Fluorine reacts vigorously with water to form oxygen/ozone and hydrofluoric acid.



Chlorine disproportionates in water to form chloric(I) acid and hydrochloric acid.



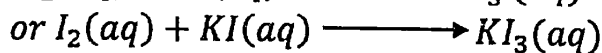
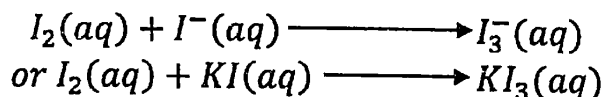
Bromine disproportionates in water to form bromic(I) acid and hydrobromic acid.



Iodine does not react with water.

(b) Explain why iodine is insoluble in water but soluble in potassium iodide solution.

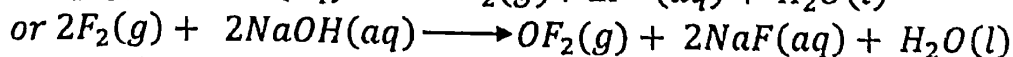
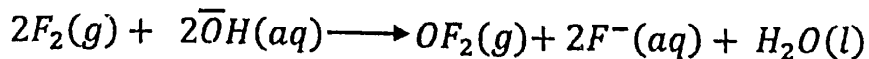
*Iodine is non-polar yet water is polar. Intermolecular forces of attraction between individual molecules of water and individual molecules of iodine are on average stronger than intermolecular forces of attraction between molecules of water and molecules of iodine. When the two are combined, repulsion occurs. However, iodine reacts with potassium iodide to a soluble complex of potassium triiodide.*



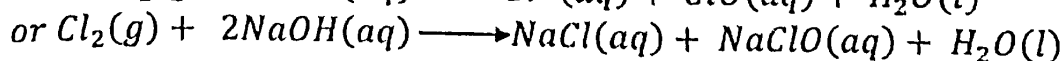
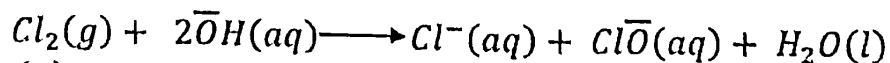
3. Describe how fluorine, chlorine, bromine and iodine react with sodium hydroxide under various conditions.

(i) cold dilute sodium hydroxide

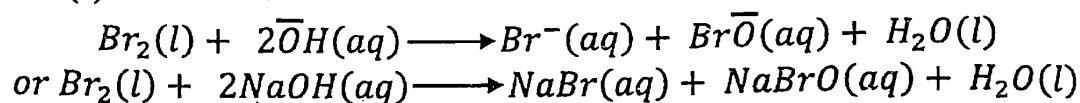
Fluorine reacts with cold dilute sodium hydroxide solution to form oxygen difluoride, fluoride ions and water.



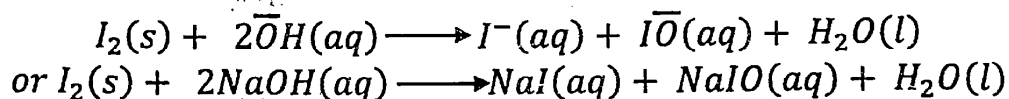
Chlorine disproportionates in cold dilute sodium hydroxide to form chloride ions, chlorate(I) ions and water.



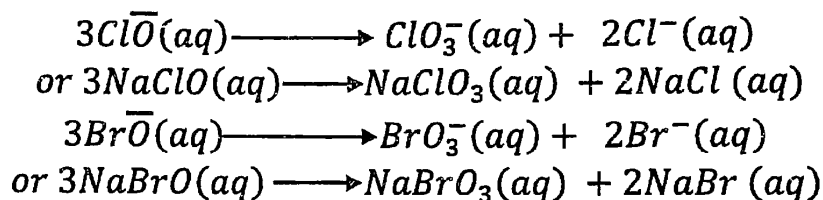
Bromine also disproportionates in cold dilute sodium hydroxide to form bromide ions, bromate(I) ions and water.



Iodine disproportionates in cold dilute sodium hydroxide to form iodide ions, iodate(I) ions and water.

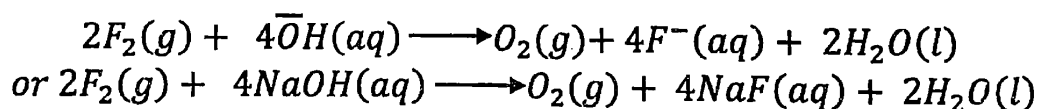


*N.B;* The chlorate(I) ions and bromate(I) ions formed by the above reactions undergo further disproportionation if heated/ warmed to form chlorate(V) ions and chloride ions, bromate(V) ions and bromide ions respectively. The yellow solution turns colourless during this reaction

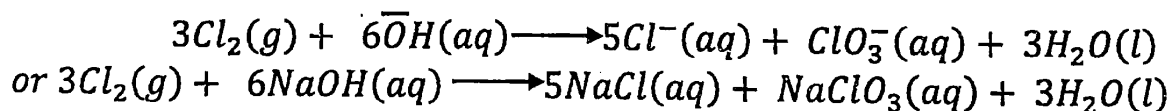


(ii) hot concentrated sodium hydroxide.

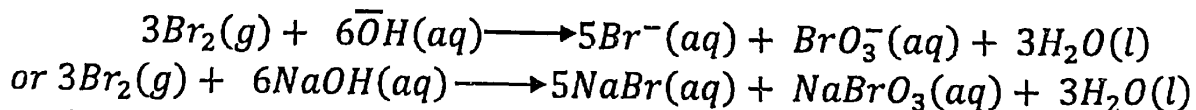
Fluorine reacts with hot concentrated sodium hydroxide to form oxygen, fluoride ions and water.



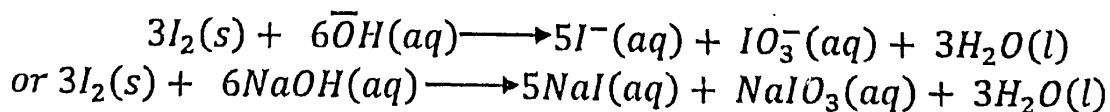
Chlorine disproportionates in hot concentrated sodium hydroxide to form chloride ions, chlorate(V) ions and water.



Bromine also disproportionates in hot concentrated sodium hydroxide to form bromide ions, bromate(V) ions and water.



Iodine also disproportionates in hot concentrated sodium hydroxide to form iodide ions, iodate(V) ions and water.



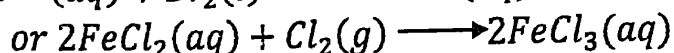
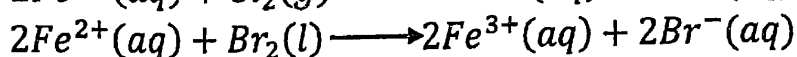
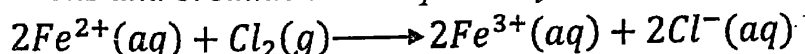
## OXIDISING ACTION OF HALOGENS

1. State what would be observed and explain your observations when;

- (i) chlorine and bromine are separately added to iron(II) chloride solution.
- (ii) chlorine is bubbled through potassium nitrite solution and silver nitrate solution followed by excess ammonia added to the resultant solution.

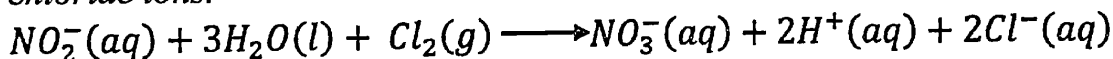
(i) **Observation;** In each case, the green solution turns brown

**Explanation;** chlorine and bromine oxidise iron(II) ions to iron(III) ions as they are reduced to chloride ions and bromide ions respectively.

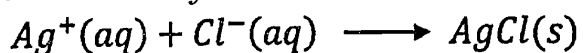


(ii) **Observation;** Greenish yellow gas dissolves and the colourless solution formed a white precipitate soluble in excess ammonia to form a colourless solution.

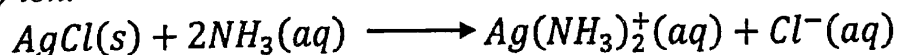
**Explanation;** chlorine oxidises nitrate ions to nitrite ions and itself reduced to chloride ions.



Silver ions react with the chloride ions to form insoluble silver chloride



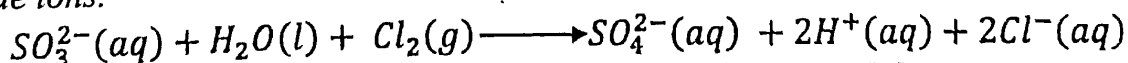
Silver chloride reacts with excess ammonia to form a soluble complex of diammine silver(I) ion.



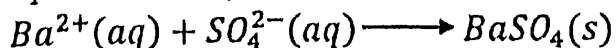
2. Chlorine gas was bubbled through sodium sulphite solution and to the resultant solution was added barium nitrate solution. State what was observed and explain your answer.

**Observation;** Greenish yellow gas dissolved and the colourless solution formed a white precipitate with barium nitrate solution.

**Explanation;** Chlorine oxidises sulphite ions to sulphate ions and itself reduced to chloride ions.



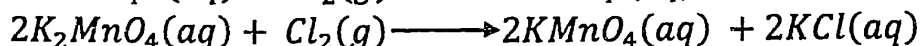
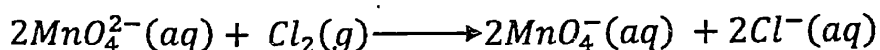
Barium ions react with sulphate ions to form insoluble barium sulphate



3. Chlorine gas was bubbled through potassium manganate(VI) solution and to the resultant solution was dilute sulphuric acid and tin(II) sulphate solution. State what was observed and explain your answer.

*Observation; Greenish yellow gas dissolved and the green solution turned to a purple solution which then turned colourless.*

*Explanation; Chlorine oxidises manganate(VI) ions to manganate(VII) ions and itself reduced to chloride ions.*



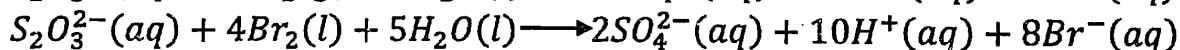
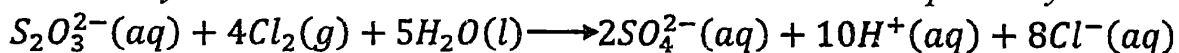
*The acidified manganate(VII) ions then oxidise tin(II) ions to tin(IV) ions as they are reduced to manganese(II) ions.*



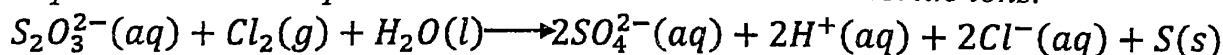
4. Describe the reactions of chlorine, bromine and iodine react with;

- (i) sodium thiosulphate solution
- (ii) hydrogen sulphide.
- (iii) sulphurous acid

- (i) Chlorine and bromine oxidise thiosulphate ions to sulphate ions as they are reduced to chloride ions and bromide ions respectively.



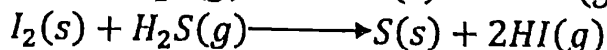
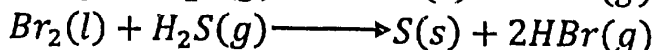
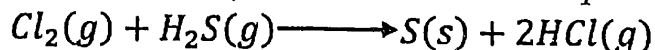
*However, if limited chlorine is used, thiosulphate ions disproportionate into sulphate ions and sulphur as the chlorine is reduced to chloride ions.*



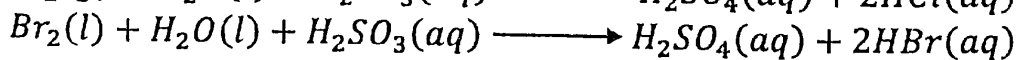
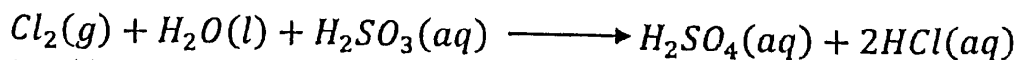
*Iodine being a weaker oxidising agent oxidises thiosulphate ions to tetrathionate ions and itself reduced to iodide ions.*



- (ii) Chlorine, bromine and iodine oxidise hydrogen sulphide to deposit a yellow solid of sulphur as they are reduced to corresponding hydrides.



- (iii) Chlorine and bromine oxidise sulphurous acid to sulphuric acid as they are reduced to hydrochloric acid and hydrobromic acid respectively.



## HYDRIDES OF GROUP VII ELEMENTS

1. The table below shows the chemical formulae of the hydrides of Group VII elements and their physical states at room temperature.

Element	Formula of hydride	Physical state at room temperature
Fluorine	<i>HF</i>	<i>Liquid</i>
Chlorine	<i>HCl</i>	<i>Gas</i>
Bromine	<i>HBr</i>	<i>Gas</i>
Iodine	<i>HI</i>	<i>Gas</i>

Explain why hydrogen fluoride is a liquid at 19°C whereas hydrogen bromide is a gas at the same temperature.

*Fluorine atom is more electronegative than the bromine atom. The fluorine atom in hydrogen fluoride has a smaller atomic radius than the bromine atom in hydrogen bromide. This makes the hydrogen-fluorine bond more polar than the hydrogen-bromine bond. The molecules of hydrogen fluoride are held by stronger intermolecular hydrogen bonds which keep the molecules closer to each other whereas the molecules of hydrogen bromide are held by weak Van der Waals' forces that keep the molecules far apart.*

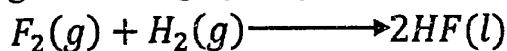
## METHODS OF PREPARATION OF THE HYDRIDES

2. (a) Describe the general methods of preparing the hydrides in above.

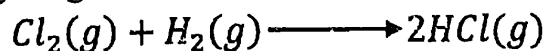
The hydrides can be formed by three main general methods;

- (i) *Direct combination of the elements with hydrogen.*

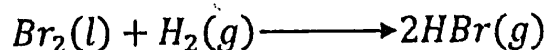
Fluorine is reacted with hydrogen forming hydrogen fluoride



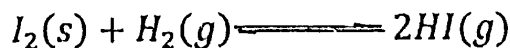
Chlorine is reacted with hydrogen and the mixture is heated or exposed to sunlight or ultraviolet light to form hydrogen chloride



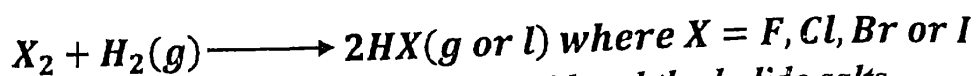
Bromine is reacted with hydrogen in the presence of platinum catalyst at 300 °C to form hydrogen bromide



Iodine is reacted with hydrogen in the presence of platinum catalyst at 400 °C to form hydrogen iodide

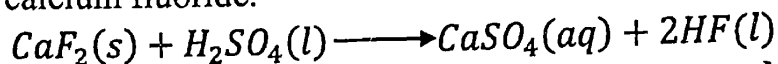


In general, the hydrides can be formed by the reaction between hydrogen and the halogen

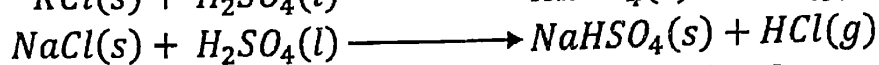
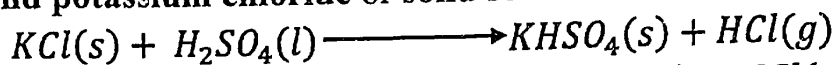


(ii) *Reaction between concentrated sulphuric acid and the halide salts*

Hydrogen fluoride can best be formed by reaction between cold concentrated sulphuric acid calcium fluoride.



Hydrogen chloride is also best formed by heating concentrated sulphuric acid with either solid potassium chloride or solid sodium chloride.

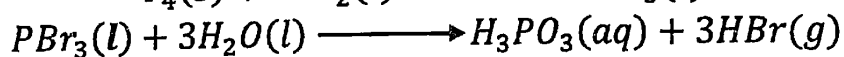


However, this method is inconvenient for preparation of hydrogen bromide and hydrogen iodide which are progressively stronger reducing agents than hydrogen chloride.

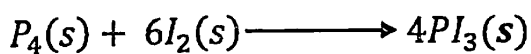
(iii) *Hydrolysis of corresponding phosphorus trihalides prepared in situ.*

This is the best method for preparation of hydrogen bromide and hydrogen iodide.

Hydrogen bromide is formed by adding bromine to a paste of red phosphorus and water forming phosphorus(III) bromide which is then hydrolysed to form hydrogen bromide and phosphorous acid



Hydrogen iodide is formed by adding water to a mixture of red phosphorus and iodine forming phosphorus(III) iodide which is then hydrolysed to form hydrogen iodide and phosphorous acid

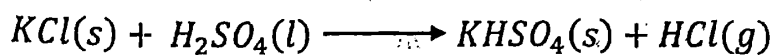


No heat is required in each of these two reactions.

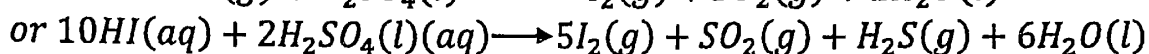
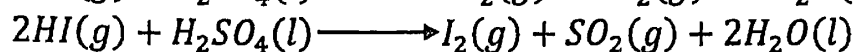
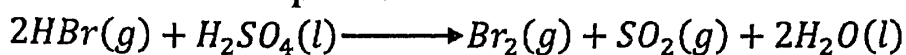
N.B. Note that although the above methods can prepare the hydrides in general, there is a more convenient method to prepare each of the hydrides.

(b) Hydrogen chloride can be prepared by the action of concentrated sulphuric acid on potassium chloride but hydrogen iodide and hydrogen bromide cannot be prepared by the action of concentrated sulphuric acid on potassium iodide and potassium bromide respectively.

Potassium chloride reacts with concentrated sulphuric acid to form hydrogen chloride gas which is a weak reducing agent due to the smaller atomic radius of chlorine.



On the other hand, hydrogen iodide and hydrogen bromide that would be formed are strong reducing agents due to the large atomic radius of iodine and bromine. They reduce sulphuric acid to sulphur dioxide as they are oxidised to iodine and bromine respectively. The iodine is observed as purple vapours and bromine as reddish brown vapours.



### BOILING POINTS/ MELTING POINTS OF THE HYDRIDES

3. The table below shows both boiling points of group VII hydrides.

Hydride	<i>HF</i>	<i>HCl</i>	<i>HBr</i>	<i>HI</i>
Boiling point(°C)	+19.9	-85.0	-66.7	-35.4

Explain the variation in melting/ boiling points, including any anomalies involved.

*Boiling points generally increase from hydrogen fluoride to hydrogen iodide. However, hydrogen fluoride has an abnormally high value of boiling point.*

*The increase in melting point from hydrogen chloride to hydrogen iodide is because the three hydrides have simple molecular structures held by weak Van der Waals' forces whose magnitude increases with the increasing molecular weight leading to an increasing amount of energy required to break the increasingly stronger forces.*

*Hydrogen fluoride has an abnormally high melting point because the fluorine atom has the highest electronegativity, the fluorine atom has the smallest atomic radius, making the hydrogen-fluorine bond highly polar. The hydrogen fluoride molecules are therefore held by strong intermolecular hydrogen bonds which require a high amount of energy to break.*

**Explain why hydrogen fluoride has a higher boiling point than hydrogen iodide.**

*The fluorine atom is more electronegative than the iodine atom. The fluorine atom also has a smaller atomic radius than the iodine atom. This makes the hydrogen-fluorine bond more polar than the hydrogen-iodine bond. The molecules of hydrogen fluoride are held by stronger intermolecular hydrogen bonds which require a higher amount of energy to break whereas the molecules of hydrogen iodide are held by weak Van der Waals' forces that require a lower amount of energy to break.*

#### **THERMAL STABILITY**

**4. (a) State and explain the trend in thermal stability of the hydrides.**

*Thermal stability of the hydrides decreases in the order  $HF > HCl > HBr > HI$ . This is because the atomic radius of the halogen atoms increases from fluorine to iodine. This makes the hydrogen-halogen bond length longer, reducing the bond strength from hydrogen fluoride to hydrogen iodide, reducing the amount of energy required to dissociate the hydrogen-halogen bond.*

#### **ACID STRENGTHS**

**5. The table below shows acid dissociation constants,  $K_a$ , of group VII hydrides.**

Hydride	<i>HF</i>	<i>HCl</i>	<i>HBr</i>	<i>HI</i>
$K_a$ ( $\text{mol dm}^{-3}$ ) at 25 °C	$6.6 \times 10^{-4}$	$1.3 \times 10^6$	$1.0 \times 10^9$	$3.2 \times 10^9$

**Explain the trend in  $K_a$  values of the hydrides.**

*The  $K_a$  values increase in the order  $HF < HCl < HBr < HI$  indicating that acid strength increases in the same order. This is because atomic radius of the halogen atoms increases from the fluorine atom to the iodine atom. This makes the hydrogen-halogen bond length longer, reducing the bond strength from hydrogen fluoride to hydrogen iodide, releasing many hydrogen ions in solution.*

*Hydrofluoric acid is the weakest acid because the fluorine atom is most electronegative and the fluorine atom has the smallest atomic radius. Therefore the hydrogen-fluorine bond is the shortest, most polar and strongest making the acid to dissociate to a considerably smaller extent.*

**Explain why hydrofluoric acid is a weaker acid than hydroiodic acid**

*The fluorine atom is more electronegative than the iodine atom and the fluoride ion in hydrofluoric acid has a smaller ionic radius than the iodide ion in hydroiodic acid. Therefore the hydrogen-fluorine bond is the shorter, more polar and stronger than the hydrogen-iodine bond in hydroiodic acid hence the hydrogen-fluorine bond does not easily break, releasing fewer hydrogen ions in solution than the hydrogen-iodine bond which easily breaks.*

**Qn. Explain why hydrofluoric acid is a weak acid in dilute solution but its acid strength increases with increasing concentration**

*The fluorine atom in hydrogen fluoride is highly electronegative due to a very small atomic radius. Therefore the hydrogen-fluorine bond is highly polar and very strong. When hydrogen fluoride is dissolved in water, the hydrofluoric acid formed only partly ionises, doesn't easily release hydrogen ions making it a weak acid.*

*In dilute solution;*  $HF(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

*However, in concentrated solution, the fluoride ions released react with hydrofluoric acid to form hydrogen difluoride ion.*

*In concentrated solution;*  $HF(l) + F^-(aq) \rightleftharpoons HF_2^-(aq)$

*This reduces the concentration of fluoride ions at equilibrium. The equilibrium shifts from left to right as more of the hydrogen fluoride dissociates releasing more hydrogen ions making the solution a strong acid at high concentration.*

### REDUCING ACTION

**6. State and explain the trend in reducing action of the hydrides**

Reducing strength increases in the order  $HF < HCl < HBr < HI$  because ionic radius halide ions increases and electronegativity decreases from fluorine to iodine. Hydrogen fluoride has no reducing action.

### ANOMALOUS BEHAVIOUR OF FLUORINE AND HYDROGEN FLUORIDE

**7. Although fluorine is an element in group VII of the Periodic Table, it behaves differently from other members of the group.**

(a) State the reasons why fluorine behaves differently from the other members of the group.

(b) State the differences between the Chemistry of fluorine as an element and other halogens

### Reasons / causes for anomalous behaviour of fluorine

(a)

- Fluorine atom has the smallest atomic radius compared to other elements
- Fluorine atom has the highest electronegativity among the elements
- Fluorine molecule has an abnormally low value of bond dissociation energy of the  $F-F$  bond compared to other halogen-halogen bonds.
- Unlike other elements, fluorine atom cannot expand its octet
- Fluorine has the largest positive standard electrode potential among the elements

(b)

- Fluorine oxidises water to oxygen and itself reduced to hydrofluoric acid. Iodine does not react with water and other halogens disproportionate in water
- Fluorine oxidises cold dilute sodium hydroxide solution to oxygen difluoride gas, itself reduced to fluoride ions. Other halogens disproportionate to form halide ions and halate(I) ions and water.
- Fluorine oxidises hot concentrated sodium hydroxide solution to oxygen gas, itself reduced to fluoride ions. Other halogens disproportionate to form halide ions and halate(V) ions and water.
- Fluorine combines directly with carbon. Other halogens do not react directly with carbon.

*Note with concern that the chemistry of compounds of fluorine is not required here as the question is specific to fluorine.*

**8. Although hydrogen fluoride is a group VII hydride, it behaves differently from hydrides of other members in the group.**

**(a) State the reasons why hydrogen fluoride behaves differently from the hydrides of other members of the group.**

**(b) State the differences between the properties on hydrogen fluoride and other group VII hydrides.**

(a)

- Hydrogen fluoride is strongly hydrogen bonded unlike other hydrides
- It has a very low value of acid dissociation constant at room temperature
- Hydrogen fluoride has the smallest bond length.
- Hydrogen fluoride has the highest electronegativity difference between its atoms among the hydrides.

(b)

- Hydrogen fluoride is a liquid at room temperature whereas other hydrides are gases
  - Hydrogen fluoride has an abnormally high value of boiling point compared to other hydrides
  - Hydrofluoric acid is a very weak acid in contrast to hydrochloric acid, hydrobromic acid and hydroiodic acid which are all strong acids
  - Hydrogen fluoride has no reducing action yet other hydrides are reducing
9. The bond angle in phosphorus trifluoride is  $96^\circ$  while that of phosphorus trichloride is  $100^\circ$ . Explain this observation.

Both phosphorus trifluoride and phosphorus trichloride adopt a trigonal pyramidal shape. However, the fluorine atom is more electronegative than the chlorine atom. The fluorine atom therefore draws away the bonded pairs of electrons from the phosphorus atom more than the chlorine atom does. This makes the bonded pairs to be far apart reducing the repulsion between them. Therefore phosphorus trifluoride has a smaller bond angle than phosphorus trichloride.

### POLARISABILITY OF HALIDE IONS

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

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

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

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

If we consider the halide ions, polarisability increases in the order



Explain why the solubility of lead(II) halides increases in the order;



The cationic radius and cationic charge are the same in all compounds. However, anionic radius decreases from the iodide ion to the chloride ion. The halide ions therefore become less polarisable and the ionic character increases from lead(II) iodide to lead(II) chloride. Since water is a polar solvent, the compounds become more soluble in that order.

**Qn.** Explain why aluminium chloride is soluble in methylbenzene and has a low melting point yet aluminium fluoride is soluble in water and has a higher melting point.

### QUALITATIVE ANALYSIS FOR $Cl^-$ , $Br^-$ AND $I^-$ IONS

ION	TEST	OBSERVATION	DEDUCTION	EXPLANATION
$Cl^-$	To a spatula endful of the solid, add 2-3 drops of concentrated sulphuric acid and heat	White fumes turn blue litmus red and form dense white fumes with concentrated ammonia	HCl gas evolved $Cl^-$ present	Concentrated sulphuric acid reacts with chloride ions to form hydrogen chloride gas. $Cl^-(s) + H_2SO_4(l) \longrightarrow HCl(g) + HSO_4^-(aq)$ Hydrogen chloride gas reacts with concentrated ammonia to form ammonium chloride $HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$
	To the solution, add dilute nitric acid followed lead(II) nitrate solution	White precipitate	$C_2O_4^{2-}$ , $SO_3^{2-}$ , $SO_4^{2-}$ , $Cl^-$ probably present	Lead(II) ions react with chloride ions to form insoluble lead(II) chloride $Pb^{2+}(aq) + 2Cl^-(aq) \longrightarrow PbCl_2(s)$
	Add lead(II) nitrate followed by dilute nitric acid	White precipitate insoluble in acid	$SO_4^{2-}$ , $Cl^-$ probably present	Lead(II) ions react with chloride ions to form insoluble lead(II) chloride $Pb^{2+}(aq) + 2Cl^-(aq) \longrightarrow PbCl_2(s)$
	To the acidified solution, lead(II) nitrate solution and heat/boil/Warm	White precipitate soluble on heating/boiling/warming and reprecipitates on cooling	$Cl^-$ present	Lead(II) ions react with chloride ions to form insoluble lead(II) chloride $Pb^{2+}(aq) + 2Cl^-(aq) \longrightarrow PbCl_2(s)$
	Add dilute nitric acid followed by silver nitrate solution	White precipitate	$C_2O_4^{2-}$ , $SO_3^{2-}$ , $Cl^-$ probably present	Silver ions react with chloride ions to form insoluble silver chloride $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

<b>Cl<sup>-</sup></b>	Add silver nitrate solution followed by dilute nitric acid	White precipitate insoluble in acid	Cl <sup>-</sup> present	Silver ions react with chloride ions to form insoluble silver chloride $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \longrightarrow \text{AgCl}(\text{s})$
	Add dilute nitric acid followed by silver nitrate solution. Then add aqueous ammonia drop wise until in excess.	White precipitate soluble in excess ammonia to form a colourless solution	Cl <sup>-</sup> confirmed	Silver ions react with chloride ions to form insoluble silver chloride $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \longrightarrow \text{AgCl}(\text{s})$ Silver chloride reacts with excess ammonia to form a soluble complex of diammine silver(I) ion. $\text{AgCl}(\text{s}) + 2\text{NH}_3(\text{aq}) \longrightarrow \text{Ag}(\text{NH}_3)_2^+(\text{aq}) + \text{Cl}^-(\text{aq})$
	To the solution, add bleaching powder then dilute nitric acid (or add chlorine water) followed by tetrachloromethane and shake. Allow to stand	Tetrachloromethane layer remains colourless	Cl <sup>-</sup> present	The acidified bleaching powder or chlorine water produces Chlorine. The chlorine cannot oxidise chloride ions. hence the tetrachloromethane layer remains colourless
<b>Br<sup>-</sup></b>	To a spatula endful of the solid, add 2-3 drops of concentrated sulphuric acid and heat (the reaction may take place even before heating)	Reddish brown vapours	Br <sub>2</sub> evolved Br <sup>-</sup> present	Bromide ions are strongly reducing due to their large ionic radius. They reduce hot concentrated sulphuric acid to sulphur dioxide as they are oxidised to bromine.
				$2\text{Br}^-(\text{aq}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \longrightarrow \text{Br}_2(\text{g}) + \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

<b>Br<sup>-</sup></b>	To the solution, add dilute nitric acid followed lead(II) nitrate solution	White precipitate	$C_2O_4^{2-}$ , $SO_3^{2-}$ , $SO_4^{2-}$ , $Cl^-$ $Br^-$ probably present	Lead(II) ions react with bromide ions to form insoluble lead(II) bromide $Pb^{2+}(aq) + 2Br^-(aq) \longrightarrow PbBr_2(s)$
	Add dilute nitric acid followed by silver nitrate solution	Pale yellow precipitate	$Br^-$ present	Silver ions react with bromide ions to form insoluble silver bromide $Ag^+(aq) + Br^-(aq) \longrightarrow AgBr(s)$
	Add silver nitrate solution followed by dilute nitric acid	Pale yellow precipitate insoluble in acid	$Br^-$ present	Silver ions react with bromide ions to form insoluble silver bromide $Ag^+(aq) + Br^-(aq) \longrightarrow AgBr(s)$
	Add dilute nitric acid followed by silver nitrate solution. Then add aqueous ammonia drop wise until in excess.	Pale yellow precipitate soluble in excess ammonia	$Br^-$ present	Silver ions react with bromide ions to form insoluble silver bromide $Ag^+(aq) + Br^-(aq) \longrightarrow AgBr(s)$ Silver bromide is sparingly soluble in ammonia.
	To the solution, add bleaching powder then dilute nitric acid (or add chlorine water) followed by tetrachloromethane and shake. Allow to stand	Reddish brown liquid in tetrachloromethane layer	$Br^-$ present	The acidified bleaching powder or chlorine water produces Chlorine which oxidises bromide ions to bromine. $Cl_2(g) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(l)$ Bromine is covalent hence dissolves in tetrachloromethane to form the reddish brown layer.

$I^-$	To a spatula endful of the solid, add 2-3 drops of concentrated sulphuric acid and heat (the reaction may take place even before heating)	Purple vapours	$I_2$ evolved $I^-$ present	Iodide ions are strongly reducing due to their large ionic radius. They reduce hot concentrated sulphuric acid to sulphur dioxide as they are oxidised to iodine. Sometimes oxidation result into formation of hydrogen sulphide gas, as well, with a smell of rotten eggs.
				$2I^-(aq) + 4H^+(aq) + SO_4^{2-}(aq) \longrightarrow I_2(g) + SO_2(g) + 2H_2O(l)$ or $10I^-(aq) + 14H^+(aq) + 2SO_4^{2-}(aq) \longrightarrow 5I_2(g) + SO_2(g) + H_2S(g) + 6H_2O(l)$
	To the solution, add dilute nitric acid followed lead(II) nitrate solution	Yellow precipitate	$I^-$ present	Lead(II) ions react with iodide ions to form insoluble lead(II) iodide $Pb^{2+}(aq) + 2I^-(aq) \longrightarrow PbI_2(s)$
	Add dilute nitric acid followed by silver nitrate solution	Yellow precipitate	$I^-$ present	Silver ions react with iodide ions to form insoluble silver iodide $Ag^+(aq) + I^-(aq) \longrightarrow AgI(s)$
	Add silver nitrate solution followed by dilute nitric acid	Yellow precipitate insoluble in acid	$I^-$ present	Silver ions react with iodide ions to form insoluble silver iodide $Ag^+(aq) + I^-(aq) \longrightarrow AgI(s)$
	Add dilute nitric acid followed by silver nitrate solution. Then add aqueous ammonia drop wise until in excess.	Yellow precipitate insoluble in ammonia	$I^-$ present	Silver ions react with iodide ions to form insoluble silver iodide $Ag^+(aq) + I^-(aq) \longrightarrow AgI(s)$ Silver iodide is insoluble in ammonia

$I^-$	To the solution, add bleaching powder then dilute nitric acid (or add chlorine water) followed by tetrachloromethane and shake. Allow to stand	Violet colouration in tetrachloromethane layer	$I^-$ present	The acidified bleaching powder or chlorine water produces Chlorine which oxidises iodide ions to iodine. $Cl_2(g) + 2I^-(aq) \longrightarrow 2Cl^-(aq) + I_2(aq)$ Iodine is covalent hence dissolves in tetrachloromethane.
	Add copper(II) sulphate solution	White precipitate in a brown solution	$I^-$ present	Copper(II) ions oxidises iodide ions to iodine and itself reduced copper(I) iodide. $2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow Cu_2I_2(s) + I_2(aq)$

### MISCELLANEOUS TOPICAL QUESTIONS

#### Short answer type questions

- Write equations to show how chlorine and iodine react with;
  - Sodium iodide solution. (03 marks)
  - Sodium thiosulphate solution (03 marks)
  - Cold dilute sodium hydroxide (03 marks)
- (a) Write equation for the reaction that takes place when hot concentrated potassium hydroxide is added to;
  - fluorine. (01 mark)
  - chlorine. (01 mark)

(b) Write equation(s) for the reaction(s) of

  - fluorine and water (1 ½ marks)
  - hydrofluoric acid and silicon(IV) oxide (1 ½ marks)

(c) Arrange the following hydrogen halides;  $HCl$ ,  $HI$  and  $HBr$  in order of decreasing acid strength. Give a reason for your answer. (03 marks)
- (a) Fluorine, chlorine, bromine and iodine are diatomic molecules of group VII elements of the Periodic Table. Briefly describe how the elements react with;
  - Potassium bromide. (02 marks)
  - Hydrogen sulphide (02 marks)

(b) The hydrides of the elements in (a) above boil at different temperatures shown in the table below.

Hydride	<i>HF</i>	<i>HCl</i>	<i>HBr</i>	<i>HI</i>
Boiling point( $^{\circ}\text{C}$ )	+20	-85	-67	-35

State and explain the trend in boiling points of the hydrides. (03 marks)

(c) (i) State the order in reducing strength of the hydrides. (01 mark)

(ii) Write a general equation for the reaction between aqueous solutions of the hydrohalic acids with sodium carbonate. (01 mark)

4. The table below gives some physical properties of hydrogen halides.

Hydride	<i>HF</i>	<i>HCl</i>	<i>HBr</i>	<i>HI</i>
Boiling point(K)	293	188	206	238
Bond length(nm)	0.086	0.128	0.142	0.160

(a) Explain the observed trend in;

(i) Boiling points (02 marks)

(ii) Bond length (02 marks)

(b) Arrange the hydrogen halides in order of the expected increase in acid strength of their aqueous solutions, giving reason for your answer.

(02 marks)

5. State what would be observed and write equation for the reaction that would take place when;

(a) Copper(II) sulphate solution was added to potassium iodide solution. (2 ½ marks)

(b) Potassium iodide solution is added to chlorine water. (02 marks)

(c) Chlorine is bubbled through iron(II) chloride solution (2 ½ marks)

(d) Solid sodium iodide is heated with concentrated sulphuric acid. (2 ½ marks)

(e) Warm concentrated hydrochloric acid is added to manganese(IV) oxide. (02 marks)

(f) Sodium iodide is added to acidified sodium chlorate(I) solution. (02 marks)

(g) Chlorine is bubbled through sodium thiosulphate solution (2 ½ marks)

(h) Sodium iodide solution is added to acidified hydrogen peroxide solution. (1 ½ marks)

(i) Chlorine is bubbled through potassium manganate(VI) solution (2 ½ marks)

6. (a) The chemistry of fluorine differs from that of chlorine.
- State two differences between the chemistry of fluorine and chlorine apart from their reactions with sodium hydroxide. (02 marks)
  - Write the equation for the reaction between cold dilute sodium hydroxide and;
    - Fluorine
    - chlorine
 (03 marks)
7. (a) The oxidising strength of group VII elements decreases in the order;  
 $F_2 \gg Cl_2 > Br_2 > I_2$
- State three reasons to account for the high oxidising strength of fluorine relative to other halogens. (1 ½ marks)
  - State two other anomalous properties of fluorine. (02 marks)
- (b) Describe the reactions of chlorine and iodine with;
- sodium thiosulphate solution. (3 ½ marks)
  - iron(II) sulphate. (02 marks)
8. (a) (i) State the condition(s) under chlorine reacts with sulphur dioxide. (01 mark)
- (ii) Write equation for the reaction. (01 mark)
- (b) Chlorine was bubbled through sodium thiosulphate solution and lead(II) nitrate solution was added to the resultant solution.
- State what was observed. (01 mark)
  - Write equation(s) for the reaction(s) that took place. (02 marks)
9. (a) State three reasons why fluorine differs in some of its properties from the rest of group VII elements. (03 marks)
- (b) Write equations for ionisation of hydrogen fluoride in aqueous solutions that are;
- dilute
  - concentrated
- (03 marks)
- (c) Explain why hydrogen fluoride is a weaker acid than hydrogen chloride. (03 marks)
10. Name the reagent(s) that can be used to distinguish between the following pair(s) of compounds. In each case state the observations made and write equation(s) for the reaction.
- $I^-$  and  $Br^-$  (4 ½ marks)
  - $Cl^-$  and  $Br^-$  (4 ½ marks)

- (iii)  $I^-$  and  $Cl^-$  (4 ½ marks)
- 11.(a) (i) What is the electronic configuration of the bromide ion. (01 mark)
- (ii) With the aid of a suitable diagram(s), show how the bonding of the chlorate(III) oxo-anion of chlorine. (1 ½ marks)
- (b) When iodine is added to aqueous sodium hydroxide, the initial product formed disproportionates. Explain the meaning of this term and write an ionic equation for the changes that take place. (2 ½ marks)
- (c) Explain why unlike other halogens, fluorine liberates oxygen from cold water. (02 marks)
- 12.(a) State what would be observed and write equation for the reaction that would take place if potassium iodide was added to acidified potassium dichromate solution. (2 ½ marks)
- (b) Sodium thiosulphate solution was added to the mixture in (a), state what was observed and write equation for the reaction that took place. (2 ½ marks)
- 13.(a) The table below shows the melting points of magnesium halides.

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

Explain the trend in melting points of the halides. (04 marks)

(b) The values of lattice energies of potassium halides are given below.

Formula of halide	$KF$	$KCl$	$KI$
Lattice energy( $kJmol^{-1}$ )	-813	-710	-643

Explain the trend in these values for the potassium halides. (03 marks)

14. Explain the following observations

- (a) Lead(IV) chloride exists but lead(IV) bromide does not. (02 marks)
- (b) Tin and lead do not form tetraiodides. (03 marks)
- (c) When hydrogen iodide is treated with concentrated sulphuric acid, iodine is liberated, whereas when hydrogen chloride is similarly treated, chlorine is not evolved. (03 marks)
- (d) When added separately to copper(II) sulphate solution, potassium iodide forms a white precipitate in a brown solution while potassium chloride gives no observable change. (03 marks)
- (e) The boiling point of hydrogen fluoride is higher than that of hydrogen chloride. (03 marks)

- (f) Both halogens and oxygen are diatomic. However, halogens react more readily with metals than oxygen. (02 marks)
- (g) Iodine is insoluble in water but soluble in potassium iodide solution. (2 ½ marks)
- (h) The bond in hydrogen chloride is polar. (1 ½ marks)
- (i) Hydrofluoric acid is weaker than hydrobromic acid. (03 marks)

**Long answer type questions**

15. Fluorine, chlorine, bromine and iodine are elements in group VII of the Periodic Table.

(a) Describe the general method of preparing chlorine, bromine and iodine in the laboratory. (02 marks)

(b) Fluorine differs in some of its properties from chlorine, bromine and iodine.

(i) Explain why fluorine differs from other Group VII elements. (02 marks)

(ii) State four properties in which fluorine differs from other Group members. (04 marks)

(c) Describe the reactions of group VII elements with:

(i) Water (04 marks)

(ii) Sodium hydroxide (08 marks)

(iii) sulphurous acid (2 ½ marks)

(d) Hydrofluoric acid is a weaker acid than hydrochloric acid. Explain.

(02 marks)

16.(a)(i) Sketch a graph of first electron affinity against atomic number of group VII elements. (3 ½ marks)

(ii) Explain the shape of the graph (6 ½ marks)

(b) State two reasons why fluorine differs in some of its properties from bromine. (02 marks)

(c) State three properties in which fluorine differs from bromine. (03 marks)

(d) Describe the reaction of sulphuric acid with hydrogen bromide. Write the equation for the reaction. (03 marks)

17.(a) The boiling points of group VII elements are in the order

$I_2 > Br_2 > Cl_2 > F_2$  whereas the dissociation energy is in the reverse order. Briefly explain this observation. (06 marks)

(b) Discuss the chemical differences between fluorine and bromine with respect to;

(i) Water

(ii) Sodium hydroxide

(08 marks)

- (c) The oxy-acids of chlorine include;  $\text{HOCl}$ ,  $\text{HClO}_2$ ,  $\text{HClO}_3$  and  $\text{HClO}_4$ .
- Write and name the shapes adopted by the oxy-acids. (04 marks)
  - Which of the oxy-acids is the strongest acid? Give a reason for your answer. (02 marks)
- 18.(a) State and explain the trend in the boiling points of group VII elements. (03 marks)
- (b) Explain why hydrogen fluoride;
- is a weaker acid in dilute aqueous solution than in concentrated solution. (03 marks)
  - has a higher boiling point than hydrogen iodide (03 marks)
- (c) Write equation for the reaction between hydrogen fluoride and silicon(IV) oxide. (01 mark)
- (d) Describe the reactions of group (VII) elements with sodium hydroxide. (07 marks)
- (e) Write the equation for the reaction between sulphuric acid
- Sodium chloride
  - Potassium bromide
  - Sodium iodide (03 marks)
- 19.(a) The bond energies of halogen acids are given in the table below.
- | $\text{H}-\text{X}$                | $\text{H}-\text{F}$ | $\text{H}-\text{Cl}$ | $\text{H}-\text{Br}$ | $\text{H}-\text{I}$ |
|------------------------------------|---------------------|----------------------|----------------------|---------------------|
| Bond energy( $\text{kJmol}^{-1}$ ) | 556                 | 431                  | 336                  | 299                 |
- Explain the variation in bond energy. (03 marks)
  - State two properties of the halogen acids whose variation is caused by the trend in bond energies. (02 marks)
- (b) Describe the reaction of the halogen acids with;
- Concentrated sulphuric acid (05 marks)
  - Sodium carbonate (2 ½ marks)
- (c) Describe the reaction of the halogens with concentrated potassium hydroxide. (7 ½ marks)
- 20.(a) Describe the industrial preparation of chlorine. (04 marks)
- (b) Describe the reaction of chlorine with;
- iron (02 marks)
  - potassium hydroxide (04 marks)
- (c) Describe the reaction of fluorine with
- Water (02 marks)
  - Potassium hydroxide (04 marks)

(d) Explain:

- (i) why hydrogen fluoride is a liquid whereas hydrogen chloride is a gas at 18 °C. (04 marks)
- (ii) why aluminium fluoride has a higher melting point than aluminium chloride. (03 marks)

21. The table below shows the hydrides of group VII elements and their boiling points.

Period number	2	3	4	5
Hydride	HF	HCl	HBr	HI
Boiling point(°C)	+20	-85	-67	-35

- (a) (i) Plot a graph of boiling point against period number. (04 marks)
- (ii) Explain the shape of the graph. (05 marks)
- (b) Describe briefly how the following hydrides are prepared in the laboratory. (*Illustrate your answers with equations*)
- (i) hydrogen chloride (2 ½ marks)
- (ii) hydrogen iodide (2 ½ marks)
- (c) Discuss the reactions of the hydrides with:
- (i) sodium hydroxide
- (ii) sulphuric acid
- (iii) silicon dioxide (06 marks)

22. Explain the following observations.

- (a) When iodine crystals are added to cold dilute sodium hydroxide solution, the grey solid dissolves to form a pale yellow solution which turned colourless on standing. (04 marks)
- (b) When acidified potassium manganate(VII) solution was added to aqueous potassium iodide solution, the solution turns brown. (03 marks)
- (c) The first electron affinities of the halogens generally decrease down the group. However, the first electron affinity of fluorine is abnormally high. (04 marks)
- (d) When a limited amount of chlorine is bubbled through sodium thiosulphate solution, a yellow precipitate is formed. (05 marks)
- (e) The fluorine molecule has a low bond dissociation enthalpy yet it has a short bond length. (04 marks)

# THE CHEMISTRY OF D-BLOCK AND TRANSITION ELEMENTS

## INTRODUCTION

All transition elements are d-block elements but not all d-block elements are transition elements.

1. (a) Define a transition element

(b) Distinguish between a transition element and a d-block element

(a) *A transition element is an element that has a partially filled d-sub energy level in its atom or at least one of its ions.*

(b) *A transition element is an element that has a partially filled d-sub energy level in its atom or at least one of its ions whereas a d-block element is an element whose outer most electrons fill the d-sub energy level.*

## ELECTRONIC CONFIGURATIONS OF TRANSITION METAL ATOMS/ IONS

The first transition series includes the elements in which the 3d sub-energy level is filled successively. It lies in the fourth period and includes the elements from scandium ( ${}_{21}\text{Sc}$ ) to zinc ( ${}_{30}\text{Zn}$ ). The table below to show the electronic configurations of the elements

ELEMENT	SYMBOL	ATOMIC NUMBER	ELECTRONIC CONFIGURATION
Scandium	<i>Sc</i>	21	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
Titanium	<i>Ti</i>	22	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
Vanadium	<i>V</i>	23	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
Chromium	<i>Cr</i>	24	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$
Manganese	<i>Mn</i>	25	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
Iron	<i>Fe</i>	26	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
Cobalt	<i>Co</i>	27	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
Nickel	<i>Ni</i>	28	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$
Copper	<i>Cu</i>	29	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
Zinc	<i>Zn</i>	30	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

*Note that for copper and chromium, the 3d sub energy level is filled first because a sub-energy level is only thermodynamically stable when half-filled or completely filled with electrons.*

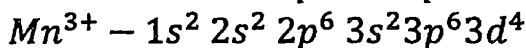
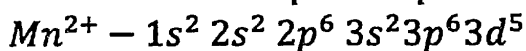
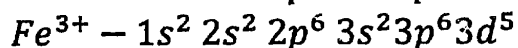
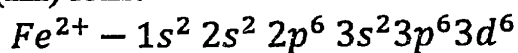
All the transition elements except zinc and scandium use the 3s as well as the 4d electrons in forming chemical bonds.

Still, all of them except zinc and scandium show variable valencies. Other properties of the elements will be discussed later.

2. The table below shows formulae of some of the ions formed by chromium, iron, cobalt, copper and manganese. Write the electronic configurations of the ions.

Ion	Electronic configuration
$Cr^{3+}$	
$Fe^{2+}$	
$Co^{2+}$	
$Cu^{+}$	
$Mn^{2+}$	

3. Explain in terms of electronic configuration why iron(II) ions are readily oxidised to iron(III) ions whereas manganese(II) ions are not readily oxidised to manganese(III) ions.



The iron(II) ion has a partially filled 3d-subenergy level, with 6 electrons hence thermodynamically unstable while the iron(III) ion has a half filled 3d-sub energy level which is more stable. Iron(II) ions are readily oxidised to iron(III) ions in order to attain a more stable electronic configuration.

The manganese(II) ion has a half filled 3d-sub energy level which is thermodynamically more stable than the manganese(III) ion that has a partially filled 3d-subenergy level, with 4 electrons hence thermodynamically unstable. The manganese(II) ion cannot readily be oxidised because the oxidation state will be changing from a relatively more stable one to less stable one.

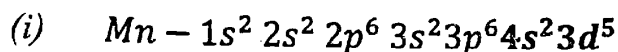
4. (a) Vanadium and Manganese are transition elements. Manganese can form compounds in the +7 oxidation state. Explain;

(i) how the +7 oxidation state arises for manganese?

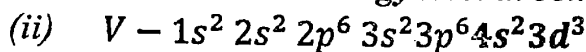
(ii) what the maximum possible oxidation state for Vanadium is likely to be.

(b) Write a formula of one compound of vanadium in which it shows the oxidation state in (ii) above. State one chemical application of the compound whose formula is written

(a)



*Manganese uses both the two electrons in the 4s sub energy level and the five unpaired electrons in the 3d sub energy level in bond formation.*

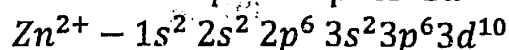
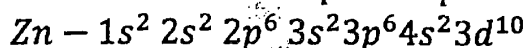
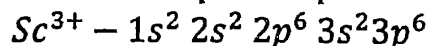
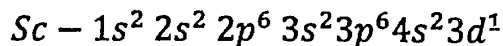


*Vanadium acquires a maximum oxidation state of +5 after using the two electrons in the 4s sub energy level and the three electrons in the 3d sub energy level in bond formation.*

(b) Formula of compound ;  $\text{V}_2\text{O}_5$

*Chemical application; In the contact process, as catalyst for oxidation Sulphur dioxide to Sulphur trioxide.*

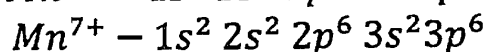
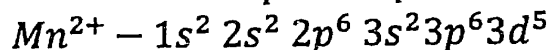
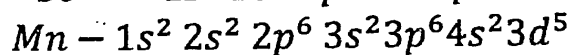
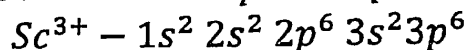
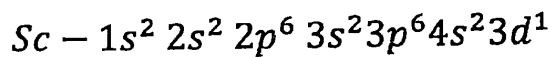
5. Explain in terms of electronic configuration why Scandium and zinc are not typical transition elements.



*Scandium form ions only in the +3 oxidation state. This involves loss of the two electrons in the 4s sub energy level and the only one electron in the 3d-sub energy level leaving its ion with an empty 3d sub energy level.*

*The zinc atom has a completely filled 3d sub energy level. The only ion formed by zinc is in the +2 oxidation state which involves loss of the two electrons in the 4s sub energy level leaving its ion with a fully filled 3d sub energy level.*

6. Explain why scandium only forms compounds in which its oxidation state is +3, while manganese can form compounds in which its oxidation states are +2 and +7.



*Manganese can form the manganese(II) ion which involves loss of the two electrons in the 4s sub energy level leaving the ion with a stable configuration in which the 3d-sub energy level is half filled. Manganese can also lose both the two electrons in the 4s sub energy level and the five unpaired electrons in the 3d sub energy level to form the manganese(VII) ion which has a completely filled 3p sub energy level and is also thermodynamically stable.*

*Scandium can only form an ion by loss of the two electrons in the 4s sub energy level and the only one electron in the 3d-sub energy level leaving the scandium(III) ion with a very stable electronic configuration in which the 3p sub energy level is completely filled.*

## PHYSICAL PROPERTIES OF THE ELEMENTS

### 1. Melting points/Boiling points

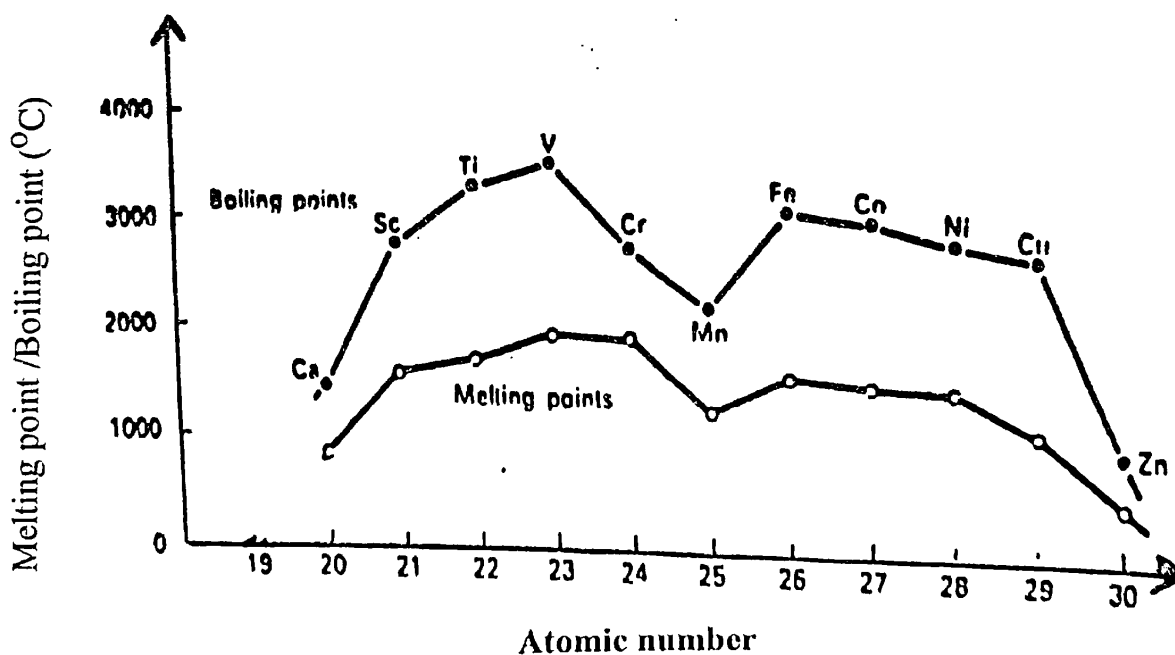
The boiling point of the first transition series follows the same trend as the melting point, showing a drop in melting point/ boiling point for manganese and zinc having the lowest melting point.

Most of the first transition series metals are harder and tougher, have higher melting and boiling points than the main block elements in the same period, i.e. potassium and calcium. This is attributed to the stronger metallic bonds they form since they use both 4s and 3d electrons in metallic bonding.

Melting point for the transition metals increases with increase in number of unpaired electrons in the 3d sub energy level and decreases as the number of unpaired electrons in the 3d sub energy level decreases.

ELEMENT	ELECTRONIC CONFIGURATION	Electron arrangement in the 3d sub energy level	No. of unpaired electrons
Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$	$\uparrow$	1
Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$	$\uparrow \uparrow$	2
V	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$	$\uparrow \uparrow \uparrow$	3
Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$	$\uparrow \uparrow \uparrow \uparrow \uparrow$	5
Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$	$\uparrow \uparrow \uparrow \uparrow \uparrow$	5
Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$	$\uparrow\downarrow \uparrow \uparrow \uparrow \uparrow$	4
Co	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$	$\uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \uparrow$	3
Ni	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow$	2
Cu	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	0
Zn	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	0

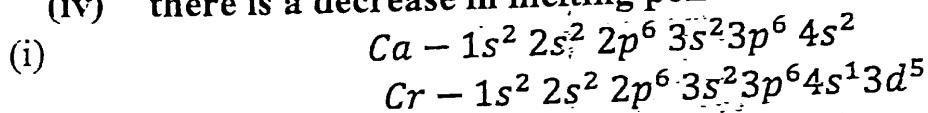
The graph below is a sketch of the variation of the melting and boiling points of some of the elements in period 4 of the Periodic Table. Use it to answer the questions that follow.



DEMYSTIFYING INORGANIC CHEMISTRY BY Joseph Jobs Kayiira, BScED(Hons.CHEM/MTC)  
 Email:josephkayirab@gmail.com Call 0782601038 WhatsApp 0753247098

Explain why;

- (i) the melting point of chromium is higher than that of calcium
- (ii) melting point generally increases from scandium to chromium
- (iii) manganese and zinc have abnormally low melting points
- (iv) there is a decrease in melting point from iron to copper



Calcium has a larger atomic radius and only contributes the two 4s electrons per atom towards metallic bonding hence forming weaker metallic bonds that require a lower amount of energy to break than chromium which has a smaller atomic radius and contributes both the one 4s electron and the five 3d electrons per atom forming stronger metallic bonds that require a higher amount of energy to break.

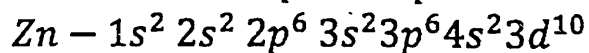
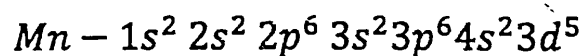
- (ii) Melting point generally increases from Scandium to Chromium because the number of unpaired electrons in the 3d sub energy level increases from one in scandium, two in Titanium, three in Vanadium to five in Chromium.

Element	Electronic configuration
Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
V	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

Electron arrangement in the 3d sub energy level				
↑				
↑	↑			
↑	↑	↑		
↑	↑	↑	↑	↑

No. of unpaired electrons
1
2
3
5

(iii)



Manganese and zinc have abnormally low melting points because manganese has a half filled 3d sub energy level, thermodynamically stable, making the 3d electrons less available for metallic bonding. It only uses the 4s electrons per atom in metallic bonding. Zinc has a completely filled 3d sub energy level which is also thermodynamically stable and the 3d electrons are also less available for metallic bonding. Zinc only uses the 4s electrons per atom in metallic bonding. Manganese and zinc therefore form weaker metallic bonds that require a low amount of energy to break.

(iv) Melting point decreases from iron to copper because the number of unpaired electrons in the 3d sub energy level decreases from four in iron, three in cobalt, two in nickel to zero in copper.

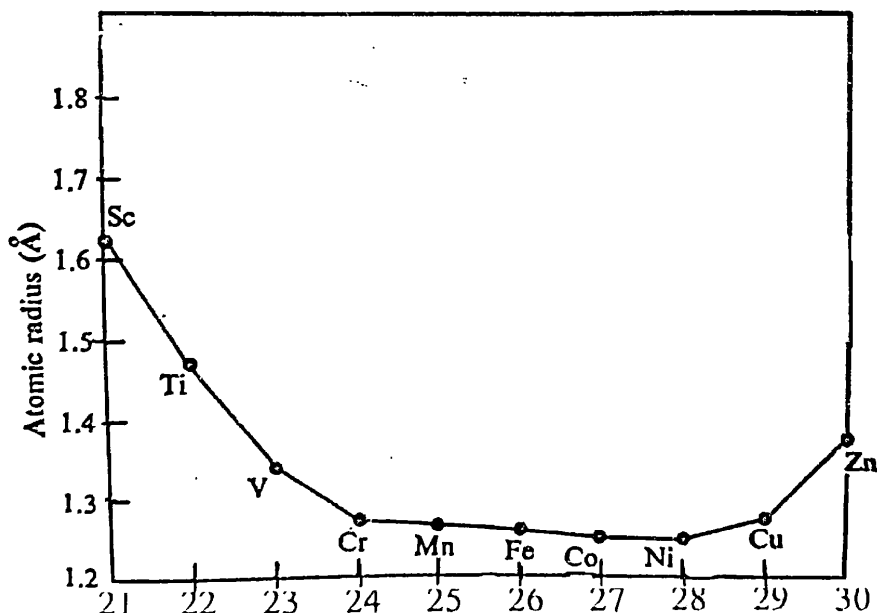
Element	Electronic configuration	Electron arrangement in the 3d sub energy level	No. of unpaired electrons					
Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$	<table border="1"> <tr><td>↑↓</td><td>↑</td><td>↑</td><td>↑</td><td>↑</td></tr> </table>	↑↓	↑	↑	↑	↑	4
↑↓	↑	↑	↑	↑				
Co	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$	<table border="1"> <tr><td>↑↓</td><td>↑↓</td><td>↑</td><td>↑</td><td>↑</td></tr> </table>	↑↓	↑↓	↑	↑	↑	3
↑↓	↑↓	↑	↑	↑				
Ni	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$	<table border="1"> <tr><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑</td><td>↑</td></tr> </table>	↑↓	↑↓	↑↓	↑	↑	2
↑↓	↑↓	↑↓	↑	↑				
Cu	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$	<table border="1"> <tr><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑↓</td></tr> </table>	↑↓	↑↓	↑↓	↑↓	↑↓	0
↑↓	↑↓	↑↓	↑↓	↑↓				

## 2. Atomic radius

The table below shows the atomic radii and ionic radii of the elements in the first transition series of the Periodic Table.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Atomic radius ( $\text{\AA}$ )	1.62	1.47	1.33	1.26	1.25	1.24	1.23	1.22	1.25	1.37

Below is a graph of atomic radius against atomic number (Advised to plot own graph)



State and explain the general trend in atomic radius of the first transition series.

*Atomic radius generally slightly decreases (remains almost constant) with increase in atomic number. This is because as atomic number increases, nuclear charge increases, electrons are added to the inner 3d sub energy level after the outer 4s sub energy level has been filled. The 3d electrons shield the outermost 4s electrons from nuclear attraction. Effective nuclear charge only slightly increases leading to a slight decrease in atomic radius.*

### 3. First ionization energy

The table below shows the first ionization energies of the elements in the first transition series of the Periodic Table. Explain the general trend in ionisation energy.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
First ionisation energy ( $\text{kJmol}^{-1}$ )	630	660	650	650	720	767	760	740	750	910

*There is a general slight increase in ionisation energy from Scandium to Zinc. This is because from one element to another nuclear charge increases, electrons are added to the inner 3d sub energy level after the outer 4s sub energy level has been filled. The 3d electrons shield the outermost 4s electrons from nuclear attraction. Effective nuclear charge only slightly increases. Nuclear attraction for outermost electron only slightly increases requiring a slightly increasing amount of energy to remove the outermost electron.*

### 4. Electropositivity

*Electropositivity generally slightly decreases from scandium to zinc.*

*This is because from scandium to zinc, nuclear charge increases, electrons are added to the inner 3d sub energy level after the outer 4s sub energy level has been filled. The 3d electrons shield the outermost 4s electrons from nuclear attraction. Effective nuclear charge only slightly increases leading to a slight decrease in atomic radius. The valence electrons experience a slightly increased nuclear attraction.*

## 5. Electrode potential

The table below shows the standard electrode potential values of the elements in the first transition series of the Periodic Table.

Element	<i>Sc</i>	<i>Ti</i>	<i>V</i>	<i>Cr</i>	<i>Mn</i>	<i>Fe</i>	<i>Co</i>	<i>Ni</i>	<i>Cu</i>	<i>Zn</i>
Standard electrode potential ( $E^\ominus$ ) (Volts) for $M^{2+}(aq)/M(s)$	-2.10	-1.63	-1.18	-0.91	<b>-1.18</b>	-0.44	-0.28	-0.25	+0.34	-0.76

*Standard electrode potential generally becomes less negative (decreases) from scandium to zinc because ionic radius generally slightly decreases, ionization energy slightly increases, atomization energy and hydration energy also generally increase. However, the increase in ionization energy and atomization energy is more rapid than increase in hydration energy.*

### GENERAL CHARACTERISTICS OF TRANSITION ELEMENTS

These include;

- a) Variable oxidation states
- b) Complex ion formation
- c) Formation of coloured compounds
- d) Paramagnetism
- e) Catalytic activity
- f) Formation of interstitial compounds

## VARIABLE OXIDATION STATES

*An oxidation state/ oxidation number is the net charge that remains on an atom in a compound when all the other atoms bonded to it are removed as ions.*

The oxidation states shown by the elements are summarised below;

SYMBOL	ELECTRONIC CONFIGURATION	OXIDATION STATES				
Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$	<b>+3</b>				
Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$	<b>+4</b>	+3	+2		
V	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$	+5	<b>+4</b>	+3	+2	
Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$	+6	<b>+3</b>	+2		
Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$	+7	+6	+4	+3	<b>+2</b>
Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$	+6	<b>+3</b>	+2		
Co	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$	+4	+3	<b>+2</b>		
Ni	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$	+4	<b>+2</b>			
Cu	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$	<b>+2</b>	+1			
Zn	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$	<b>+2</b>				

Note that;

- (i) The **bold** oxidation state for each element is the most stable one
- (ii) All elements except Scandium show an oxidation state of +2 in which the two 4s electrons are used are used for bonding.
- (iii) All elements except nickel, copper and zinc show the +3 oxidation state
- (iv) Transition metal cations with charges greater than +3 are rarely formed
- (v) The maximum oxidation state shown by the elements is equal to the sum of the number of the 4s electrons and number of unpaired 3d

electrons present in the neutral atom with an exception of Cobalt. It is only manganese that reaches the maximum oxidation state of +7.

- (vi) When a transition metal element forms a compound using an oxidation state higher than the most stable oxidation state, the compound can easily be reduced to a lower more stable oxidation state. The compound formed is therefore an oxidising agent. Examples include;

- Potassium manganate(VII) ( $KMnO_4$ )
- Potassium dichromate(VI) ( $K_2Cr_2O_7$ )
- Potassium chromate(VI) ( $K_2CrO_4$ )

Compounds in the lower oxidation states are generally reducing. These include iron(II) sulphate, copper(II) ions and manganese(II) ions.

- (vii) Compounds with higher oxidation states are mainly covalent i.e. Titanium(IV) chloride ( $TiCl_4$ ) and manganese(VII) oxide ( $Mn_2O_7$ ). Whereas those with lower oxidation states are mainly basic, higher oxidation states yield acidic compounds.

**Why do transition metal elements form variable oxidation states?**

*This is because their atoms can easily lose both the 4s and 3d electrons due to the very small energy difference between the 3d and 4s sub energy levels.*

### COMPLEX ION FORMATION

*A complex is a substance in which a metal atom or ion is associated with an atom or a group of atoms that are negatively charged or have a lone pairs of electrons by formation of coordinate covalent bonds.*

Transition metals form complexes because of;

- (i) *Small ionic radius of the cations*
- (ii) *High charge density of the cations*
- (iii) *Presence of vacant 3d-orbitals to accommodate lone pairs of electrons donated by ligands.*

*A ligand is an ion or neutral molecule that is capable of forming coordinate covalent bonds with a central atom or ion by donating a lone pair of electrons into empty orbitals of the central atom or ion.*

The central atom in every complex has a maximum **coordination number**.

*The coordination number is the number of coordinate bonds a central metal atom or ion is able to form with ligands.*

**N.B.** Coordination number should not be confused with number of ligands bonded to central metal atom or ion.

### Types of ligands

Ligands are classified according to the number of coordinate bonds it can form with the central atom or ion. They include;

- i. *Monodentate ligands*
- ii. *Bidentate ligands*
- iii. *Polydentate ligands*

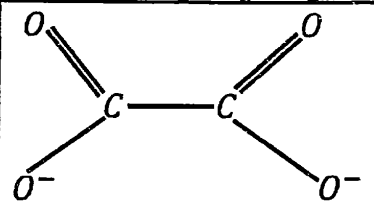
#### (i) Monodentate ligands

*A monodentate ligand is one which forms only one coordinate bond with the central atom or ion. Examples include;*

Name of ligand	Formula
<i>ammine</i>	$NH_3$
<i>aqua</i>	$H_2O$
<i>bromo</i>	$Br^-$
<i>carbonyl</i>	$CO$
<i>chloro</i>	$Cl^-$
<i>cyano</i>	$CN^-$
<i>fluoro</i>	$F^-$
<i>hydroxo</i>	$\bar{O}H$
<i>nitro</i>	$NO_2^-$
<i>nitrito</i>	$\bar{O}NO$
<i>nitrosyl</i>	$NO$
<i>thiocyano</i>	$SCN^-$

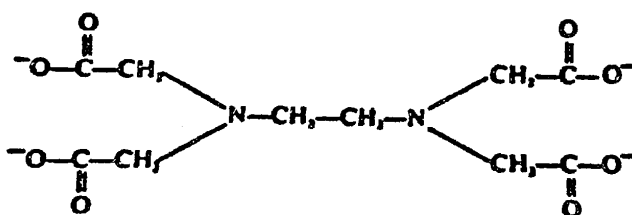
(ii) Bidentate ligands

A bidentate ligand is a ligand which forms only two coordinate bonds with a central atom or ion. Examples include;

Name of ligand	Formula
ethane-1,2-diamine	$NH_2CH_2CH_2NH_2$
Oxalato	

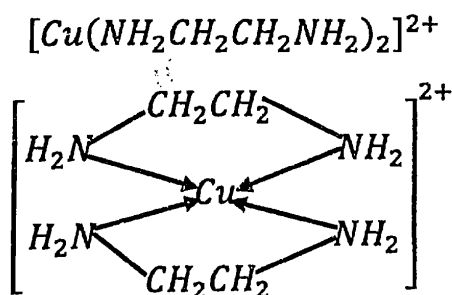
(iii) Polydentate ligands

A polydentate ligand is a ligand which forms more than two coordinate bonds with the central metal atom or ion. For example, EDTA (Ethylenediaminetetraacetic acid) which is a hexadentate ligand.



N.B. The coordination number of a complex corresponds to the number of ligands only if they monodentate. However, for bidentate ligands in a given complex, the coordination number is twice the number of ligands.

Consider the complex with a bidentate ligand below;



Since the each of the two ligands forms two coordinate bonds with copper, making a total of four coordinate bonds, the coordination number is four, corresponding to the number of coordinate bonds, but twice the number of ligands.

## Determining oxidation state of central metal atom in a complex and the coordination number

Rules to consider;

- Oxidation numbers must be written with symbols (+ or -) but superscripts (+3), subscripts (+3), mere numbers (3) or words(three) are not allowed
- The neutral ligands such as  $H_2O$ ,  $NH_3$ ,  $CO$ ,  $NO$ ,  $NH_2CH_2CH_2NH_2$ , etc are assigned a charge of zero in their complexes
- The ligands  $OH$ ,  $Cl$ ,  $Br$ ,  $F$ ,  $I$ ,  $CN$ ,  $ONO$ ,  $SCN$ , etc hold a (-1) charge. Those that are dinegatively charged like the oxalato ligand hold a (-2) charge.
- Atoms that are monoatomic can be assigned an oxidation number equal to their charge
- The oxidation state of the central atom is assigned an unknown letter say,  $x$ , and the sum of the oxidation numbers on all atoms in the species is equated to the overall charge on the species.
- The central atom is that atom that appears the least number of times in the species.

### Examples

Calculate the oxidation state of the central metal atom in the following complexes. State the coordination number as well.

Complex	Oxidation state	Coordination number
(i) $[Fe(H_2O)_5(OH)]^{2+}$	+3	6
(ii) $[Co(NH_3)_4Cl_2]Br$	+3	6

*Fe* and *Co* appear the least number of times i.e. once; hence they are the central metal atoms

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

$$y + (5 \times \text{charge of } H_2O) + (1 \times \text{charge of } OH) = +2$$

$$y + (4 \times 0) + (1 \times -1) = +2$$

$$y - 1 = +2$$

$$y = +3$$

The oxidation state of Fe is therefore +3.

Let the oxidation state of Co in  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$  be  $q$

The overall charge on the complex is +1 because the whole complex bonds to one Br to neutralise that charge. This Br is not considered in either calculating the oxidation state or determining the coordination number since it's not directly bonded to the central atom.

$$q + (4 \times \text{charge of } \text{NH}_3) + (2 \times \text{charge on Cl}) = +1$$

$$q + (4 \times 0) + (2 \times -1) = +1$$

$$q - 2 = +1$$

$$q = +3$$

The oxidation state of Co is therefore +3.

For each of the following complexes, state the oxidation state of the central atom and the coordination number of the complex.

No.	Formula of complex	Oxidation state	Coordination number
1	$\text{Cu}(\text{H}_2\text{O})_4^{2+}$		
2	$\text{Cr}(\text{OH})_4^-$		
3	$\text{Cr}_2\text{O}_7^{2-}$		
4	$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$		
5	$[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]^{3+}$		
6	$[\text{Mn}(\text{CN})_6]^{4-}$		
7	$[\text{MnO}_4]^{2-}$		
8	$[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]^{2+} \text{SO}_4^{2-}$		
9	$\text{Fe}(\text{CO})_5$		
10	$\text{Cr}(\text{CO})_6$		
11	$\text{K}_4[\text{Fe}(\text{CN})_6]$		
12	$[\text{Fe}(\text{CN})_6]^{3-}$		
13	$[\text{CoCl}_4]^{2-}$		
14	$[\text{Fe}(\text{CN})_6]^{4-}$		
15	$[\text{Ni}(\text{CN})_4]^{2-}$		
16	$[\text{Cr}(\text{NH}_3)_6]^{3+}$		
17	$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+} 2\text{Cl}^-$		
18	$[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$		
19	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$		

20	$[CrCl_2(H_2O)_4]^+$		
21	$[Cr(H_2O)_6]^{3+}(Cl^-)_3$		
22	$Ni(CO)_5$		
23	$[PtCl(NO_2)(NH_3)_4]^+$		
24	$Co(NH_3)_5(H_2O)Cl_3$		
25	$[Cu(NH_2CH_2CH_2NH_2)_2]^{2+}$		
26	$[Cr(NH_2CH_2CH_2NH_2)_3]^{3+}$		
27	$[Co(NH_3)_5SO_4]^+Br^-$		
28	$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$		
29	$[Cr(C_2O_4)_3]^{3-}$		
30	$Ag(NH_3)_2^+$		
31	$[Ni(NH_3)_6](NO_3)_3$		

### Nomenclature of complexes

The formula of any complex normally has a central atom and a ligand(s).

There are three types of complexes i.e. cation complexes, anion complexes and neutral complexes.

*Cation complexes are positively charged complex ions*

*Anion complexes are negatively charged complex ions*

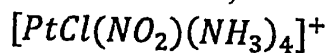
*Neutral complexes are those such that the charge on the central atom is equal and opposite to the total charge on the complex*

The table below shows common ligands and their names. They are divided into neutral anionic and neutral ligands.

Charged ligands		Neutral ligands	
Name	Formula	Name	Formula
hydroxo	$\bar{O}H$	Aqua	$H_2O$
chloro	$Cl^-$	ethane-1,2-diamine	$NH_2CH_2CH_2NH_2$
fluoro	$F^-$	hexane-1,6-diamine	$NH_2CH_2(CH_2)_4CH_2NH_2$
iodo	$I^-$	pyridine	$C_5H_5N$
bromo	$Br^-$	dinitrogen	$N_2$
cyano	$CN^-$	ammine	$NH_3$
nitro	$NO_2^-$	nitrosyl	$NO$
nitrito	$ONO^-$	carbonyl	$CO$
oxalato	$C_2O_4^{2-}$	dioxygen	$O_2$
thiocyanato	$SCN^-$		
oxo	$O^{2-}$		
carbonato	$CO_3^{2-}$		
sulphato	$SO_4^{2-}$		
ethanoato	$CH_3COO^-$		

### Rules for naming complexes;

Consider the cation complex with the formula;



1. Identify the names of the ligands i.e. *chloro*, *nitro* and *ammine*
2. Prefix the ligands according to their number i.e. *mono*, *di*, *tri*, *tetra*, *penta*, *hexa*, and so on. For the above case we have *monochloro*, *mononitro*, *tetraammine*
3. If more than one ligands are present, like in the case above, arrange the ligands in alphabetical order to make one word but disregarding the numerical prefixes i.e. *mono*, *di*, *tri*, *tetra*, *penta*, *hexa*, ...  
For the above case we have *tetraamminemonochloromononitro*...
4. For a cation complex, add the usual name of the central atom with its oxidation state indicated in roman numerals in brackets and end with the word *ion*. The name now becomes *tetraamminemonochloromononitroplatinum(III) ion*

5. If it is a neutral complex, i.e.  $[\text{PtCl}(\text{NO}_2)(\text{NH}_3)_4]\text{Br}$ , the name ends with the name of the radical attached, that is **tetraamminemonochloromononitroplatinum(III) bromide**.
6. If the complex is anionic, follow rules 1-3, but the name of the central atom ends as **...ate** (or **...ic** for acids) and the oxidation state written in brackets in roman numerals. For example the complex  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$  has a name **pentacyanomomonitrosylferrate(III) ion**.  
The table below shows names taken central atoms in anionic complexes.

Central atom	Name in anionic complex
Fe	ferrate
Ni	nickelate
Ag	argentate
Cr	chromate
Cu	cuprate
Pb	plumbate
Au	aurate
Sn	stannate
Si	silicate
Pt	platinate
Co	cobaltate
Mn	manganate
Zn	zincate
Be	beryllate
Al	aluminate

7. If the number prefix e.g. di, tri has already been used in the name of the ligand such as ethane-1,2-diamine; the name of the ligand is put in brackets and prefixed by the words bis, tris, tetrakis, ... respectively. For examples the complex  $[\text{Co}(\text{NH}_2\text{CH}_2(\text{CH}_2)_4\text{CH}_2\text{NH}_2)_3]^{3+}$  has a name;

**Tris(hexane-1,6-diamine) cobalt(III) ion.**

8. Correct spellings should be considered when naming complexes. **ammine** is used for complexes where the ligand  $\text{NH}_3$  appears such as  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  (hexaamminechromium(III) ion) whereas **amine** is used for complexes where the ligand is an amine such as  $[\text{Cu}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2]^{2+}$  bis(ethane-1,2-diamine)copper(II) ion. Check for spellings of central atoms, ligands, use of commas, numbers, hyphens and the order of ligands if more than one.

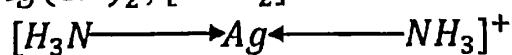
State the names of the following complexes.

No.	Formula of complex	Name of complex
1.	$Cu(H_2O)_4^{2+}$	
2.	$[Cr(H_2O)_5Cl]^{2+}$	
3.	$[Cr(NH_3)_3(H_2O)_3]^{3+}$	
4.	$[Cr(NH_3)_6]^{3+}$	
5.	$[Fe(H_2O)_5SCN]^{2+}$	
6.	$[CrCl_2(H_2O)_4]^+$	
7.	$[PtCl(NO_2)(NH_3)_4]^+$	
8.	$Ag(NH_3)_2^+$	
9.	$[Fe(H_2O)_4(OH)_2]^+$	
10.	$[Cr(NH_3)_4Cl_2]^+$	
11.	$Zn(NH_3)_4^{2+}$	
12.	$[CoCl_4]^{2-}$	
13.	$[CuCl_4]^{2-}$	
14.	$[Fe(CN)_6]^{3-}$	
15.	$Cr(OH)_4^-$	
16.	$Cr_2O_7^{2-}$	
17.	$[MnO_4]^{2-}$	
18.	$[Mn(CN)_6]^{4-}$	
19.	$[Fe(CN)_6]^{3-}$	
20.	$[Cr(C_2O_4)_3]^{3-}$	
21.	$AlF_6^{3-}$	
22.	$SiF_6^{2-}$	
23.	$CrF_6^{3-}$	
24.	$[Ni(CN)_4]^{2-}$	
25.	$[FeCl(CN)_5]^{3-}$	
26.	$K_4[Fe(CN)_6]$	
27.	$[Co(NH_3)_4Cl_2]Cl$	
28.	$Co(NH_3)_5(H_2O)Cl_3$	
29.	$[Pt(NH_3)_2Cl_2]Cl_2$	
30.	$[Cr(H_2O)_6]^{3+}(Cl^-)_3$	

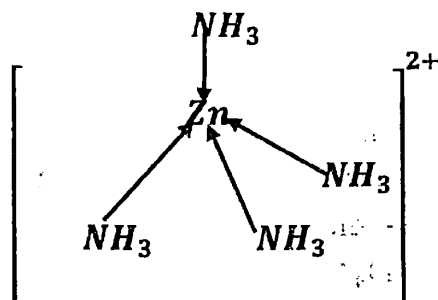
31.	$Ni(CO)_4$	
32.	$[Fe(NO)(H_2O)_5]^{2+}SO_4^{2-}$	
33.	$[Co(NH_3)_5SO_4]^+Br^-$	
34.	$[Pt(NH_3)_5Cl]Br_3$	
35.	$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$	
36.	$[Ni(NH_3)_6](NO_3)_3$	
37.	$[Ag(NH_3)_2](NO_3)_2$	
38.	$[Co(NH_3)_5(ONO)]Cl_2$	
39.	$Fe(CO)_5$	
40.	$[Cr(H_2O)_5Cl]^{2+}2Cl^-$	
41.	$[Co(ONO)(NH_3)_5]Br$	
42.	$[Co(NO_2)(NH_3)_5]Cl$	
43.	$[Co(NH_3)_3(CO_3)]Cl$	
44.	$K_3CoF_6$	
45.	$H_2SiF_6$	
46.	$Cr(CO)_6$	
47.	$[Co(NH_2CH_2CH_2NH_2)_3]^{3+}$	
48.	$[Cu(NH_2CH_2CH_2NH_2)_2]^{2+}$	
49.	$[Ni(NH_2CH_2CH_2NH_2)_3]^{3+}$	
50.	$[Cr(NH_2CH_2CH_2NH_2)_3]^{3+}$	
51.	$[Co(NH_2CH_2CH_2NH_2)_2Cl_2]^+$	
52.	$[Pt(NH_2(CH_2)_6NH_2)_2Cl_2]Cl_2$	

### Shapes of complexes

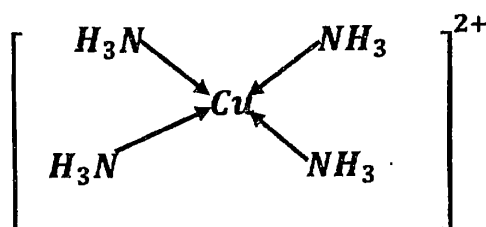
- Complexes with coordination number 2 adopt a **linear** structure. These include  $Ag(NH_3)_2^+$ ,  $Ag(CN)_2^-$ ,  $[CuCl_2]^-$  etc



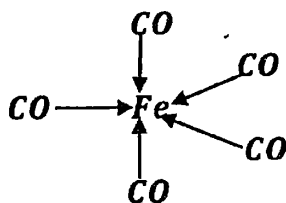
- Some complexes with coordination number 4 may adopt a **tetrahedral** structure. These include  $Zn(NH_3)_4^{2+}$ ,  $[NiCl_4]^{2-}$ ,  $Ni(CO)_4$  and  $MnO_4^{2-}$



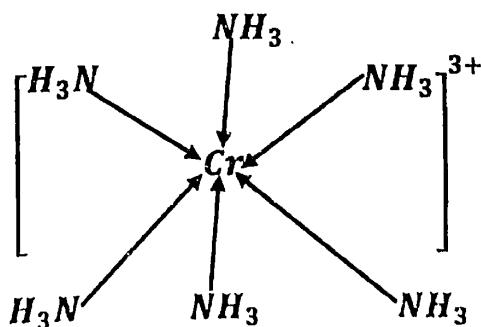
Some other complexes with coordination number 4 adopt a square planar structure e.g.  $\text{Cu}(\text{NH}_3)_4^{2+}$ ,  $\text{Ni}(\text{CN})_4^{2-}$



5. Complexes with coordination number 5 like  $\text{Fe}(\text{CO})_5$  are trigonal bipyramidal



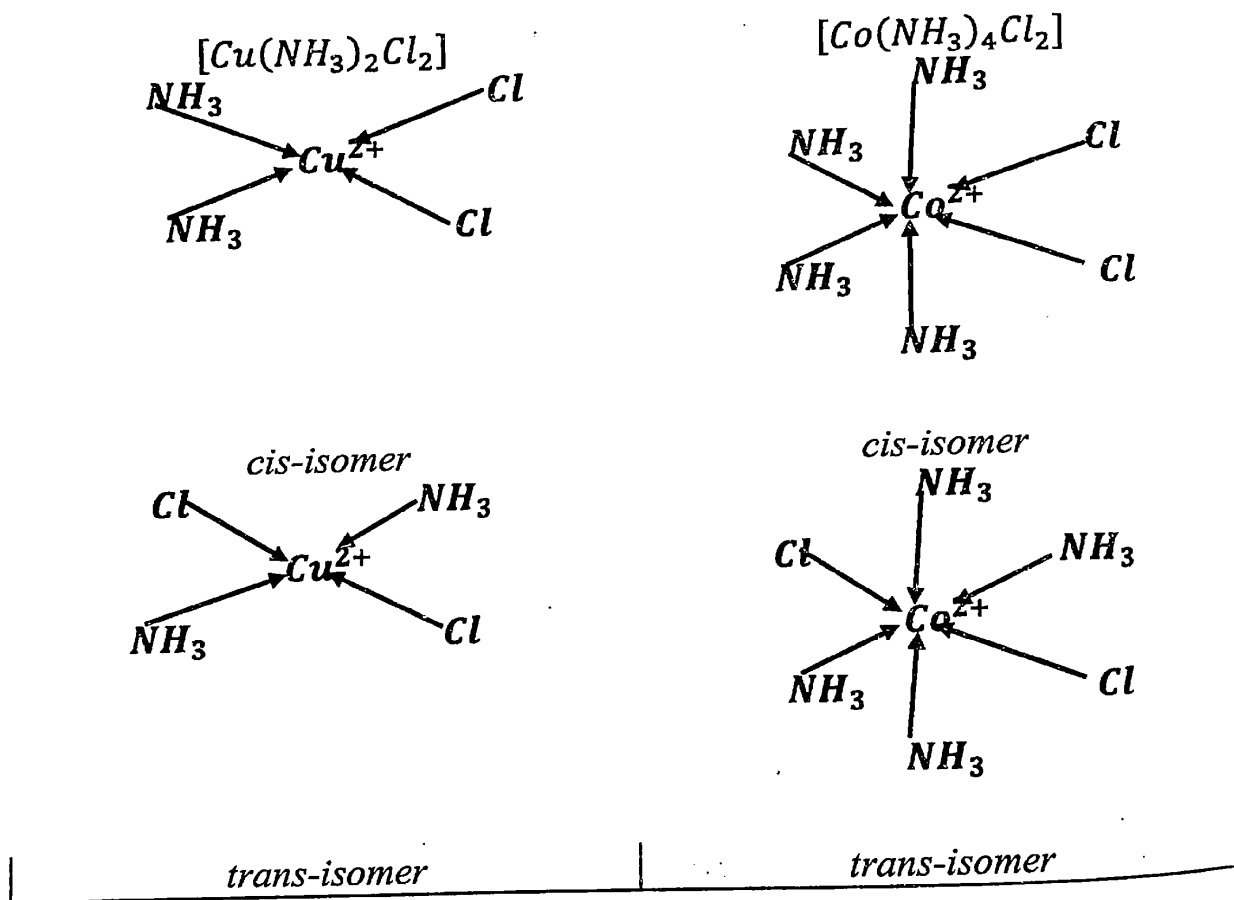
6. Complexes with coordination number 6 are generally octahedral e.g.  $\text{Cr}(\text{NH}_3)_6^{3+}$ ,  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{Fe}(\text{CN})_6^{3-}$ ,  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ ,  $\text{Cr}(\text{CO})_6$



## Isomerism in complexes

### 1. Geometric isomerism

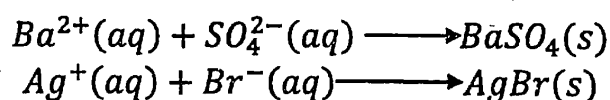
Geometric isomers are compounds with the same molecular formula but differ by the arrangement of ligands in space. Geometric isomerism occurs in square planar and octahedral complexes. *cis*- and *trans*- isomers are formed. For example  $[Cu(NH_3)_2Cl_2]$  and  $[Co(NH_3)_4Cl_2]$



### 2. Ionisation isomerism.

Ionisation isomers are compounds with the same molecular formula but form different ions in solution. For example  $Co(NH_3)_5BrSO_4$  has two isomers  $[Co(NH_3)_5Br]^{2+}SO_4^{2-}$  and  $[Co(NH_3)_5SO_4]^+Br^-$ . The two isomers may be distinguished by separately treating their solutions with barium nitrate solution and silver nitrate solution.

Isomer	$[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}\text{SO}_4^{2-}$		$[\text{Co}(\text{NH}_3)_5\text{SO}_4]^+\text{Br}^-$	
Reagent used	<i>barium nitrate solution</i>	<i>silver nitrate solution</i>	<i>barium nitrate solution</i>	<i>silver nitrate solution</i>
Observation	<i>White precipitate</i>	<i>No observable change</i>	<i>No observable change</i>	<i>Pale yellow precipitate</i>
Explanation	<i>The bromide ion is directly bonded to the cobalt(III) ion whereas the sulphate ion is free and reacts with barium ions to form insoluble barium sulphate</i>	<i>The bromide ion is directly bonded to the cobalt(III) ion hence cannot be precipitated by silver ions</i>	<i>The sulphate ion is directly bonded to the cobalt(III) ion hence cannot be precipitated by barium ions</i>	<i>The sulphate ion is directly bonded to the cobalt(III) ion whereas the bromide ion is free and reacts with silver ions to form insoluble silver bromide</i>



### 3. Hydrate isomerism.

Hydrate isomers are compounds with the same molecular formula but differ by number of water molecules directly bonded to the central metal ion. This type of isomerism can occur in compounds like cobalt(III) bromide hexahydrate ( $\text{CoBr}_3 \cdot 6\text{H}_2\text{O}$ ) and chromium(III)chloride hexahydrate ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ).

$\text{CoBr}_3 \cdot 6\text{H}_2\text{O}$  has the isomers whose formulae and properties are shown in the table below.

Formula of isomer	or	Formula of isomer	Number of moles of $\text{Br}^-$ ions removed as $\text{AgBr}$ by $\text{AgNO}_3$	Total number of conducting ions in solution	No. of $\text{H}_2\text{O}$ molecules removed by drying in dessicator over concentrated $\text{H}_2\text{SO}_4$
$[\text{Co}(\text{H}_2\text{O})_6]\text{Br}_3$		$[\text{Co}(\text{H}_2\text{O})_6]^{3+}(\text{Br}^-)_3$	3	4	0
$[\text{Co}(\text{H}_2\text{O})_5\text{Br}]\text{Br}_2 \cdot \text{H}_2\text{O}$		$[\text{Co}(\text{H}_2\text{O})_5\text{Br}]^{2+}(\text{Br}^-)_2 \cdot \text{H}_2\text{O}$	2	3	1
$[\text{Co}(\text{H}_2\text{O})_4\text{Br}_2]\text{Br} \cdot 2\text{H}_2\text{O}$		$[\text{Co}(\text{H}_2\text{O})_4\text{Br}_2]^+(\text{Br}^-) \cdot 2\text{H}_2\text{O}$	1	2	2

As shown in the table above the following conclusions can be made about the isomers;

- The coordination number of cobalt in all the complexes does not change and is 6.
- The number of moles /mass of silver bromide precipitated is in the ration 3:2:1 respectively and depends on the number of free bromide ions respectively
- The number of conducting ions is in the ratio 4:3:2 respectively
- The colour of the complexes also changes as the number of water molecules directly bonded to the central atom changes.

#### 4. Optical isomerism

This occurs in complexes with bidentate ligands. The isomers are not superimposable on others.

## FORMATION OF COLOURED COMPOUNDS

Most transition metal ions are coloured due to;

- (i) *Incompletely filled 3d sub-energy levels in which are unpaired electrons that can make d-d electronic transitions.*
- (ii) *The nature of ligand bonded to the central metal atom*
- (iii) *The oxidation state of the central metal element.*

The ions that are colourless are either due to completely filled or completely empty 3d- sub energy level.

For transition metal ion with incompletely filled 3d sub energy level, electronic transitions occur in the 3d sub energy level of transition metal ions. This is because light in the visible region has the right energy to promote d- electrons from a lower energy level to a higher energy level. When light falls on the metal ion, the 3d- sub energy level splits into two. The unpaired electrons in the lower energy level absorb energy and jump to a higher energy level. The remaining part of the visible light that is not absorbed is reflected in form of electromagnetic radiation whose wavelength corresponds to the colour of the ion.

Explain why copper(I) ions are colourless in solution but iron(II) ions and manganese(II) ions are coloured?

Element	Electronic configuration	Electron arrangement in the 3d sub energy level	No. of unpaired electrons					
$\text{Cu}^+$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$	<table style="margin: auto; border-collapse: collapse;"> <tr> <td style="border: 1px solid black; padding: 2px;">↑↓</td> <td style="border: 1px solid black; padding: 2px;">↑↓</td> <td style="border: 1px solid black; padding: 2px;">↑↓</td> <td style="border: 1px solid black; padding: 2px;">↑↓</td> <td style="border: 1px solid black; padding: 2px;">↑↓</td> </tr> </table>	↑↓	↑↓	↑↓	↑↓	↑↓	0
↑↓	↑↓	↑↓	↑↓	↑↓				
$\text{Fe}^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$	<table style="margin: auto; border-collapse: collapse;"> <tr> <td style="border: 1px solid black; padding: 2px;">↑↓</td> <td style="border: 1px solid black; padding: 2px;">↑</td> <td style="border: 1px solid black; padding: 2px;">↑</td> <td style="border: 1px solid black; padding: 2px;">↑</td> <td style="border: 1px solid black; padding: 2px;">↑</td> </tr> </table>	↑↓	↑	↑	↑	↑	4
↑↓	↑	↑	↑	↑				
$\text{Mn}^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$	<table style="margin: auto; border-collapse: collapse;"> <tr> <td style="border: 1px solid black; padding: 2px;">↑</td> <td style="border: 1px solid black; padding: 2px;">↑</td> <td style="border: 1px solid black; padding: 2px;">↑</td> <td style="border: 1px solid black; padding: 2px;">↑</td> <td style="border: 1px solid black; padding: 2px;">↑</td> </tr> </table>	↑	↑	↑	↑	↑	5
↑	↑	↑	↑	↑				

*The copper(I) ion has a completely filled 3d-subenergy level in which all the electrons are paired; no d-d electronic transitions can occur hence the ion has no colour. The iron(II) ion has and manganese(II) ion have incompletely filled 3d-sub energy levels with 4 unpaired electrons and 5 unpaired electrons in their 3d-subenergy levels respectively, d-d electronic transitions can occur, hence coloured.*

Explain why;

(i) scandium(III) ions and zinc ions are colourless in solution.

Element	Electronic configuration	Electron arrangement in the 3d sub energy level	No. of unpaired electrons
$Sc^{3+}$	$1s^2 2s^2 2p^6 3s^2 3p^6$		0
$Zn^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	0

The scandium(III) ion has a completely empty 3d sub energy level and no electronic d-d electronic transitions can occur since it has no 3d electrons. The zinc ion has a completely filled 3d sub energy level in which all the electrons are paired hence no possible d-d electronic transitions can occur.

(ii) Copper(I) ions are colourless whereas copper(II) ions are coloured.

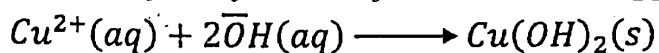
Element	Electronic configuration	Electron arrangement in the 3d sub energy level	No. of unpaired electrons
$Cu^+$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	0
$Cu^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$	↑↓ ↑↓ ↑↓ ↑↓ ↑	1

The copper(I) ion has a completely filled 3d sub energy level in which all the electrons are paired hence no d-d electronic transitions can occur whereas the copper(II) ion has a partly filled 3d sub energy level with an unpaired electron. d-d electronic transitions are possible.

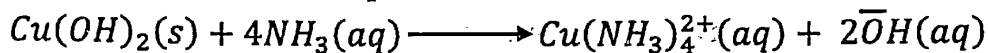
The nature of the ligand also affects the colour of the compound. A transition metal ion may show different colours when surrounded by different ligands. This normally happens due to ligand exchange shown by the three reactions below.

- To a solution of copper(II) sulphate was added aqueous ammonia drop wise until in excess, the pale blue solution formed a blue precipitate soluble in excess ammonia to form a deep blue solution. On addition of water, the deep blue solution slowly turned back to a pale blue solution. Explain.

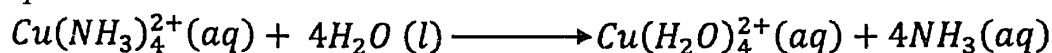
*Copper (II) ions react with hydroxyl ions to form insoluble copper(II) hydroxide.*



*Copper(II) hydroxide reacts with excess ammonia to form a soluble complex of tetraamminecopper(II) ions, deep blue in colour.*



*On addition of water, ligand exchange occurs and the ammino ligands in the complex are replaced with aqua ligands to form tetraaquacopper(II) ions, which are pale blue.*



2. Copper(II) sulphate crystals were dissolved in water and then concentrated hydrochloric acid was added drop wise to the solution. The resultant solution was then diluted with water.

(a) Name the chemical species present in;

- (i) the solution before hydrochloric acid was added
- (ii) after concentrated hydrochloric acid was added
- (iii) the resultant solution was diluted.

(b) State what was observed on;

- (i) dissolution of the crystals in water
- (ii) addition of concentrated hydrochloric acid
- (iii) dilution of the resultant solution

(c) Write equation for the reaction in

- (i) b(i)
- (ii) b(ii)

(d) Name the reaction that took place in b(iii)

(a)

- (i) Tetraaquacopper(II) ion
- (ii) Tetrachlorocuprate(II) ion
- (iii) Tetraaquacopper(II) ion

(b)

- (i) Blue crystals completely dissolved to form a pale blue solution
- (ii) The pale blue solution turned yellow
- (iii) The yellow solution turned back to pale blue

(c)

- (i)  $\text{Cu}(\text{H}_2\text{O})_4^{2+}(\text{aq}) + 4\text{Cl}^{-}(\text{aq}) \longrightarrow \text{CuCl}_4^{2-}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
- (ii)  $\text{CuCl}_4^{2-}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) \longrightarrow \text{Cu}(\text{H}_2\text{O})_4^{2+}(\text{aq}) + 4\text{Cl}^{-}(\text{aq})$

(d) Ligand exchange.

3. Cobalt(II) nitrate crystals dissolve in water to form a pink solution.

(a) State what would be observed when to a solution of cobalt(II) nitrate was added;

- (i) Concentrated hydrochloric acid
- (ii) the resultant solution in a (i) is diluted.

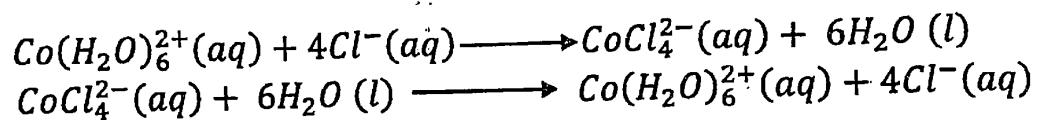
(b) Explain your observations in (a) (i) and (ii) above.

(a)

(i) the pink solution turned blue

(ii) the blue solution turned back to pink

(b) Cobalt(II) ions in solution exist as hexaaquacobalt(II) ions which react with excess chloride ions to form tetrachlorocobaltate(II) ions. On addition of water, ligand exchange occurs and the chloro ligands in the complex are replaced with aqua ligands to form hexaaquacobalt(II) ions, which are pink.



The colour of the transition metal ion may also depend on the **oxidation state** of the central metal element.

Iron(III) ions are yellow whereas iron(II) ions are green

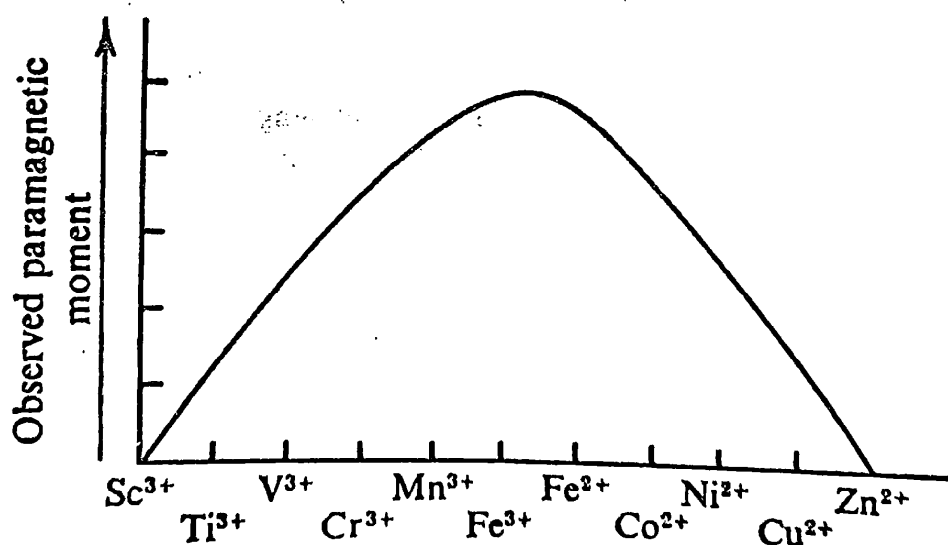
Manganate(VII) ions ( $\text{MnO}_4^-$ ) are purple whereas manganate(VI) ions ( $\text{MnO}_4^{2-}$ ) are green.

The colours of some transition metal ions are summarised in the table below

ION	COLOUR
$Sc^{3+}$	Colourless
$Ti^{3+}$	Purple
$V^{3+}$	Green
$Cr^{3+}$	Green
$Mn^{2+}$	Pink
$Fe^{3+}$	Yellow
$Fe^{2+}$	Green
$Co^{2+}$	Pink
$Ni^{2+}$	Green
$Cu^{2+}$	Blue
$Zn^{2+}$	Colourless

### PARAMAGNETISM

Most substances are weakly repelled from a strong magnetic field (diamagnetic) while others are weakly attracted to it (paramagnetic). In cases where the force of attraction is so large, the materials are then ferromagnetic. The magnitude of paramagnetic effect varies according to the transition metal ion. The attraction of a magnetic effect is strongest for the iron(III) ion and manganese(II) ion and is lowest for scandium(III) ion and zinc(II) ion, both of which are diamagnetic.



Paramagnetism increases with the increase in the number of unpaired electrons in the 3d sub energy level of the ions. The unpaired electrons spin on their axes thus inducing a paramagnetic moment. The table below shows number of unpaired electrons in different ions of transition metal elements of the first series. The observed paramagnetic moment directly corresponds with the graph above according to the observed number of unpaired electrons.

ION	ELECTRONIC CONFIGURATION	Electron arrangement in the 3d sub energy level	No. of unpaired electrons
$Sc^{3+}$	$1s^2 2s^2 2p^6 3s^2 3p^6$		0
$Ti^{3+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$	↑	1
$V^{3+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$	↑ ↑	2
$Cr^{3+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$	↑ ↑ ↑	3
$Mn^{3+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$	↑ ↑ ↑ ↑	4
$Mn^{2+}, Fe^{3+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$	↑ ↑ ↑ ↑ ↑	5
$Fe^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$	↑↓ ↑ ↑ ↑ ↑	4
$Co^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$	↑↓ ↑↓ ↑ ↑ ↑	3
$Ni^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$	↑↓ ↑↓ ↑↓ ↑ ↑	2
$Cu^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$	↑↓ ↑↓ ↑↓ ↑↓ ↑	1
$Zn^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	0

$Mn^{2+}$  and  $Fe^{3+}$  with the electronic configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$  have the highest paramagnetic moment because they have 5 unpaired electrons which is the highest number.

The  $Zn^{2+}$  ion with electronic configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$  and the  $Sc^{3+}$  ion with the electronic configuration  $1s^2 2s^2 2p^6 3s^2 3p^6$  have no paramagnetic moment because they have no unpaired electrons.

## CATALYTIC ACTIVITY

*A catalyst is a substance which although present in small proportions alters the speed of a chemical reaction but remains chemically unchanged at the end of the reaction.*

Catalysts function by providing an alternative path for a reaction.

A positive catalyst is one which increases the rate of a chemical reaction by providing an alternative path with lower activation energy.

A negative catalyst or an inhibitor on the other hand decreases the rate of a chemical reaction as the alternative path has higher activation energy.

There are certain peculiarities about catalysts;

- A catalyst may increase the rate of a chemical reaction (positive catalyst) or decrease it (negative catalyst)
- A catalyst remains chemically unchanged at the end of the reaction
- A catalyst is usually specific in action. A catalyst which may increase the rate of a particular reaction may not have any effect on another reaction.
- Usually a small amount of a catalyst often affects the rate of a chemical reaction. When a solid catalyst is used, it is usually in finely divided state.
- A catalyst does not affect the total amount of substance decomposed. It only speeds up the action.
- If a catalyst is used in a reversible reaction, it does not affect the yield of the product in the equilibrium mixture. It favours both forward and backward reactions equally.

A catalyst can be **heterogeneous** or **homogeneous**.

A **heterogeneous catalyst** is one whose phase is different from that of the reactants whereas a **homogeneous catalyst** is one which is in the same phase as the reactants

Most of the transition metals or their compounds are used as solids to catalyse gaseous reactions.

### How catalysts work;

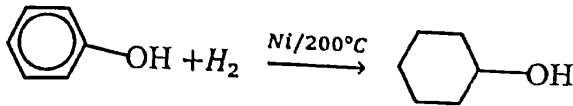
**Heterogeneous catalysts** are commonly used in solid form and in processes like hydrogenation, cracking and polymerisation. It's the surface of the catalysts that help in catalysis.

The transition elements use both the 3d and 4s electrons in bonding. This enables their ions to form they form weak temporary bonds with the reactant molecules. This weakens the internal bonding of the reactant molecules and

also increases the concentration of the reactant molecules at the surface of the catalyst thereby reducing the activation energy hence increasing the rate of reaction.

**Homogeneous catalysts** are commonly used for reactions in aqueous solution. The catalytic activity of such catalysts depends on the ability of transition metals to form ions in variable oxidation states in solution. In such cases the catalyst reacts with one of the reactants to form an intermediate compound in which the transition element exists in a different oxidation state from its original one. The intermediate compound then reacts with the other reactant or decomposes to form the final product, regenerating the catalyst with the original oxidation state of the central metal ion.

The table below shows common catalysts and some examples of reactions catalysed

Heterogeneous catalysts		
Catalyst	Reaction catalysed	Equation for the reaction
Manganese(IV) oxide	Decomposition of hydrogen peroxide to form oxygen	$2\text{H}_2\text{O}_2(\text{aq}) \longrightarrow \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
Finely divided iron	Manufacture of ammonia by the Haber process	$3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
Vanadium(V) oxide	Catalytic oxidation of sulphur dioxide to sulphur trioxide in the contact process	$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
Nickel	Hydrogenation of ethene to form ethane at $150^\circ\text{C}$	$\text{H}_2\text{C} = \text{CH}_2 + \text{H}_2 \xrightarrow{\text{Ni}/150^\circ\text{C}} \text{CH}_3\text{CH}_3$
	Hydrogenation of phenol to form cyclohexanol	

Nickel	Reduction of propanone and propanal to propan-1-ol and propan-2-ol respectively at 150 °C	$\text{CH}_3\text{CH}_2\text{CHO} + \text{H}_2 \xrightarrow{\text{Ni}/150^\circ\text{C}} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ $\text{CH}_3\text{COCH}_3 + \text{H}_2 \xrightarrow{\text{Ni}/150^\circ\text{C}} \text{CH}_3\underset{\text{OH}}{\text{CH}}\text{CH}_3$
	Reaction between Bromine and hydrogen to form hydrogen bromide OR iodine and hydrogen to form hydrogen iodide	$\text{Br}_2(\text{l}) + \text{H}_2(\text{g}) \rightleftharpoons 2\text{HBr}(\text{g})$ $\text{I}_2(\text{s}) + \text{H}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

### Homogeneous catalysts

Catalyst	Reaction catalysed	Equation for the reaction
Iron(II) ions	Reaction between peroxodisulphate (persulphate ions) and iodide ions.	$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq}) \longrightarrow 2\text{SO}_4^{2-}(\text{aq}) + 2\text{Fe}^{3+}(\text{aq})$ $2\text{Fe}^{3+}(\text{aq}) + 2\text{I}^{-}(\text{aq}) \longrightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{aq})$ <p>Overall equation</p> $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{I}^{-}(\text{aq}) \longrightarrow 2\text{SO}_4^{2-}(\text{aq}) + \text{I}_2(\text{aq})$
Iron(III) chloride solution	Decomposition of hydrogen peroxide to form oxygen	$2\text{H}_2\text{O}_2(\text{aq}) \longrightarrow \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
Copper(II) ions	Oxidation of vanadium(III) ions to Vanadium(V) ions by iron(III) ions	$\text{V}^{3+}(\text{aq}) + 2\text{Fe}^{3+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{VO}_2^{+}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq}) + 4\text{H}^{+}(\text{aq})$
Manganese(II) ions	Autocatalysis of the reaction between manganate(VII) ions and oxalate ions in acidic medium	$2\text{MnO}_4^{-}(\text{aq}) + 16\text{H}^{+}(\text{aq}) + 5\text{C}_2\text{O}_4^{2-}(\text{aq}) \longrightarrow 2\text{Mn}^{2+}(\text{aq}) + 10\text{CO}_2(\text{g}) + 8\text{H}_2\text{O}(\text{l})$

## FORMATION OF INTERSTITIAL COMPOUNDS

*Interstitial compounds are compounds with non-stoichiometric composition formed between transition metals and elements of atoms with small atomic radius such as hydrogen, carbon and nitrogen.*

These small atoms are able to fit in the interstices of the transition metal lattices forming materials which are chemically similar to the metals themselves but differ greatly in physical properties especially hardness.

The composition of interstitial compounds is variable and therefore cannot be expressed in by a simple chemical formula. Examples include  $TiH_{1.73}$ ,  $VH_{0.56}$  etc

## CHEMISTRY OF EACH ELEMENT

### SCANDIUM

- *Symbol Sc.*
- *A rare soft silvery metallic element*
- *group IIIA of the Periodic Table*
- *Atomic number 21*
- *Melting point 1541°C*
- *Boiling point 2831°C*
- *Because of the metal's high reactivity and high cost no substantial uses have been found for either the metal or its compounds except in high-intensity lights and in electronic devices.*

It only forms compounds in the +3 oxidation state

Some of these include **scandium oxide** ( $Sc_2O_3$ ) which is an amphoteric oxide that dissolves in excess alkali to form **hexahydroxoscandiate(III) ions**,  $Sc(OH)_6^{3-}$ .

**Scandium chloride** is a white solid formed by the element too.

**Qn. Explain why;**

- i. Scandium and zinc are not typical transition elements.
- ii. scandium only forms compounds in which its oxidation state is +3, while manganese can form compounds in which its oxidation states are +2 and +7
- iii. scandium(III) ion and zinc(II) ions are colourless in solution
- iv. scandium(III) ion and zinc(II) ions are non-paramagnetic

DEMYSTIFYING INORGANIC CHEMISTRY BY Joseph Jobs Kayiira, BScED(Hons. CHEM/MTC)  
Email: josephkaylirab@gmail.com Call 0782601038 WhatsApp 0753247098



## TITANIUM

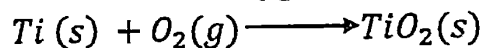
- *Symbol Ti.*
- *A white metallic transition element*
- *Atomic number 22*
- *Group IVA of the Periodic Table*
- *Melting point  $1660 \pm 10^\circ\text{C}$*
- *Boiling point  $3287^\circ\text{C}$ .*
- *The main use is making strong light corrosion resistant alloys for aircraft, ships and chemical plants as it is strong and resistant to corrosion.*
- *The element forms a passive oxide coating in air.*

### Chemical properties of titanium

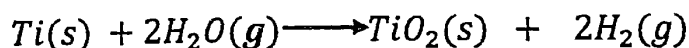
Describe the reactions of titanium with;

- air
- water
- acids
- sodium hydroxide
- chlorine

(a) Red hot Titanium reacts with oxygen to form titanium(IV) oxide



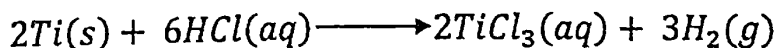
(b) Strongly heated Titanium reacts with steam to form Titanium(IV) oxide and hydrogen



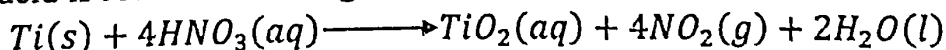
(c) Reaction with acids

Cold hydrochloric acid or cold nitric acid of any concentration have no effect on Titanium.

Hot concentrated hydrochloric acid reacts with Titanium to form Titanium(III) chloride and hydrogen gas. Titanium(III) chloride solution is purple.

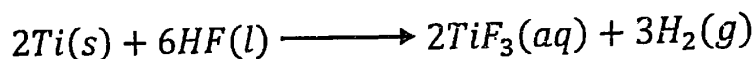


Titanium is oxidised by hot concentrated nitric acid to titanium(IV) oxide as the acid is reduced to nitrogen dioxide and water



*C.f Sn and Ge*

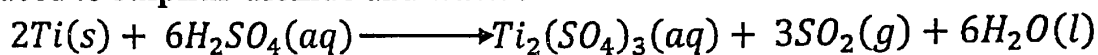
Cold hydrofluoric acid reacts with titanium to form titanium(III) fluoride and hydrogen



Cold dilute sulphuric acid reacts with Titanium to form titanium(III) sulphate and hydrogen



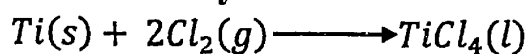
Cold concentrated sulphuric acid oxidises titanium to titanium(III) sulphate, itself reduced to sulphur dioxide and water.



*c. f ; Cr, Al and Fe*

(d) Sodium hydroxide **does not react** with Titanium under any condition.

(e) Heated Titanium reacts with **dry chlorine** to form Titanium(IV) chloride

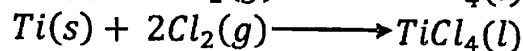
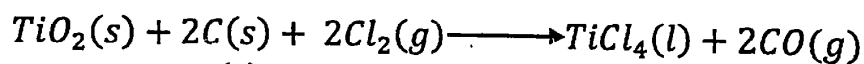


### COMPOUNDS OF TITANIUM

Common compounds are Titanium(IV) oxide, Titanium(IV) chloride and Titanium(III) chloride.

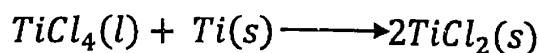
Compounds in +2 oxidation state like Titanium(II) chloride are unstable.

Titanium(IV) chloride is a volatile colourless liquid formed by heating titanium(IV) oxide with carbon in a stream of dry chlorine or passing dry chlorine over heated titanium. The same methods can be used to prepare silicon tetrachloride.



Titanium(III) chloride is formed by the reaction between titanium and hot concentrated hydrochloric acid as seen above.

Titanium(II) chloride is obtained by reducing titanium(IV) chloride by titanium metal



#### Question:

Titanium forms compounds with oxidation states +4, +3, and +2, the +4 state being the most stable.

(a) Write the formula and the electronic configuration of the ions of Titanium in each of the above oxidation states

(b) Explain why the +4 oxidation state is most stable for Titanium.

(c) Apart from variable oxidation states, with suitable examples, state three reasons why Titanium is a typical transition element.

(d) For each of the oxidation states above, write the formula of a compound in which titanium exhibits the oxidation state.

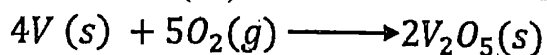
## VANADIUM

- *Symbol V*
- *A silvery white metallic element*
- *Atomic number 23*
- *Group VA*
- *Melting point 1890°C*
- *Boiling point 3380°C*
- *The element is used in a large number of steel alloys.*
- *Chemically, it reacts with non-metals at high temperatures but is not affected by hydrochloric acid or alkalis.*
- *Maximum oxidation state is +5 and compounds in this state are oxidising agents*
- *The +4 oxidation state is most stable*
- *+3 and +2 oxidation states exist and compounds in these states are ionic.  $V^{3+}$  and  $V^{2+}$  are both reducing agents.*
- *Vanadium therefore forms compounds with oxidation states +5, +4, +3, and +2.*

### Chemical properties of vanadium

Vanadium is relatively inert under normal conditions. Unlike its neighbours; titanium and chromium, it is corrosion resistant.

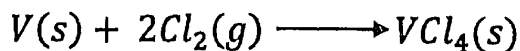
Heated Vanadium reacts with oxygen to form mainly vanadium(V) oxide. But vanadium(IV) oxide and vanadium(III) oxide are also formed



Vanadium does not react with non-oxidising acids like hydrochloric acid but dissolves in nitric acid and concentrated sulphuric acid.

Vanadium does not react with alkalis

Heated vanadium reacts with dry chlorine to form vanadium(IV) chloride.

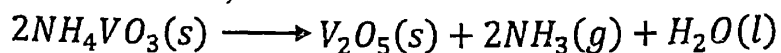


## COMPOUNDS OF VANADIUM

### Vanadium(V) compounds

Ammonium vanadate(V), a white solid and vanadium(V) oxide, an orange solid are the commonly known compounds of vanadium in the +5 oxidation state.

Vanadium(V) oxide is prepared by heating ammonium vanadate(V) which decomposes to form the oxide, ammonia and water.



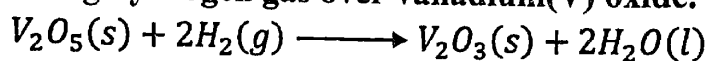
Vanadium(V) oxide is amphoteric and a useful catalyst in the catalytic oxidation of sulphur dioxide to sulphur trioxide in the contact process.

### Vanadium(IV) compounds

Vanadium(IV) oxide( $\text{VO}_2$ ), which is a dark blue amphoteric solid is a common vanadium compound in the +4 oxidation state.

### Vanadium(III) compounds

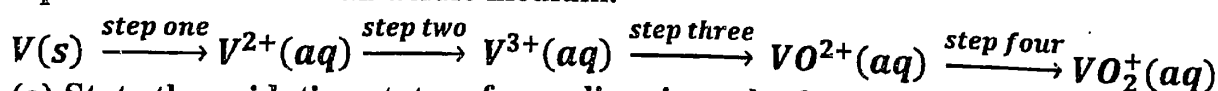
Vanadium(III) oxide( $\text{V}_2\text{O}_3$ ), a black solid and basic in nature is known. It is formed by passing hydrogen gas over vanadium(V) oxide.



### Vanadium(II) compounds

Vanadium(III) oxide( $\text{VO}$ ), a black solid and basic in nature

**Qn.** The following scheme shows changes in oxidation states of vanadium in aqueous solutions in an acidic medium.



- State the oxidation states of vanadium in each of the ions above.
- Write the half-cell reaction equations to show how each of the conversions in the following steps occur
  - step two
  - step three
  - step four
- Explain why the  $\text{V}^{4+}$  and  $\text{V}^{5+}$  ions cannot independently exist in solution.
- State what is observed and write an equation for the reaction that occurs when ammonium vanadate is heated strongly.

## CHROMIUM

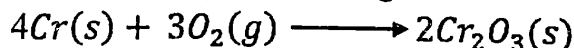
- *Symbol Cr.*
- *A hard silvery element.*
- *Atomic number 24*
- *Group VIA*
- *Melting point 1857°C*
- *Boiling point 2672°C*
- *It is used in making alloy steels, as a shiny decorative electroplated coating and in the manufacture of certain chromium compounds.*
- *The oxidation states are +6 in chromates( $\text{CrO}_4^{2-}$ ) and dichromates( $\text{Cr}_2\text{O}_7^{2-}$ ), +3 (the most stable and ionic), and +2(ionic)*
- *Compounds in +2 oxidation state are reducing agents while those in +6 oxidation state for example Potassium dichromate(VI) ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) and Potassium chromate(VI) ( $\text{K}_2\text{CrO}_4$ ) are oxidising agents.*

### Chemical properties of chromium

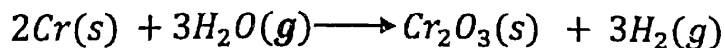
Describe the reactions of chromium with;

- air
- water
- dilute acids
- concentrated acids
- sodium hydroxide
- chlorine
- hydrogen chloride

a) Heated chromium reacts with oxygen to form green chromium(III) oxide.

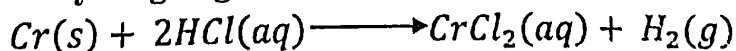


b) Red hot chromium reacts with steam to form chromium(III) oxide and hydrogen.

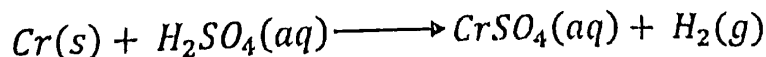


c) dilute acids

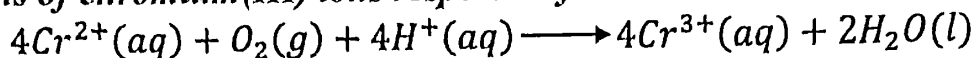
Chromium reacts with dilute hydrochloric acid to form chromium(II) chloride and hydrogen gas.



Chromium reacts with dilute sulphuric acid to form chromium(II) sulphate and hydrogen gas.



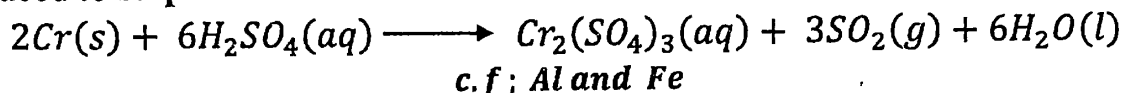
*Note; The solutions formed above are blue but are rapidly oxidised by air to green solutions of chromium(III) ions respectively.*



Chromium does not react with dilute nitric acid

d) concentrated acids

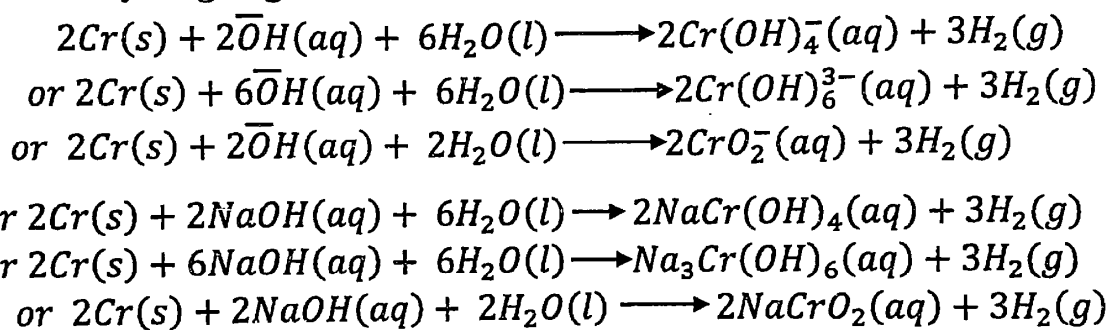
Hot concentrated sulphuric acid oxidises chromium to chromium(III) sulphate, itself reduced to sulphur dioxide and water.



Chromium is rendered passive by concentrated nitric acid

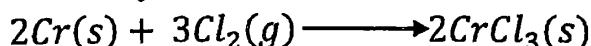
e) sodium hydroxide

Chromium reacts slowly with aqueous sodium hydroxide to form sodium chromite and hydrogen gas.



f) chlorine

Heated chromium reacts with dry chlorine to form chromium(III) chloride



g) hydrogen chloride

Heated chromium reacts with dry hydrogen chloride to form chromium(II) chloride and hydrogen.



## COMPOUNDS OF CHROMIUM

### Chromium(II) compounds

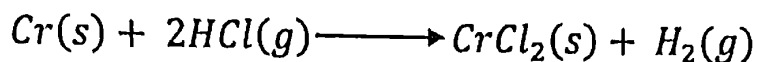
Chromium(II) oxide is a black solid and basic in nature.

It is insoluble in water but reacts with acids to form chromium(II) salts which are unstable hence readily oxidised by air to chromium(III) salts

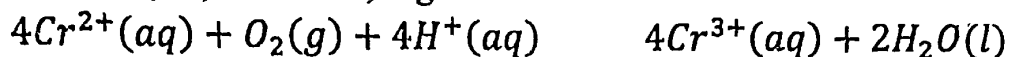


### Chromium(II) chloride

Anhydrous chromium(II) chloride can be prepared by passing dry hydrogen chloride over heated chromium.

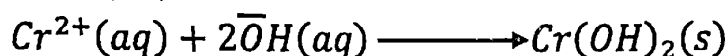


An aqueous solution of chromium(II) chloride is blue and is oxidised by air on standing to chromium(III) chloride, a green solution.



### Chromium(II) hydroxide

This is prepared as a yellow precipitate by adding sodium hydroxide solution to a solution of chromium(III) ions.

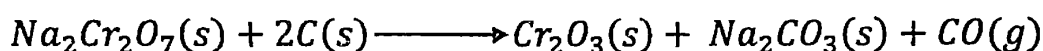


### Chromium(III) compounds

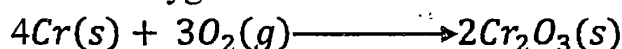
Chromium(III) oxide is a green solid and amphoteric in nature

It is prepared by

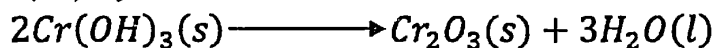
(i) reduction of sodium dichromate with carbon



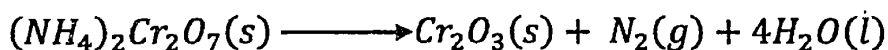
(ii) burning the chromium in oxygen



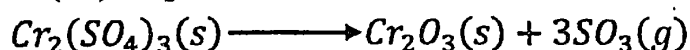
(iii) heating chromium(III) hydroxide



(iv) heating ammonium dichromate.



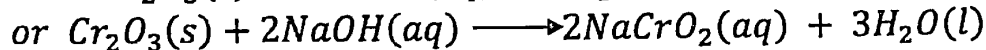
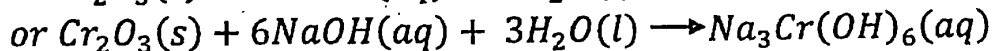
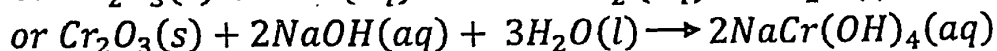
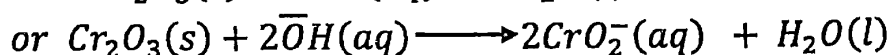
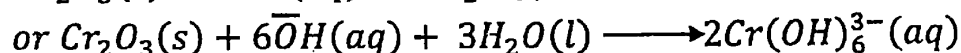
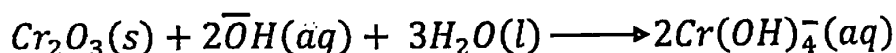
(v) heating chromium(III) sulphate



Chromium(III) oxide does not dissolve in water but reacts with acids e.g. hot concentrated hydrochloric acid to form chromium(III) salts and water



Being amphoteric, it also reacts with fused sodium hydroxide to form sodium chromate(III).

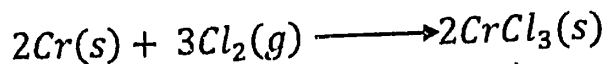


cf.  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$

### Chromium(III) chloride

Anhydrous chromium(III) chloride is a reddish brown solid

Anhydrous chromium(III) chloride is made by passing dry chlorine over heated chromium.



The hydrated chloride ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ), exhibits hydrate isomerism in which the three isomers have different colours as shown in the table below

Formula of isomer	or	Formula of isomer	Number of moles of $\text{Cl}^-$ ions removed as $\text{AgCl}$ by $\text{AgNO}_3$	Total number of conducting ions in solution	Colour
$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$		$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{Cl}^-)_3$	3	4	violet
$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$		$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}(\text{Cl}^-)_2 \cdot \text{H}_2\text{O}$	2	3	Pale green
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$		$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+\text{Cl}^- \cdot 2\text{H}_2\text{O}$	1	2	Dark green

The three isomers can therefore be distinguished by;

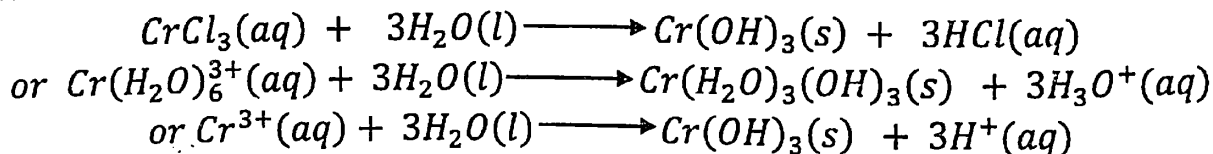
- Titrating equimolar quantities with a standard solution of silver nitrate using potassium chromate(VI) as indicator
- Measuring conductivity of equimolar solutions of each isomer.

Like other highly charged small cations such as aluminium ions and iron(III) ions, the chromium(III) ion in solution is hydrated.

**Qn.** Explain why an aqueous solution of Chromium(III) chloride has a pH below 7?

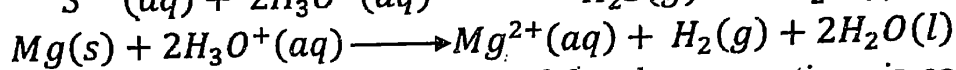
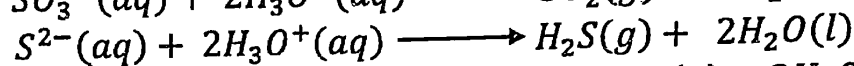
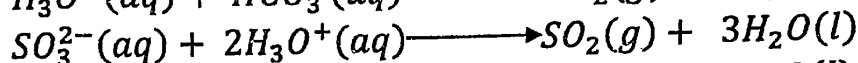
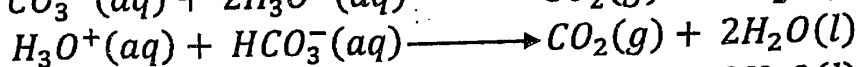
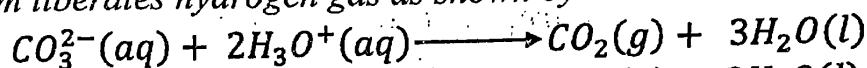
The chromium(III) ion in chromium(III) chloride has a high charge and a small ionic radius.

It has a high charge density and high polarising power, exists as hexaaquachromium(III) ion in solution. Chromium(III) ion therefore undergoes cationic hydrolysis forming hydrogen ions hence making the resultant solution acidic.



N.B;

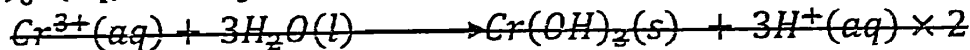
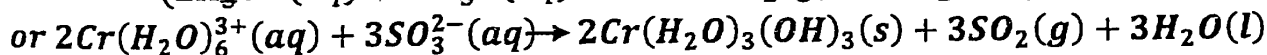
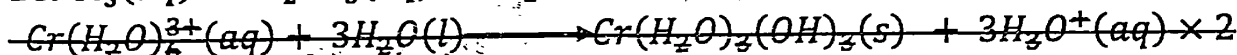
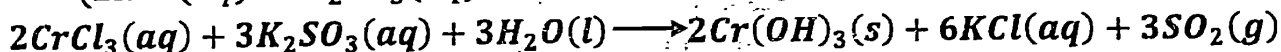
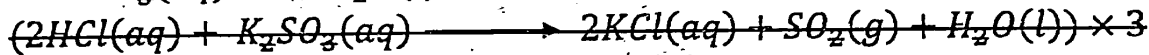
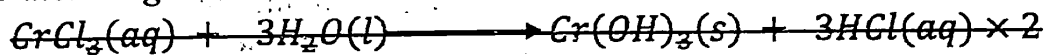
- a. Small highly charged cations precipitate as hydroxides in water on addition of a basic substance. The basic substances include; sodium carbonate or potassium carbonate, sodium hydrogen carbonate or potassium hydrogen carbonates, sodium sulphite or potassium sulphite, sodium sulphide/ ammonium sulphide, magnesium powder, or an alkali.
- b. The carbonates or hydrogen carbonates evolve carbon dioxide, the sulphites produce sulphur dioxide, sulphides liberate hydrogen sulphide gas and magnesium liberates hydrogen gas as shown by the reactions below;

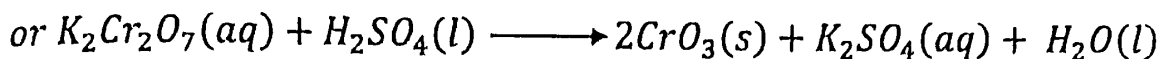


- c. When writing the overall equation, one of the above equations is combined with the equation for the hydrolysis of the salts by eliminating the acid ( $\text{H}_3\text{O}^+$  or  $\text{H}^+$ ) in the half cell reaction equations. A well balanced molecular equation can as well be written.

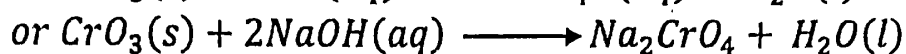
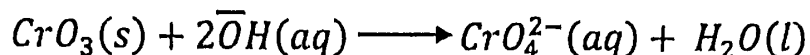
Qn. When potassium sulphite is added to a solution of chromium(III) chloride, a green precipitate and bubbles of a colourless gas that turns acidified potassium dichromate solution from orange to green are observed. Explain this observation.

The chromium(III) ion in chromium(III) chloride has a high charge and a small ionic radius. It has a high charge density and high polarising power, exists as hexaaquachromium(III) ion in solution. The ion therefore undergoes cationic hydrolysis forming insoluble chromium(III) hydroxide and hydrogen ions making the resultant solution acidic. The hydrogen ions react with sulphite ions forming sulphur dioxide gas.





It is acidic hence reacts with **sodium hydroxide** to form **sodium chromate(VI)**



It is a **mild oxidising agent in acidic medium** and on heating used in organic chemistry to **oxidise primary alcohols to aldehydes** and **secondary alcohols to ketones**. For oxidation of primary alcohols to carboxylic acids, the reagent is used in excess.

**Chromyl chloride ( $CrO_2Cl_2$ )**, a red liquid, is an acid chloride of chromium in the +6 oxidation state.

It is an **oxidising agent** that **commonly oxidises methylbenzene to benzaldehyde** in organic synthesis.

### The Oxo-salts of chromium

The common Oxo salts of chromium are:

1. **Sodium dichromate ( $Na_2Cr_2O_7 \cdot 2H_2O$ )**, which is a **red crystalline solid**, soluble in water.

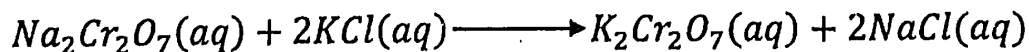
Sodium dichromate is cheaper than the corresponding potassium compound but has the disadvantage of being **highly deliquescent** hence not a good primary standard in volumetric analysis.

It is used as an **oxidizing agent in organic chemistry** when its solution is **acidified and heated** to oxidise primary alcohols to aldehydes or carboxylic acid, secondary alcohols to ketones and aldehydes to carboxylic acids.

It is also used in volumetric analysis to estimate iron(II) ions and iodide ions.

2. **Potassium dichromate ( $K_2Cr_2O_7$ )**, which is **orange crystalline solid**, soluble in water.

It is prepared by **mixing hot concentrated solutions of sodium dichromate and potassium chloride**



Potassium dichromate is used as an oxidizing agent both in volumetric analysis and in organic chemistry just as seen for sodium dichromate. The crystals are anhydrous, and non-deliquescent.

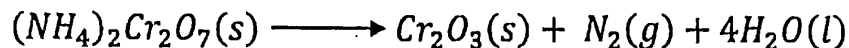
It is a **good reagent for volumetric analysis** because it is;

- *Highly soluble in water*
- *Not deliquescent*
- *Easily obtained in pure state*

### 3. Ammonium dichromate ( $(NH_4)_2Cr_2O_7$ )

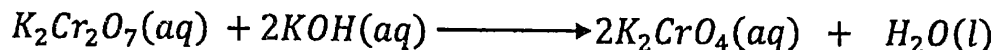
This is an **orange crystalline solid** that can be used to prepare **chromium(III) oxide**, a **green solid** on gentle heating.

The solid decomposes with flashes of light.

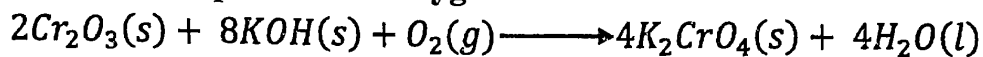


### 4. Potassium chromate ( $K_2CrO_4$ ) which is a yellow solid that is extremely soluble in water.

It can be made by adding a solution of potassium hydroxide to a solution of potassium dichromate.



Potassium chromate can also be made by fusing chromium(III) oxide with potassium hydroxide in presence of oxygen.



The salt is used as an indicator in silver nitrate titrations.

### 5. Chromates of lead, barium and silver are also known but insoluble.

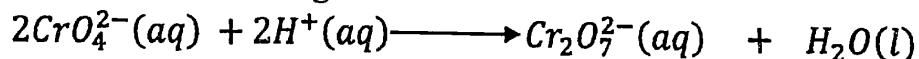
## The Oxo-anions of chromium

There are two known oxo-anions of chromium. They include the;

#### 1. Chromate ion ( $CrO_4^{2-}$ )

Chromate ions are **yellow in solution**.

The chromate(VI) ions are **only stable in alkaline medium** but in **acidic medium they are converted to dichromate(VI) ions**. Once an acidic solution is added, the **yellow solution turns orange**.



#### 2. Dichromate ion ( $Cr_2O_7^{2-}$ )

Dichromate ions are **orange in solution**

The dichromate(VI) ions are **only stable in acidic medium** but in **alkaline medium they are converted to chromate(VI) ions**. Once an alkaline solution is added, the **orange solution turns yellow**.



This principle has been in preparation of potassium chromate above.

*Note the inter conversion reactions above are not redox reactions since there is no change in oxidation state.*

### Shapes of the oxo-anions

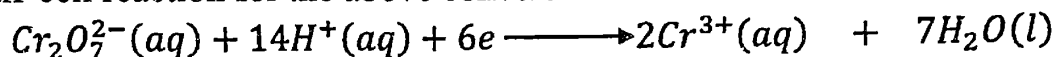
Oxo anion	$CrO_4^{2-}$	$Cr_2O_7^{2-}$
Structure		
Shape	Tetrahedral	Two chromate(VI) ions tetrahedrally linked through an oxygen atom

### Redox reactions of the oxo-anions

Dichromate ions are **strongly oxidising in acidic medium**.

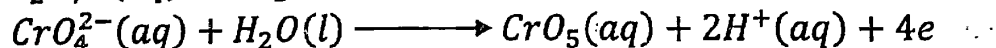
The **orange dichromate ions** being reduced to **green chromium(III) ions**

The half-cell reaction for the above conversion is shown below

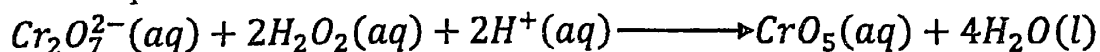


The reaction of dichromate ions and chromate ions with hydrogen peroxide is unique

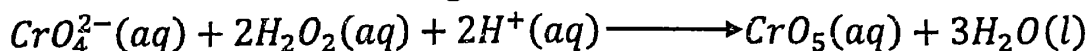
Instead of chromium(III) ions, the dichromate and chromate ions are converted to chromium pentoxide (a blue solution) with hydrogen peroxide as shown by the half-cell reactions below.



The overall equations can therefore be deduced as;



*The orange solution turns blue*



*The yellow solution also turns blue*

The chromium pentoxide is unstable and decomposes to form green chromium(III) ions and oxygen after some time. To avoid this, it is stabilized in a water-immiscible organic solvent such as an ether or butan-1-ol in which it dissolves.

Other words, dichromate(VI) ions oxidise each of the following in acidic medium as they are reduced to chromium(III) ions

- (i) sulphite ions to sulphate ions
- (ii) iodide ions to iodine

- (iii) hydrogen sulphide gas to sulphur
- (iv) tin(II) ions to tin(IV) ions
- (v) iron(II) ions to iron(III) ions
- (vi) oxalate ions to carbon dioxide
- (vii) nitrite ions to nitrate ions
- (viii) sulphur dioxide to sulphate ions
- (ix) hydrazine to nitrogen

**Qn. State what would be observed and write equations when to acidified potassium dichromate solution;**

- (i) was bubbled hydrogen sulphide gas
- (ii) sodium sulphite was added
- (iii) hydrogen peroxide was added
- (iv) was added potassium nitrite solution
- (v) anhydrous sodium oxalate was added
- (vi) a solution of hydrazine was added
- (vii) potassium iodide solution was added
- (viii) sulphur dioxide was bubbled
- (ix) tin(II) sulphate solution was added
- (x) iron(II) sulphate solution was added.

### TEST TUBE EXPERIMENTS TO IDENTIFY CHROMIUM(III) IONS, CHROMATE(VI) IONS AND DICHROMATE(VI) IONS.

The tests are arranged in a way that the chromate ions are got after oxidation of chromium(III) ions and the dichromate got after adding an acid to the chromate ions.

ION	TEST	OBSERVATION	DEDUCTION	EXPLANATION
$Cr^{3+}$	Add sodium hydroxide drop wise until in excess	Green gelatinous precipitate soluble in excess to form a green solution	$Cr^{3+}$ present	Chromium(III) ions react with hydroxyl ions to form insoluble chromium(III) hydroxide. chromium(III) hydroxide is amphoteric hence reacts with excess sodium hydroxide to form a soluble complex of chromate(III) ions. $Cr^{3+}(aq) + 3\bar{O}H(aq) \rightarrow Cr(OH)_3(s)$ $Cr(OH)_3(s) + \bar{O}H(aq) \rightarrow Cr(OH)_4^-(aq)$ or $Cr(OH)_3(s) + 3\bar{O}H(aq) \rightarrow Cr(OH)_6^{3-}(aq)$

	Add ammonia solution drop wise until in excess	Green precipitate soluble in excess to form a violet solution	$Cr^{3+}$ present	Chromium(III) ions react with hydroxyl ions to form insoluble chromium(III) hydroxide. chromium(III) hydroxide reacts with excess ammonia to form a soluble complex of hexaamminechromium(III) ions. $Cr^{3+}(aq) + 3\bar{O}H(aq) \rightarrow Cr(OH)_3(s)$
	$Cr(OH)_3(s) + 6NH_3(aq) \rightarrow Cr(NH_3)_6^{3+}(aq) + 3\bar{O}H(aq)$			
$Cr^{3+}$	To the solution, add sodium hydroxide solution drop wise until in excess followed by hydrogen peroxide. Boil the mixture and allow to cool. Then add butan-1-ol followed by 2-3 drops of dilute sulphuric acid	A green precipitate soluble in excess sodium hydroxide to form a green solution. A yellow solution is formed on warming with hydrogen peroxide.  A deep blue solution is formed in the organic layer	$Cr^{3+}$ confirmed present	Chromium(III) ions react with hydroxyl ions to form insoluble chromium(III) hydroxide. chromium(III) hydroxide is amphoteric hence reacts with excess sodium hydroxide to form a soluble complex of chromate(III) ions. Some of the hydrogen peroxide oxidises green chromate(III) ions to yellow chromate(VI) ions in alkaline medium. The sulphuric acid added then provides an acidic medium for the remaining hydrogen peroxide to react with the chromate(VI) ions to form an unstable chromium pentoxide (Chromium(VI) peroxide) which is a blue solution and water. The chromium(VI) peroxide decomposes to form green chromium(III) ions and oxygen after some time. To avoid this, it is stabilized in a water-immiscible organic solvent such as an ether or butan-1-ol in which it dissolves. It can be observed over a much longer period then. $Cr^{3+}(aq) + 3\bar{O}H(aq) \rightarrow Cr(OH)_3(s)$ $Cr(OH)_3(s) + \bar{O}H(aq) \rightarrow Cr(OH)_4^-(aq)$
	$\begin{aligned} & (Cr(OH)_4^-(aq) + 4\bar{O}H(aq) \rightarrow CrO_4^{2-}(aq) + 4H_2O(l) + 3e^-) \times 2 \\ & (H_2O_2(aq) + 2e^- \rightarrow 2\bar{O}H(aq)) \times 3 \\ & 2Cr(OH)_4^-(aq) + 2\bar{O}H(aq) + 3H_2O_2(aq) \rightarrow 2CrO_4^{2-}(aq) + 8H_2O(l) \\ & CrO_4^{2-}(aq) + 2H_2O_2(aq) + 2H^+(aq) \rightarrow CrO_5(aq) + 3H_2O(l) \end{aligned}$			

$Cr^{3+}$	To the solution, add sodium hydroxide solution drop wise until in excess followed by hydrogen peroxide. Boil the mixture and allow to cool. Divide the resultant solution into four parts for further tests	A green precipitate soluble in excess sodium hydroxide to form a green solution. A yellow solution is formed on warming with hydrogen peroxide.	$Cr^{3+}$ present	Chromium(III) ions react with hydroxyl ions to form insoluble chromium(III) hydroxide. chromium(III) hydroxide is amphoteric hence reacts with excess sodium hydroxide to form a soluble complex of chromate(III) ions. Hydrogen peroxide oxidises green chromate(III) ions to yellow chromate(VI) ions in alkaline medium.  $Cr^{3+}(aq) + 3\bar{O}H(aq) \longrightarrow Cr(OH)_3(s)$ $Cr(OH)_3(s) + \bar{O}H(aq) \longrightarrow Cr(OH)_4^-(aq)$
			$Cr^{3+}$ oxidised to $CrO_4^{2-}$	

*In the previous test chromium(III) ions were complexed to chromate(III) ions and then oxidised to chromate(VI) ions. The tests below now investigate the behaviour of chromate(VI) ions*

$CrO_4^{2-}$	To the first part, add barium nitrate or barium chloride solution	A yellow precipitate	$CrO_4^{2-}$ present	Barium ions react with chromate ions to form insoluble barium chromate $Ba^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow BaCrO_4(s)$
	To the second part, add lead(II) nitrate or lead(II) ethanoate solution	A yellow precipitate	$CrO_4^{2-}$ present	lead(II) ions react with chromate ions to form insoluble lead chromate $Pb^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow PbCrO_4(s)$
	To the third part, add silver nitrate solution	A brick red precipitate	$CrO_4^{2-}$ present	Silver ions react with chromate ions to form insoluble silver chromate $2Ag^+(aq) + CrO_4^{2-}(aq) \longrightarrow Ag_2CrO_4(s)$

$\text{CrO}_4^{2-}$	To the fourth part, add dilute hydrochloric acid. Keep the resultant solution for further tests.	The yellow solution turns orange	$\text{Cr}_2\text{O}_7^{2-}$ formed from $\text{CrO}_4^{2-}$	The chromate(VI) ions are only stable in alkaline medium but unstable in acidic medium. They are converted to dichromate(VI) ions in an acidic medium. Note that this is not a redox reaction since there is no change in oxidation state(+6). It is rather an acid-base reaction(proton transfer)
	$2\text{CrO}_4^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \longrightarrow \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$			

In the previous test, chromate(VI) ions have been changed to dichromate(VI) ions. The tests below now investigate the behaviour of dichromate(VI) ions. Since dichromate(VI) ions are strong oxidising agents, addition of any reducing agent will give a positive test.

$\text{Cr}_2\text{O}_7^{2-}$	Add dilute sulphuric acid to make the solution acidic. Divide the solution into 5 portions. To the first part, add hydrogen peroxide. Boil the mixture and allow to cool. Then add butan-1-ol.	A deep blue solution is formed in the organic layer	$\text{Cr}_2\text{O}_7^{2-}$ present	Dichromate(VI) ions react with hydrogen peroxide in acidic medium to form chromium pentoxide, a blue solution. The chromium pentoxide is unstable hence decomposes to form green chromium(III) ions and oxygen after some time. To avoid this, it is stabilized in a water-immiscible organic solvent such as an ether or butan-1-ol in which it dissolves. It can be observed over a much longer period then.
	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 4\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) \longrightarrow 2\text{CrO}_5(\text{aq}) + 5\text{H}_2\text{O}(\text{l})$			
	To second part, add tin(II) sulphate solution	Orange solution turned green	$\text{Cr}_2\text{O}_7^{2-}$ present	Dichromate(VI) ions in acidic medium, oxidise tin(II) ions to tin(IV) ions as they are reduced to chromium(III) ions
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 3\text{Sn}^{2+}(\text{aq}) + 14\text{H}^+(\text{aq}) \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 3\text{Sn}^{4+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$				
To third part, add sodium sulphite solution	Orange solution turns green	$\text{Cr}_2\text{O}_7^{2-}$ present	Dichromate(VI) ions in acidic medium, oxidise sulphite ions to sulphate ions as they are reduced to chromium(III) ions	
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 3\text{SO}_3^{2-}(\text{aq}) + 8\text{H}^+(\text{aq}) \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 3\text{SO}_4^{2-}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$				

$Cr_2O_7^{2-}$	To fourth part, add potassium nitrite solution	Orange solution turns green	$Cr_2O_7^{2-}$ present	Dichromate(VI) ions in acidic medium, oxidise nitrite ions to nitrate ions as they are reduced to chromium(III) ions
	$Cr_2O_7^{2-}(aq) + 3NO_2^-(aq) + 8H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3NO_3^-(aq) + 4H_2O(l)$			
	To the fifth part, add iron(II) sulphate solution	Orange solution turns green	$Cr_2O_7^{2-}$ present	Dichromate(VI) ions in acidic medium, oxidise nitrite ions to nitrate ions as they are reduced to chromium(III) ions
$Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$				

### Questions

- Chromium forms many complex ions including  $Cr(NH_3)_6^{3+}$ 
  - (i) Name the complex
    - State how an aqueous solution of the complex can be formed.
  - (i) Explain the reasons that enable chromium to form many complex ions
    - Apart from complex ion formation, state any three other reasons that make chromium a typical transition element, giving suitable examples.
  - State the common oxidation states exhibited by chromium in its compounds and mention its most stable oxidation state.
  - (i) Write the formulae of the oxide of chromium in each of the above oxidation states
    - Write equations to show how each of the above oxides can be formed.
  - Discuss how the chemistry of chromium relates to that of aluminium, with suitable examples. Include equations where necessary
  - Explain the amphoteric behaviour of chromium and any of its oxides in (d) (i) above.
- Chromium can form compounds in +2, +3 and +6 oxidation states.
  - (i) Write the electronic configuration of chromium ions in each of the oxidation states above.
    - Write the formula of a chloride of chromium in each of the oxidation states above
  - Chromium(III) potassium sulphate (chrome alum),  $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$  is a double salt formed by chromium. A few

crystals of the salt were dissolved in water and divided into three equal portions.

- (i) to the first portion was added magnesium powder. State what was observed and explain your observation.
  - (ii) to the second portion was added ammonia solution drop wise until a green precipitate was formed. The mixture was filtered and to the filtrate was added lead(II) nitrate solution. State what was observed and write an equation for the reaction.
  - (iii) to the third portion was added sodium hydroxide solution drop wise until in excess. Hydrogen peroxide was then added to the resultant solution and the mixture warmed and allowed to cool. The drops of silver nitrate solution were added. Explain the reactions that took place.
- (c) (i) Write the formulae of the two known oxyanions of chromium.  
(ii) Describe the reactions that can make the two oxyanions interchange in solution.

3. Potassium dichromate is a common oxosalt formed by chromium. It is a useful reagent in volumetric analysis and organic synthesis.

- (a) State the reasons why potassium dichromate is commonly used in volumetric analysis.
- (b) Explain any three reactions, giving specific examples and conditions, where potassium dichromate is useful in organic synthesis.
- (c) To a solution of Chromium(III) chloride was added sodium hydroxide drop wise to form a green precipitate, Q. Q was heated strongly to form a green solid, R. When R was fused with potassium hydroxide, a yellow solid, T, was formed. T readily dissolved in water to form a yellow solution.
  - (i) Name Q, solid R and solid T.
  - (ii) Write equations for the reactions leading to formation of Q, R and T.
- (d) When dilute sulphuric acid was added to a solution of T in water, the yellow solution turned an orange solution, W. Write equation for the reaction for formation of W.
- (e) Explain why;

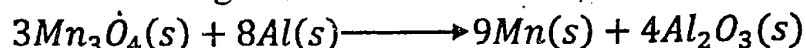
- (i) addition of sodium sulphite to solution W results into a green solution but bubbling hydrogen sulphide through it forms a yellow solid deposit.
- (ii) addition of sodium hydroxide solution turns the solution from orange back to yellow.
4. (a) (i) State what is observed when magnesium metal is placed into an aqueous solution of chromium(III) sulphate.
- (ii) Write equation(s) of the reactions that take place in a(i) above.
- (b) State what is observed and write equations of reactions that take place in each case when:
- (i) ammonium dichromate is heated
- (ii) dilute sodium hydroxide is added to an aqueous solution of ammonium dichromate.

## MANGANESE

- Symbol Mn.
- A grey brittle metallic element.
- Atomic number 25
- Group VIIA
- Melting point 1244°C
- Boiling point 1962°C
- Its main use is in alloy steels.
- The oxidation states are +7, +6, +4, +3 and +2 which is the most stable.
- But +7, +4 and +2 are most common in its compounds.

### Extraction

The metal can be extracted through the thermite process by reduction of the trimanganese tetraoxide using aluminium

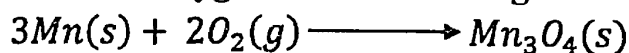


### Chemical properties of manganese

Describe the reactions of manganese with;

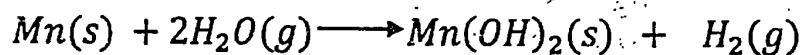
- air
- water
- dilute acids
- concentrated acids
- sodium hydroxide
- chlorine
- hydrogen chloride

a) Heated manganese reacts with oxygen to form trimanganese tetraoxide.



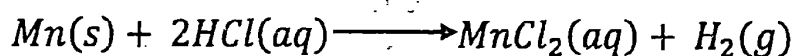
*c.f Fe*

b) Red hot manganese reacts with steam to form manganese(II) hydroxide and hydrogen.

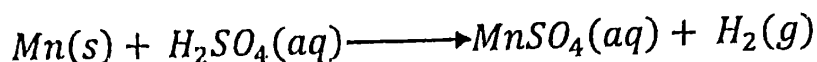


c) dilute acids

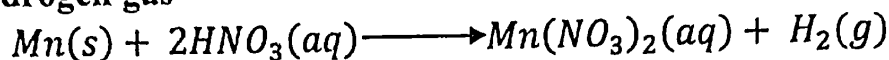
Manganese reacts with dilute hydrochloric acid to form manganese(II) chloride and hydrogen gas.



Manganese reacts with **dilute sulphuric acid** to form **manganese(II) sulphate** and **hydrogen gas**.

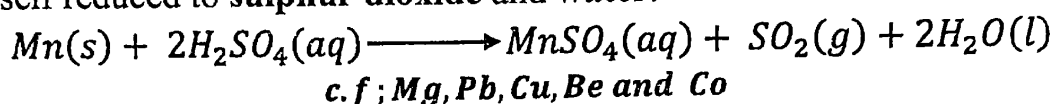


Manganese reacts with **cold very dilute nitric acid(1%)** to form **manganese(II) nitrate** and **hydrogen gas**

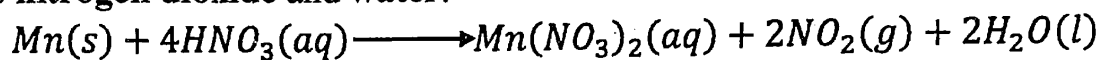


**d) concentrated acids**

**Hot concentrated sulphuric acid** oxidises manganese to **manganese(II) sulphate**, itself reduced to **sulphur dioxide** and **water**.



**Hot concentrated nitric acid** oxidises manganese to **manganese(II) nitrate**, itself reduced to **nitrogen dioxide** and **water**.

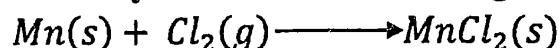


**e) sodium hydroxide**

Manganese **doe not react** with sodium hydroxide.

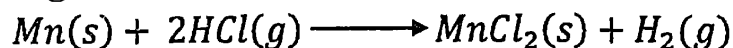
**f) chlorine**

**Heated manganese** reacts with **dry chlorine** to form **manganese(II) chloride**



**g) hydrogen chloride**

**Heated manganese** reacts with **dry hydrogen chloride** to form **manganese(II) chloride** and **hydrogen**.

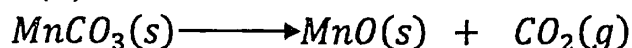


## COMPOUNDS OF MANGANESE

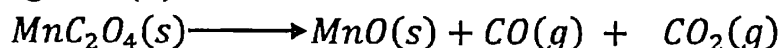
### Manganese(II) compounds

**Manganese(II) oxide** is a **green powder** insoluble in water. **Manganese(II) oxide** can be prepared by;

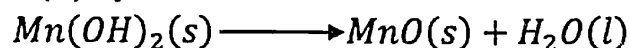
(i) heating manganese(II) carbonate **in the absence of air**



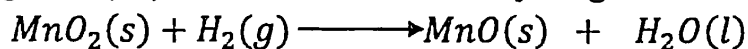
(ii) heating manganese(II) oxalate **in the absence of air**.



(iii) heating manganese(II) hydroxide **in absence of air**

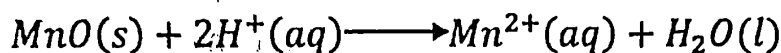


(iv) heating manganese(IV) oxide **in a stream of hydrogen**



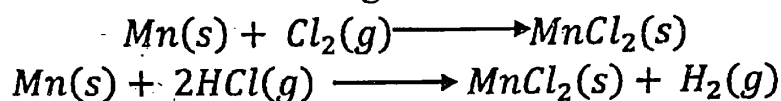
The compounds from which manganese(II) oxide is obtained are heated in absence of air because manganese(II) oxide is easily oxidised to manganese(III) oxide by air.

It is a strongly basic oxide, dissolving in acids to form manganese(II) ions and water.



### Manganese(II) chloride

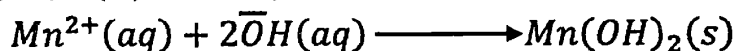
Anhydrous manganese(II) chloride can be prepared by passing dry chlorine or dry hydrogen chloride over heated manganese.



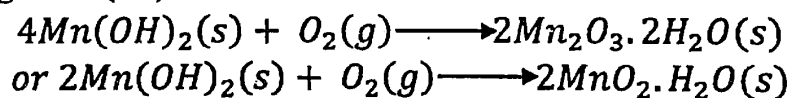
An aqueous solution of the chloride and other salts containing manganese(II) ions is pale pink.

### Manganese(II) hydroxide

This is formed as a white precipitate by adding sodium hydroxide solution to a solution of manganese(II) ions



Manganese(II) hydroxide is insoluble in excess sodium hydroxide since it is basic. It is easily oxidised by air to form brown hydrated manganese(III) oxide or hydrated manganese(IV) oxide.

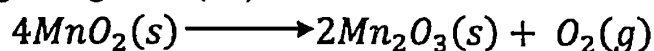


### Manganese(III) compounds

Compounds of manganese in the +3 oxidation state are not common, unstable and not important.

**Manganese(III) oxide** is a black or dark brown powder and is basic in nature.

It is made by heating manganese(IV) oxide in air at 700 °C for a long time.

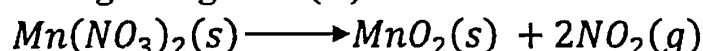


It dissolves in cold moderately concentrated sulphuric acid to form unstable green manganese(III) sulphate.

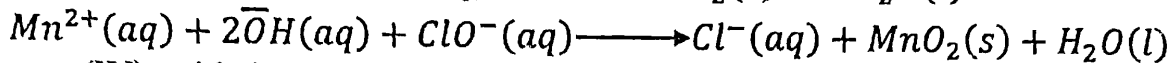
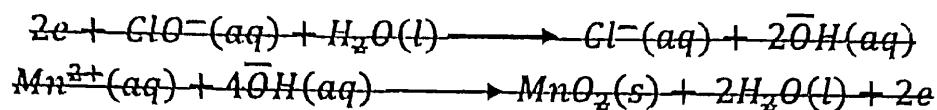
### Manganese(IV) compounds

**Manganese(IV) oxide** is a black solid, amphoteric and insoluble in water.

It is prepared by heating manganese(II) nitrate.



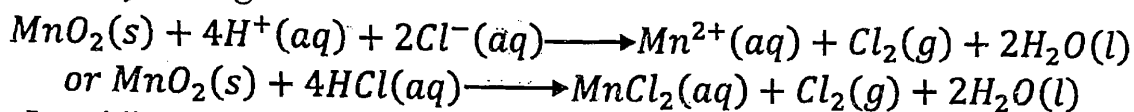
Manganese(IV) oxide can also be prepared by alkaline oxidation of manganese(II) ions by sodium chlorate(I)



Manganese(IV) oxide is an oxidising agent in acidic medium.

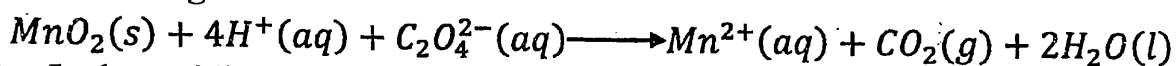
- (i) It oxidises hot concentrated hydrochloric to chlorine gas itself reduced to manganese(II) ions.

*The black solid dissolves forming a colourless solution and bubbles of a greenish yellow gas.*



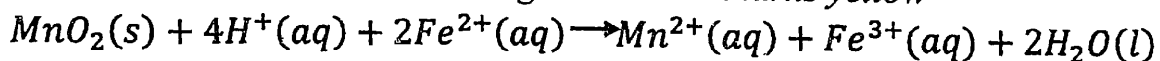
- (ii) It oxidises hot acidified solution of oxalate ions or oxalic acid to carbon dioxide, itself reduced to manganese(II) ions.

*The black solid dissolves forming a colourless solution and bubbles of a colourless gas.*

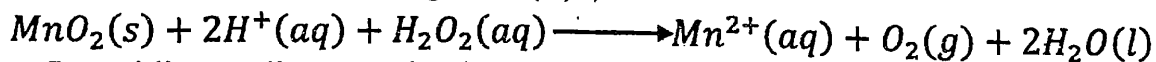


- (iii) It also oxidises cold iron(II) sulphate solution to iron(III) sulphate solution in presence of dilute sulphuric acid.

*The black solid dissolves and the green solution turns yellow*

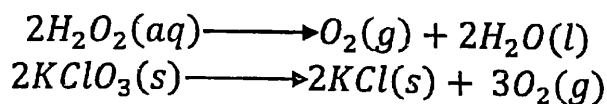


- (iv) Manganese(IV) oxide also, in acidic medium, oxidises hydrogen peroxide in acidic medium to manganese(II) ions.



- (v) In acidic medium, and when heated, manganese(IV) oxide is used in organic chemistry to oxidise primary alcohols to aldehydes and secondary alcohols to ketones. For oxidation of primary alcohols to carboxylic acids, the reagent is used in excess.

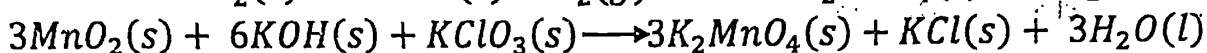
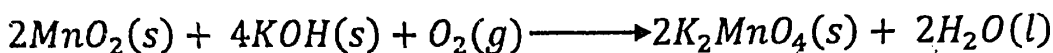
It is used as a catalyst in the decomposition of potassium chlorate to potassium chloride and oxygen and also in the decomposition of hydrogen peroxide to oxygen and water.



## Manganese(VI) compounds

Potassium manganate(VI) ( $K_2MnO_4$ ), is the common oxosalt of manganese in the +6 oxidation state. It is a dark green solid, very soluble in water to form a green solution and a strong oxidising agent.

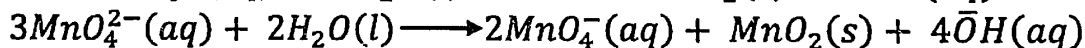
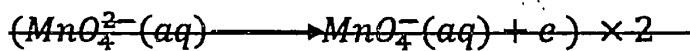
It can be prepared by fusing manganese(IV) oxide with potassium hydroxide and an oxidising agent which can be plenty of oxygen or potassium chlorate or potassium nitrate.



Potassium manganate(VI) contains the manganate(VI) ion, ( $MnO_4^{2-}$ ), one of the two oxyanions of manganese. The manganate(VI) ion is only stable in strongly alkaline medium. It disproportionates in neutral or acidic medium to form manganate(VII), ( $MnO_4^-$ , a purple solution), and manganese(IV) oxide, a brown solid.

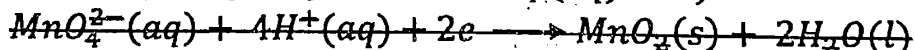
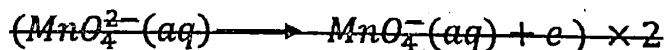
*Therefore, in neutral or acidic medium, the green solution turns purple with a black solid formed.*

*In neutral medium;*

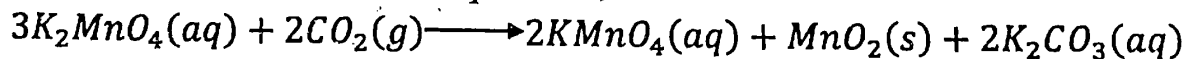


*The reaction above occurs on dilution of a solution potassium manganate(VI)*

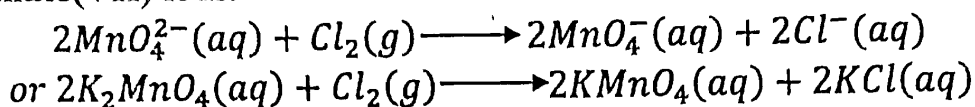
*In acidic medium;*



*This reaction occurs if to a solution of potassium manganate(VI) is bubbled carbon dioxide or when it is left standing in air for a long time. The carbon dioxide dissolves in the solution to form a carbonic acid that provides the acidic medium for disproportionation of manganate(VI) ions according to the above ionic equation or the molecular equation below.*



Similarly, when chlorine is bubbled through the green solution of potassium manganate(VI), it turns purple. This is due to oxidation of manganate(VI) ions to manganate(VII) ions.



### Manganese(VII) compounds

Manganese(VII) oxide ( $\text{Mn}_2\text{O}_7$ ) is the oxide of manganese in the +7 oxidation state.

It is a green oily liquid and strongly acidic in nature. It is formed by the action of cold concentrated sulphuric acid on powdered potassium permanganate.

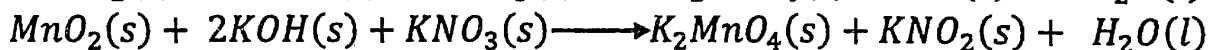
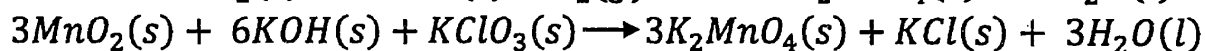
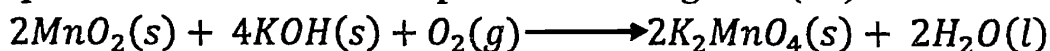
*(Caution; do not try out this in the laboratory due to explosion danger)*



Potassium manganate(VII) (potassium permanganate,  $\text{KMnO}_4$ )

These are purple crystals, soluble in water to form an intense purple solution.

The compound is prepared by fusing manganese(IV) oxide with potassium hydroxide and an oxidising agent which can be *plenty of oxygen* or *potassium chlorate* or *potassium nitrate* to form potassium manganate(VI).

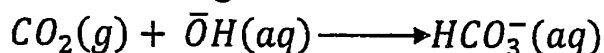


The green potassium manganate (VII) crystals formed can then be treated in one of the following ways;

- (i) dissolved in water, the mixture diluted and then boiled to form purple potassium manganate(VII) solution and manganese(IV) oxide.

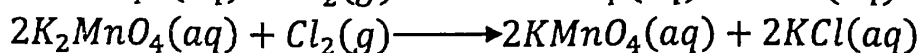


Carbon dioxide is bubbled through the mixture to remove hydroxide ions.



The mixture is filtered and heated to crystallisation.

- (ii) dissolved in water to form a green solution through which chlorine is bubbled. The chlorine oxidises the manganate(VI) ions to purple manganate(VII) ions.



It is commonly used in volumetric analysis because;

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

However, it is not a good primary standard because;

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

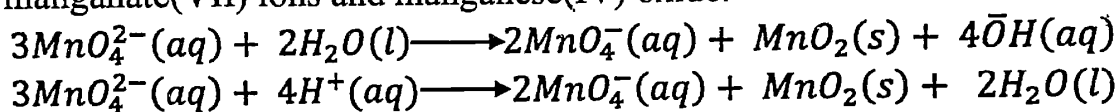
### The Oxo-anions of manganese

There are two known oxo-anions of manganese. They include the;

#### 1. Manganate(VI) ion ( $MnO_4^{2-}$ )

Manganate(VI) ions are green in solution.

The manganate(VI) ions are only stable in strongly alkaline medium but in neutral or acidic medium they disproportionate (undergo self-oxidation and reduction) to form manganate(VII) ions and manganese(IV) oxide.



#### 2. Manganate(VII) ion ( $MnO_4^{-}$ )

Manganate(VII) ions are purple in solution.

The manganate(VII) ion is a powerful oxidising agent in acidic medium.

### Shapes of the oxo-anions

Oxo anion	$MnO_4^{2-}$	$MnO_4^{-}$
Structure		
Shape	Tetrahedral	Tetrahedral

## Redox reactions of permanganate ion

The permanganate ion is a powerful oxidizing agent in acidic medium both in volumetric analysis and in organic synthesis.

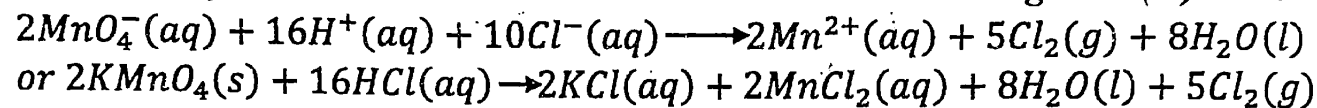
During the redox reactions, the manganate(VII) ions are reduced to manganese(II) ions in the acidic medium.

The half-cell reactions for the above conversion is shown below



It is always acidified with sulphuric acid but not hydrochloric acid or nitric acid because;

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



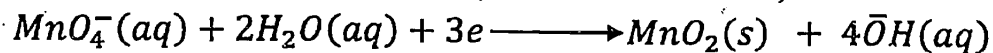
*Nitric acid is itself an oxidising agent hence interferes with the oxidising ability of manganate(VII) ions.*

Manganate(VII) ions oxidise each of the following in acidic medium as they are reduced to manganese(II) ions. The reactions can occur at room temperature hence heating may not be required.

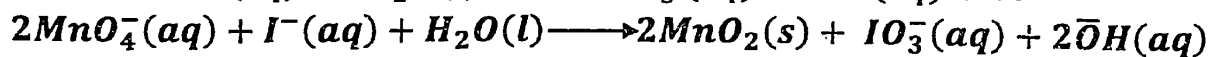
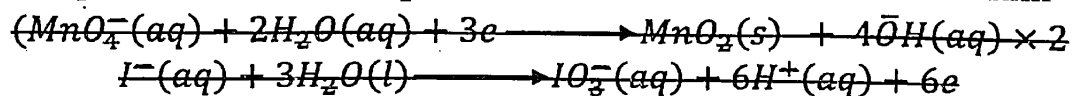
- (i) hydrochloric acid
- (ii) sulphite ions to sulphate ions
- (iii) iodide ions to iodine
- (iv) hydrogen sulphide gas to sulphur
- (v) tin(II) ions to tin(IV) ions
- (vi) iron(II) ions to iron(III) ions
- (vii) nitrite ions to nitrate ions
- (viii) sulphur dioxide to sulphate ions
- (ix) hydrogen peroxide to oxygen
- (x) hydrazine to nitrogen

The manganate(VII) ions however oxidise oxalic acid and oxalates on heating to carbon dioxide and water.

In neutral or weakly alkaline medium, the half reaction is;



It oxidises potassium iodide to potassium iodate in the alkaline medium



DEMISTIFYING INORGANIC CHEMISTRY BY Joseph Jobs Kayiira, BScED(Hons.CHEM/MTC)  
Email;josephkayirab@gmail.com Call 0782601038 WhatsApp 0753247098

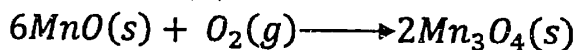
Qn. State what would be observed and write equations when to acidified potassium manganate(VII) solution;

- (i) was bubbled hydrogen sulphide gas
- (ii) sodium sulphite was added
- (iii) hydrogen peroxide was added
- (iv) was added potassium nitrite solution
- (v) sodium oxalate was added and the mixture heated.
- (vi) a solution of hydrazine was added
- (vii) sulphur dioxide was bubbled
- (viii) tin(II) sulphate solution was added
- (ix) iron(II) sulphate solution was added.
- (x) was added potassium iodide

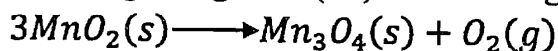
#### Trimanganese tetraoxide ( $Mn_3O_4$ )

It is a mixed oxide of manganese containing manganese(II) oxide and manganese(IV) oxide in a ratio 2:1

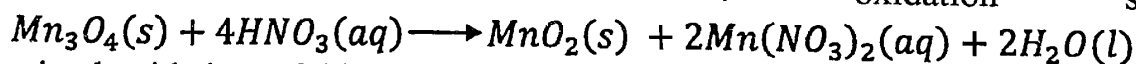
It is formed by heating manganese(II) oxide in excess air



It can also be formed by heating manganese(IV) oxide at high temperatures



Its reaction with nitric acid to form manganese(IV) oxide and manganese(II) nitrate well shows that it is mixed oxide. Two products are formed, one in +2 oxidation state and another in +4 oxidation state.



The mixed oxide is useful in the thermite process for extraction of manganese where it is reduced by aluminium to form manganese and aluminium oxide.



### TEST TUBE EXPERIMENTS TO IDENTIFY MANGANESE(II) IONS.

ION	TEST	OBSERVATION	DEDUCTION	EXPLANATION
<b>Mn<sup>2+</sup></b>	Add sodium hydroxide drop wise until in excess	White precipitate insoluble in excess and turns brown on standing	Mn <sup>2+</sup> present	Manganese(II) ions react with hydroxyl ions to form insoluble manganese(II) hydroxide. Manganese(II) hydroxide is basic hence insoluble excess sodium hydroxide. $\text{Mn}^{2+}(\text{aq}) + 2\bar{\text{O}}\text{H}(\text{aq}) \rightarrow \text{Mn}(\text{OH})_2(\text{s})$ Manganese(II) hydroxide is oxidised by air to form hydrated manganese(III) oxide or hydrated manganese(IV) oxide. $4\text{Mn}(\text{OH})_2(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{Mn}_2\text{O}_3 \cdot 2\text{H}_2\text{O}(\text{s})$ or $2\text{Mn}(\text{OH})_2(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{MnO}_2 \cdot \text{H}_2\text{O}(\text{s})$
	Add ammonia solution drop wise until in excess	White precipitate insoluble in excess and turns brown on standing	Mn <sup>2+</sup> present	Manganese(II) ions react with hydroxyl ions to form insoluble manganese(II) hydroxide. Manganese(II) hydroxide is insoluble excess ammonia solution. $\text{Mn}^{2+}(\text{aq}) + 2\bar{\text{O}}\text{H}(\text{aq}) \rightarrow \text{Mn}(\text{OH})_2(\text{s})$ Manganese(II) hydroxide is oxidised by air to form hydrated manganese(III) oxide or hydrated manganese(IV) oxide. $4\text{Mn}(\text{OH})_2(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{Mn}_2\text{O}_3 \cdot 2\text{H}_2\text{O}(\text{s})$ or $2\text{Mn}(\text{OH})_2(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{MnO}_2 \cdot \text{H}_2\text{O}(\text{s})$
	Add sodium carbonate solution	A white precipitate is formed	Mg <sup>2+</sup> , Ca <sup>2+</sup> , Ba <sup>2+</sup> Zn <sup>2+</sup> , Pb <sup>2+</sup> , Mn <sup>2+</sup> Probably present (depending on previous tests)	Manganese(II) ions react with carbonate ions to form insoluble manganese(II) carbonate. $\text{Mn}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{MnCO}_3(\text{s})$
	Add lead(IV) oxide followed by concentrated nitric acid and heat	A purple solution is formed.	Mn <sup>2+</sup> present	Manganese(II) ions are oxidised by lead(IV) oxide to manganate(VII) ions in acidic medium, the lead(IV) oxide being reduced to lead(II) ions.
				$(\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})) \times 5$ $(\text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) \rightarrow \text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^-) \times 2$ $5\text{PbO}_2(\text{s}) + 2\text{Mn}^{2+}(\text{aq}) + 4\text{H}^+(\text{aq}) \rightarrow 5\text{Pb}^{2+}(\text{aq}) + 2\text{MnO}_4^-(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$

Add a few drops of concentrated nitric acid followed by solid sodium bismuthate and heat	A purple solution formed	$Mn^{2+}$ confirmed present	Manganese(II) ions are oxidised by sodium bismuthate to manganate(VII) ions in acidic medium, the sodium bismuthate being reduced to bismuth(III) ions.
	<del><math>(BiO_3^-(aq) + 6H^+(aq) + 2e \rightarrow Bi^{3+}(aq) + 3H_2O(l)) \times 5</math></del> <del><math>(Mn^{2+}(aq) + 4H_2O(l) \rightarrow MnO_4^-(aq) + 8H^+(aq) + 5e) \times 2</math></del> $5BiO_3^-(aq) + 2Mn^{2+}(aq) + 14H^+(aq) \rightarrow 5Bi^{3+}(aq) + 2MnO_4^-(aq) + 7H_2O(l)$		

### Questions

- Manganese is both a d-block element and a first series transition element with atomic number 25.
  - (i) Distinguish between a transition element and a d-block element.  
(ii) State any three reasons that classify manganese a transition element.
  - (i) State the common oxidation states exhibited by manganese in its compounds.  
(ii) Write a formula of one compound of manganese in each of the oxidation states stated in c (i) above.
  - State the reagents and conditions that can effect each of the following conversions.
    - manganese dioxide to manganate(VI) ions
    - manganate(VI) ions to manganate(VII) ions
  - Write equations to show how each of the conversions in d (i) and d (ii) can be effected.
  - Discuss how the chemistry of manganese(IV) oxide relates to that of lead(IV) oxide, with suitable examples. Include equations where necessary.
- A pink crystalline solid J when heated decomposed to form a black residue, K. Some few crystals of J were dissolved in water and the resultant solution divided into 3 portions. The first portion formed a dirty white precipitate, L, insoluble in excess ammonia and turned to a brown solid, M, after a few minutes. The second portion evolved ammonia gas when heated with dilute sodium hydroxide solution and zinc powder.
  - (i) Name the substances K, L and M.  
(ii) Deduce the chemical formula of J.
  - Write the equations for formation of K, L, and M
  - Explain the reaction(s) that led to formation of ammonia.

Write equation(s) to illustrate your answer.

(d) Describe a test that can be used to confirm the cation in J using lead(IV) oxide. State any observations and write equation for the reaction.

3. Potassium manganate(VII) is a common oxosalt formed by manganese. It is a useful reagent in volumetric analysis.

(a) (i) State the reasons why potassium manganate(VII) is commonly used in volumetric analysis.

(ii) Mention two reasons why the compound cannot make primary standards

(b) Explain why solutions of potassium manganate(VII) are never acidified with nitric acid or hydrochloric acid.

4. (a) Write the electronic configuration of manganese.

(Atomic number of manganese = 24).

(b) Explain why manganese:

(i) is a transition element

(ii) has variable oxidation states.

(iii) has a higher melting point (1890°C) than calcium (860°C).

(c) Describe the reaction(s) of manganese with:

(i) water

(ii) sulphuric acid

(d) Aqueous sodium hydroxide solution was added to manganese(II) sulphate solution drop wise until in excess and the resultant mixture allowed to stand.

(i) State what was observed.

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

(iii) Write equation for the reaction between trimanganese tetroxide and aluminium.

## IRON

- Symbol *Fe*.
- A silvery malleable and ductile metallic transition element.
- Atomic number 26
- Group *VIIIA*
- Melting point  $1535^{\circ}\text{C}$
- Boiling point  $2750^{\circ}\text{C}$
- It is the fourth most abundant in the earth's crust.
- It is required as a trace element by living organisms.
- It forms ionic salts and numerous complexes in the +2 (green) or +3 (yellow) oxidation states. Its most stable oxidation state is +3. The +6 (purple) oxidation state though not common, also exists in the ferrate ion ( $\text{FeO}_4^{2-}$ ), and the element also forms complexes in which its oxidation number is zero (e.g.  $\text{Fe}(\text{CO})_5$ ).
- Iron is used as a catalyst in the Haber process for ammonia production.
- Most stable oxidation state is +3 (yellow/brown), but +2 (green) and +6 (purple, easily reduced) also exist.

### Extraction

The main sources are the ones whose names and formulae are given below: Haematite is the chief ore but iron can be extracted from the other ores as well.

Name of ore	Chemical formula
Haematite	$\text{Fe}_2\text{O}_3$
Magnetite	$\text{Fe}_3\text{O}_4$
Siderite (spathic iron ore)	$\text{FeCO}_3$
Iron pyrite	$\text{FeS}_2$

The main impurities in the ores are;

Name of impurity	Formula
Silicon(IV) oxide	$\text{SiO}_2$
Aluminium oxide	$\text{Al}_2\text{O}_3$

### Extraction from iron pyrites

The ore is roasted/heated in air to form iron(III) oxide.



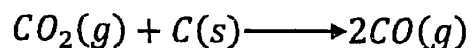
The iron(III) oxide, coke and limestone are fed into the blast furnace from the top.

Hot air is blown into the furnace from the bottom

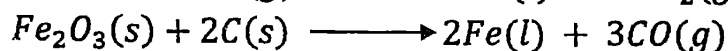
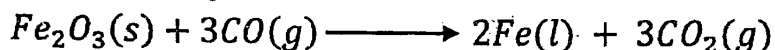
Coke burns in air to form carbon dioxide. This reaction liberates a very large quantity of heat and it is this heat that keeps up the high temperature required for the reduction process.



The carbon dioxide formed is reduced by unburnt coke to form carbon monoxide.

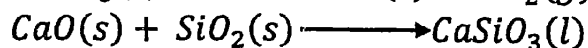
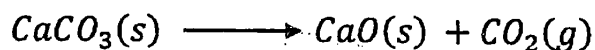


Iron(III) oxide is reduced by either carbon or carbon monoxide to form iron



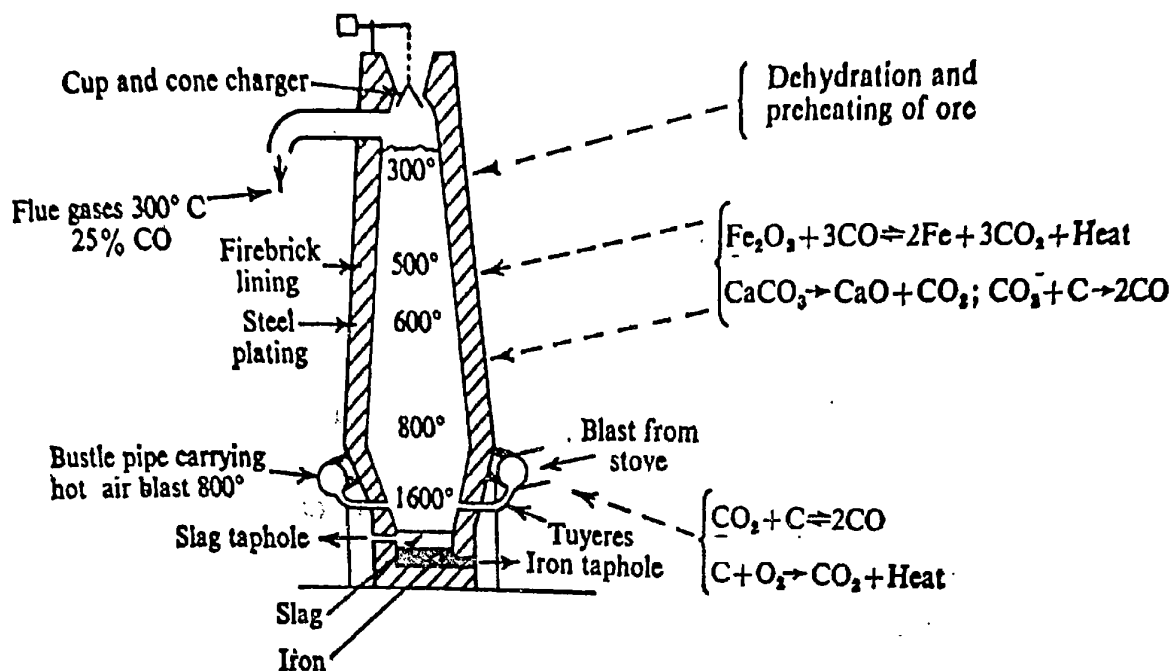
Limestone is decomposed at the high temperature in the furnace to form calcium oxide.

The calcium oxide is a basic oxide hence reacts with the acidic silicon(IV) oxide or amphoteric aluminium oxide impurities to form slag (calcium silicate/calcium aluminate)



Slag floats on top of molten iron which sinks at the bottom of the furnace and each is tapped off separately.

The molten iron is called pig/ cast iron.



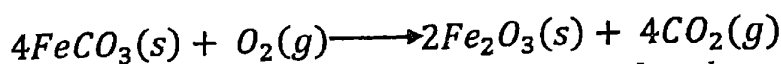
### Note;

If haematite is used, the ore is just fed into the furnace directly, together with coke and limestone.

If magnetite is used, it is also fed directly into the furnace and reduction occurs as shown by the equation below;



If spathic iron ore/ siderite is used, it is first roasted in air to form iron(III) oxide and carbon dioxide.



The iron(III) oxide is then fed into the furnace with coke and limestone as stated above.

Iron cannot be extracted by electrolysis but by reduction because iron is less reactive than carbon hence forms a less stable oxide, easily reduced by carbon.

### Pig iron/Cast iron

This is impure iron obtained after extraction of iron and contains varying amounts of impurities such as carbon (4%) and smaller quantities of silicon, phosphorus, sulphur and manganese.

This impure iron has a lower melting point than pure iron, brittle, cannot be welded and has a low tensile strength.

It can therefore not be used for bridge and motor car construction.

However, it is used for;

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Email;josephkayirab@gmail.com Call 0782601038 WhatsApp 0753247098

- Making fire grates
- Making Railings
- Making hot water pipes
- Making Bunsen burner bases
- Making refrigerator plates
- Making stoves
- Manufacture of steel

### **Wrought iron**

This is the purest form of iron obtained by heating pig iron with iron(III) oxide in a furnace.

The oxygen in iron(III) oxide oxidises the impurities, carbon and sulphur to gaseous oxides which escape. Silicon and phosphorus are oxidised to silicates and phosphates respectively, which form as a slag.

The semi- molten mass is then hammered and rolled so that the slag is squeezed out and almost pure iron remains.

Wrought iron has a higher melting point than pig iron, it is malleable. It can be hammered and welded when hot. It is tough and if subjected to great strain, it can bend. Wrought iron is used for making;

- Iron nails
- Iron sheets
- Ornamental work
- Horse-shoes
- Agricultural implements

It has been replaced to a large extent in the recent years by mild steel, which can be made more cheaply.

#### **A distinction between pig/ cast iron and wrought iron**

<b>Pig iron</b>	<b>Wrought iron</b>
has a lower melting point	has a higher melting point
cannot be welded	can be welded
low tensile strength	high tensile strength
Brittle	Malleable

## Steel

Ordinary steel contains mainly **iron** and a small proportion of **carbon**. The proportion of carbon is determined by the intended use of the steel. Steel is hard tough and strong. Steel is used in making;

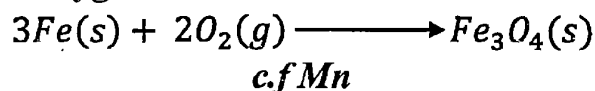
- Battleships and military tanks
- Making cutting tools like knives
- Modern motor cars
- Bridges, etc.

## Chemical properties of iron

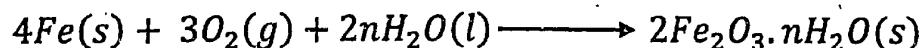
Describe the reactions of iron with;

- air
- water
- dilute acids
- concentrated acids
- sodium hydroxide
- chlorine
- hydrogen chloride
- sulphur
- carbon monoxide

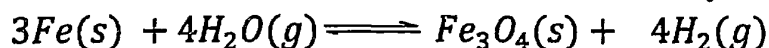
a) Heated iron reacts with oxygen to form triiron tetraoxide



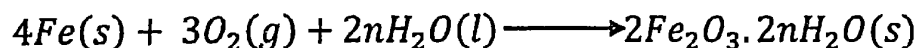
Iron also reacts with **moist air** to form **hydrated iron(III) oxide**, a reddish brown solid; also called rust.



b) Red hot iron reacts with steam to form triiron tetroxide and hydrogen.

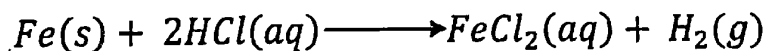


Iron also reacts with **cold water** in presence of oxygen to form **hydrated iron(III) oxide**.



c) dilute acids

Iron reacts with **dilute hydrochloric acid** to form **iron(II) chloride** and **hydrogen gas**.

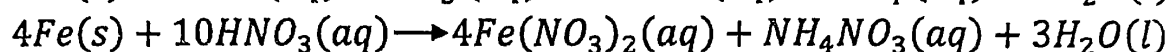
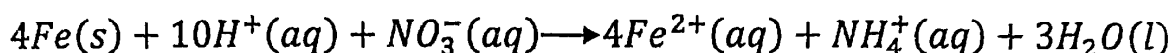


Iron reacts with dilute sulphuric acid to form iron(II) sulphate and hydrogen gas.



*Iron(II) salts are obtained instead of iron(III) salts because the hydrogen given off during the reaction is a reducing agent.*

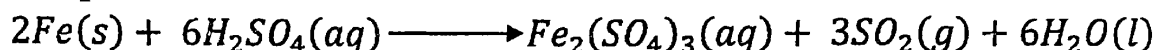
Cold dilute nitric acid oxidises iron to iron(II) nitrate, itself reduced to ammonium nitrate and water.



*C.f Sn and Zn*

#### d) concentrated acids

Hot concentrated sulphuric acid oxidises iron to iron(III) sulphate, itself reduced to sulphur dioxide and water.

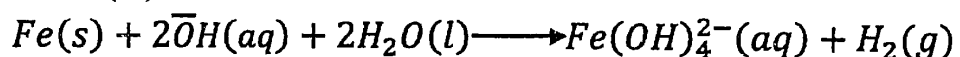


*c. f ; Cr and Al*

Hot or cold concentrated nitric acid renders iron passive due to a protective layer of iron tetroxide.

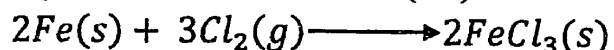
#### e) Sodium hydroxide

Hot concentrated sodium hydroxide reacts with iron to form tetrahydroxoferrate(II) ions.



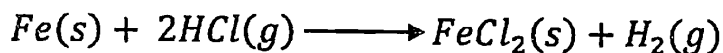
#### (f) chlorine

Heated iron reacts with dry chlorine to form iron(III) chloride.

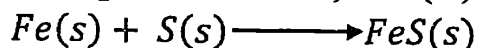


#### g) hydrogen chloride

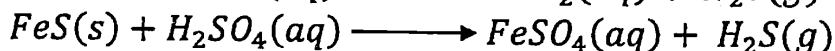
Heated iron reacts with dry hydrogen chloride to form iron(II) chloride and hydrogen.



h) When a mixture of iron and sulphur is heated, iron(II) sulphide is formed.



*The iron(II) sulphide reacts with warm dilute hydrochloric acid or warm dilute sulphuric acid to form hydrogen sulphide gas.*



(i) Iron reacts with carbon monoxide to form pentacarbonyliron(0)

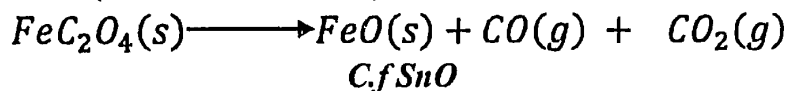


## COMPOUNDS OF IRON

### Iron(II) compounds

#### Iron(II) oxide

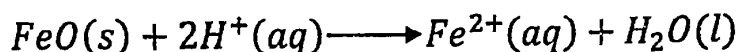
It is a black solid, ionic and basic. It can be prepared by heating iron(II) oxalate in an inert atmosphere (in absence of air)



The carbon monoxide formed produces a reducing atmosphere thus preventing oxidation to iron(III) oxide.

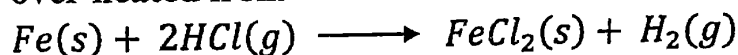
When exposed to air, it is oxidized to iron(III) oxide.

Since it is a basic oxide, it dissolves readily in dilute acids to form iron(II) salt solutions and water.



#### Iron(II) chloride

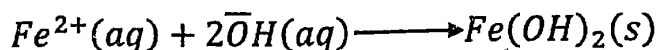
Anhydrous iron(II) chloride, a white solid, can be prepared by passing dry hydrogen chloride over heated iron.



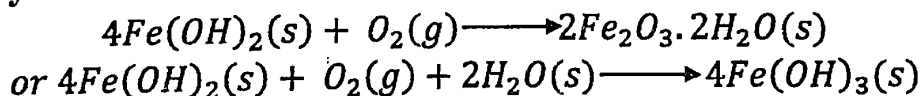
The hydrated chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) is a pale green solid

#### Iron(II) hydroxide

It is insoluble in water and is formed as a dirty green gelatinous precipitate by adding sodium hydroxide solution or ammonia solution to a solution of iron(II) ions.



It is easily oxidised by air to form yellow/brown hydrated iron(III) oxide or iron(III) hydroxide.

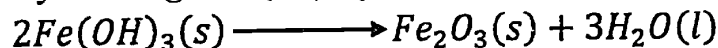


### Iron(III) compounds

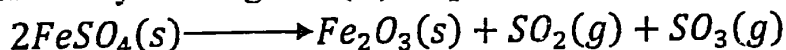
Compounds of iron in the +3 oxidation state are most stable.

Iron(III) oxide is a reddish brown insoluble solid.

It can be prepared by heating iron(III) hydroxide.



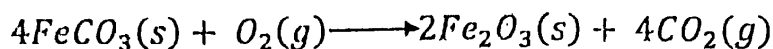
It can also be formed by heating iron(II) sulphate



Industrially, it is obtained by roasting iron pyrites in air.

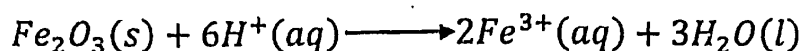


or roasting spathic iron in air

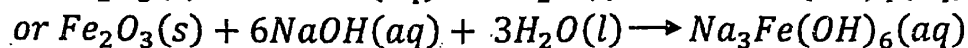
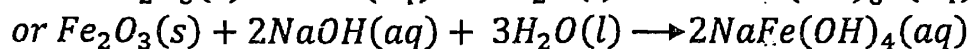
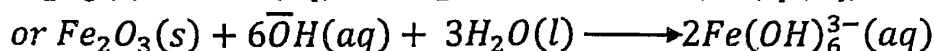
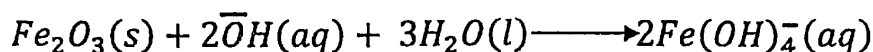


Iron(III) oxide is amphoteric hence reacts with both dilute acids to produce solutions of iron(III) salts and alkalis to form ferrate(III) ions.

With acids;



With alkalis;

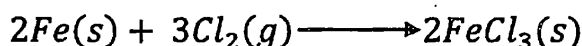


cf.  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$

### Iron(III) chloride

It is a dark brown solid.

Anhydrous iron(III) chloride is prepared by passing dry chlorine over heated iron wire.



*In many ways the compound resembles aluminium chloride, which it may replace in Friedel-Crafts reactions for alkylation of benzene.*

Iron(III) chloride is very soluble in water and undergoes salt hydrolysis.

At temperatures below 400°C the anhydrous salt exists as a dimer,  $\text{Fe}_2\text{Cl}_6$ .

**Qn.** When 0.13g of a chloride of iron was vapourised at 600K and 760mmHg, 20 cm<sup>3</sup> of a vapour was formed.

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

(d) Determine the;

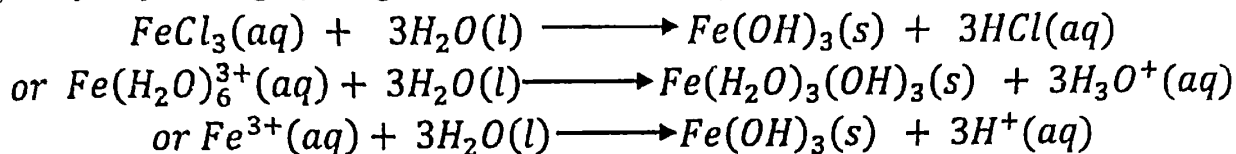
(iii) Molecular formula of the chloride of iron,

(iv) Structural formula of the chloride of iron in vapour phase.

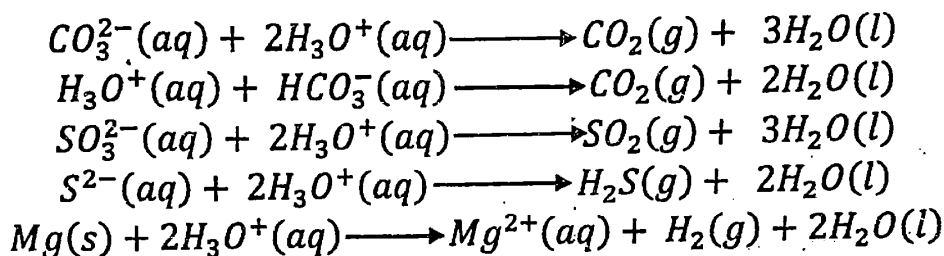
Like other highly charged small cations including aluminium(III) ions and chromium(III) ions, iron (III) ions undergo hydrolysis to form acidic solutions and a brown precipitate of iron(III) hydroxide.

**Qn.** Explain why an aqueous solution of iron(III) chloride turns litmus solution to red?

The iron(III) ion in iron(III) chloride has a high charge and a small ionic radius. It has a high charge density and high polarising power, exists as hexaaquairon(III) ion in solution. Iron(III) ion therefore undergoes cationic hydrolysis forming hydrogen ions hence making the resultant solution acidic.



Addition of a basic substance to a solution of iron(III) ions in solution will precipitate iron(III) hydroxide. The carbonates or hydrogen carbonates evolve carbon dioxide, the sulphites produce sulphur dioxide, sulphides liberate hydrogen sulphide gas and magnesium liberates hydrogen gas as shown by the reactions below;

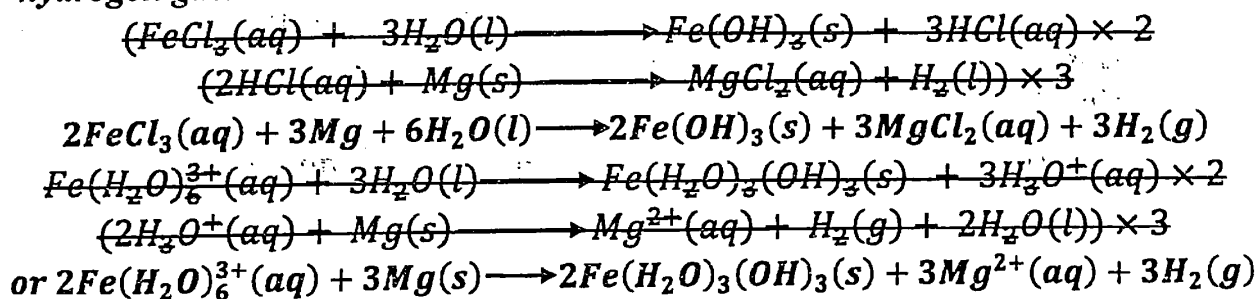


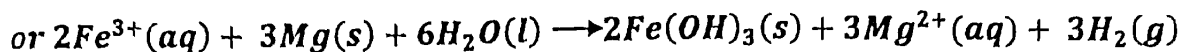
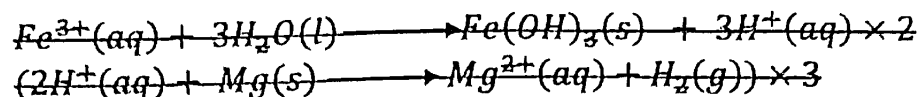
Qn. State what will be observed and explain your observation for what will happen when magnesium ribbon is added to a solution of iron(III) chloride.

*Observation; A brown precipitate and bubbles of a colourless gas.*

*Explanation;*

The iron(III) ion in iron(III) chloride has a high charge and a small ionic radius. It has a high charge density and high polarising power, exists as hexaaquairon(III) ion in solution. The ion therefore undergoes cationic hydrolysis forming insoluble iron(III) hydroxide and hydrogen ions making the resultant solution acidic. The hydrogen ions react with magnesium forming hydrogen gas.





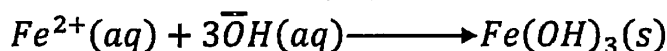
**Qn.** State what would be observed and explain your observation when to a solution of iron(III) sulphate was added;

Sodium hydroxide solution drop wise until in excess

- (a) Ammonia solution drop wise until in excess
- (b) Sodium hydroxide solution drop wise until in excess
- (c) Potassium sulphite
- (d) Sodium carbonate
- (e) Sodium sulphide
- (f) Potassium hydrogen carbonate

### Iron(III) hydroxide

This is formed as a **brown precipitate** by adding sodium hydroxide solution or ammonia solution to a solution of iron(III) ions.

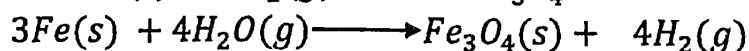
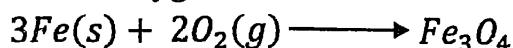


Iron(III) ions can be reduced to iron(II) ions and iron(II) ions can easily be oxidised to iron(III) ions. More of such reactions to be seen in the table below.

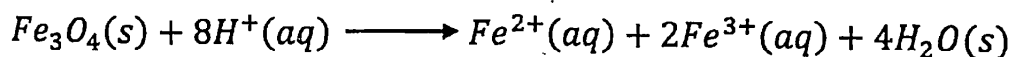
### Triiron tetraoxide( $Fe_3O_4$ )

It is a **black solid** and a **mixed oxide** of iron containing iron(II) oxide and iron(III) oxide in a ratio 1:1. It is also called iron(II,III) oxide.

It is formed by heating iron in oxygen or steam.



Its reaction dilute acids to form both iron(II) ions and iron(III) ions well shows that it is **mixed oxide**. Two products are formed, one in +2 oxidation state and another in +3 oxidation state.



## TEST TUBE EXPERIMENTS TO IDENTIFY IRON(II) AND IRON(III) IONS.

ION	TEST	OBSERVATION	DEDUCTION	EXPLANATION
$Fe^{2+}$	Add sodium hydroxide drop wise until in excess	Dirty green precipitate insoluble in excess and turns brown on standing	$Fe^{2+}$ present	<p>Iron(II) ions react with hydroxyl ions to form insoluble iron(II) hydroxide. Iron(II) hydroxide is insoluble excess sodium hydroxide.</p> $Fe^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Fe(OH)_2(s)$ <p>Iron(II) hydroxide is oxidised by air to form hydrated iron(III) oxide or iron(III) hydroxide.</p> $4Fe(OH)_2(s) + O_2(g) \longrightarrow 2Fe_2O_3 \cdot 2H_2O(s)$ <p>or <math>4Fe(OH)_2(s) + O_2(g) + 2H_2O(l) \longrightarrow 4Fe(OH)_3(s)</math></p>
	Add ammonia solution drop wise until in excess	Dirty green precipitate insoluble in excess and turns brown on standing	$Fe^{2+}$ present	<p>Iron(II) ions react with hydroxyl ions to form insoluble iron(II) hydroxide. Iron(II) hydroxide is insoluble excess ammonia solution</p> $Fe^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Fe(OH)_2(s)$ <p>Iron(II) hydroxide is oxidised by air to form hydrated iron(III) oxide or iron(III) hydroxide.</p> $4Fe(OH)_2(s) + O_2(g) \longrightarrow 2Fe_2O_3 \cdot 2H_2O(s)$ <p>or <math>4Fe(OH)_2(s) + O_2(g) + 2H_2O(l) \longrightarrow 4Fe(OH)_3(s)</math></p>
	Add acidified potassium dichromate solution	The orange solution turns green	$Cr_2O_7^{2-}$ reduced to $Cr^{3+}$ by $Fe^{2+}$ present	Dichromate ion is an oxidising agent in acidic medium. It is therefore reduced by iron(II) ions to chromium(III) ions as the iron(II) are oxidised to iron(III) ions.
	$Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$			
	Add dilute sulphuric acid and then concentrated nitric acid and heat.	The green solution turns brown. Brown fumes are also formed.	$Fe^{2+}$ oxidised to $Fe^{3+}$	Concentrated nitric acid oxidises iron(II) ions to iron(III) ions and itself reduced to nitrogen monoxide. The nitrogen monoxide is oxidised by air to form nitrogen dioxide.
	$6FeSO_4(aq) + 3H_2SO_4(aq) + 2HNO_3(aq) \longrightarrow 3Fe_2(SO_4)_3(aq) + 4H_2O(l) + 2NO(g)$ <p>or <math>3Fe^{2+}(aq) + 4H^+(aq) + NO_3^-(aq) \longrightarrow 3Fe^{3+}(aq) + 2H_2O(l) + NO(g)</math></p> $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$			
Add dilute sulphuric acid and hydrogen peroxide solution	Green solution turns brown	$Fe^{2+}$ oxidised to $Fe^{3+}$	In acidic medium, hydrogen peroxide oxidises iron(II) ions to iron(III) ions and itself reduced to water.	
$2Fe^{2+}(aq) + 2H^+(aq) + H_2O_2(aq) \longrightarrow 2Fe^{3+}(aq) + 2H_2O(l)$				

$Fe^{2+}$	Add chlorine water or bromine water	Green solution turns brown	$Fe^{2+}$ oxidised to $Fe^{3+}$	Chlorine/bromine is an oxidising agent. It oxidises iron(II) ions to iron(III) ions as it is reduced to chloride/bromide ions $2Fe^{2+}(aq) + Cl_2(aq) \rightarrow 2Fe^{3+}(aq) + 2Cl^{-}(aq)$ $2Fe^{2+}(aq) + Br_2(aq) \rightarrow 2Fe^{3+}(aq) + 2Br^{-}(aq)$
	Add potassium hexacyanoferrate (III) solution	A dark blue precipitate is formed	$Fe^{2+}$ confirmed present	Potassium hexacyanoferrate(III) reacts with iron(II) ions to form insoluble potassium iron(II)hexacyanoferrate(III) $K^{+}(aq) + Fe(CN)_6^{3-}(aq) + Fe^{2+}(aq) \longrightarrow K[Fe(Fe(CN)_6)](s)$
$Fe^{3+}$	Add sodium hydroxide solution drop wise until in excess	Brown precipitate insoluble in excess	$Fe^{3+}$ present	Iron(III) ions react with hydroxyl ions to form insoluble iron(III) hydroxide. $Fe^{3+}(aq) + 3OH^{-}(aq) \rightarrow Fe(OH)_3(s)$
	Add ammonia solution drop wise until in excess	Brown precipitate insoluble in excess	$Fe^{3+}$ present	Iron(III) ions react with hydroxyl ions to form insoluble iron(III) hydroxide. $Fe^{3+}(aq) + 3OH^{-}(aq) \rightarrow Fe(OH)_3(s)$
	Add potassium thiocyanate solution	Intense deep red colouration	$Fe^{3+}$ present	Iron(III) ions react with thiocyanate ions to form insoluble thiocyanate iron(III) $Fe^{3+}(aq) + 3SCN^{-}(aq) \longrightarrow Fe(SCN)_3(aq)$
	Add dilute hydrochloric acid and zinc powder and boil	Brown solution turned green	$Fe^{3+}$ reduced to $Fe^{2+}$	Zinc, in acidic medium, reduces iron(III) ions to iron(II) ions, itself oxidised to zinc ions $Zn(s) + 2Fe^{3+}(aq) \longrightarrow Zn^{2+}(aq) + 2Fe^{2+}(aq)$
	Add tin(II) sulphate solution	Brown solution turned green	$Fe^{3+}$ reduced to $Fe^{2+}$	Tin(II) ions reduce iron(III) ions to iron(II) ions, as the tin(II) ions are oxidised to tin(IV) ions $2Sn^{2+}(aq) + 2Fe^{3+}(aq) \longrightarrow 2Sn^{4+}(aq) + 2Fe^{2+}(aq)$
	Add potassium hexacyanoferrate (II) solution	A dark blue precipitate is formed	$Fe^{3+}$ confirmed present	Potassium hexacyanoferrate(II) reacts with iron(III) ions to form insoluble potassium iron(III)hexacyanoferrate(II) $K^{+}(aq) + Fe(CN)_6^{4-}(aq) + Fe^{3+}(aq) \longrightarrow K[Fe(Fe(CN)_6)](s)$

## Questions

- Write the names and chemical formulae of the iron compounds contained in two important iron ores
    - Give the chemical formulae of two impurities commonly present in iron ores which have to be removed before turning the ores into cast iron.
  - The magnetic iron ore is one of the ores in which iron is extracted. It is mixed together with coke and limestone and fed into the blast furnace from the top. Hot air is blown into the furnace from the bottom. Describe the processes that lead to formation of cast iron from the magnetic iron ore
  - State the difference between wrought iron and cast iron
    - Mention any two uses of cast iron and two uses of wrought iron
    - State the main components of steel
  - Describe how pure iron can be converted to anhydrous;
    - iron(II) chloride
    - iron(III) chloride
- Write the name and chemical formula of the principal ore from which iron can be extracted
    - Explain why iron cannot be purified by electrolysis but rather by reduction
  - A hydrated iron(III) sulphate  $Fe_2(SO_4)_3 \cdot xH_2O$  contains 19.9% by mass of iron. Find the value of  $x$
  - Explain why an aqueous solution of iron(III) sulphate has pH less than 7
- Diammonium iron(III) sulphate,  $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$ , is a double salt formed by iron. Crystals of the salt were dissolved in water and the solution formed divided into three portions.
  - to the first portion was added sodium hydroxide solution drop wise until in excess and the mixture heated. Explain the reactions that took place and state any observations made.

(5 ½ marks)
  - to the second portion was added some drops of potassium thiocyanate. State what was observed and write equation(s) for the reaction(s) that took place.

(02 marks)
  - to the third part was added a few drops of potassium ferrocyanide solution. State what was observed and write equation(s) to illustrate your answer.

(2 ½ marks)

## COBALT

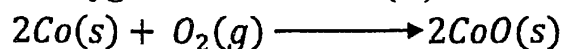
- *Symbol Co.*
- *A lustrous silvery-white hard transition element.*
- *Atomic number 27*
- *Group VIIIA*
- *Melting point 1495°C*
- *Boiling point 2870°C*
- *Cobalt is ferromagnetic*
- *Cobalt is usually alloyed for use. Alnico is a well-known magnetic alloy containing aluminium, nickel and cobalt used in making generators, electric motors and mass spectrometers.*
- *Artificially produced cobalt-60 is an important radioactive tracer and also used in cancer-treatment.*
- *Cobalt has oxidation states +2 and +3 but +2 is the most stable oxidation state*
- *Cobalt(III) ions are used as catalyst in oxidation of 2,3-dihydroxybutanedioate by hydrogen peroxide*

### Chemical properties of cobalt

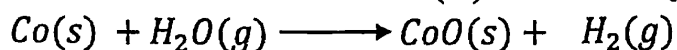
Describe the reactions of cobalt with;

- air
- water
- dilute acids
- concentrated acids
- sodium hydroxide
- chlorine

a) Heated cobalt reacts with oxygen to form cobalt(II) oxide



b) Red hot cobalt reacts with steam to form cobalt(II) oxide and hydrogen.

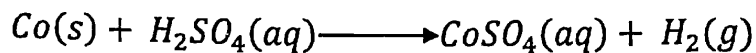


c) dilute acids

Cobalt reacts with dilute hydrochloric acid to form cobalt(II) chloride and hydrogen gas.



Cobalt reacts with dilute sulphuric acid to form cobalt(II) sulphate and hydrogen gas.



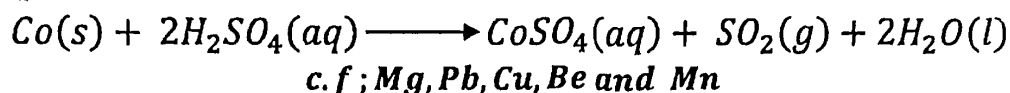
DEMYSTIFYING INORGANIC CHEMISTRY BY Joseph Jobs Kayiira, BScED(Hons. CHEM/MTC)  
Email: josephkayirab@gmail.com Call 0782601038 WhatsApp 0753247098

Dilute nitric acid oxidises cobalt to cobalt(II) nitrate, itself reduced to oxides of nitrogen and water.

*Cobalt(II) ions are pink in solution.*

d) concentrated acids

Hot concentrated sulphuric acid oxidises cobalt to cobalt(II) sulphate, itself reduced to sulphur dioxide and water.



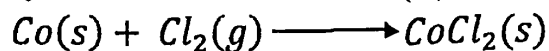
Concentrated nitric acid renders cobalt passive.

e) Sodium hydroxide

Cobalt does not react with sodium hydroxide

f) chlorine

Heated cobalt reacts with dry chlorine to form cobalt(II) chloride

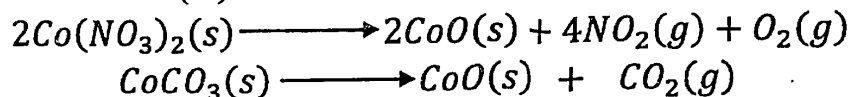


## COMPOUNDS OF COBALT

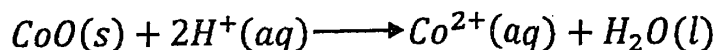
### Cobalt(II) compounds

**Cobalt(II) oxide**

Cobalt(II) oxide is a green solid prepared by the thermal decomposition of cobalt(II) nitrate or cobalt(II) carbonate in the absence of air.

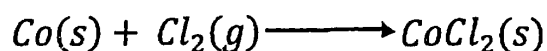


Cobalt(II) oxide is a basic oxide, reacting with acids to give pink solutions of cobalt(II) salts.



**Cobalt(II) chloride**

Anhydrous cobalt(II) chloride, a blue solid, can be prepared by passing dry chlorine over heated cobalt.



Anhydrous cobalt(II) chloride paper is used as a qualitative test for presence of water and as a heat-sensitive ink.

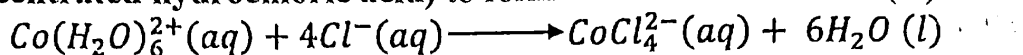
When water gets into contact with blue cobalt chloride paper, it turns from blue to pink.

The hydrated chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) is a pink solid.

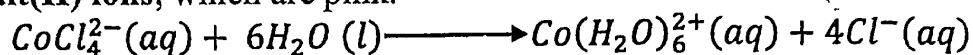
Cobalt(II) chloride and other soluble cobalt(II) salts dissolve in water to form pink solutions of cobalt(II) ions.

Cobalt(II) ions in solution exist as hexaaquacobalt(II) ions,  $\text{Co}(\text{H}_2\text{O})_6^{2+}$

And undergo ligand exchange reaction on addition of excess chloride ions (concentrated hydrochloric acid) to form tetrachlorocobaltate(II) ions:

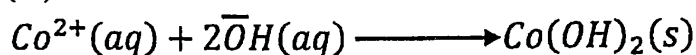


On dilution of the product with water, ligand exchange occurs and the chloro ligands in the complex are replaced with water molecules to form hexaaquacobalt(II) ions, which are pink.



### Cobalt(II) hydroxide

It is formed as a blue precipitate by adding sodium hydroxide solution to a solution of cobalt(II) ions.



It turns from blue to pink when exposed to air due to aerial oxidation.

### Cobalt(III) compounds

These are mostly complexes which include hexaamminecobalt(III) chloride ( $[\text{Co}(\text{NH}_3)_6]^{3+}3\text{Cl}^-$ ), hexanitrocobaltate(III) ion ( $[\text{Co}(\text{NO}_2)_6]^{3-}$ ), hexacyanocobaltate(III) ion, ( $[\text{Co}(\text{CN})_6]^{3-}$ ), etc.

### TEST TUBE EXPERIMENTS TO IDENTIFY COBALT(II) IONS

ION	TEST	OBSERVATION	DEDUCTION	EXPLANATION
$\text{Co}^{2+}$	Add sodium hydroxide drop wise until in excess	Pink solution forms a blue precipitate insoluble in excess and turns pink on standing	$\text{Co}^{2+}$ present	Cobalt(II) ions react with hydroxyl ions to form insoluble cobalt(II) hydroxide. $\text{Co}^{2+}(\text{aq}) + 2\overline{\text{O}}\text{H}(\text{aq}) \longrightarrow \text{Co}(\text{OH})_2(\text{s})$ Cobalt(II) hydroxide is oxidised by air to hydrated cobalt(III) oxide. $4\text{Co}(\text{OH})_2(\text{s}) + \text{O}_2(\text{g}) \longrightarrow 2\text{Co}_2\text{O}_3 \cdot 2\text{H}_2\text{O}(\text{s})$
	Add ammonia solution drop wise until in excess	Pink solution forms a blue precipitate soluble in excess to form a brown solution that turns red on standing	$\text{Co}^{2+}$ present	Cobalt(II) ions react with hydroxyl ions to form insoluble cobalt(II) hydroxide. $\text{Co}^{2+}(\text{aq}) + 2\overline{\text{O}}\text{H}(\text{aq}) \longrightarrow \text{Co}(\text{OH})_2(\text{s})$ Cobalt(II) hydroxide reacts with excess ammonia to form a soluble complex of hexaamminecobalt(II) ions.
				$\text{Co}(\text{OH})_2(\text{s}) + 6\text{NH}_3(\text{aq}) \longrightarrow \text{Co}(\text{NH}_3)_6^{2+}(\text{aq}) + 2\overline{\text{O}}\text{H}(\text{aq})$

Add potassium thiocyanate or ammonium thiocyanate solution	Pink solution forms blue solution	$Co^{2+}$ confirmed present	Cobalt(II) ions react with thiocyanate ions to form cobalt(II)thiocyanate solution. $Co^{2+}(aq) + 2SCN^{-}(aq) \rightarrow Co(SCN)_2(aq)$
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### Questions

- Cobalt(II) nitrate crystals heated strongly until no further change.
  - State what was observed and write an equation for the reaction.
  - Some crystals of the nitrate were dissolved in water to form pink solution. The resultant solution was divided into four parts.
    - To the first part was added concentrated hydrochloric acid and the resultant solution diluted. Explain the reactions that took place and write equations to illustrate your answer.
    - The second part was treated with ammonium thiocyanate solution. State what was observed and write equation for the reaction
    - To the third part was added aqueous ammonia drop wise until in excess and the mixture left to stand. Explain the reactions that took place.
    - To the fourth part was added copper turnings followed concentrated sulphuric acid and the mixture heated. State what was observed.
  - Cobalt(III) chloride hexammine,  $CoCl_3 \cdot 6NH_3$  is isomeric.
    - Write the chemical formulae and names of three possible isomers that can be formed by  $CoCl_3 \cdot 6NH_3$ .
    - State any two chemical tests that can be done to distinguish the isomers in above.
- Cobalt forms a complex of formular,  $Co(NH_3)_5SO_4Br$ .
  - State the oxidation state and the coordination number of cobalt in the complex.
  - Write the formulae for the ionisation isomers of the complex.
  - Name a reagent that can be used to distinguish the isomers in (b) above.
  - In each case, state what is observed when the isomers are separately treated with the reagent you have named in (c).

## NICKEL

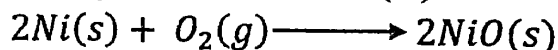
- Symbol Ni.
- A malleable ductile silvery metallic transition element
- Atomic number 28
- Group VIIIA
- Melting point 1450°C
- Boiling point 2732°C
- Nickel metal is used in special steels, in Invar, and, being ferromagnetic, in magnetic alloys, such as Mumetal.
- It is also an effective catalyst, particularly for hydrogenation reactions.
- Nickel mainly forms compounds in the +2 oxidation state (green); the +3 state also exists.

### Chemical properties of Nickel

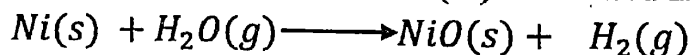
Describe the reactions of nickel with;

- air
- water
- dilute acids
- concentrated acids
- sodium hydroxide
- chlorine
- carbon monoxide

a) Heated nickel reacts with oxygen to form nickel(II) oxide.

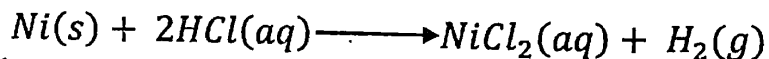


b) Red hot nickel reacts with steam to form nickel(II) oxide and hydrogen.

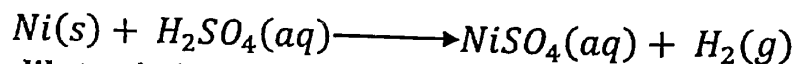


c) dilute acids

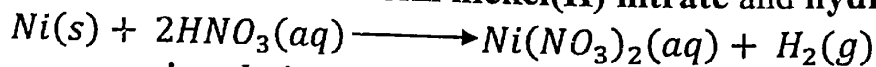
Nickel reacts with dilute hydrochloric acid to form nickel(II) chloride and hydrogen gas.



Nickel reacts with dilute sulphuric acid to form nickel(II) sulphate and hydrogen gas.



Nickel reacts with dilute nitric acid to form nickel(II) nitrate and hydrogen.



Nickel (II) ions are green in solution.

**d) concentrated acids**

Nickel does not react with concentrated sulphuric acid or hydrochloric acid

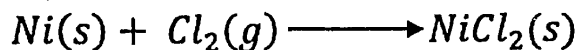
Concentrated nitric acid renders nickel passive.

**e) Sodium hydroxide**

Nickel does not react with sodium hydroxide

**f) chlorine**

Heated nickel reacts with dry chlorine to form nickel(II) chloride



**g) Nickel reacts with carbon monoxide to form tetracarbonylnickel(0)**

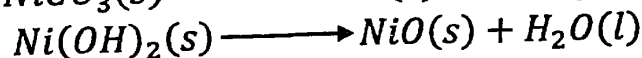
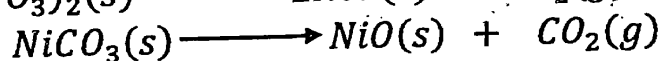
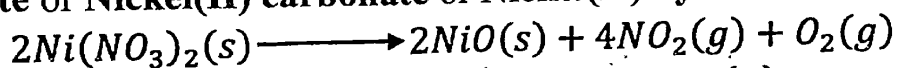


## COMPOUNDS OF NICKEL

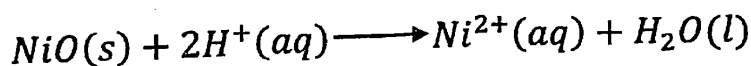
### Nickel (II) compounds

#### Nickel (II) oxide

Nickel(II) oxide is a green solid prepared by the thermal decomposition of Nickel(II) nitrate or Nickel(II) carbonate or Nickel(II) hydroxide.

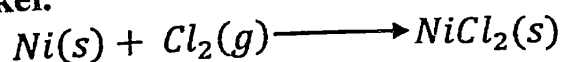


Nickel(II) oxide is a basic oxide, reacting with acids to give green solutions of Nickel(II) salts.



#### Nickel(II) chloride

Anhydrous nickel(II) chloride, a yellow solid, can be prepared by passing dry chlorine over heated Nickel.

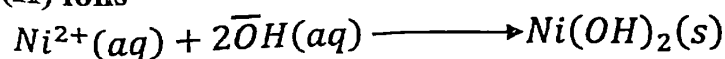


The hydrated chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) is a green solid.

Nickel(II) chloride and other soluble Nickel(II) salts dissolve in water to form green solutions.

#### Nickel(II) hydroxide

It is formed as a green precipitate by adding sodium hydroxide solution to a solution of nickel(II) ions



### TEST TUBE EXPERIMENTS TO IDENTIFY NICKEL(II) IONS.

ION	TEST	OBSERVATION	DEDUCTION	EXPLANATION
<b>Ni<sup>2+</sup></b>	Add sodium hydroxide drop wise until in excess	Green precipitate insoluble in excess	Ni <sup>2+</sup> present	Nickel(II) ions react with hydroxyl ions to form insoluble nickel(II) hydroxide. $\text{Ni}^{2+}(\text{aq}) + 2\overline{\text{O}}\text{H}(\text{aq}) \longrightarrow \text{Ni}(\text{OH})_2(\text{s})$
	Add ammonia solution drop wise until in excess	Green precipitate soluble in excess to form a blue solution.	Ni <sup>2+</sup> present	Nickel(II) ions react with hydroxyl ions to form insoluble nickel(II) hydroxide. $\text{Ni}^{2+}(\text{aq}) + 2\overline{\text{O}}\text{H}(\text{aq}) \longrightarrow \text{Ni}(\text{OH})_2(\text{s})$
				Nickel(II) hydroxide reacts with excess ammonia to form a soluble complex of hexaamminenickel(II) ions. $\text{Ni}(\text{OH})_2(\text{s}) + 6\text{NH}_3(\text{aq}) \longrightarrow \text{Ni}(\text{NH}_3)_6^{2+}(\text{aq}) + 2\overline{\text{O}}\text{H}(\text{aq})$
	Add potassium hexacyanoferrate (II) solution.	Green precipitate	Ni <sup>2+</sup> present	Nickel(II) ions react with hexacyanoferrate(II) ions to form insoluble nickel(II) hexacyanoferrate(II) $2\text{Ni}^{2+}(\text{aq}) + \text{Fe}(\text{CN})_6^{4-}(\text{aq}) \longrightarrow \text{Ni}_2[\text{Fe}(\text{CN})_6](\text{s})$
				Add potassium hexacyanoferrate (III) solution
	Add excess ammonia solution and dimethylglyoxime solution (butanedionedioxime solution).	A red precipitate is formed	Ni <sup>2+</sup> confirmed present	Not required

## Questions

1. A green solid J when heated decomposed to form a solid residue, K and a gas Y, which has a sweet smell and forms a yellow precipitate with 2,4-dinitrophenyl hydrazine in acidic medium. When a sample of J was dissolved in water, a pale green solution was formed which formed a green precipitate, L, soluble in excess ammonia and turned to a purplish blue solution, M.
- (a) (i) Name the species present as K, Y, L and M.  
(ii) Deduce the chemical formula of J.
- (b) Write the equation(s) for;
- (i) formation of K, L, and M  
(ii) reaction between Y and 2,4-dinitrophenylhydrazine in acidic medium
- (c) Describe a test that can be used to confirm the cation in J. State any observations made (*no equation required*)
2. When a pale green solid K was heated, it decomposed to form a green solid L and a gas that forms a white precipitate when bubbled through calcium hydroxide solution. L dissolves in dilute sulphuric acid to form a green solution M, which forms a green precipitate, N that is insoluble in excess sodium hydroxide but soluble in excess ammonia to form a purplish blue solution.
- (a) Write the formulae of the compounds K, L, M and N.
- (b) Write the equation(s) for the;
- (i) decomposition of K on heating  
(ii) reaction between L and dilute sulphuric acid  
(iii) formation of N  
(iv) reaction leading to formation of the purplish blue solution.

## COPPER

- *Symbol Cu.*
- *A brown transition element*
- *Atomic number 29*
- *Group IB*
- *Melting point 1083.4°C*
- *Boiling point 2567°C*
- *Copper compounds contain the element in the +1 and +2 oxidation states. Copper(I) compounds are mostly white (except the oxide, which is red). Copper(II) salts are blue in solution. The metal also forms a large number of coordination complexes.*
- *Copper is an excellent conductor of heat and electricity, used to make electric cables and wires and in its alloys, brass (copper–zinc) and bronze (copper–tin), used extensively.*

### Extraction

Copper can be extracted from the ores whose names and formulae are given below. **Copper pyrites** (also called *chalcopyrite*) is the **chief ore** from which the element can be extracted.

Name of ore	Chemical formula
Copper pyrites	$CuFeS_2$
Malachite	$CuCO_3 \cdot Cu(OH)_2$
Azurite	$2CuCO_3 \cdot Cu(OH)_2$
Copper glance	$Cu_2O$

The main impurity in the ores is;

Name of impurity	Formula
Iron(II) oxide	$FeO$

This is removed from the ore as slag during the smelting stage.

## Extraction from copper pyrites

The extraction involves five main stages which include; concentration, roasting, smelting, reduction and refining.

### 1. Concentration by froth flotation

The ore is crushed/ pulverised into powder and mixed with water containing a frothing agent like palm oil in a concentration tank.

Water wets the impurities, making them sink to the bottom

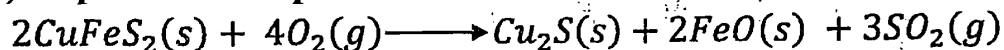
The frothing agent wets the ore making it float on the surface.

Compressed air is blown through the mixture to agitate it, making air bubbles rise to the surface with the froth.

The froth is skimmed off, an acid is added to break it down, filtered off and dried.

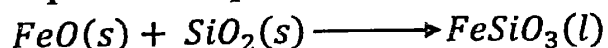
### 2. Roasting

The concentrated and dried ore is roasted in air to obtain iron(II) oxide, copper(I) sulphide and sulphur dioxide.



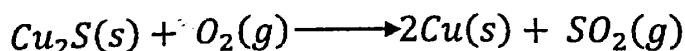
### 3. Smelting

The roasted product is heated in a reverberatory furnace with silicon(IV) oxide in absence of air to remove the iron(II) oxide impurity in form iron(II) silicate, called slag, a liquid that is poured away.



### 4. Reduction

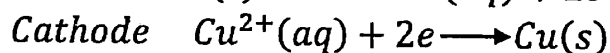
The smelted product is heated in a controlled amount of air to convert it to form impure copper.



### 5. Refining

The impure/ blister copper formed is purified by electrolysis using impure copper as anode and pure copper as cathode in an electrolytic cell containing acidified copper(II) sulphate solution as electrolyte.

Impure copper dissolves to form copper(II) ions and pure copper is deposited at the cathode.



**Note:** A Sulphuric acid manufacturing plant is needed near a site for extraction of copper because sulphur dioxide, a by-product of the process is a poisonous gas but a raw material for the manufacture of sulphuric acid.

### Uses of copper

- In electrical circuits and appliances since it is exceptionally able to conduct electricity
- Making ornaments, being little attacked by air
- Making steam pipes and boilers because it is a very good conductor of heat
- Making alloys such as brasses, bronzes, coinage metal.

### Alloys of copper

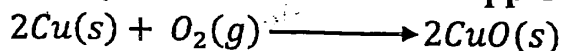
Name	Composition	Use
Brass	Copper and zinc	Machine bearings, jewellery, electrical objects, metallic parts of door furniture, water pipes.
Bronze	Copper and tin	Machine parts, ornaments e.g. necklaces and medals
Duralumin	Aluminium, copper and magnesium	Aircraft construction, bicycle parts and small boats
Copper coinage	Copper, tin and zinc	Making coins

### Chemical properties of copper

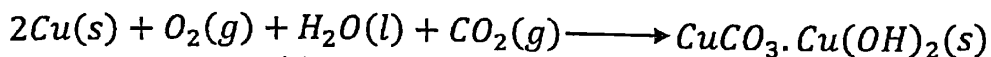
Describe the reactions of iron with;

- air
- water
- dilute acids
- concentrated acids
- sodium hydroxide
- chlorine
- hydrogen chloride

(a) Heated copper reacts with dry air at 300 °C to form copper(II) oxide.



Copper also reacts slowly with moist air to form to form basic copper(II) carbonate.

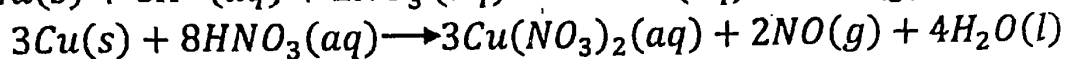
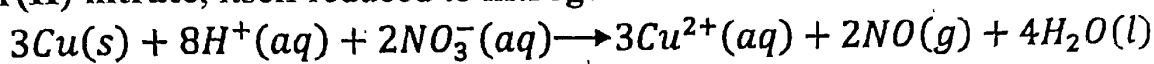


b) Copper does not react with water under any condition.

### c) dilute acids

Copper has a greater positive standard electrode potential than that of hydrogen hence unable to liberate hydrogen from dilute acids in the absence of an oxidising agent.

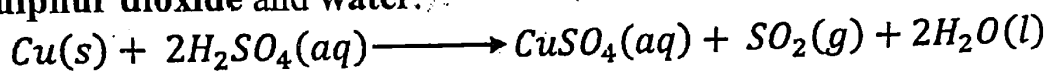
**Dilute/ moderately concentrated/ half concentrated nitric acid oxidises copper to copper(II) nitrate, itself reduced to nitrogen monoxide and water.**



*C.f Mg and Pb*

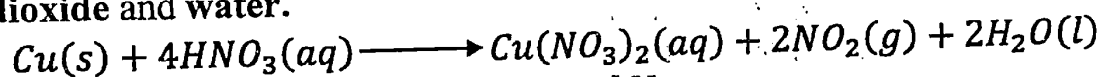
### d) concentrated acids

**Hot concentrated sulphuric acid oxidises copper to copper(II) sulphate, itself reduced to sulphur dioxide and water.**



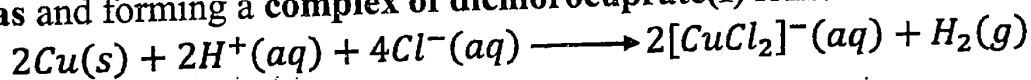
*c. f ; Pb, Mg, Be, Cu and Co*

**Concentrated nitric acid oxidises copper to copper(II) nitrate, itself reduced to nitrogen dioxide and water.**



*c. f ; Pb and Mg*

**Boiling concentrated hydrochloric acid dissolves copper with evolution of hydrogen gas and forming a complex of dichlorocuprate(I) ions.**

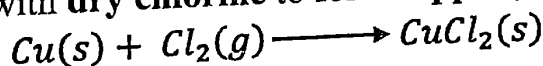


### e) Sodium hydroxide

Copper does not react with sodium hydroxide

### f) Chlorine

**Heated copper reacts with dry chlorine to form copper(II) chloride.**



### g) Hydrogen chloride

**Heated copper reacts with dry hydrogen chloride to form copper(II) chloride and hydrogen.**

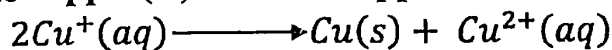


## COMPOUNDS OF COPPER

### Copper(I) compounds

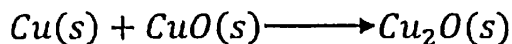
Copper(I) compounds are white apart from copper(I) oxide, which is red.

In solution copper(I) ions ( $\text{Cu}^+$ ) are colourless and very unstable hence easily disproportionate into copper(II) ions and copper.



### Copper(I) oxide

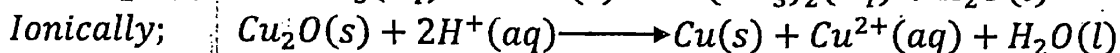
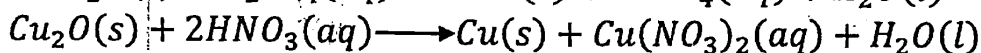
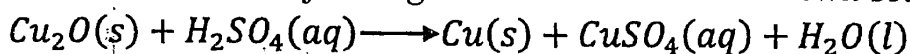
Copper(I) oxide ( $\text{Cu}_2\text{O}$ ) is a red solid prepared by the heating of copper with copper(II) oxide or by reduction of an alkaline solution of copper(II) sulphate.



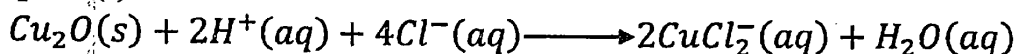
Copper(I) oxide is easily reduced by hydrogen when heated and is oxidized to copper(II) oxide when heated in air.

Copper(I) oxide undergoes disproportionation when reacted with dilute acids (dilute nitric acid and dilute sulphuric acid), producing copper(II) ions and copper.

*The red solid dissolves forming a blue solution and a brown solid.*



However, the oxide dissolves in concentrated hydrochloric acid to form a complex of dichlorocuprate(I) ions.



In this case, disproportionation does not occur as the copper(I) ion is held in solution as a complex ion.

### Copper(I) chloride

Copper(I) chloride ( $\text{CuCl}$ ) is a white solid compound obtained by boiling a solution containing copper(II) chloride, excess copper turnings, and hydrochloric acid. When the solution is colourless, it is poured into air-free water and a white precipitate of copper(I) chloride is obtained.

On exposure to air this precipitate turns green due to the formation of basic copper(II) chloride

In the vapour phase, the dimeric species ( $\text{Cu}_2\text{Cl}_2$ ) is present.

In organic synthesis, copper(I) chloride is used;

- (i) *together with hydrochloric acid converting benzene diazonium chloride to chlorobenzene (the Sandmeyer reaction)*
- (ii) *together with ammonia solution (ammoniacal copper(I) chloride solution) to test for terminal alkynes. A red precipitate is formed.*

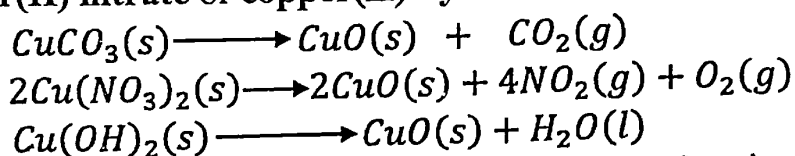
Qn. Name a reagent, apart from ammoniacal silver nitrate solution that can be used to distinguish between each of the following and in each case state what is observed and write an equation for the reaction.

- (i) ethyne and ethane
- (ii) propane and propyne
- (iii) But-1-yne and But-2-yne

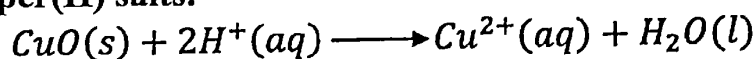
### Copper(II) compounds

#### Copper(II) oxide

Copper(II) oxide is a black solid. It is obtained by heating either copper(II) carbonate or copper(II) nitrate or copper(II) hydroxide.

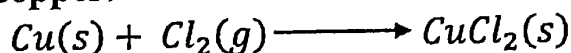


Copper(II) oxide is a basic oxide hence soluble in dilute acids forming blue solutions of copper(II) salts.

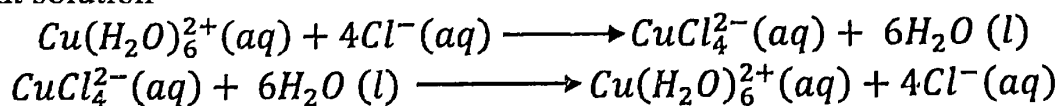


#### Copper(II) chloride

Anhydrous copper(II) chloride, a brown solid, can be prepared by passing dry chlorine over heated copper.



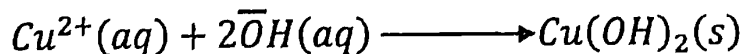
Copper(II) ions from copper(II) chloride or other soluble copper(II) salts exist in solution as blue hexaaquacopper(II) ions and react with excess chloride ions from concentrated hydrochloric acid to form a yellow solution of tetrachlorocuprate(II) ions. On addition of water, ligand exchange occurs and the chloro ligands in the complex are replaced with aqua ligands to form hexaaquacopper(II) ions. The solution therefore turns from blue to yellow on addition of concentrated hydrochloric acid and back to blue on dilution of resultant solution



The hydrated chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) is a green solid

#### Copper (II) hydroxide

It is formed as a blue precipitate by adding sodium hydroxide solution or ammonia solution to a solution of copper(II) ions.



## TEST TUBE EXPERIMENTS TO IDENTIFY COPPER(II) IONS

ION	TEST	OBSERVATION	DEDUCTION	EXPLANATION
<b>Cu<sup>2+</sup></b>	Add sodium hydroxide drop wise until in excess	Pale blue precipitate insoluble in excess.	Cu <sup>2+</sup> present	Copper(II) ions react with hydroxyl ions to form insoluble copper(II) hydroxide. $\text{Cu}^{2+}(\text{aq}) + 2\overline{\text{O}}\text{H}(\text{aq}) \longrightarrow \text{Cu}(\text{OH})_2(\text{s})$
	Add ammonia solution drop wise until in excess	Pale blue precipitate soluble in excess to form a deep blue solution	Cu <sup>2+</sup> confirmed present	Copper(II) ions react with hydroxyl ions to form insoluble copper(II) hydroxide. $\text{Cu}^{2+}(\text{aq}) + 2\overline{\text{O}}\text{H}(\text{aq}) \longrightarrow \text{Cu}(\text{OH})_2(\text{s})$ Copper(II) hydroxide reacts with excess ammonia to form a soluble complex of tetraamminecopper(II) ions. $\text{Cu}(\text{OH})_2(\text{s}) + 4\text{NH}_3(\text{aq}) \longrightarrow \text{Cu}(\text{NH}_3)_4^{2+}(\text{aq}) + 2\overline{\text{O}}\text{H}(\text{aq})$
	Add potassium iodide solution	White precipitate in a brown solution	Cu <sup>2+</sup> present	Copper(II) ions are reduced by iodide ions to copper(I) iodide as the iodide ions are oxidised to iodine. $2\text{Cu}^{2+}(\text{aq}) + 4\text{I}^{-}(\text{aq}) \longrightarrow \text{Cu}_2\text{I}_2(\text{s}) + \text{I}_2(\text{aq})$
	Add potassium hexacyanoferrate (II) solution	A reddish brown precipitate	Cu <sup>2+</sup> present	Copper(II) ions react with hexacyanoferrate(II) ions to form insoluble copper(II) hexacyanoferrate(II). $2\text{Cu}^{2+}(\text{aq}) + \text{Fe}(\text{CN})_6^{4-}(\text{aq}) \longrightarrow \text{Cu}_2[\text{Fe}(\text{CN})_6](\text{s})$

### Questions

1. (a) Write the formula and name of one ore from which copper can be extracted.
- (b) During the process of extraction, the copper ore is concentrated; roasted, smelted, reduced and then refined to obtain pure copper.
- (c) Describe the processes of concentration, roasting and smelting of the ore.
- (d) Write equations to show how the smelted product can be converted to impure copper.
- (e) Explain the processes that lead to formation of pure copper from impure copper during the refining process (No diagram required)
- (f) Copper is used to make alloys of important use in daily life.
  - (i) State any two alloys formed by copper
  - (ii) Apart from alloy formation, mention any two other uses of copper.
- (g) Describe how copper reacts with;
  - (i) nitric acid
  - (ii) chlorine

## ZINC

- *Symbol Zn*
- *A bluish-white transition metal*
- *Atomic number 30*
- *Group IIB*
- *Melting point 419.58°C*
- *Boiling point 907°C*
- *Zinc compounds contain the element only in the +2 oxidation state and are white, colourless in solution.*
- *The metal is used in galvanizing iron and in a number of alloys (brass, bronze, etc.) and in dry batteries.*

### Extraction

Zinc can be extracted from the ores whose names and formulae are given below. Zinc blende is the chief ore from which the element can be extracted. The other ore is Calamine

Name of ore	Chemical formula
Zinc blende	$ZnS$
Calamine	$ZnCO_3$
Zincite	$ZnO$

### Extraction from Zinc blende

#### 1. Concentration by froth flotation

The ore is crushed/ pulverised into powder and mixed with water containing a frothing agent like palm oil in a concentration tank.

Water wets the impurities, making them sink to the bottom

The frothing agent wets the ore making it float on the surface.

Compressed air is blown through the mixture to agitate it, making air bubbles rise to the surface with the froth.

The froth is skimmed off, an acid is added to break it down, filtered off and dried.

#### 2. Roasting

The concentrated and dried ore is roasted in air to obtain zinc oxide and sulphur dioxide.

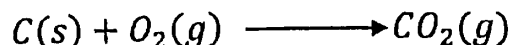


### 3. Reduction

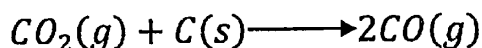
The zinc oxide obtained after roasting, coke and limestone are fed into the blast furnace from the top.

Hot air is blown into the furnace from the bottom

Coke burns in air to form carbon dioxide.



The carbon dioxide formed is reduced by unburnt coke to form carbon monoxide.



The zinc oxide is reduced by either coke or carbon monoxide to form zinc vapour.

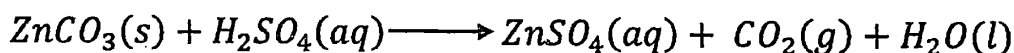


The zinc vapour distils off from the furnace, cooled by a spray of molten lead and then purified by redistillation.

*Note: The sulphur dioxide, a by-product of the process is a poisonous gas but a raw material for the manufacture of sulphuric acid.*

#### Extraction from Calamine

The ore is dissolved in dilute sulphuric acid to form zinc sulphate, carbon dioxide and water.

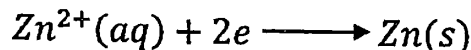


Milk of lime is added to precipitate the hydroxides of the elements such as aluminium, iron(II) and lead(II) ions.

The mixture is filtered to obtain zinc sulphate solution as filtrate.

The zinc sulphate solution is acidified and electrolysed using aluminium cathode and lead anode. A very high current density is required.

Pure zinc is deposited at the cathode.



#### Uses of zinc

- Galvanising of iron to prevent it from rusting
- Making dry batteries
- Making alloys such as brass.

## Alloys of zinc

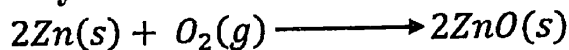
Name	Composition	Use
Brass	Copper and zinc	Machine bearings, jewellery, electrical objects, metallic parts of door furniture, water pipes.
Copper coinage	Copper, tin and zinc	Making coins

## Chemical properties of zinc

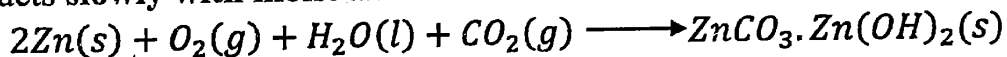
Describe the reactions of zinc with;

- a) air
- b) water
- c) dilute acids
- d) concentrated acids
- e) sodium hydroxide
- f) chlorine
- g) sodium nitrate solution in presence of sodium hydroxide solution.

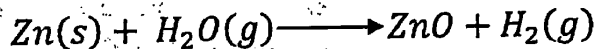
a) Heated zinc reacts with dry air to form zinc oxide.



Zinc also reacts slowly with moist air to form to form basic zinc carbonate.



b) Red hot zinc reacts with steam to form zinc oxide and hydrogen.



c) dilute acids

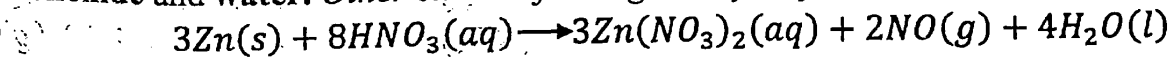
Zinc reacts with dilute hydrochloric acid to form zinc chloride and hydrogen gas.



Zinc also reacts with dilute sulphuric acid to form zinc sulphate and hydrogen gas.



Dilute nitric acid oxidises zinc to zinc nitrate, itself reduced to nitrogen monoxide and water. Other oxides of nitrogen may be formed too.

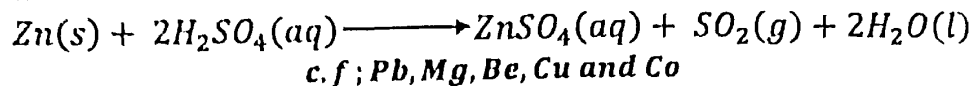


d) concentrated acids

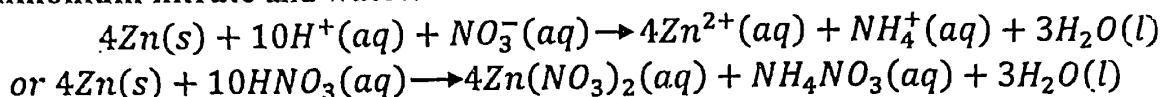
Zinc reacts with concentrated hydrochloric acid to form zinc chloride and hydrogen.



Hot concentrated sulphuric acid oxidises zinc to zinc sulphate, itself reduced to sulphur dioxide and water.

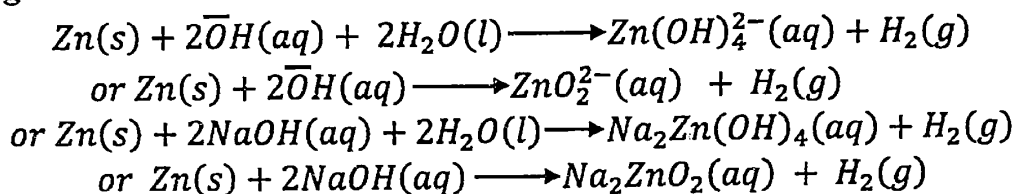


Hot concentrated nitric acid oxidises zinc to zinc nitrate, itself reduced to ammonium nitrate and water.



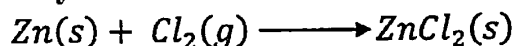
#### e) Sodium hydroxide

Zinc reacts with hot concentrated sodium hydroxide to form sodium zincate and hydrogen gas.



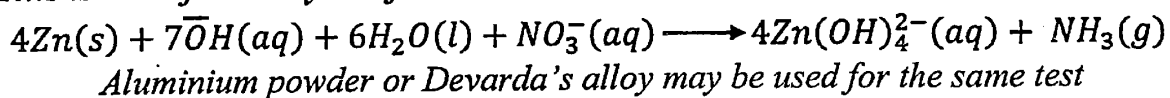
#### f) Chlorine

Heated zinc reacts with dry chlorine to form zinc chloride.



#### g) sodium nitrate solution in presence of sodium hydroxide solution.

When zinc powder is added to a solution containing nitrate ions followed by sodium hydroxide solution and the mixture heated, Zinc reduces the nitrate ions, in the alkaline medium to ammonia and itself oxidised to zincate ions. *This is a confirmatory test for nitrate ions.*



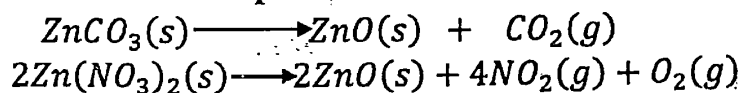
### COMPOUNDS OF ZINC

All compounds occur in only the +2 oxidation state

#### Zinc oxide

It is a white powder when cold and yellow when hot.

It is prepared by the thermal decomposition of zinc carbonate or zinc nitrate.

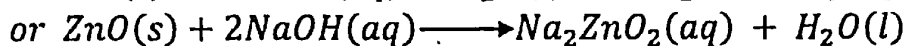
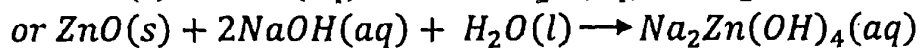
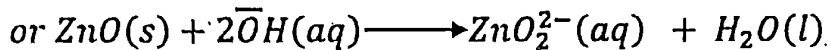
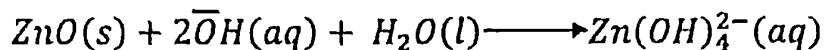


Zinc oxide is amphoteric hence soluble in dilute acids forming colourless solutions of zinc ions and soluble in hot concentrated sodium hydroxide solution to form sodium zincate.

With acids:

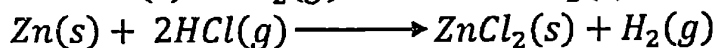
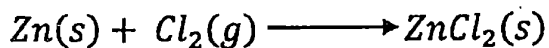


With hot concentrated sodium hydroxide:



### Zinc chloride

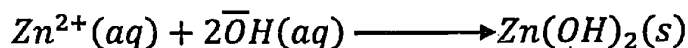
Anhydrous zinc chloride, a white solid, can be prepared by passing dry chlorine or dry hydrogen chloride over heated zinc.



The hydrated chloride ( $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ ) is a white solid and deliquescent.

### Zinc hydroxide

It is formed as a white precipitate by adding sodium hydroxide solution or ammonia solution to a solution of zinc ions.



Zinc hydroxide is soluble in both sodium hydroxide and ammonia solution

### TEST TUBE EXPERIMENTS TO IDENTIFY ZINC IONS

ION	TEST	OBSERVATION	DEDUCTION	EXPLANATION
$\text{Zn}^{2+}$	Add sodium hydroxide drop wise until in excess	White precipitate soluble in excess to form a colourless solution.	$\text{Zn}^{2+}, \text{Al}^{3+}, \text{Pb}^{2+}$ probably present	Zinc ions react with hydroxyl ions to form insoluble zinc hydroxide. $\text{Zn}^{2+}(aq) + 2\text{OH}^-(aq) \longrightarrow \text{Zn}(\text{OH})_2(s)$ Zinc hydroxide is amphoteric hence reacts with excess hydroxide ions to form a soluble complex of zincate ions. $\text{Zn}(\text{OH})_2(s) + 2\text{OH}^-(aq) \longrightarrow \text{Zn}(\text{OH})_4^{2-}$
	Add ammonia solution drop wise until in excess	White precipitate soluble in excess to form a colourless solution	$\text{Zn}^{2+}$ present	Zinc ions react with hydroxyl ions to form insoluble zinc hydroxide. $\text{Zn}^{2+}(aq) + 2\text{OH}^-(aq) \longrightarrow \text{Zn}(\text{OH})_2(s)$ Zinc hydroxide reacts with excess ammonia to form a soluble complex of tetraamminezinc(II) ions. $\text{Zn}(\text{OH})_2(s) + 4\text{NH}_3(aq) \longrightarrow \text{Zn}(\text{NH}_3)_4^{2+}(aq) + 2\text{OH}^-(aq)$

$Zn^{2+}$	Add potassium hexacyanoferrate (II) solution	A white precipitate	$Zn^{2+}$ present	Zinc ions react with hexacyanoferrate(II) ions to form insoluble zinc hexacyanoferrate(II).
			$2Zn^{2+}(aq) + Fe(CN)_6^{4-}(aq) \longrightarrow Zn_2[Fe(CN)_6](s)$	
	Add potassium hexacyanoferrate (III) solution	A yellow precipitate	$Zn^{2+}$ present	Zinc ions react with hexacyanoferrate(III) ions to form insoluble zinc hexacyanoferrate(III).
			$3Zn^{2+}(aq) + 2Fe(CN)_6^{3-}(aq) \longrightarrow Zn_3[Fe(CN)_6]_2(s)$	
	Add solid ammonium chloride and disodium hydrogenphosphate and then excess aqueous ammonia solution	White precipitate soluble in excess ammonia to form a colourless solution	$Zn^{2+}$ confirmed present	Not required

### Questions

1. (a) Write the formula and name of the carbonate ore from which zinc can be extracted.
- (b) Describe the processes that lead to extraction of zinc from the carbonate ore in (a) above.
- (c) Scandium and zinc are part of the first transition series but are not typical transition elements
  - (i) State two reasons why the elements are not typical transition elements
  - (ii) State two properties in which zinc behaves as a transition element.
- (d) Describe how zinc reacts with;
  - (i) sulphuric acid
  - (ii) air

### THE MAIN STAGES INVOLVED IN METAL EXTRACTION

Most metals are extracted from substances called ores from which they normally exist.

*An ore is a naturally occurring substance from which an element can be extracted using a suitable method.*

The chief ores from which most elements are extracted are; **oxides, sulphides, chlorides and carbonates.**

It is usual to convert the sulphides and carbonates into oxides before reduction because oxides are more efficiently reduced than sulphides.

Most attention therefore will be given to the oxide ores.

The overall process of metal extraction involves **three main stages** namely;

1. **Concentration of the ore**
2. **Reduction**
3. **Refining**

### **CONCENTRATION OF THE ORE**

Often, ores are found contaminated with earthly impurities. Methods are employed to remove the impurities. The ores are always **first crushed to form fine powder** suitable for the next treatment. The ore can **then be concentrated** by either **physical methods** or **chemical methods**.

*The physical methods make use of difference in density or magnetic properties. They include washing, magnetic separation and froth flotation.*

**Washing.** This is done if the ore is denser than gangue (rock and other waste material present in an ore) for example galena ( $PbS$ )

**Magnetic separation.** This normally used in the separation of wolframite, the tungsten ore, from cassiterite, in which it is found.

**Froth flotation.** This is the widely used and important method for the sulphide ores.

The ore is crushed into fine powder and mixed with water containing a frothing agent like palm oil. The oil wets the sulphide particles and the water wets the gangue. Air is then blown through the mixture and the air bubbles attach themselves to the oiled particles are buoyed up and carried to the surface, leaving the gangue at the bottom. The froth is skimmed off, an acid is added to break it down, filtered off and dried.

This process is normally used in concentration of copper pyrites, zinc blende and galena.

*The chemical methods for concentration of ores include heating or roasting and leaching.*

**Heating or roasting.** The hydrated ores like Bauxite are heated to drive off water of crystallisation. Roasting in air is sometimes used to remove water, carbonaceous matter, and to convert sulphides and carbonates to oxides for example zinc blende, calamine, copper pyrites, iron pyrites and siderite.

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**Leaching.** The ore may be leached with aqueous solvents to extract the metal as a soluble salt. For example, Bauxite is digested with hot concentrated sodium hydroxide under pressure to form sodium aluminate.

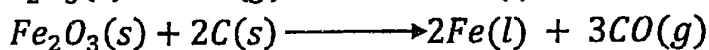
Zinc ores, oxide and carbonate ores of copper may also be leached with dilute sulphuric acid.

## REDUCTION

Reduction normally occurs by two processes;

### *High temperature reduction with carbon or carbon monoxide*

This depends on the fact that carbon monoxide exists and is stable at high temperature. Therefore, carbon or carbon monoxide can reduce less stable metal oxides to the metals. For example, reduction of iron(III) oxide and zinc oxide to iron and zinc respectively.



### *Electrolysis of molten compounds of metals or their aqueous solutions*

Metals may be obtained from solutions or molten compounds by electrolysis due to the very high temperatures required for reduction over their oxides with carbon. They also form stable oxides which cannot easily be reduced by carbon or carbon monoxide. For example, aluminium, which is obtained from molten aluminium oxide by electrolysis in presence of molten cryolite.

## REFINING

The product of reduction is not often a pure specimen of the metal. A pure metal can be obtained by any of the following methods;

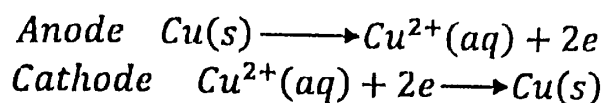
### *Preferential oxidation of impurities*

Removal of impurities as gaseous oxides or slag is done for impurities that have greater affinity for oxygen than the metal. Manufacture of steel from pig iron is an example.

### *Electrolysis using impure metal as anode*

Impure copper is purified by electrolysis using impure copper as anode and pure copper as cathode in an electrolytic cell containing acidified copper(II) sulphate solution as electrolyte.

Impure copper dissolves to form copper(II) ions and pure copper is deposited at the cathode



### *Distillation*

Zinc can be purified by distillation. Distillation usually in a vacuum gives a very pure product.

### *Formation of carbonyls*

Very pure iron and nickel are made by forming their volatile carbonyls,  $\text{Ni}(\text{CO})_4(g)$ , and  $\text{Fe}(\text{CO})_5(l)$  which are then decomposed by heating.

**Qn. Concentration, reduction and refining are the three main stages ores undergo during metal extraction.**

**(a) Describe the;**

- (i) physical methods used during concentration of metal ores**
- (ii) importance of heating, roasting and leaching in ore concentration**

*(Illustrate your answers with the principles underlying the above methods)*

**(b) With reference to one ore describe how the ore is reduced to obtain the metal from it**

**(c) Briefly describe how impure copper can be refined to pure copper.**

## **MISCELLANEOUS TOPICAL QUESTIONS**

### *Short answer type questions*

1. (a) State two properties in which chromium behaves as a transition element. (01 mark)
- (b) Write the equation for the reaction that takes place when chromium(III) sulphate is dissolved in water. (1 ½ marks)
- (c) Magnesium ribbon was added to a solution of chromium(III) sulphate.
  - (i) State what was observed. (01 mark)
  - (ii) Write equation for the reaction that took place. (1 ½ marks)
- (d) To a dilute solution of chromium(III) sulphate was added dilute aqueous sodium hydroxide drop wise until in excess followed by 3 drops of hydrogen peroxide and the mixture warmed. Explain the reaction(s) that took place. (04 marks)

2. (a) Chromium like other transition elements forms an orange coloured solution of potassium dichromate and a complex of formula  $[Cr(C_2O_4)_3]^{3-}$ .
- (i) State any two other properties to show that chromium is a typical transition element. Illustrate each answer with an example. (02 marks)
- (ii) Explain why chromium can form complexes. (1 ½ marks)
- (b)(i) State the coordination number and oxidation state of chromium in  $[Cr(C_2O_4)_3]^{3-}$ . (01 mark)
- (ii) Name the donor atom in the ligand in  $[Cr(C_2O_4)_3]^{3-}$ . (½ mark)
- (c) State what would be observed and write an equation for the reaction that occurs when each of the following is added to an aqueous solution of potassium dichromate.
- (i) acidified hydrogen peroxide solution. (02 marks)
- (ii) dilute sodium hydroxide solution. (02 marks)
3. (a) Calculate the oxidation state of chromium in each of the following oxides.
- (i)  $Cr_2O_3$
- (ii)  $CrO_3$  (02 marks)
- (b) Write the equation to show the reaction between aqueous sodium hydroxide and
- (i)  $Cr_2O_3$
- (ii)  $CrO_3$  (02 marks)
4. Potassium dichromate(VI) is used as a reagent in volumetric analysis:
- (a) State two reasons why potassium dichromate(VI) is used as a primary standard. (02 marks)
- (b) Name one substance that can be standardised using potassium dichromate(VI) (01 mark)
- (c) To acidified potassium dichromate(VI) was bubbled hydrogen sulphide gas.
- (i) State what was observed. (01 mark)
- (ii) Write an ionic equation for the reaction. (1 ½ marks)
5. Potassium chromate(VI) solution was added to barium chloride solution followed by dilute nitric acid drop wise until in excess.
- (i) State what was observed. (01 mark)
- (ii) Write equation(s) for the reaction(s) that took place. (03 marks)

6. Manganese is a d-block element in the Periodic Table.

(a) Define a d-block element. (01 mark)

(b) (i) Write the electronic configuration of manganese (½ mark)

(ii) State the common oxidation states exhibited by manganese in its compounds. (1 ½ marks)

(iii) Write the formulae of the oxides of manganese in each of the oxidation states you have stated in (b) (ii). (1 ½ marks)

(c) An oxide of manganese, Q was fused with a mixture of potassium hydroxide and potassium nitrate to give a compound which when treated with water gave a green solution. The green solution turned purple when acidified with sulphuric acid. Identify;

(i) Q (01 mark)

(ii) the ion that gives the green solution its colour. (01 mark)

(iii) the ion that gives the purple solution its colour. (01 mark)

(d) Write ionic equation for the reaction leading to the formation of the purple solution. (1 ½ marks)

7. (a) State the oxidation state of manganese in each of the following compounds (02 marks)

Compound	Oxidation state
$Mn_2O_7$	
$Na_2MnO_4$	
$KMnO_4$	
$MnN_2O_4$	

(b) Write a half equation for the reduction of the permanganate ion in;

(i) Acidic medium (01 mark)

(ii) Alkaline medium (01 mark)

(c) An acidified solution of potassium iodide was added to a solution of potassium permanganate.

(i) State what was observed. (01 mark)

(ii) Write the ionic equation for the reaction that took place. (1 ½ mark)

(d) State;

(i) Two advantages of using potassium permanganate as a reagent in volumetric analysis (01 mark)

(ii) Two reasons why potassium permanganate is not a primary standard. (01 mark)

(e) Name two compounds that are used to standardise potassium manganate(VII). (01 mark)

8. (a) A compound Z contained 19.1% nitrogen, 43.6% oxygen and the rest being manganese.
- (i) Calculate the empirical formula of Z. (02 marks)
- (ii) 10g of Z in 1000g of water lowered the freezing point by  $0.127^{\circ}\text{C}$ . Calculate the molecular formula of Z ( $k_f$  for water is  $1.86^{\circ}\text{Cmol}^{-1}\text{kg}^{-1}$ ) (02 marks)
- (b) When Z was strongly heated, brown fumes were given off. Z dissolved in water to form a pink solution which decolourises acidified potassium manganate(VII) solution. Identify Z. (01 mark)
- (c) State what would be observed and write equation(s) for the reaction(s) that took place when to the solution in (b) was;
- (i) added concentrated nitric acid and lead(IV) oxide and the mixture boiled. (02 marks)
- (ii) sodium carbonate solution was added (02 marks)
9. Solid M dissolved in water to form a pale pink solution. Addition of excess sodium hydroxide to the solution formed a dirty white precipitate that rapidly turned brown on standing. When nitric acid was added to the solution of M followed by sodium bismuthate solution, the solution changed from pink to purple.
- (a) Identify the cation in M. ( $\frac{1}{2}$  mark)
- (b) Write equation for the reaction;
- (i) when ammonia solution was added to the pink solution. (1  $\frac{1}{2}$  marks)
- (ii) leading to formation of the brown solid. (1  $\frac{1}{2}$  marks)
- (iii) leading to the formation of the purple solution. (1  $\frac{1}{2}$  marks)
10. State what would be observed and write an equation(s) for the reaction that would take place when to a solution of iron(II) sulphate was added;
- (i) aqueous sodium hydroxide drop wise until in excess and the mixture allowed to stand. (3  $\frac{1}{2}$  marks)
- (ii) a few drops of concentrated nitric acid and the mixture boiled. (2  $\frac{1}{2}$  marks)
11. (a)(i) State how iron(III) chloride can be prepared. (01 mark)
- (ii) Write equation for the reaction that takes place. (01 mark)
- (b) To an aqueous solution of iron(III) chloride solution was added a few drops of saturated solution of sodium carbonate solution.
- (i) State what was observed. (01 mark)
- (ii) Write equation for the reaction that takes place. (1  $\frac{1}{2}$  marks)

12.(a) Substance X dissolved in water to form a yellow solution. When aqueous sodium hydroxide solution was added drop wise to the solution, a brown precipitate insoluble in excess alkali was formed.

(i) Identify the cation in X. (01 mark)

(ii) Write equation for the formation of the brown precipitate. (1 ½ marks)

(c) (i) Name one reagent that can be used to confirm the cation you have identified in (a) and state the observation made when the cation is treated with the reagent. (02 marks)

(ii) Write an equation for the reaction in c (i) above. (1 ½ marks)

(d) The pH of the solution formed in (a) above is less than 7. Explain this observation and write an equation to illustrate your answer. (4 ½ mark)

13.(a) Iron metal is extracted from one of its ore siderite. The ore is mixed with coke and limestone and then heated strongly in a blast furnace. Write equations for the reactions that lead to formation of iron metal in the blast furnace.

(4 ½ marks)

(b) 1.6 g of an impure sample of tin(II) chloride is added to an aqueous solution of iron(III) chloride and the mixture heated until no further change. The solution was diluted to 250cm<sup>3</sup> with water. 25cm<sup>3</sup> of the solution was acidified with dilute sulphuric acid and titrated with 0.02M potassium permanganate solution. 16.0cm<sup>3</sup> of oxidant was required to reach end point. Determine the percentage purity of tin(II) chloride. (4 ½ marks)

14.(a) Write the electronic configuration of cobalt. (½ mark)

(b) Write the formulae and electronic configuration of the common ions formed by cobalt. (02 marks)

(c) Give reasons why cobalt is classified as a transition metal element. (01 mark)

(d) To an aqueous solution of  $CoCl_2 \cdot 6H_2O$  was added concentrated hydrochloric acid drop wise until in excess.

(i) State what was observed. (01 mark)

(ii) Write equation(s) for the reaction(s) that took place. (01 mark)

(e) Name the species present in the;

(i) Solution before hydrochloric acid was added. (01 mark)

(i) Solution containing excess hydrochloric acid. (01 mark)

(f) The solution containing concentrated hydrochloric acid was diluted with water.

(i) State what was observed. (01 mark)

(ii) Write equation for the reaction that took place. (1 ½ mark)

- (g) Concentrated ammonia solution was added drop wise until in excess to an aqueous solution of cobalt(II) sulphate and the resulting solution allowed to stand in air. (04 marks)
- 15.(a) Cobalt(III) ions form a wide range of complexes with coordination number 6
- Define the term coordination number. (01 mark)
  - Write the formula of the complex formed between cobalt(III) ions and ethane-1,2-diamine ( $H_2NCH_2CH_2NH_2$ ). (01 mark)
  - State two reasons why cobalt forms complexes. (01 mark)
- (b) 2.033g of an isomer of  $CoBr_3 \cdot 6H_2O$  were dissolved in water and the resultant solution treated with excess silver nitrate solution. The mixture was filtered and the mass of the dry pale yellow residue was 2.8185g.
- Explain how the pale yellow residue is formed. (1 ½ marks)
  - Determine the structural formula of the isomer that gave the results above and deduce its IUPAC name. (04 marks)
  - State one other method by which the isomers of  $CoBr_3 \cdot 6H_2O$  can be distinguished from each other. (½ mark)
- 16.(a) State Graham's law of gaseous diffusion. (01 mark)
- (b) Nickel forms a gaseous carbonyl;  $Ni(CO)_n$ . Deduce the value of n if carbon monoxide diffuses 2.46 times faster than the carbonyl compound. (03 marks)
- (c) State;
- name of the nickel carbonyl
  - coordination number of nickel in the compound. (01 mark)
17. Compound Q is a green solid which dissolves in water to give a pale green solution. The solution of Q formed a red precipitate with butanedionedioxime solution and a reddish brown solution when a few drops of iron(III) chloride solution were added to it. When Q was heated with concentrated sulphuric acid, methanoic acid was formed.
- Identify Q. (01 mark)
  - Write equation for the reaction that took place when Q was heated with concentrated sulphuric acid. (1 ½ marks)
  - Write equation(s) for the reaction(s) that take place when excess ammonia solution is added to a solution of Q. (2 ½ marks)

18. When a pale green solid Y was heated, it decomposed to a green solid Q and a gas that turns limewater milky was evolved. Q dissolves in nitric acid to form a green solution R. On addition of dilute sodium hydroxide to R, a green precipitate S insoluble in excess alkali was obtained. S dissolved in aqueous ammonia to form a purplish blue solution.

(a) Identify the compounds Y, Q, R and S. (02 marks)

(b) Write the equations for the reactions between

(i) Q and nitric acid (1 ½ marks)

(ii) R and sodium hydroxide. (1 ½ marks)

19. State what will be observed and write equations for the reaction that takes place when;

(a) Nickel ethanoate is heated strongly and the gaseous product passed through acidified 2,4-dinitrophenyl hydrazine. (04 marks)

(b) Ammonia solution is added drop wise until in excess to aqueous solution of nickel ethanoate. (04 marks)

20. During the extraction of copper from copper pyrites, copper pyrites is crushed and agitated with water/oil mixture. Compressed air is bubbled through the mixture which is then filtered, roasted and finally impure molten copper is obtained.

(a) State the role of;

(i) Oil (01 mark)

(ii) Compressed air. (01 mark)

(b) Write equation for the reaction that occurs when copper pyrites is roasted. (1 ½ marks)

(c) Explain briefly how copper pyrites is refined. (04 marks)

(d) Explain why it is advantageous to have a sulphuric acid manufacturing plant near a copper extraction plant. (1 ½ marks)

21. (a) Copper like other transition elements forms compounds in oxidation states +1 and +2. Write the electronic configuration of;

(i) copper(I) ions

(ii) copper(II) ions (01 mark)

(b) The enthalpies of reduction of copper(I) and copper(II) ions are given below.



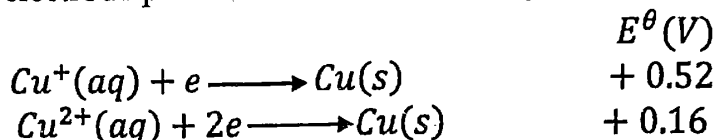
(i) Calculate the enthalpy for the disproportionation of copper(I) ions to copper(II) ions and copper. (02 marks)

(ii) Using your answer in b(i), comment on the stability of copper(I) ions with respect to copper(II) ions. Give a reason for your answer. (01 mark)

(c) State any two other properties that make copper a typical transition metal. (01 mark)

22.(a) State three factors which determine the magnitude of electrode potential of a metal (1 ½ marks)

(b) The standard electrode potentials for the following reactions are given



Write;

(i) the cell notation for the cell formed when the two half cells are connected. (01 mark)

(ii) the overall cell reaction (1 ½ marks)

(c) (i) calculate the emf of the cell. (01 mark)

(ii) what deduction do you make from your answer in (d) (i) (01 mark)

(d) When dilute sulphuric acid is added to copper(I) oxide, a brown solid and a pale blue solution were formed. Explain the observation. (2 ½ marks)

23. Compound X is a greenish blue solid which dissolves in water to form a pale blue solution. The pale blue solution forms a deep blue solution with excess ammonia and a reddish brown colour with a few drops of neutral iron(III) chloride. When X is heated with concentrated sulphuric acid, compound Y, which has a sharp distinctive smell is formed. Compound Y was isolated and reacted with ethanol in presence of an acid giving compound Z which has a sweet fruity smell.

(a) Identify compounds X, Y and Z. (03 marks)

(b) Write the equations for the reactions that took place when;

(i) excess ammonia solution was added to a solution of X. (1 ½ marks)

(ii) X was heated with concentrated sulphuric acid. (01 mark)

(iii) Y was heated with ethanol and an acid. (01 mark)

(c) State what would be observed and write equation for the reaction that would take place when concentrate hydrochloric acid was added to an aqueous solution of X followed by water. (3 ½ marks)

24.(a) In the extraction of zinc from its ores, the ore is first concentrated and then roasted in air. The roasted material is mixed with coke and limestone and heated by hot air in a blast furnace producing zinc.

(i) Write the name of the ore from which zinc can be extracted. (½ mark)

- (ii) Describe the process by which the ore named in (a) can be concentrated. (03 marks)
- (b) Write equation for the reaction ;
- (i) that takes place when the ore is roasted in air (01 mark)
- (ii) that leads to the formation of zinc in the blast furnace. (01 mark)
- (c) State what would be observed and write equation for the reaction when zinc metal is added to;
- (i) Copper(II) sulphate solution. (2 ½ marks)
- (ii) Aqueous sodium hydroxide solution (2 ½ marks)
- (iii) Aqueous iron(III) sulphate. (02 marks)
- 25.(a) During the extraction of zinc from its sulphide ore, the ore is first concentrated, then roasted and reduced.
- (i) Name the process by which the ore is concentrated. (½ mark)
- (ii) Write the equations for roasting and reduction of the concentrated ore. (02 mark)
- (b) State the process by which the zinc formed after reduction can be purified. (01 mark)
- (c) Zinc powder was added to potassium nitrate solution followed by sodium hydroxide and the resultant mixture warmed.
- (i) State what was observed. (01 mark)
- (ii) Write an equation for the reaction. (1 ½ marks)
- (d) Describe the reaction of zinc with sulphuric acid. (03 marks)
26.  $[Cr(NH_3)_6]^{3+}$  and  $[Co(CN)_4]^{2-}$  are complexes formed when chromium(III) ions and cobalt(II) ions are respectively treated with aqueous ammonia and potassium thiocyanate.
- (a) Name the complexes. (02 marks)
- (b) State what would be observed when;
- (i) Chromium(III) ions are treated with excess concentrated ammonia solution. (1 ½ marks)
- (ii) Cobalt(II) ions are treated with excess concentrated hydrochloric acid. (01 mark)
- (c) Write equation(s) for the reaction(s) that take(s) place in (b)(i) (02 marks)

27. State what would be observed and write equation for the reaction that would take place when;

(a) Carbon dioxide is bubbled through a solution of potassium manganate(VI) (2 ½ marks)

(b) Dilute sulphuric acid is added to aqueous solution of potassium manganate(VI) (03 marks)

(c) Concentrated hydrochloric acid is added drop wise until excess to aqueous copper(II) sulphate solution. (2 ½ marks)

(d) Ethyne is bubbled through ammoniacal copper(I) chloride solution (02 marks)

(e) Hydrogen peroxide is added to acidified potassium manganate (VII) solution. (02 marks)

(f) Aqueous ammonia is added to iron(II) sulphate solution drop wise until in excess and the solution left to stand in air for some time. (03 marks)

(g) A spatula endful of sodium hydrogencarbonate is added to iron(III) chloride solution. (2 ½ marks)

28. (a) Define the term ore. (01 mark)

(b) Name the **chief ores** for the following metals

(i) Aluminium

(ii) Copper

(iii) Iron

(iv) Zinc (02 marks)

(c) State the role of the following processes in extraction of metals.

(i) Froth flotation (03 marks)

(ii) roasting

(iii) Smelting

29. (a) What is a catalyst? (01 mark)

(b) Differentiate between a positive catalyst and a negative catalyst. (02 marks)

(c) State four general properties of a positive catalyst. (02 marks)

(d) State the difference between a homogeneous and a heterogeneous catalyst. (02 marks)

30. (a) Explain why transition elements commonly act as catalysts. (02 marks)

(b) In each case write equation for the reaction catalysed by each of the following substances.

(i) vanadium(V) oxide (1 ½ marks)

(ii) finely divided iron (1 ½ marks)

- (iii) iron(III) chloride (1 ½ marks)
- (c) Explain the action of a positive catalyst. (2 ½ marks)
31. Explain each of the following observations. Illustrate your answers with equations where necessary.
- (a) Iron(III) chloride and Tin(II) chloride cannot exist together in solution. (2 ½ marks)
- (b) The aqueous solutions of chromium(III) and chromium(II) ions are coloured whereas that of copper(I) is not. (03 marks)
- (c) Manganese, iron, cobalt and nickel form ions in the +2 oxidation state whose size decreases from manganese to nickel (02 marks)
- (d) When sodium carbonate solution was added to a solution of chromium(III) sulphate, bubbles of a colourless gas and a green precipitate were observed. (03 marks)
- (e) When potassium methanoate solution is added to copper(II) sulphate solution, a blue precipitate is formed. (03 marks)
- (f) When iron is heated with sulphur, the product is iron(II) sulphide but when chlorine gas is passed over heated iron, the product is iron(III) chloride. (1 ½ marks)

**Long answer type questions.**

32. In the chemistry of d-block and their compounds, respect is given to the properties mentioned below. Discuss each property briefly, with examples and exceptionalities involved. (20 marks)
- Variable oxidation states
  - Coloured compounds
  - Formation of interstitial compounds
  - Catalytic behaviour
  - Paramagnetism
  - Complex ion formation
33. (a) (i) Write the electronic configuration of chromium. (Atomic number 24) (½ mark)
- (ii) State the oxidation states of chromium. (01 mark)
- (b) Explain why chromium has a high melting point. (01 mark)
- (c) Describe the reaction of chromium with;
- water (02 marks)
  - sulphuric acid (04 marks)

- (d) Explain the reactions that take place when the following solutions are added to an aqueous solution of potassium chromium(III) sulphate.
- (i) sodium hydrogencarbonate (4 ½ marks)
- (ii) sodium hydroxide until in excess (04 marks)
- (e) Hydrogen peroxide was added to the solution formed in c(ii) above.
- (i) State what was observed. (½ mark)
- (ii) Write the equation for the reaction that took place. (1 ½ marks)
- 34.(a) Chromium is a transition element with atomic number 24.
- (i) Define a transition element. (01 mark)
- (ii) Write the electronic configuration of chromium. (01 mark)
- (b) (i) What do you understand by the term paramagnetism? (01 mark)
- (ii) Explain why chromium(III) ion has a higher paramagnetic moment than copper(II) ion. (02 marks)
- (c) Describe the reactions of chromium with;
- (i) air (02 marks)
- (ii) water (02 marks)
- (iii) Sulphuric acid (3 ½ marks)
- (iv) Nitric acid (02 marks)
- (d) Write ionic equation for the reaction between sodium hydroxide and;
- (i) chromium (1 ½ marks)
- (ii) chromium(III) oxide (1 ½ marks)
- (e) Potassium carbonate was added to a solution of chromium(III) chloride. State and explain what was observed. (3 ½ marks)
35. Magnetite is one of the ores from which iron can be extracted.
- (a) Describe how iron is extracted from magnetite. (09 marks)
- (b) Describe the reaction of iron with;
- (i) water (03 marks)
- (ii) chlorine (03 marks)
- (iii) Sulphuric acid (05 marks)
- 36.(a) (i) What is meant by the term an ore? (01 mark)
- (ii) Write the formula and name of one ore from which copper is extracted. (01 mark)
- (b) Describe how;
- (i) The ore in a(ii) can be concentrated. (03 marks)
- (ii) Pure copper can be obtained from the concentrated ore. (6 ½ marks)
- (c) Discuss the reactions of copper with;
- (i) Hydrochloric acid

- (ii) Sulphuric acid (06 marks)
- (d) A few drops of potassium hexacyanoferrate(II) solution was added to copper(II) sulphate solution;
- (i) State what was observed. (01 mark)
- (ii) Write the equation for the reaction. (1 ½ marks)
- 37.(a)(i) What is meant by a transition element? (01 mark)
- (ii) Write the electronic configurations of  $Cu$ ,  $Fe^{2+}$ , and  $Mn^{2+}$  (03 marks)
- (iii) Explain why iron(II) ions are readily oxidised to iron(III) ions but manganese(II) ions are not readily oxidised to manganese(III) ions. (02 marks)
- (b) 0.005 moles of a compound  $[Co(NH_3)_x]^{3+}3Cl^-$  was heated with excess alkali and ammonia liberated absorbed in  $50\text{ cm}^3$  of 0.5M sulphuric acid. After complete absorption of ammonia, the excess acid required  $20.0\text{ cm}^3$  of 1M sodium hydroxide for complete neutralisation. Calculate the value of  $x$ . (04 marks)
- (c) Z is a purple solid which dissolves in water to give a solution that turns green on warming. When sodium hydroxide solution is added to a solution of Z, a green precipitate Y is formed soluble in excess of the alkali to form a green alkaline solution. On adding hydrogen peroxide to the alkaline solution, the green solution turned yellow. On adding more hydrogen peroxide and acidifying with dilute sulphuric acid, a blue solution is formed but later turns green with evolution of oxygen on standing. The solution of Z gives a white precipitate with barium chloride which is soluble in dilute hydrochloric acid.
- (i) Identify X, Y and Z.
- (ii) Explain the reactions that took place. (07 marks)
38. Zinc is a d-block element.
- (a) (i) Write the electronic configuration of zinc ( $Zn=30$ ) (01 mark)
- (ii) State the common oxidation state of zinc (01 mark)
- (b) Briefly explain why zinc is not a transition metal (02 marks)
- (c) (i) List down three chemical properties of zinc or its compounds that are not shared with group IIA metals. (03 marks)
- (ii) List down three chemical properties of zinc or its compounds that are similar to those of magnesium. (03 marks)
- (d) With the aid of equations, describe the reactions of zinc with;
- (i) sodium hydroxide. (03 marks)



## ABOUT THE AUTHOR

Joseph Jobs Kayiira is a graduate of BSCED (Hons), Uganda Martyrs University who majored in chemistry but also teaches Mathematics.

He went to Masaka SS for both 'O' and 'A' Levels

He has facilitated various schools in Entebbe, Wakiso and Kampala. Currently, he heads the Chemistry Department at Bulu Parents S.S and also teaches at Makerere College School and other Schools.

## SPECIAL FEATURES OF THIS BOOK

- Variety of examples (options) are given where required to choose the samples to one's understanding
- Content about qualitative analysis incorporated
- Miscellaneous topical short answer and long answer type questions at the end of each topic
- Fully compatible with the 2013 NCDC chemistry A'Level syllabus

## CONTACTS

Tel: +256 753 247 098 | +256 782 601 038

Email: josephkayirab@gmail.com



joseph jobs kayiira



joskabmtwit



Joseph Jobs Kayiira Chemistry Channel