

# STRAIGHTFORWARD REVIEW CHEMISTRY

## FAMILIAR FLAT CHEMISTRY

### REVIEWED NOTES

Still have glitches or weedy in the subject?  
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Objective

helping you understand Fundamental  
Principles of the subject,

RUBANGAKENE Js FELIX Jr GEOFREY.

100% LUO ACHOLIBOY

**IN THE NAME OF GOD MOST GRACIOUS & MERCIFUL,**

## ***PERSEVERANCE:***

I pledge this book to my **foster parent Rev.Fr.Francis Ocaya** the late (RIP), Atanga Christ the king, Gulu Archdiocese for continued love, moral, financial, & spiritual assistance rendered to me since childhood and throughout my life to-date.

There are those special people in this world who give & give without taking who offer without asking for much in return, I dedicate this book to the best of them.

***MAY THE ALMIGHTY FATHER REWARD ALL OF YOU  
ABUNDANTLY.***

## ***ACKNOWLEDGEMENTS:***

I am grateful to my parents for whatever they have rendered to me. And I am also so grateful to my special and beloved wife **Tutor Bridget Baseke**.

Work of this nation is by no means a single person's effort. It has been a result of many kind and helpful people who have willingly assisted me whenever approached.

I am also glad to my prodigious teachers, **Mr. Otto Stephen, Mr.Obala Peter, Okello Charles Waliky & Mr.Kilama Stephen** of Sir Samuel Baker School, who awkward to take me thought the impenetrable maze of science to make me appreciate it to the point of producing work of this nature.

I am also particularly grateful to **senior Chemist Mr. Otto Stephen** for the tireless efforts, advice & guidance he accorded to me during the writing of this book so as to reach this customary.

Am grateful to him for keeping everything going while I am off in my academic pursuance and university.

More so I am grateful for his sharp tabloid eye.

I can't forget to move a show of hands of cheers to my colleagues, **Dr.Oyo Benedict & Dr.Bongomin Felix** of Gulu University, **Mr. Keith Obot** &

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**Mr.Onen Tony** of St. Mary's College Kisubi, **Mr.Wokorach Godfrey** of St. Joseph's College Layibi for the support and advice they rendered to me when I was carrying out research on the subject.  
To my prior apprentices of **Lira Integrated Senior Secondary School**, Principally **Adopo Julius** was my greatest instigators.

## PREAMBLE:

In this era of scientific advancement, Chemistry becomes unavoidable.

This book is intended for use in secondary especially advanced level. It will facilitate both the teachers and the students to focus intensively on each practical.  
It contains detailed scientific approaches, experiments, explanations and illustrations.

Revision questions and Answers are provided topic by topic meanwhile UNEB sample questions are also provided.

These questions are intended to form the basics of interactions between teachers and students or student discussion groups.

To emphasize this, the simplified language and approach used in this book aims at making chemistry as a subject easy to **understand, straight forward, attractive friendly to students**.

This book has been developed in line with the most recent developments of Uganda national curriculum center teaching syllabus and UNEB syllabus. It is therefore of great pro to all secondary schools most especially those which may not be able to afford a wide range of text books for use by their teachers, students & the discussion groups.

The trial queries are intended to enhance group dialogue for students, reference questions are for exams & seminars.

We hope that the student who follows the layout of this paperback will in the end have got enough familiarity in enabling a wide range of questions in exams.

The students will be fully prepared to both **mock** and **UNEB examinations**. We have a **vision** as most students will turn as scientists to meet the ever increased demand for science graduate in various technical castigation of medicine, agriculture & forestry.

# REVISION GUIDE TO INORGANIC CHEMISTRY.

- ☛ **BONDING AND STRUCTURES.**
- ☛ **DIAGONAL RELATIONSHIP.**
- ☛ **PERIODIC PROPERTIES.**
  - ✓ **IONISATION ENERGY.**
  - ✓ **ELECTRON AFFINITY.**
  - ✓ **ELECTRONEGATIVITY.**
  - ✓ **ATOMIC RADIUS.**
  - ✓ **MELTING POINT.**
  - ✓ **BOILING POINT.**
- ☛ **GROUP (II) ELEMENTS.**
- ☛ **GROUP (IV) ELEMENTS.**
- ☛ **GROUP (VII) ELEMENTS.**
- ☛ **PERIOD (III) ELEMENTS.**
- ☛ **PERIOD (IV) ELEMENTS [Transition metals].**
- ☛ **EXTRACTION OF METALS.**
  - ✓ **IRON.**
  - ✓ **COPPER.**
  - ✓ **SODIUM.**
  - ✓ **CHLORINE.**
  - ✓ **ALUMINIUM.**
  - ✓ **SODIUM HYDROXIDE.**
- ☛ **OXIDATION STATES & REDOX REACTIONS.**

Please make sure that you revise effectively so that you have conducive environment or atmosphere in the examination room.

FAQS ON INORGANIC CHEMISTRY YEARLY:

BY  
BA

TR.JS FELIX RUBANGAKENE JR.GEOFREY.  
TRJS FELIX RUBANGAKENE JR.GEOFREY

## **INTRODUCTION:**

**Inorganic chemistry** is the study of chemical substances other than carbon compounds (Hydrocarbons) and their derivatives.

**Inorganic chemistry** gives a relative factual information concerning modes of preparation, manufacture, properties and uses of other inorganic chemicals.

### **Golden tips:**

The study of inorganic chemistry explains the specific characteristics, similarities, differences and trend in observation.

### **Periodic Table**

The original form of the periodic table was first put forward by **Mendeleev** in 1869 when he arranged the known elements in the order of their relative atomic masses.

The elements fall into 8 vertical groups numbered from I-VIII and horizontal rows of elements are known as periods which 7 are numbered 1-7.

Those periods containing 8 elements are known as short periods and the others as long periods

The elements in any one vertical group have similar chemical and physical properties  
Therefore the properties of elements are periodic function of their atomic number *which is Periodic table.*

**Periodic table:** is a list of all the elements, in order of increasing atomic number, giving their names and symbols.

### **Importance points to notes in a periodic table:**

- ✓ When arranged in this order, the elements show periodicity: elements with similar properties appear at regular intervals. So the list is set out with these similar elements together, in the numbered columns.
- ✓ The columns are called groups, and numbered 0 to 7. Note where group 0 is.
- ✓ The rows are called periods. They too are numbered 0 to 7.
- ✓ The heavy zigzag line above separates metals from non-metals, with the non-metals to the right.

### **Golden tips on the groups:**

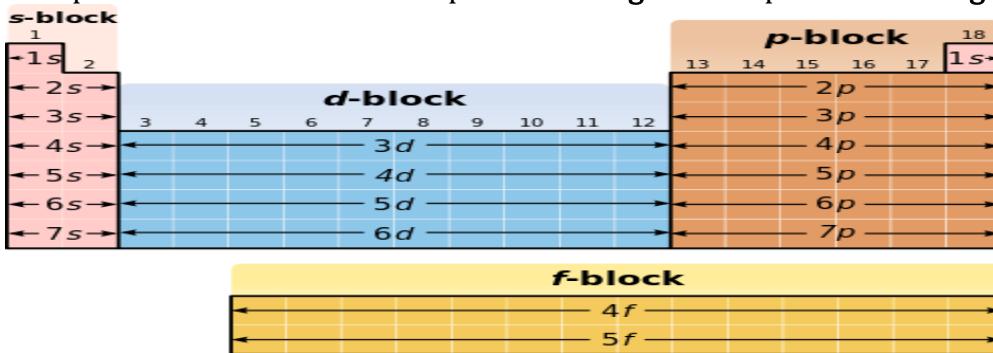
- ✓ The group number tells you how many electrons there are in the outer shell of the atoms. The atoms of Group 1 elements have one outer shell electron. The atoms of Group 2 elements have two, and so on.
- ✓ The outer-shell electrons are also called valency electrons. And their number dictates how the elements behave.
- ✓ So all the elements in a group have similar properties.
- ✓ The atoms of the Group 0 elements have **full outer shells**. This makes them unreactive, hence periodic table's elements are sub divided in to four groups namely:
- ✓ **s-block elements, p-block elements, d-block elements & f-block elements.**

# Periodic Table of the Elements

## **1. Define what is meant by the following terms?**

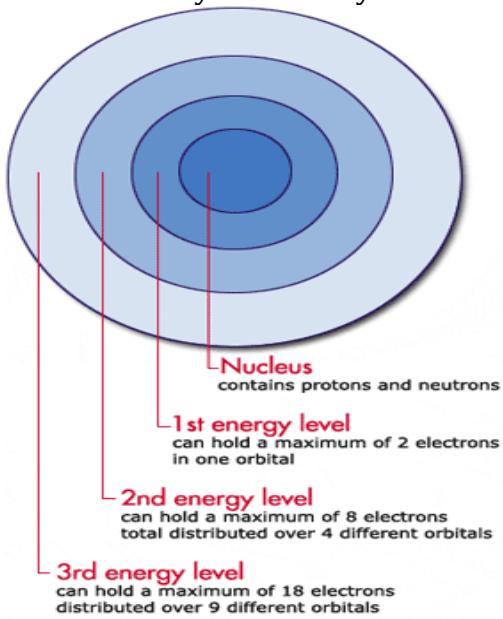
- ✓ **s-Block elements:** these are elements which have got their outer most electrons in s-sub energy level; they are mostly elements in Group 1, Group 2 & only Helium in Group 0.i.e elements with atomic no 1 to 88.
  - ✓ **p-Block elements:** these are elements which have got their outer most electrons in p-sub energy level; they are mostly elements starting from Group 3 to the rest of the remaining elements in Group 0.i.e elements with atomic no 5 to 118.
  - ✓ **d-Block elements:** these are elements which have got their outer most electrons in d-sub energy level; they are mostly all the transitional metal elements i.e elements with atomic no 21 to 111.
  - ✓ **f-Block elements:** these are elements which have got their outer most electrons in f-sub energy level; they are mostly called inner transitional metal elements, why? Because they have 3d orbital partially filled energy levels. Their properties are determined by electrons in the three outer most sub energy level i.e. s, p, d & f.they are also called Lanthanides and Actinides.
  - ✓ Some of the groups have special names:

Group 1 - the alkali metals Group 7 – the halogens Group 0 – the noble gases.



Row

2. Describes how the electrons of an atom are arranged (distributed) in the energy levels, sub shells and orbitals.  
Electrons lie outside the nucleus and occupy energy levels. The number of energy levels an atom should have depends on the number of electrons present in the atom. Energy levels are numbered as they move away from the nucleus.



Within each energy level, there are sub energy levels or sub shells designated as s, p, d & f, which differ in energy.

In a given energy level there is only one s-sub energy level and the energy of s-sub energy level is greater than the any other sub energy levels of p, d & f; why?

**Because:**

- ✓ The s-sub energy level is closer to the nucleus than the other sub energy levels hence strongly attracted by the nucleus, leading to high energy.
- ✓ The s-sub energy level screens the other sub energy levels of p, d & f from the nucleus attraction hence they have less energy.
- ✗ The s-sub shell has 1 orbital and takes up 2 electrons.
- ✗ The p-sub shell has 3 orbitals and takes up 6 electrons.
- ✗ The d-sub shell has 5 orbitals and takes up 10 electrons.
- ✗ The f-sub shell has 7 orbitals and takes up 14 electrons.

#### Golden tips:

- ✓ The 1<sup>st</sup> energy level n = 1 has 1 sub shell given as 1s
- ✓ The 2<sup>nd</sup> energy level n = 2 has 2 sub shells given as 2s,2p
- ✓ The 3<sup>rd</sup> energy level n = 3 have 3 sub shells given as 3s,3p,3d
- ✓ The 4<sup>th</sup> energy level n = 4 have 4 sub shells given as 4s,4p,4d,4f
- ✓ The 5<sup>th</sup> energy level n = 5 and beyond have 4-subshells.

#### Golden tips:

- ✗ An orbital can accommodate a maximum of two electrons with opposite spins ie.
- ✗ Electron 1<sup>st</sup> occupies each orbital singly 1<sup>st</sup> with parallel spins before pairing starts.
- ✗ Half-filled orbital's are thermodynamically **VERY** stable.i.e p<sup>3</sup>, d<sup>5</sup> & f<sup>7</sup>.

### **ELECTRONIC CONFIGURATION:**

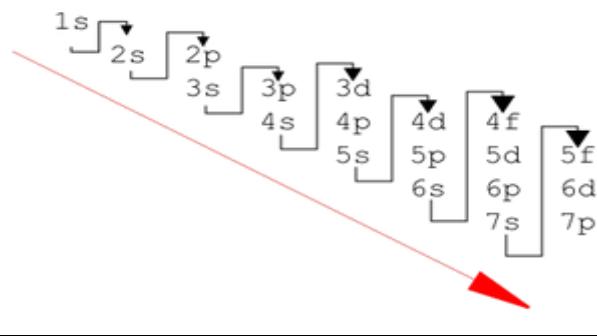
Electron configuration of atoms and ions.

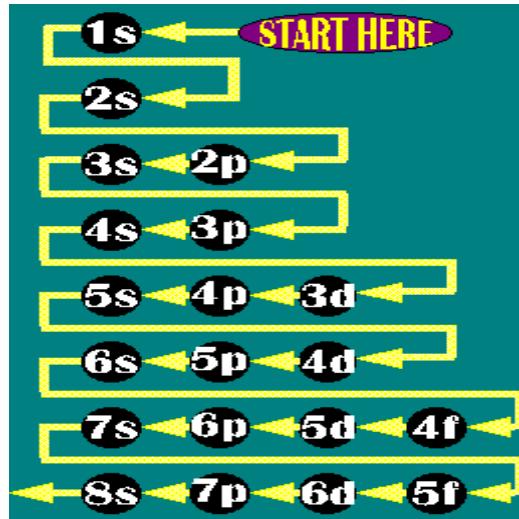
Electron configuration describes the distribution of electrons among different orbitals (including shells and subshells) within atoms and molecules.

#### **Introduction:**

There are four principle orbitals (s, p, d, and f) which are filled according to the energy level and valence electrons of the element. All four orbitals can hold different number of electrons.

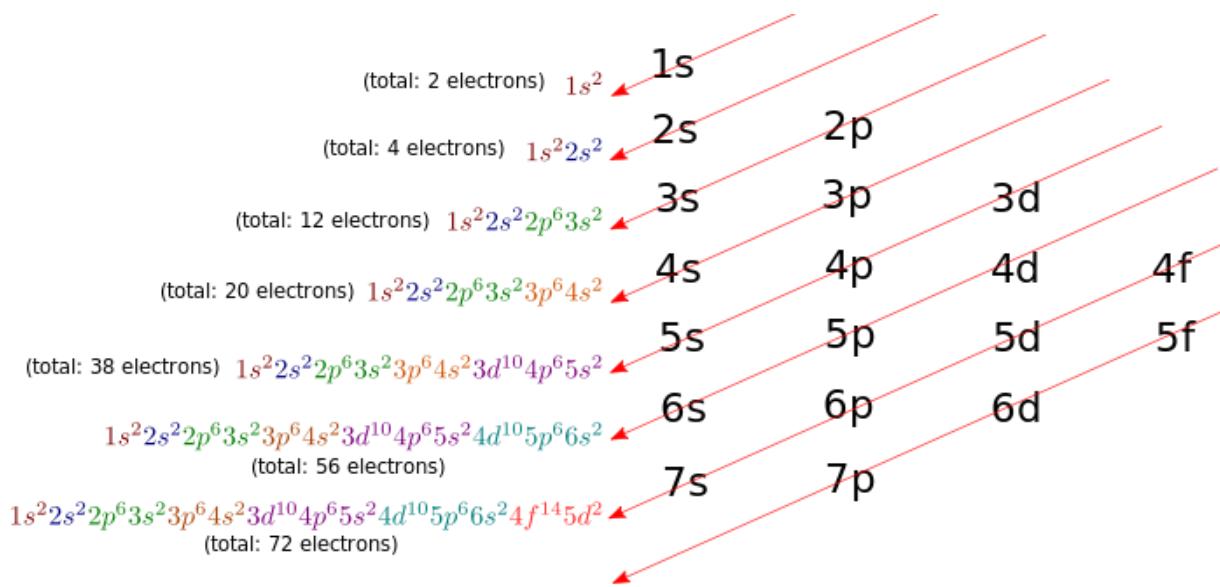
The s-orbital can hold 2 electrons, and the other three orbitals can hold up to 6, 10, and 14 electrons, respectively. The s-orbital primarily denotes group (I) or group (II) elements, the p-orbital denotes group 13, 14, 15, 16, 17, or 18 elements, and f-orbital denotes Lanthanides and Actinides group.





The order of increasing energy of the orbitals is then read off by following these arrows, starting at the top of the first line and then proceeding on to the second, third, fourth lines, and so on. This diagram predicts the following order of increasing energy for atomic orbitals.

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p \dots$$



The  $4f^t$  principal quantum number  $m_s$  (electron spin quantum number) has the valence of  $+\frac{1}{2}, -\frac{1}{2}$  which are the two possible values of  $m_s$ . meaning that there are two electrons spinning in opposite directions in an orbital. i.e an orbital is occupied by two electrons. Therefore:

s-sub energy level is filled by 2 electrons.  
p-sub energy level is filled by 6 electrons.

d-sub energy level is filled by 10 electrons.  
f-sub energy level is filled by 14 electrons

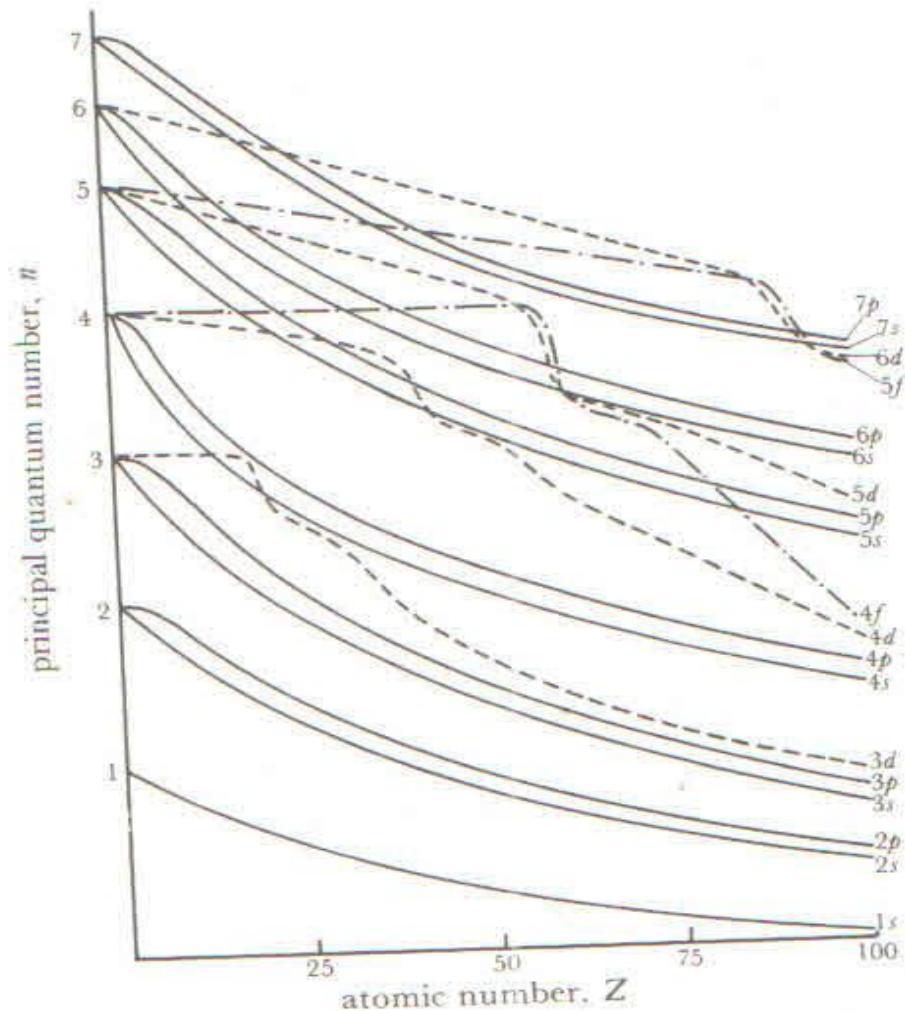


f  14 electrons

d  10 electrons

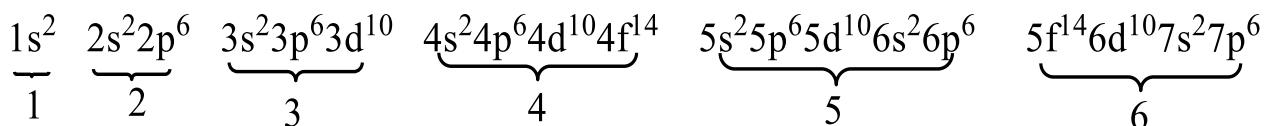
p  6 electrons

s  2 electrons



## Attentions please Boys & Women:

But because of overlapping then, the abnormal filling of the orbital is as shown below which is not right:



## The right order is below

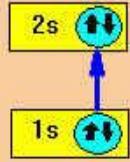
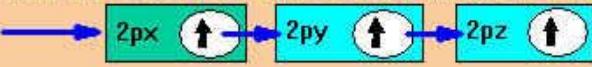
1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p

3. What are the meaning of the followings s< p < d < f?
  - ✓ s stands for sharp
  - ✓ p stands for principal
  - ✓ d stands for diffuse
  - ✓ f stands for fundamental
4. State and explain the principle rules for filling electrons of an atom arranged in the energy levels, sub shells and orbital's in their ground states.

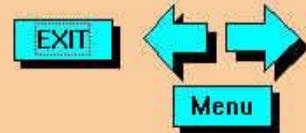
### **Electron Configuration of Hydrogen**

Energy Level → 1 Number of Electrons in This Orbital (Subshell)  
**1 S** Type of Orbital (Subshell)

## **Electron Configuration Rules:**

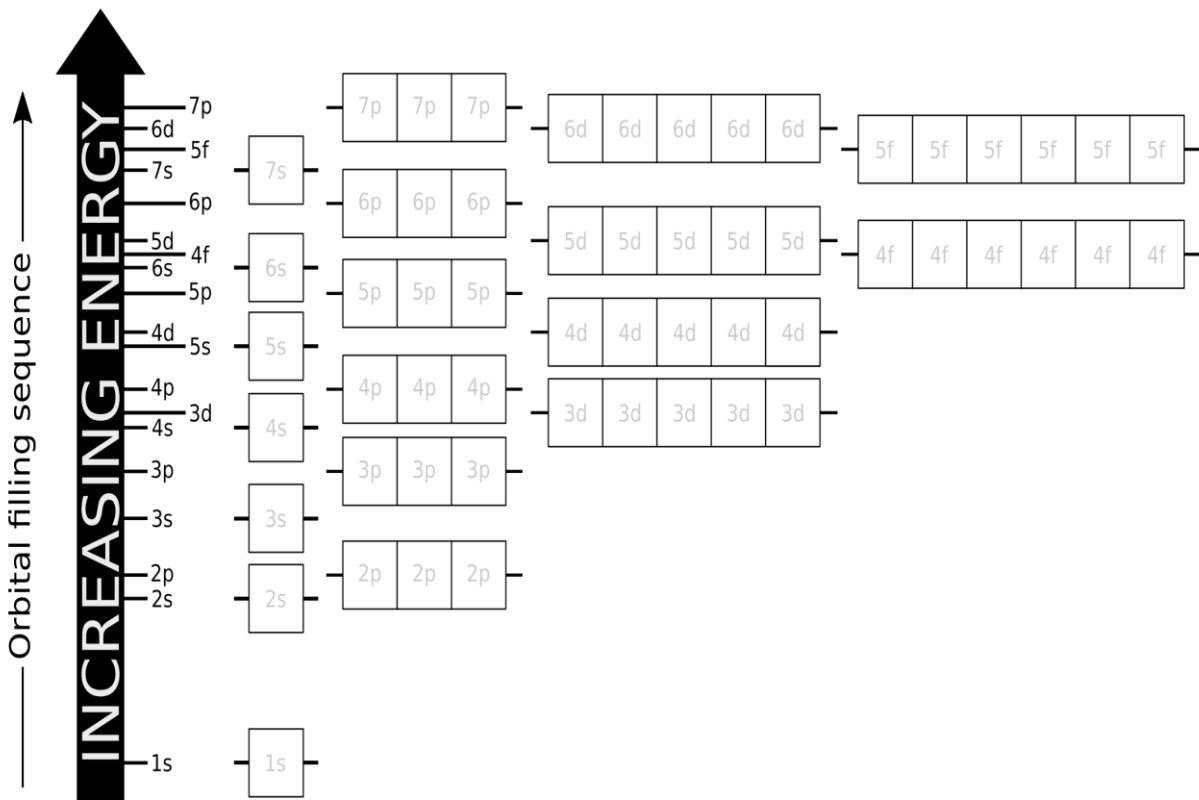
1. **Fill each subenergy level before placing an electron into a higher energy sublevel:**
  - a. **fill 1s before proceeding to 2s**
  - b. **fill 2s before proceeding to 2p**
  - c. **fill 2p before proceeding to 3s**
2. **Electrons in a subenergy level remain unpaired as long as orbitals of the same energy are available:**
  - a. **half fill 2px, 2py, 2pz before filling each orbital**
  - b. **half fill 3px, 3py, 3pz before filling each orbital**
  - c. **half fill each of the 3d orbitals before pairing 3ds**

\* Orbitals may contain either zero, one or two total electrons. However, when a second electron enters an orbital, it must have an opposite spin using the up and down arrows to indicate the spin.



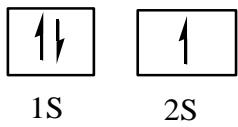
## Rules for filling electrons

Rule 1: Aufbau Principle:



The electrons in the ground state occupy orbital's in order of the orbital energy levels. The lowest energy orbital's are always filled first.

e.g. for  ${}^3Li$



Rule 2: Pauli Exclusion Principle.

## Pauli exclusion principle

- The fourth quantum number refers to the **spin of the electrons**.
- Electrons in an orbital can either be spinning in one direction or in the opposite direction.
- The **Pauli exclusion principle** states that no two electrons in the same atom can have exactly the same four quantum numbers.
- Hence each orbital can contain a maximum of only two electrons, because if they hold more, at least two of the electrons would have the same four quantum numbers.

## Many-Electron Atoms: The First Two Rules

The **quantum state** of an electron is specified by the orbital quantum numbers,  $n$ ,  $l$ , and  $m_l$ , **plus** an electron spin quantum number  $s$ . So far we have neglected this property of electrons, and we will not say any more about it at this stage except to note that  $s$  can have one of two values,  $+1/2$  or  $-1/2$ .

The **Pauli Exclusion Principle** says that no two electrons in an atom may have be in the same **quantum state**.

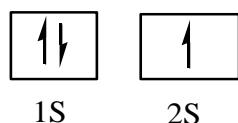
- That is, no two electrons can have the same four quantum numbers,  $n$ ,  $l$ ,  $m_l$ , and  $s$ .
- This is equivalent to saying that no orbital (specified by  $n$ ,  $l$ , and  $m_l$ ) can be occupied by more than two electrons.

The **second rule** is that electrons in atoms (and molecules) generally exist in their lowest possible energy state. This is called the **ground state**.

*This is enough to begin to handle multi-electron atoms, at least He.*

This states that an orbital cannot contain more than two electrons and then **ONLY** if they have opposite spins.

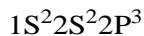
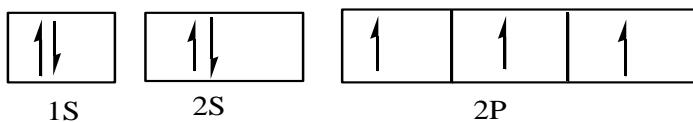
e.g.  ${}^3 Li$



### Rule 3: Hunds Rule

This states that the orbital's of a sub shell must be occupied **singly first** and with parallel spins before they can be occupied in pairs.

e.g.  ${}^7 N$



### Rule 4:

Electrons in degenerate orbital's which are singly occupied have parallel spins

The order of filling in the electrons in atoms is:

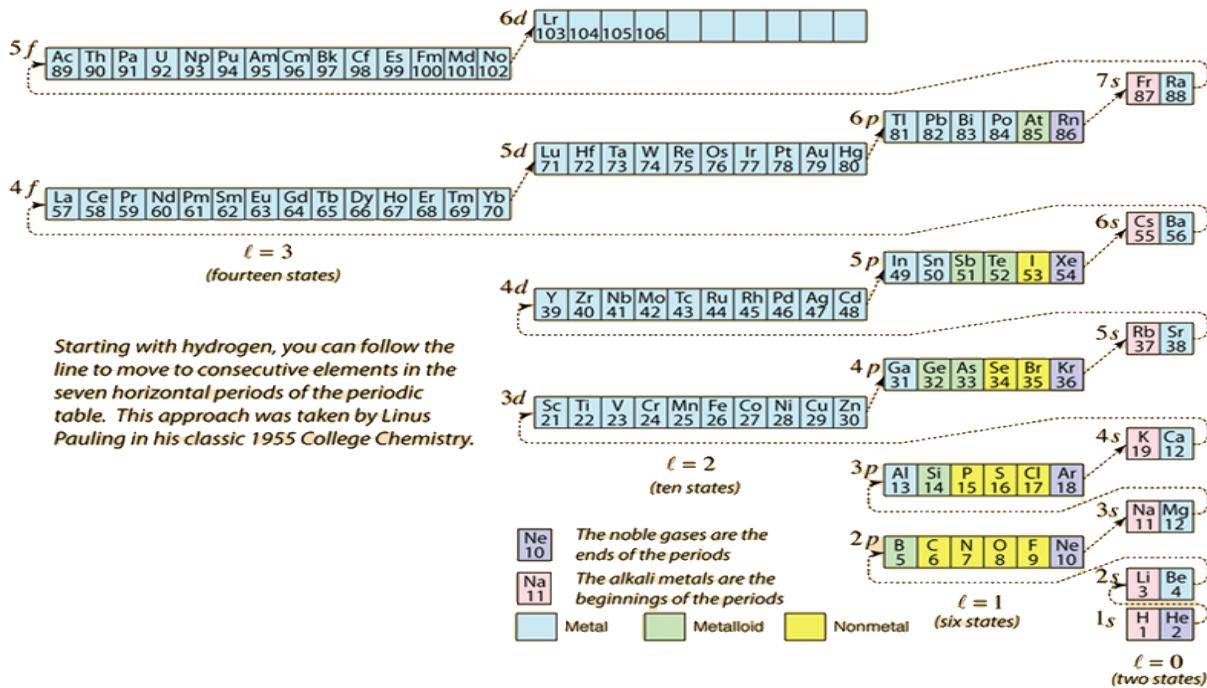
**The order of filling is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p.**

As the [periodic table](#) of the elements is built up by adding the necessary electrons to match the [atomic number](#), the electrons will take the lowest energy consistent with the [Pauli Exclusion Principle](#). The maximum population of each shell is determined by the [quantum numbers](#) and the diagram at left is one way to illustrate the order of filling of the electron energy states.

For a single electron, the energy is determined by the [principal quantum n](#) number and that quantum number is used to indicate the "[shell](#)" in which the electrons reside. For a given shell in multi-electron atoms, those electrons with lower [orbital quantum number l](#) will be lower in energy because of [greater penetration](#) of the shielding cloud of electrons in inner shells. These energy levels are specified by the principal and orbital quantum numbers using the [spectroscopic notation](#). When you reach the 4s level, the dependence upon orbital quantum number is so large that the 4s is lower than the 3d. Although there are minor exceptions, the level crossing follows the scheme indicated in the diagram, with the arrows

indicating the points at which one moves to the next shell rather than proceeding to higher orbital quantum number in the same shell.

The electron configuration for any element may be found by clicking on that element in the [periodic table](#). The first exception to the above scheme that is encountered is [chromium](#), where the fifth 3d electron state is occupied instead of the second 4s state.



## Filling of Electronic States

- Usual filling sequence:

$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^2 \ 3d^{10} \ 4p^6 \ 5s^2 \ 4d^{10} \ 5p^6 \ 6s^2 \ 4f^{14} \ 5d^{10} \ 6p^6 \ 7s^2 \ 6d^{10} \ 5f^{14}$

- consider potassium (K): the 4s shell is filled before the 3d shell because of the stronger binding of the 4s electrons

- the transition elements have electrons in the 3d or 4d sub shells respectively

- the lanthanides (rare earths) have identical  $5s^2 \ 5p^6 \ 6s^2$  configurations and differ by the number of electrons in the in the 4f shell

- the actinides have identical  $6s^2 \ 6p^6 \ 7s^2$  configurations and differ only in the 5f and 6d electrons

- for both lanthanides and actinides the chemical properties are dominated by the outer s and p electrons and thus result in very similar properties for all of them

## Hund's Rule

When filling electrons in any sub shell spins first remain unpaired in every quantum state and have parallel spin.

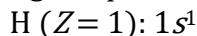
## ELECTRON CONFIGURATIONS

**The Aufbau Principle, Pauli Exclusion, Degenerate Orbitals, and Hund's Rule.**

The electron configuration of an atom describes the orbitals occupied by electrons on the atom. The basis of this prediction is a rule known as the **Aufbau principle**, which assumes that electrons are added to an atom, one at a time, starting with the lowest energy orbital, until all of the electrons have been placed in an appropriate orbital.

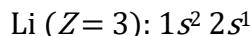
### **Examples:**

A hydrogen atom ( $Z=1$ ) has only one electron, which goes into the lowest energy orbital, the  $1s$  orbital. This is indicated by writing a superscript "1" after the symbol for the orbital.



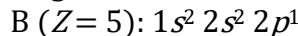
The next element has two electrons and the second electron fills the  $1s$  orbital because there are only two possible values for the spin quantum number used to distinguish between the electrons in an orbital.  $\text{He } (Z=2): 1s^2$

The third electron goes into the next orbital in the energy diagram, the  $2s$  orbital.

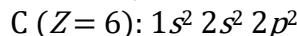


The fourth electron fills this orbital.  $\text{Be } (Z=4): 1s^2 2s^2$

After the  $1s$  and  $2s$  orbitals have been filled, the next lowest energy orbitals are the three  $2p$  orbitals. The fifth electron therefore goes into one of these orbitals.

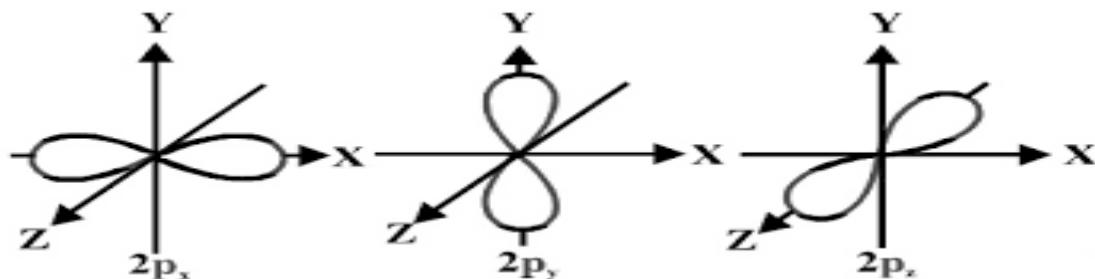


When the time comes to add a sixth electron, the electron configuration is obvious.



However, there are three orbitals in the  $2p$  sub shell. Does the second electron go into the same orbital as the first, or does it go into one of the other orbitals in this sub shell?

To answer this, we need to understand the concept of **degenerate orbitals**. By definition, orbitals are *degenerate* when they have the same energy. The energy of an orbital depends on both its size and its shape because the electron spends more of its time further from the nucleus of the atom as the orbital becomes larger or the shape becomes more complex. In an isolated atom, however, the energy of an orbital doesn't depend on the direction in which it points in space. Orbitals that differ only in their orientation in space, such as the  $2p_x$ ,  $2p_y$ , and  $2p_z$  orbitals, are therefore degenerate.



An orbital diagram uses boxes to designate individual orbitals, and a group of boxes to designate sub shells.

An arrow pointing up ( $\uparrow$ ) stands for an electron spinning in one direction, and an arrow pointing downward ( $\downarrow$ ) indicates an electron spinning in the opposite direction.

**Golden tips:**

Orbital diagram indicates the number of unpaired electrons in an atom. The presence of unpaired electrons is detected experimentally by the behavior of a substance when placed in a magnetic field. Hence two terms arises:

- ✓ Diamagnetism
- ✓ Paramagnetism

**Diamagnetism:** is the property of repulsion by a magnetic field.

**Paramagnetism:** is the property of attraction to a magnetic field.

Notes:

The atoms of **paramagnetism** substances contains unpaired electron **WHILE** those of **diamagnetism** substances contains paired electrons.

### Using:

The three stated principles that have been given the electron configurations of the ground states of most atoms can be estimated.

Electrons fill degenerate orbitals according to rules first stated by Friedrich Hund. **Hund's rules** can be summarized as follows.

- One electron is added to each of the degenerate orbitals in a sub shell before two electrons are added to any orbital in the sub shell.
- Electrons are added to a sub shell with the same value of the spin quantum number until each orbital in the sub shell has at least one electron.

### Orbital diagram:

The electronic configurations tend to hide some information about the number of electrons in any outer orbital.

	1s	2s	2p	3s	3p	4s	3d
H	1						
He	2						
Li	1	1					
Na	1	1	111111	1			
O	2	11	111111		3		
Cr	11	11	111111	11	111111	1	111111

### Examples: Z configuration spin of p electrons

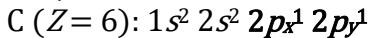
The Coulomb repulsion between electrons gives rise to Hund's rule. Electrons with the same spin in the same sub shell must have different magnetic quantum numbers  $m_l$  which has different spatial distributions minimizing the overlap and thus the Coulomb energy.

- Ferromagnetism of the 3d metals iron ( $_{26}\text{Fe}$ ), cobalt ( $_{27}\text{Co}$ ) and nickel ( $_{28}\text{Ni}$ ) is a consequence of Hund's rule.  $_{26}\text{Fe}: 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

Examples:

The 2p-sub shell consists of three 2p-orbitals ie  $2p_x$ ,  $2p_y$  and  $2p_z$ . Hence its capacity is 6 electrons. If we use an orbital diagram, a choice arises about where to place the electrons.

When the time comes to place two electrons into the  $2p$  sub shell we put one electron into each of two of these orbitals. (The choice between the  $2p_x$ ,  $2p_y$ , and  $2p_z$  orbitals is purely arbitrary.)

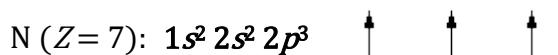


The fact that both of the electrons in the  $2p$  sub shell have the same spin quantum number can be shown by representing an electron for which  $s = +\frac{1}{2}$  with an arrow pointing up and an electron for which  $s = -\frac{1}{2}$  with an arrow pointing down.

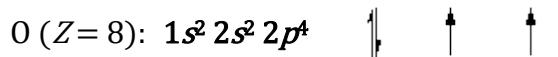
The electrons in the  $2p$  orbitals on carbon can therefore be represented as follows.



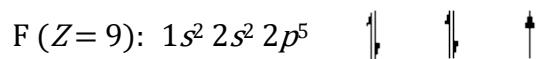
When we get to N (Z=7), we have to put one electron into each of the three degenerate  $2p$  orbitals.



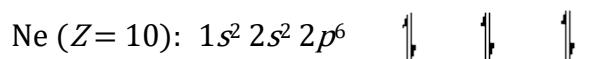
Because each orbital in this sub shell now contains one electron, the next electron added to the sub shell must have the opposite spin quantum number, thereby filling one of the  $2p$  orbitals.



The ninth electron fills a second orbital in this sub shell.



The tenth electron completes the  $2p$  sub shell.



Element	Configuration	Orbital Notation	©NCSSM 2003
H	$1s^1$	$\begin{array}{c} 1 \\ \hline \end{array}$	
He	$1s^2$	$\begin{array}{c} 1 \\ \hline \end{array} \quad \begin{array}{c} 1 \\ \hline \end{array}$	
Li	$1s^2 2s^1$	$\begin{array}{c} 1 \\ \hline \end{array} \quad \begin{array}{c} 1 \\ \hline \end{array}$	
Be	$1s^2 2s^2$	$\begin{array}{c} 1 \\ \hline \end{array} \quad \begin{array}{c} 1 \\ \hline \end{array}$	
B	$1s^2 2s^2 2p^1$	$\begin{array}{c} 1 \\ \hline \end{array} \quad \begin{array}{c} 1 \\ \hline \end{array} \quad \begin{array}{c} 1 \\ \hline \end{array}$	
C	$1s^2 2s^2 2p^2$		
N	$1s^2 2s^2 2p^3$	$\begin{array}{c} 1 \\ \hline \end{array} \quad \begin{array}{c} 1 \\ \hline \end{array} \quad \begin{array}{c} 1 \\ \hline \end{array} \quad \begin{array}{c} 1 \\ \hline \end{array}$	
O	$1s^2 2s^2 2p^4$	$\begin{array}{c} 1 \\ \hline \end{array} \quad \begin{array}{c} 1 \\ \hline \end{array} \quad \begin{array}{c} 1 \\ \hline \end{array} \quad \begin{array}{c} 1 \\ \hline \end{array}$	
Cr	$[\text{Ar}]4s^1 3d^5$	$\begin{array}{c} 1 \\ \hline \end{array} \quad \begin{array}{c} 1 \\ \hline \end{array}$	

Atom	1s	2s	2p		Electronic configuration
Li	↑↓	↑			1s <sup>2</sup> 2s <sup>1</sup>
Be	↑↓	↑↓			1s <sup>2</sup> 2s <sup>2</sup>
B	↑↓	↑↓	↑		1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>1</sup>
C	↑↓	↑↓	↑	↑	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup>
N	↑↓	↑↓	↑	↑	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>3</sup>
O	↑↓	↑↓	↑↓	↑	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>4</sup>
F	↑↓	↑↓	↑↓	↑	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup>
Ne	↑↓	↑↓	↑↓	↑↓	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup>

There is something unusually stable about atoms, such as He and Ne, which have electron configurations with filled shells of orbitals. By convention, we therefore write abbreviated electron configurations in terms of the number of electrons beyond the previous element with a filled-shell electron configuration. Electron configurations of the next two elements in the periodic table, for example, could be written as follows.



**Principal quantum number, n where  $n = 1, 2, 3, 4$  etc**

This denotes the principal quantum energy shell in which the electron in an atom is found. Within the principal quantum energy shell there are shells but the total number of electrons that can occupy any principal quantum shell is given by  $2n^2$

#### PRINCIPAL QUANTUM NUMBER:

**The Quantum Characteristics of an Electron.**

The Bohr Theory gave the four electron shells K, L, M & N the quantum number n, whereby n equals 1,2, 3& 4 respectively. These numbers represented the increasing energy levels of the shells.

However, an atomic spectrum shows that the lines representing transition metal elements between these quantized energy levels are in fact split in to finer lines. This indicates that the electron shells are split in to **sub-shells**, each with its own quantized energy level. These sub-shells have been labeled after the types of lines in the atomic spectra to which they correspond.

The atomic spectra of elements, under certain conditions can be split, spin of an electron. All electrons spin about their own axis. The spin can be either clockwise or anticlockwise. N.B. Fully filled and half-filled orbital's are regarded as thermodynamically more stable therefore the electronic configuration of Chromium ( $Z=24$ ) and Copper ( $Z=29$ ) follow this.

#### **Determination of Block of an element**

The block to which an element belongs is determined by the orbital's which are in the process of filling up. E.g.

$_{11}Na - 1S^2 2S^2 2P^6 3S^1$  Belongs to the s- block.

5. Define the following terms:

- (a) **Shell**: is a group of orbital with the same principal quantum number.
- (b) **Sub shell**: is a group of orbitals with the same principal and second quantum numbers, Examples: 1s, 2s-orbitals, 3p, 3d-orbitals.  
**Sub shell**: is a group of orbital's designated by a particular  $l$  values within a particular shell.
- (c) **Electron density**: refer to the possibility of finding the electrons in a certain region of atom.  
**Electron density (Probability density)**: is the probability that the electrons are present in a given small region of space.
- (d) **Atomic orbital**: is the volume of space in which there is 95% chance of finding the electrons.
- (e) **Orbital (Atomic orbital)**: are region in atom within which electrons have a high probability, usually 90% of being found.
- (f) **Hybridization**: is the process of mixing up orbital on a single atom in a molecule.
- (g) **Principal quantum number**: is the existence of the energy level where an electron of an atom in a given shell can be found.

**Noble gas core abbreviations::**

The electronic configurations of the Noble gas elements can be used as abbreviations when writing electron configuration.

**The Electron Configurations of the Elements (1st, 2nd, 3rd, and 4th Row Elements)**

<i>Atomic Number</i>	<i>Symbol</i>	<i>Electron Configuration</i>
1	H	$1s^1$
2	He	$1s^2 = [\text{He}] = 02$ electrons
3	Li	$[\text{He}] 2s^1$
4	Be	$[\text{He}] 2s^2$
5	B	$[\text{He}] 2s^2 2p^1$
6	C	$[\text{He}] 2s^2 2p^2$
7	N	$[\text{He}] 2s^2 2p^3$
8	O	$[\text{He}] 2s^2 2p^4$
9	F	$[\text{He}] 2s^2 2p^5$
10	Ne	$[\text{He}] 2s^2 2p^6 = [\text{Ne}] = 10$ electrons
11	Na	$[\text{Ne}] 3s^1$
12	Mg	$[\text{Ne}] 3s^2$
13	Al	$[\text{Ne}] 3s^2 3p^1$
14	Si	$[\text{Ne}] 3s^2 3p^2$
15	P	$[\text{Ne}] 3s^2 3p^3$
16	S	$[\text{Ne}] 3s^2 3p^4$
17	Cl	$[\text{Ne}] 3s^2 3p^5$
18	Ar	$[\text{Ne}] 3s^2 3p^6 = [\text{Ar}] = 18$ electrons
19	K	$[\text{Ar}] 4s^1$
20	Ca	$[\text{Ar}] 4s^2$
21	Sc	$[\text{Ar}] 4s^2 3d^1$
22	Ti	$[\text{Ar}] 4s^2 3d^2$
23	V	$[\text{Ar}] 4s^2 3d^3$
24	Cr	$[\text{Ar}] 4s^1 3d^5$
25	Mn	$[\text{Ar}] 4s^2 3d^5$
26	Fe	$[\text{Ar}] 4s^2 3d^6$
27	Co	$[\text{Ar}] 4s^2 3d^7$
28	Ni	$[\text{Ar}] 4s^2 3d^8$
29	Cu	$[\text{Ar}] 4s^1 3d^{10}$
30	Zn	$[\text{Ar}] 4s^2 3d^{10}$
31	Ga	$[\text{Ar}] 4s^2 3d^{10} 4p^1$
32	Ge	$[\text{Ar}] 4s^2 3d^{10} 4p^2$
33	As	$[\text{Ar}] 4s^2 3d^{10} 4p^3$
34	Se	$[\text{Ar}] 4s^2 3d^{10} 4p^4$
35	Br	$[\text{Ar}] 4s^2 3d^{10} 4p^5$

### ***Exceptions to Predicted Electron Configurations***

There are several patterns in the electron configurations listed in the table in the previous section. One of the most striking is the remarkable level of agreement between these configurations and the configurations we would predict. There are only two exceptions among the first 40 elements: chromium and copper.

Strict adherence to the rules of the Aufbau process would predict the following electron configurations for chromium and copper.

predicted electron configurations: Cr ( $Z=24$ ): [Ar]  $4s^2 3d^4$

Cu ( $Z=29$ ): [Ar]  $4s^2 3d^9$

The experimentally determined electron configurations for these elements are slightly different.

actual electron configurations: Cr ( $Z=24$ ): [Ar]  $4s^1 3d^5$

Cu ( $Z=29$ ): [Ar]  $4s^1 3d^{10}$

In each case, one electron has been transferred from the  $4s$  orbital to a  $3d$  orbital, even though the  $3d$  orbitals are supposed to be at a higher level than the  $4s$  orbital.

Once we get beyond atomic number 40, the difference between the energies of adjacent orbitals is small enough that it becomes much easier to transfer an electron from one orbital to another. Most of the exceptions to the electron configuration predicted from the [Aufbau diagram](#) shown earlier therefore occur among elements with atomic numbers larger than 40. Although it is tempting to focus attention on the handful of elements that have electron configurations that differ from those predicted with the Aufbau diagram, the amazing thing is that this simple diagram works for so many elements.

### ***Electron Configurations and the Periodic Table***

When electron configuration data are arranged so that we can compare elements in one of the horizontal rows of the periodic table, we find that these rows typically correspond to the filling of a shell of orbitals. The second row, for example, contains elements in which the orbitals in the  $n=2$  shell are filled.

Li ( $Z=3$ ): [He]  $2s^1$

Be ( $Z=4$ ): [He]  $2s^2$

B ( $Z=5$ ): [He]  $2s^2 2p^1$

C ( $Z=6$ ): [He]  $2s^2 2p^2$

N ( $Z=7$ ): [He]  $2s^2 2p^3$

O ( $Z=8$ ): [He]  $2s^2 2p^4$

F ( $Z=9$ ): [He]  $2s^2 2p^5$

Ne ( $Z=10$ ): [He]  $2s^2 2p^6$

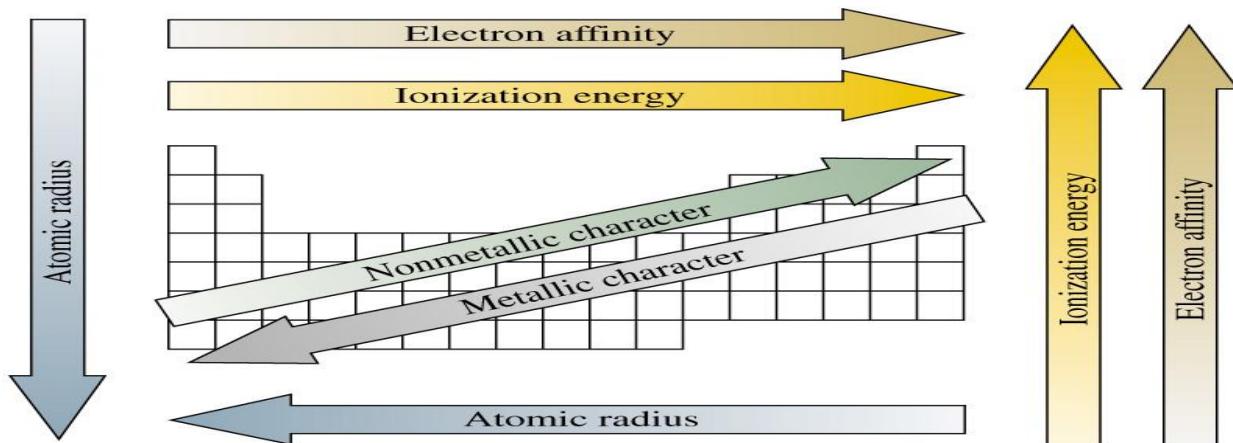
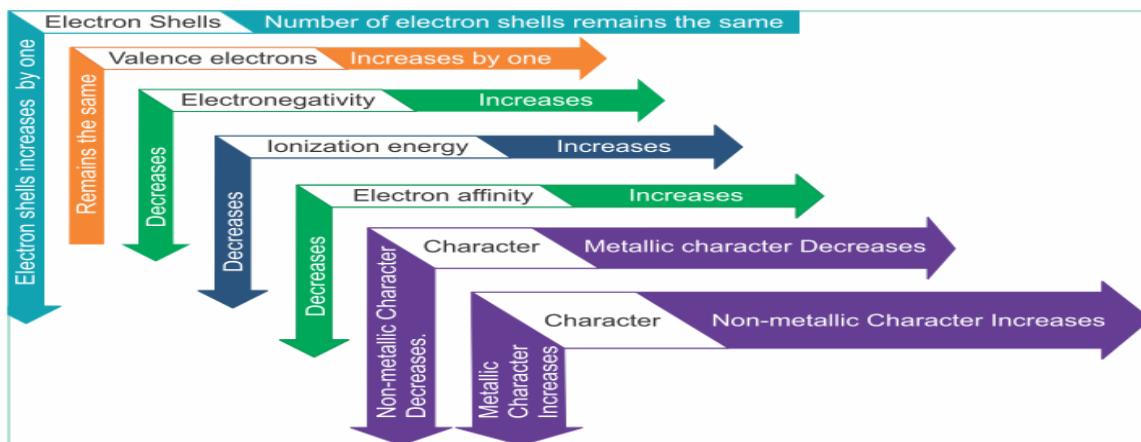
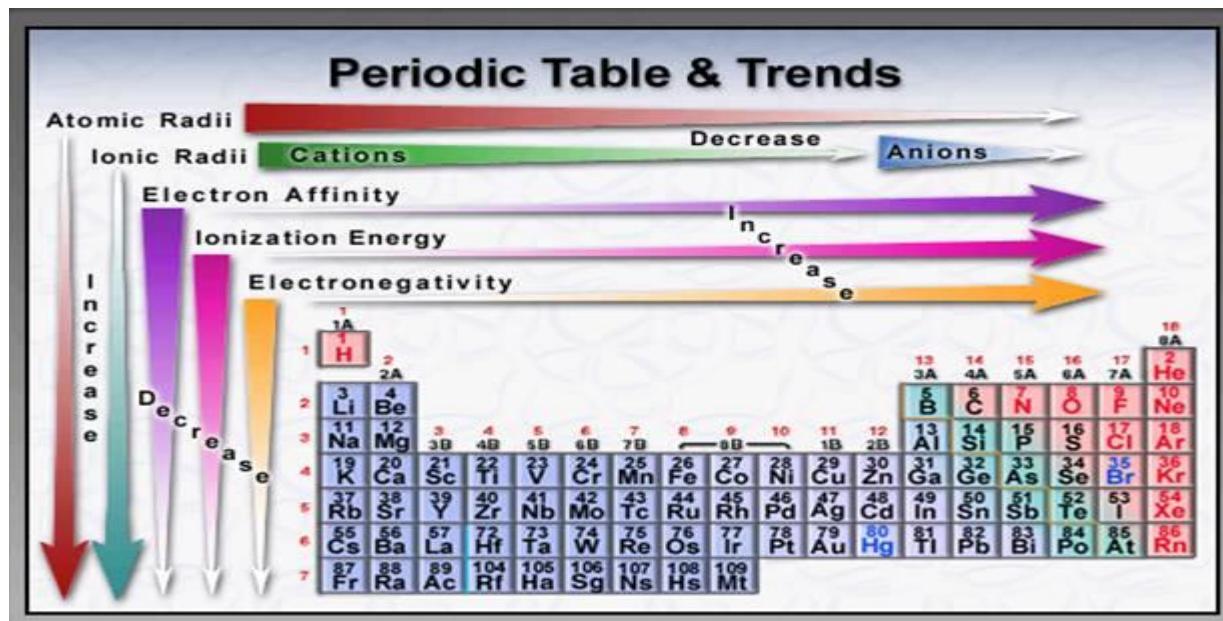
There is an obvious pattern within the vertical columns, or groups, of the periodic table as well. The elements in a group have similar configurations for their outermost electrons. This relationship can be seen by looking at the electron configurations of elements in columns on either side of the periodic table.

<i>Group IA</i>	<i>Group VIIA</i>
H	$1s^1$
Li	[He] $2s^1$ F
Na	[Ne] $3s^1$ Cl
K	[Ar] $4s^1$ Br
Rb	[Kr] $5s^1$ I
	[He] $2s^2$ $2p^5$
	[Ne] $3s^2$ $3p^5$
	[Ar] $4s^2$ $3d^{10}$ $4p^5$
	[Kr] $5s^2$ $4d^{10}$ $5p^5$

The figure below shows the relationship between the periodic table and the orbitals being filled during the Aufbau process. The two columns on the left side of the periodic table correspond to the filling of an *s* orbital. The next 10 columns include elements in which the five orbitals in a *d* sub shell are filled. The six columns on the right represent the filling of the three orbitals in a *p* sub shell. Finally, the 14 columns at the bottom of the table correspond to the filling of the seven orbitals in an *f* sub shell.

Name	Atomic Number	Electron Configuration
<b>Period 1</b>		
Hydrogen	1	$1s^1$
Helium	2	$1s^2$
<b>Period 2</b>		
Lithium	3	$1s^2 2s^1$
Beryllium	4	$1s^2 2s^2$
Boron	5	$1s^2 2s^2 2p^1$
Carbon	6	$1s^2 2s^2 2p^2$
Nitrogen	7	$1s^2 2s^2 2p^3$
Oxygen	8	$1s^2 2s^2 2p^4$
Fluorine	9	$1s^2 2s^2 2p^5$
Neon	10	$1s^2 2s^2 2p^6$
<b>Period 3</b>		
Sodium	11	$1s^2 2s^2 2p^6 3s^1$
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$
Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$
Silicon	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Phosphorus	15	$1s^2 2s^2 2p^6 3s^2 3p^3$
Sulfur	16	$1s^2 2s^2 2p^6 3s^2 3p^4$
Chlorine	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
<b>Period 4</b>		
Potassium	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Calcium	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

## GENERAL PROPERTIES OF PERIODIC TABLE:



6. State the properties of periodic table.

- ✗ Atomic radii.
- ✗ Ionization energy.
- ✗ Electron affinity.
- ✗ Electronegativity.
- ✗ Electropositivity.
- ✗ Melting and boiling points

### 1) Atomic radii

7. What is an atomic radius?

**Atomic radii:** is defined as the distance of closest approach to another identical atom.

**Atomic radii:** is the half the inter-nuclear distance between two covalently bonded atoms.

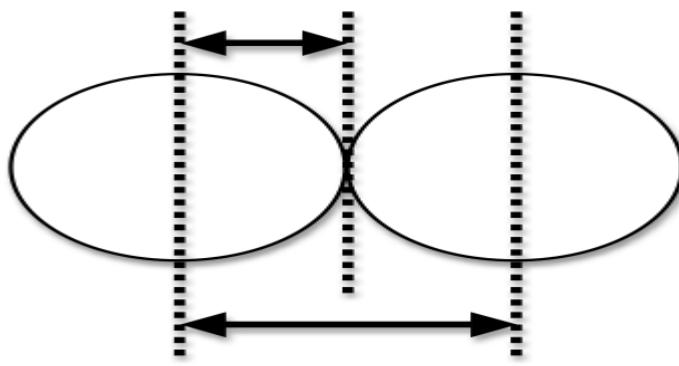
**Atomic radii:** is the distance of closest approach to another nucleus.

**Atomic radii:** is half the distance between the two nucleus in bonded atoms

**Atomic radii:** is half the inter-nuclear distance between atoms of the same element joined by singly covalent bond.

#### Illustration:

This is the metallic radius. It is  $\frac{1}{2}$  the distance between the nuclei of two atoms in a crystalline structure.



This is the distance between the nuclei of two metallic atoms.

#### Points to note:

The electron cloud of an atom has no definite limit. Because of this, the atom cannot be defined simply and easily.

By the definition of atomic radii, it means that the size of an atom is determined by the effective radius of the outer electrons.

But, what do we mean when we say the atomic radius of iodine in the solid is 0.133nm? Is it the distance between the two iodine atoms in an I<sub>2</sub> molecule or half the distance between two bonded atoms in adjacent molecules which are not chemically bonded.

#### Hence:

**Covalent radius:** is half the distance between two covalently bonded atoms.

**Van der Waal's radius:** is half the distance between two atoms which are not chemically bonded.

**Metallic radius:** is half the inter-nuclear distance between neighbouring ions in the crystalline metals.

**Notes:**

The term '**ATOMIC RADIUS**' is normally considered to be the covalent radius of non metallic atoms and the metallic radius for metallic atoms.

8. State and explain the factors affecting atomic radius.

- ✗ Nuclear charge.
- ✗ Screening effect (shielding effect).
- ✗ Effective nuclear charge.

## Trends in Atomic Size

### ◆ Influenced by three factors:

#### 1. Energy Level

- Higher energy level is further away.

#### 2. Charge on nucleus

- More charge pulls electrons in closer.

#### ◆ 3. Shielding effect    $e \leftrightarrow e$ repulsion

### Explanations:

- 1) **Nuclear charge:** is the attraction of the positively charged nucleus for the outermost electrons.

**Nuclear charge:** is the number of protons in the nucleus and it is positively charged.

**Notes:**

The nucleus exerts an attraction for the electrons that pulls the electron towards the nucleus and this tends to decrease the atomic radius of an atom.

Or:

The greater the nuclear charge, the outermost electrons are strongly attracted closer to the nucleus and hence, the smaller atomic radius.

**Notes:**

The smaller the nucleus charge, the outermost electrons are less attracted strongly closer to the nucleus and hence atomic radius will be larger.

- 2) **Effective nuclear charge.**

This is the resultant attractive force exerted by the nucleus on the outer electrons.

### *Mathematically,*

Effective nuclear charge = Nuclear charge – Screening or Shielding effect.

- 3) **Screening or (Shielding effect):** is the repulsion of the outermost electrons from the nucleus by the inner energy levels.

**Screening or shielding effect:** is the tendency of inner electrons to shield outer electrons from nuclear attraction.

**Screening or shielding effect:** is the repulsion of the outermost electron by those in the innermost shells.

**Notes:**

This reduces (decreases) the nuclear attraction for the outer electrons.

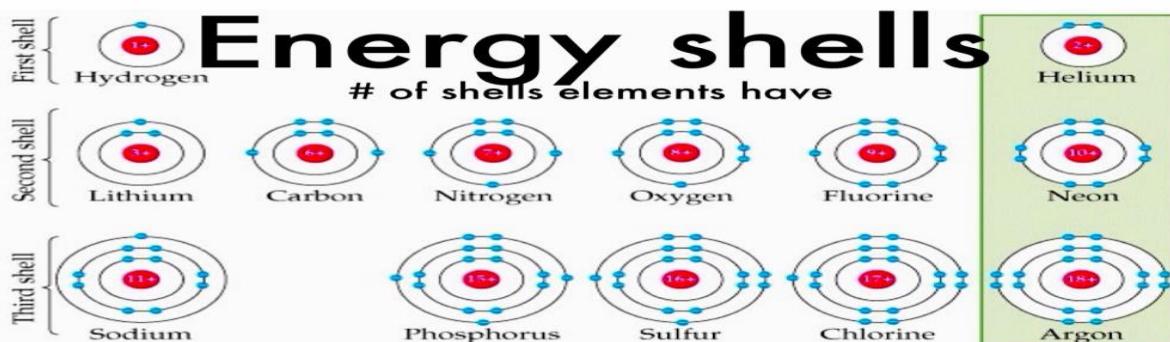
The repulsion between different energy level is great; therefore it causes a great increase in atomic radius.

Or:

The greater the shielding effect, the outermost electrons are less closely attracted and are further away from the nucleus hence greater atomic radius. The smaller the screening effect, the outermost electrons are more closely attracted by the nucleus hence smaller atomic radius.

### VARIATION OF ATOMIC RADIUS.

- Explain the variation of atomic radius.



Across the period from lithium to neon, electrons are added to the outer second shell. The charge on the nucleus is increasing from 3+ to 10+ (or 1+ to 8+ allowing the shielding of the inner shell). This tends to pull the electrons closer to the nucleus. So the size of the atom decreases across the period. On moving from neon, where the second shell is full, to sodium, the extra electron goes in to the third shell. The nuclear charge is 11+ but the shielding of the inner shells is 10 and the outer electron feels a shielded charge of 1+. Hence for two reasons we get a sudden jump in size: firstly the outer electron in sodium is one shell further out than those in neon, and secondly it feels a shielded nuclear charge of 1+ rather 8+.

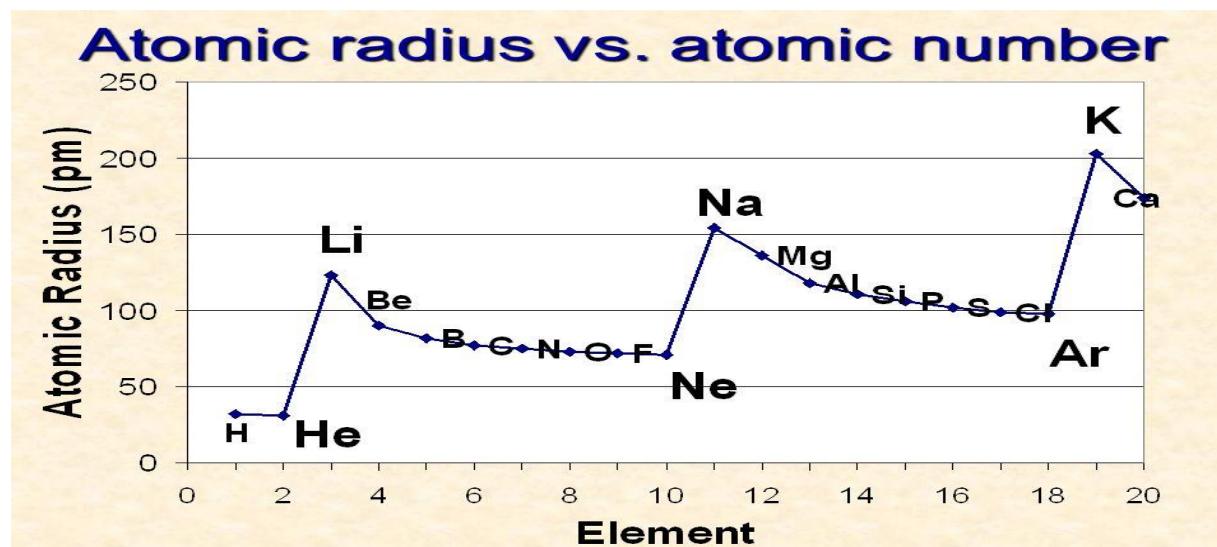
(i). Across the period.

a) Period (II) elements.

Elements	3Li	4Be	5B	6C	7N	8O	9F	10Ne
Radius(nm)	0.152	0.111	0.088	0.077	0.070	0.066	0.064	0.070

a) Period (III) elements.

Elements	11Na	12Mg	13Al	14Si	15P	16S	17Cl	18Ar
Radius(nm)	0.186	0.160	0.143	0.117	0.110	0.104	0.099	0.094



b) **Explanation.**

Atomic radius decreases across the period. This is because the nuclear charge increases due to the addition of protons to the nucleus. For every proton added, an electron is added to the same energy level and almost screening effect almost remains constant. The effective nuclear charge increases thus the electrons become more strongly attracted and closer to the nucleus.

Or:

Atomic radius decreases across the period. Across the period, the nuclear charge increases and electrons are attracted closer to the nucleus.

Across the period, electrons are being added to the same energy level making the screening effect almost constant.

The increase in nuclear outweighs that of screening effect. This leads to an increase in effective nuclear charge causing the nucleus to strongly attract the outer shell electrons, hence decrease in atomic radius.

Or:

Generally, Atomic radius reduces from left to right across each period as shown above in the diagram.

In moving from one element to the next element across each period, an electron is added to the same shell and proton added to the nucleus.

Therefore, across a period nuclear charge increases while shielding effect does not almost change so that effective nuclear charge increases such that electrons are pulled closer to the nucleus, hence the size of each atom decreases.

**The table below shows the variation of atomic radius amongst transition metals with their electronic configuration.**

Elements	Symbol	1s	Atomic radius	Electronic configurations			
				K	L	M	N
Scandium	$_{21}\text{Sc}$	1.62		$1\text{s}^2$	$2\text{s}^22\text{p}^2$	$3\text{s}^23\text{p}^63\text{d}^1$	$4\text{s}^2$
Titanium	$_{22}\text{Ti}$	1.50		$1\text{s}^2$	$2\text{s}^22\text{p}^6$	$3\text{s}^23\text{p}^63\text{d}^2$	$4\text{s}^2$
Vanadium	$_{23}\text{V}$	1.35		$1\text{s}^2$	$2\text{s}^22\text{p}^6$	$3\text{s}^23\text{p}^63\text{d}^3$	$4\text{s}^2$
Chromium	$_{24}\text{Cr}$	1.30		$1\text{s}^2$	$2\text{s}^22\text{p}^6$	$3\text{s}^23\text{p}^63\text{d}^5$	$4\text{s}^1$
Manganese	$_{25}\text{Mn}$	1.29		$1\text{s}^2$	$2\text{s}^22\text{p}^6$	$3\text{s}^23\text{p}^63\text{d}^5$	$4\text{s}^2$
Iron	$_{26}\text{Fe}$	1.29		$1\text{s}^2$	$2\text{s}22\text{p}6$	$3\text{s}^23\text{p}^63\text{d}^6$	$4\text{s}^2$
Cobalt	$_{27}\text{Co}$	1.29		$1\text{s}^2$	$2\text{s}^22\text{p}^6$	$3\text{s}^23\text{p}^63\text{d}^7$	$4\text{s}^2$
Nickel	$_{28}\text{Ni}$	1.29		$1\text{s}^2$	$2\text{s}^22\text{p}^6$	$3\text{s}^23\text{p}^63\text{d}^8$	$4\text{s}^2$
Copper	$_{29}\text{Cu}$	1.31		$1\text{s}^2$	$2\text{s}^22\text{p}^6$	$3\text{s}^23\text{p}^63\text{d}^{10}$	$4\text{s}^1$
Zinc	$_{30}\text{Zn}$	1.41		$1\text{s}^2$	$2\text{s}^22\text{p}^6$	$3\text{s}^23\text{p}^63\text{d}^{10}$	$4\text{s}^2$

'Inner building' of d sub-shell

Outer shell

## Explanation:

The metallic radius decreases from scandium to nickel and it slightly increases from nickel to Zinc.

As atomic number increases, the nuclear charge increases. However, the electrons are being added to inner 3d-subshell which poorly shields 4s electrons from the nuclear charge hence the nuclear attraction for the outermost electron increases resulting into increase in atomic radius/ metallic radius.

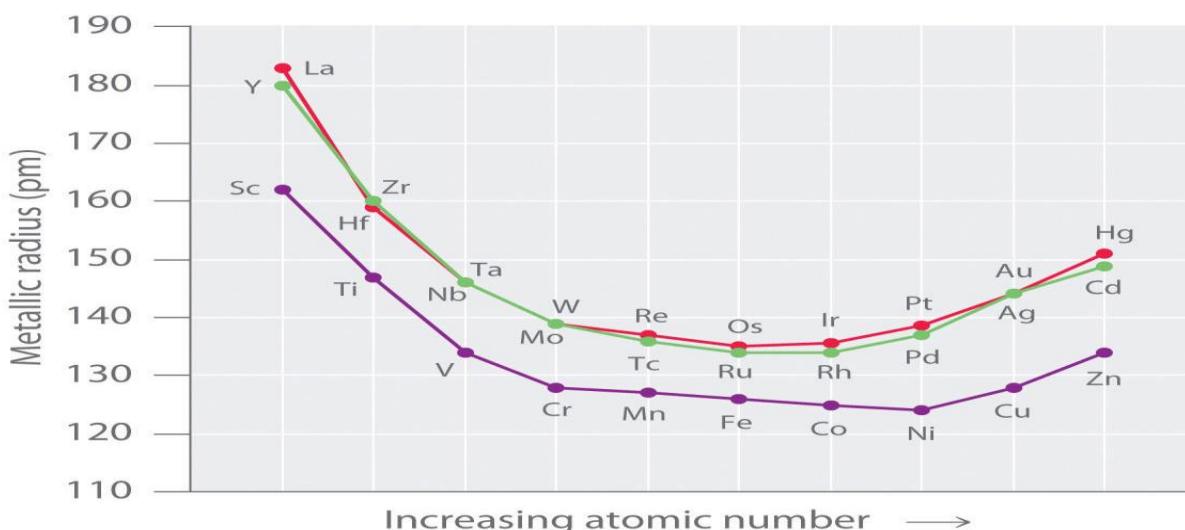
From scandium to vanadium, the 3d is occupied singly and do not screen the 4s effectively. From chromium to nickel, the atomic radius is almost constant because the 3d is being paired and this adds to the screening effect to balance the increase in nuclear charge.

The slightly increase from nickel via copper to zinc is because the 3d-subenergy levels is completely full or fully filled with electrons leading to increased shielding effect and decrease in effective nuclear charge, hence atomic radius increases.

### Notes:

The decrease in radius is coupled with increasing atomic mass causes an increase in the density and decrease in atomic volume in passing from Scandium to Nickel.

**\*Note that the  $3d^5$  and  $3d^{10}$  arrangements seem to be preferred-half full and full shells seem to have extra stability which makes it worth transferring an electron from 4s. the 3d and 4s levels are very close in energy.**



## Explanation:

- ✗ The graph shows a general slight decrease in atomic radii as atomic number increases. As the atomic number increases, the nuclear charge also increases. However, the electrons are being added to the inner 3d sub energy level. These electrons are poorly shielded from the nuclear charge. The nuclear attraction for the outer electrons therefore increases leading to a slight decrease in atomic radii.
- ✗ There is a slight increase in atomic radii from nickel to copper because the 3d sub energy level in copper is fully filled with electrons. This increases the shielding of the outer electrons from the nuclear charge hence atomic increases.

(ii).Down the group.

Group (I) elements	Atomic radius (A°)	Electron configuration
${}^3\text{Li}$	1.23	[He] $2s^1$ $1s^2, 2s^1$
${}^{11}\text{Na}$	1.57	[Ne] $3s^1$ $1s^2, 2s^2 2p^6, 3s^1$
${}^{19}\text{K}$	2.03	[Ar] $4s^1$ $1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^1$
${}^{37}\text{Rb}$	2.16	[Kr] $5s^1$ $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6, 5s^1$
${}^{55}\text{Cs}$	2.37	[Xe] $6s^1$ $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6, 5s^2 5p^6 6s^1$
${}^{87}\text{Fr}$	2.49	[Rn] $7s^1$ $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6 5d^{10}, 6s^2 6p^6 7s^1$

Generally, Atomic radius increases down the group as shown above in the table.

Explanation:

Atomic radius increases down the group, why? Because both nuclear charge and screening effect increases down the group. Down the group, new full energy levels are added. There is much repulsion between the energy levels leading to the screening effect to outweigh the nuclear charge. The effective nuclear charge decreases, hence atomic radius increases.

Or:

Atomic radius increases down the group. Both nuclear charge and screening effect increases. However the increase in screening effect outweighs the increase in nuclear charge due to addition of extra energy level of electrons thus the effective nuclear charge decreases such that the outermost electrons are less strongly attracted towards the nucleus.

Or:

Atomic radius increases down the group. Down the group, Nuclear charge increases and so it shields out (off) the inner electrons.

Because a full shell of inner electrons are added. The shielding effects outweighs increased nuclear charge hence attraction of the outer electrons by the nucleus decreases, hence increase in atomic radius.

Or:

Down the group, both nuclear charge and number of electrons are increasing.

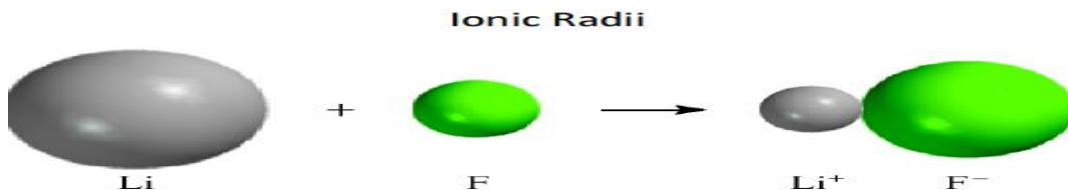
The increase in number of electrons are as a result of extra shells of electrons being added causes the increase in shielding effect which outweighs the increase in nuclear charge.

Therefore, effective nuclear charge decreases such that electrons are less attracted by the nucleus resulting in the increase of the size of atoms.

## IONIC RADIUS:

10. What is Ionic radius?

- **Ionic radius:** is the half distance between the nuclei of two adjacent ions in an ionic crystal. Its variation is in line with atomic radius.
- **Ionic radius:** is half the internuclear distance between two neighbouring monoatomic ions in a crystalline salt.



A cation is always smaller than atom from which it is formed.

An anion is always larger than atom from which it is formed.

### The sizes of ions:

- ✓ **Cations (positive)** are formed by the loss of one or more electrons from an atom. A cation is smaller than the atom from which it is formed. When electrons are lost, the nuclear charge is constant. The effective nuclear charge on the remaining few electrons increases leading to a decrease in the ionic radius of the ion formed.

### Golden tips

The figure below shows roughly to scale the sizes of the covalent radii of the atoms sodium to chlorine (even metals can form covalent bonds in the gas phase). Below these are sizes of the ions they form.

You will see that positive ions (cations) are smaller than the parent atom because:

- ✗ The whole outer shell of electrons has been lost.
- ✗ The nuclear charge can pull the remaining electrons closer to the nucleus because there is now less electron-electron repulsion.



The ions of Na<sup>+</sup> and Mg<sup>2+</sup> have the same electronic configuration, yet the ionic radius of Mg<sup>2+</sup> is smaller than Na<sup>+</sup>.

Both Na<sup>+</sup> and Mg<sup>2+</sup> have 10 electrons but different number of protons.

Mg<sup>2+</sup> ion with 12 protons attracts the 10 electrons more strongly than Na<sup>+</sup> ion with only 11 protons making Mg<sup>2+</sup> having a smaller ionic radius.

- ✓ **Anions (Negative)** are formed by addition (given) of one or more electrons to a neutral atom.

Anion is bigger than the atom from which is formed.

This is because, the nuclear charge remains constant, the effective nuclear charge decreases because the added electrons results in increased screening effect, making the ion formed bigger than the corresponding atom.

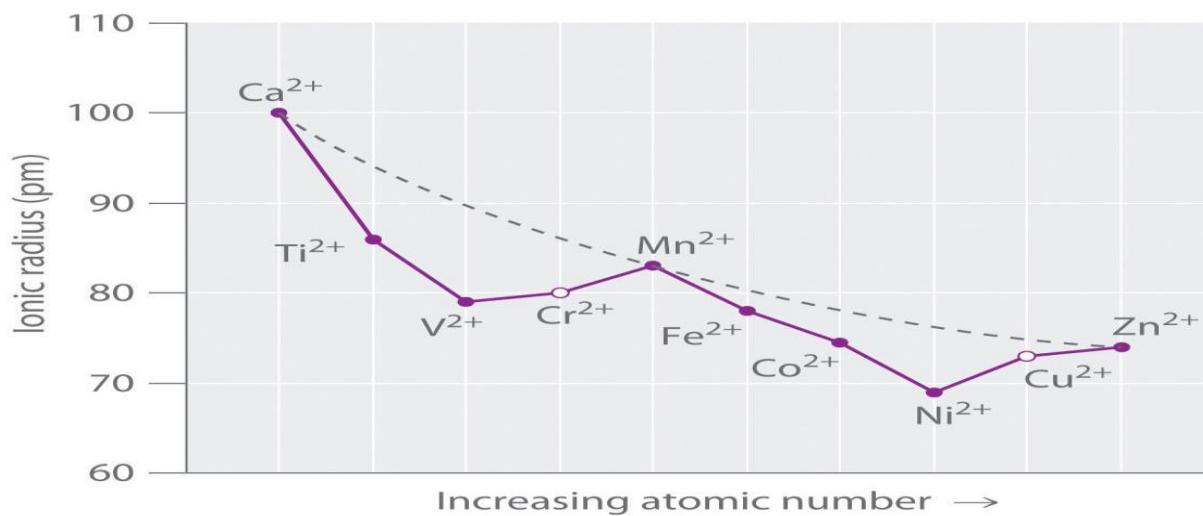
### Golden tips:

The negative ions (anions) are larger than the parent atoms as they have gained electrons, resulting in more electron-electron repulsion.

The periodicity of atomic and ionic radii is shown below. Notice that atomic radii peak at the Group (I) metals where a new shell starts, while ionic radii peak at the most negatively charged ion.

When one or more electrons are added to the outer shell of an atom forming a positive ion, there is an increase in the repulsion between negative charge clouds. Hence resulting in an overall increase in size and that is why the ionic size of  $F^-$ ,  $Cl^-$ ,  $Br^-$  &  $I^-$  are larger than their corresponding parent atoms.

Atomic size	Increases down group	F	Cl	Br	I
	Covalent radius / nm	0.064	0.099	0.111	0.128
Ionic size	Increases down group	$F^-$	$Cl^-$	$Br^-$	$I^-$
	Ionic radius / nm	0.136	0.181	0.195	0.216



## Sizes of Ions

- In an **isoelectronic series**, ions have the same number of electrons.
  - In an isoelectronic series, the most positive charge is the smallest



## **2) Ionization Energy:**

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

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

**Ionization energy:** is the amount of energy needed to remove one electron from an atom.

**Ionization energy:** is the amount of energy required to lift an electron from its ground state and detach it from its atom.

**Ionization energy:** is the minimum energy required to remove an electron from the ground state of an atom in the gas phase.

### **Equation:**

**1<sup>st</sup> ionization energy:** is the minimum amount of energy required to remove an electron from a free gaseous atom to form a unipositively charged gaseous cation.

**1<sup>st</sup> ionization energy:** is the energy required to remove one mole of electron from one mole of a free gaseous atom to produce one mole of a univalent positively charged gaseous ion.

**1<sup>st</sup> ionization energy:** is the minimum energy required to detach the most loosely held electron from a gaseous atom.

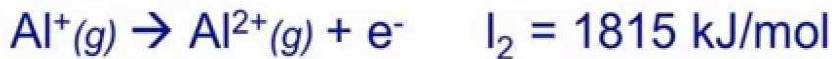
**1<sup>st</sup> ionization energy:** is the energy required to remove one mole of electrons from one mole of atoms of an element.

### **Equation:**



**2<sup>nd</sup> ionization energy:** is the energy required to remove one mole of electrons from one more singly charged positively.

### **Equation:**



### **Golden tips:**

If the electron removed is 1<sup>st</sup> to be removed from that atom, then the energy is referred to as ionization energy. If it is second electron, then it is second ionization energy and so on. Figure below shows a plot of ionization energy against number of electrons removed from a gaseous atom of magnesium.

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

The 2<sup>nd</sup> ionization energy is always higher than the 1<sup>st</sup> ionization energy and the 3<sup>rd</sup> ionization energy is higher than the 2<sup>nd</sup> I.E. This is because each succeeding electron has to be withdrawn against the attractive force of a more strongly charged positive ion.

It's then more difficult to form ions with higher positive charge.

That is why simple cations are limited to a charge of +4 and such highly charged ions are only formed by large atoms like tin and lead.

11. State and explain the factors affecting ionization energy.

- ☞ Atomic radius.
- ☞ Effective Nuclear charge.
- ☞ The net charge on the atom or ion.
- ☞ The screening effect of inner electrons.
- ☞ Electron configuration of the atom or ion.
- ☞ The penetrating power of the valence electrons.

Before we can explain these factors one by one, it is essential to understand that outermost electrons (valence electrons) are removed 1<sup>st</sup> when ionizing an atom.

## Factors Affecting Ionization Energy

1. **Nuclear charge**—the larger the nuclear charge, the greater the ionization energy.
2. **Shielding effect**—the greater the shielding effect, the less the ionization energy.
3. **Radius**—the greater the distance between the nucleus and the outer electrons of an atom, the less the ionization energy.
4. **Sublevel**—an electron from a full or half-full sublevel requires additional energy to be removed.

## IONIZATION ENERGY

- Again, when we say the **radius** is the determining factor for **ionization energy**, we are also saying that the balance between the **nuclear charge**, **electron shielding**, and the number of **energy levels** determines ionization energy.
- Because they determine radius!

### What determines IE

- ◆ **The greater the nuclear charge, the greater IE.**
- ◆ **Greater distance from nucleus decreases IE**
- ◆ **Filled and half-filled orbitals have lower energy, so achieving them is easier, lower IE.**
- ◆ **Shielding effect**

### Atomic radius.

Ionization energy increases with decrease in atomic radius because the outer shell electrons are closer to the nucleus and experience stronger nuclear attraction than atoms with bigger atomic radius, hence high ionization energy.

Or:

Atoms with small radius the electrons are strongly bound by the nuclear attraction and thus require more energy to be removed.

### Effective Nuclear charge.

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

Or;

Ionization energy increases with increase in effective nuclear charge. This is because of the increased nuclear attraction for the electrons.

### The net charge on the atom or ion.

Ionization energy increases with increase in charge on the atom or ion.

Consequently, ionization energies increases in the order of  $1^{\text{st}} < 2^{\text{nd}} < 3^{\text{rd}} < 4^{\text{th}}$  and so on.

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

Examples:

(a) The  $1^{\text{st}}$ ,  $2^{\text{nd}}$  and  $3^{\text{rd}}$  ionization energies (in KJ/Mol<sup>1</sup>) of aluminium are 577, 1816 and 2745 respectively. Explain this trend:

The ionization energies increases from the  $1^{\text{st}}$  to the  $3^{\text{rd}}$  via  $2^{\text{nd}}$ . This are because as electrons are removed, the nuclear charge remains constant. This increases the effective nuclear charge hence the outer electrons become more strongly attracted by the nucleus. Ionization energy therefore increases.

- a. The ionization energies of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  are in the order of  $\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$ . Explain this observation:

From  $\text{Na}^+$  via  $\text{Mg}^{2+}$  to  $\text{Al}^{3+}$ , nuclear charge increase (since protons are 11, 12 & 13 respectively). However, the number of electrons remains constant (all the ions have 10 electrons). Therefore the nuclear attraction for the electrons (effective nuclear charge) increases from  $\text{Na}^+$  via  $\text{Mg}^{2+}$  to  $\text{Al}^{3+}$ . This causes an increase in ionization energy in the same direction.

Or:

For a given successive ionization energies increases in the order of  $1^{\text{st}} < 2^{\text{nd}} < 3^{\text{rd}} < 4^{\text{th}}$  and so on. This is due to increased effective nuclear charge as the nuclear charge in the nucleus remains constant but the number of electrons to be attracted decreases leading to increase in the magnitude of ionization energy.

12. Successive ionization energy increases in the order of  $1^{\text{st}} \text{ I.E} < 2^{\text{nd}} \text{ I.E} < 3^{\text{rd}} \text{ I.E} < 4^{\text{th}} \text{ I.E}$  etc. Consider successive ionization energy of element T.

$1^{\text{st}} \text{ I.E}$	$2^{\text{nd}} \text{ I.E}$	$3^{\text{rd}} \text{ I.E}$	$4^{\text{th}} \text{ I.E}$
+494	+1350	+1500	+1700

Explain the trend in the variation of the ionization energies of element T.

- 1<sup>st</sup> ionization energy is low because it involves removing an electron from a neutral atom whereas the other successive ionization energy involves removing an electron from positively charged ions.
- Although the nuclear charge (number of protons) remains the same in all cases, the attraction of the nucleus for the few remaining electrons increases leading to increase in successive ionization energy.

**The screening (shielding) effect of inner electrons**

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

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

Or:

- The screening of the outer electrons by the inner electrons in an atom will facilitate the removal of electrons from the valence shell.  
Effective screening reduces the value of ionization energy as the outer electrons experience less nuclear attraction.  
Within a given shell, the screening efficiency of the inner electrons decreases in the order of [s<p<d<f].

**Electron configuration of the atom or ion.**

Electron configurations with half-filled sub energy levels or fully filled sub energy levels are relatively stable.

Example:

1<sup>st</sup> ionization energy of Nitrogen, <sub>7</sub>N:1s<sup>2</sup>, 2s<sup>2</sup>2p<sup>3</sup> is higher than that of Oxygen, <sub>8</sub>O:1s<sup>2</sup>, 2s<sup>2</sup>2p<sup>4</sup> although Oxygen has a higher nuclear charge than Nitrogen. This is because Nitrogen has a half-filled 2p<sup>3</sup> sub energy level which is more stable than partially filled 2p<sup>4</sup> sub energy level in Oxygen.

Similarly, 1<sup>st</sup> ionization energy of helium (with 2s<sup>2</sup> sub energy level is fully filled) is higher than that of lithium.

The concept of ionization energy is very essential in understanding the chemistry of elements.

**The penetrating power of the valence electrons.**

In a given shell, the penetrating power of electrons towards the nucleus decreases in the orders of [s<p<d<f], therefore the s-electrons are more penetrating and more firmly held than p-electrons and so on. Consequently in a given shell, ionization energies increase in the orders of [s<p<d<f].

- Given the ionization energies of elements A, B, C & D.

Elements	Ionization energies (KJ/Mol)		
	1 <sup>st</sup> I.E	2 <sup>nd</sup> I.E	3 <sup>rd</sup> I.E
A	730	1500	7730
B	500	4560	6900
C	580	1815	4620
D	1310	3460	5300

- Elements B & C have typical metallic character because their 1<sup>st</sup> ionization energies are below 800KJ/Mol.
- Element A shows some little metallic character.

- ☞ Element D is a typical nonmetallic element why? Because its 1<sup>st</sup> ionization energy is above 800KJ/Mol.
- ☞ Element A belongs to group 2 because there is a big rise in energy to remove the 3<sup>rd</sup> electron implying that the 3<sup>rd</sup> electron comes from a different full new energy level, its valency is 2.
- ☞ Element B belongs to group 1 why? Because there is a big rise in energy to remove the 2<sup>nd</sup> electron, implying that the 2<sup>nd</sup> electron comes from a stable energy level, hence B has single electron in its outermost shell, its valency is 1.
- ☞ Element C shows a similar rise in energy. This implies that the 3<sup>rd</sup> electrons are same shell.it has 3 electrons in the outermost shell. Its valency is 3.
- ☞ Formation of compounds formed between:
  - i. A and B =  $A^2B^1 = AB_2$
  - ii. B and C =  $B^1C^3 = B_3C$
  - iii. A and C =  $A^2C^3 = A_3C_2$
  - iv. C and D =  $C^3D^x = C_xD_3$

### VARIATION OF IONIZATION ENERGY:

14. Explain the variation of ionization energy.

❖ Across a period:

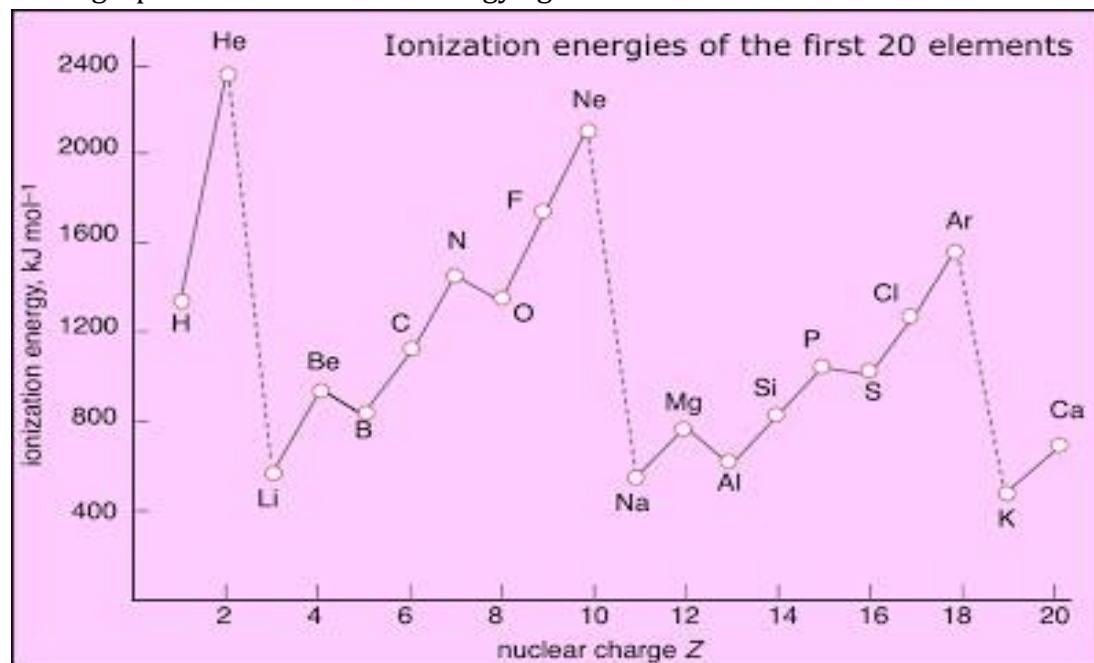
Across a period, ionization energy increases with increase in atomic number. Electrons are added to the same main energy level as nuclear charge increases. These electrons shield each other poorly from the increasing nuclear charge therefore atomic radius decreases resulting into increase in ionization energy along the period

However, beryllium, neon and nitrogen have abnormally high ionization energy because the electrons are removed from 2s<sup>2</sup>, 2p<sup>6</sup> and 2p<sup>3</sup> which are fully filled and half-filled respectively and are regarded as thermodynamically stable.

15. The table below shows the elements in period 3 of the periodic table.

Element,Z	11Na	12Mg	13Al	14Si	15P	16S	17Cl	18Ar
1 <sup>st</sup> I.E	502	745	587	791	1020	1000	1260	1530
Element,Z	3Li	3Be	5B	6C	7N	8O	9F	10Ne
I.E(KJmol <sup>-1</sup> )	520	899	801	1086	1403	1310	1681	2080

(a) Plot a graph of first ionization energy against atomic number.



(b) Explain the shape of your graph in (a).

P.T.E

## Explaining the Graph

### 1. The maximum values are for the noble gases.

Reason: Their atoms are very stable because of their electronic configuration [full outer (sub) level], so it is difficult to remove an electron.

### 2. The minimum values are for the group one metals (alkali metals).

Reason: Their atoms have only one electron in their outer level, so it is easily removed (as when this is lost it will have noble gas configuration.) This is why group one are so reactive.

### 3. In general, ionisation energies increase in moving across a period from the alkali metal to the next noble gas.

Reason: 1. Increase in nuclear charge.  
(greater pull for electrons)  
2. Decrease in atomic radius.

### 4. Ionisation energies gradually decrease in moving down a group.

Reason: 1. Increase in atomic radius.  
2. Screening effect.  
(This is where the inner shell or shells of electrons help to shield the outer electrons from the positive charge in the nucleus.)

Unit 7, 94

- There is a general increase in 1<sup>st</sup> ionization energy from sodium to argon as atomic numbers increases with abnormal behavior shown by magnesium and phosphorous.
- Across the period, atomic radius decreases, the nuclear charge increases and the electrons are attracted closer to the nucleus, electrons are being added to the same energy level, they screens each other poorly (screening within the same energy level is secondary) from the increasing nuclear charge. Therefore there is an increase in effectively nuclear charge from sodium to argon and atomic radius reduces. Hence increase in 1<sup>st</sup> ionization energy along the series.
- For magnesium, the 3s sub energy level is full ( $1s^2, 2s^2 2p^6, 3s^2$ ) and it is thermodynamically stable which require more energy to electrons.
- For phosphorous, the 3p sub energy level is half filled ( $1s^2, 2s^2 2p^3$ ) and has a special stability, hence require higher energy to remove the electrons.
- Also aluminium and sulphur has lower 1<sup>st</sup> ionization energy than expected why?
- Aluminium ( $1s^2, 2s^2 2p^6, 3s^2 3p^1$ ), the fully filled 3s<sup>2</sup> has a stable electronic configuration and shields the 3p<sup>1</sup> electron hence lower 1<sup>st</sup> ionization energy.
- Also sulphur ( $1s^2, 2s^2 2p^6, 3s^2 3p^4$ ), the half-filled 3p<sup>4</sup> sub energy level has stable configuration and relatively good shield hence lower 1<sup>st</sup> ionization energy.

16. Explain why beryllium atom has higher 1<sup>st</sup> ionization energy than boron?

- ☞ The electron structure of beryllium is:  $1s^2, 2s^2$ .
- ☞ Write out the structure of boron in the same notation.
- ☞ The electron structure of boron is:  $1s^2, 2s^2 2p^1$ .
- ☞ Which of the two elements, ie beryllium and boron has more stable electron structure?

### Explanation:

- ☞ All the sub shells in beryllium are filled but the outer sub shell of boron contains only 1 electron.
- ☞ We all know that filled electron shells are associated with extra stability.

- ☞ There is also some extra stability associated with filled sub shells.
- ☞ This means that the electron structure in beryllium is rather more stable than we might have expected and its 1<sup>st</sup> ionization energy is greater than that of boron.

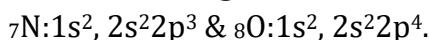
17. Explain why the 1<sup>st</sup> ionization energy of aluminium is less than that of magnesium?

- ☞ This is due to their electronic configurations:  
 $_{13}\text{Al}:1\text{s}^2, 2\text{s}^22\text{p}^6, 3\text{s}^23\text{p}^1$  &  $_{12}\text{Mg}: 1\text{s}^2, 2\text{s}^22\text{p}^6, 3\text{s}^2$ .
- ☞ The 1<sup>st</sup> ionization energy of aluminium is lower than that of magnesium is because it involves removing an electron from partly filled 3p-sub energy level which is shielded by a full 3s-sub energy level.
- ☞ The 1<sup>st</sup> ionization energy of magnesium is high because it involves removing an electron from a full 3s-sub energy level which is stable.

18. Explain why 1<sup>st</sup> ionization energy of nitrogen is higher than that of oxygen?

- ☞ Special explanation for abnormality between nitrogen and oxygen atoms.

### Electron configuration:



- ☞ The half-filled 2p-sub shell in nitrogen atom with one electron in each of the 3 boxes of 2p-orbitals are evenly or uniformly distributed hence charge is more stable than the 2p-sub shell in oxygen atom which contains four electrons resulting in a higher 1<sup>st</sup> ionization energy for nitrogen atom than oxygen atom.

### ❖ Down the group:

Elements	Be	Mg	Ca	Sr	Ba
1 <sup>st</sup> Ionization energy(KJ/Mol)	900	738	590	549	502

#### Explanation:

- Ionization energy decreases down the group. Both nuclear charge and screening effect increase down the group. Due to extra energy level of electrons being added, the increase in screening effect exceeds the increase in nuclear charge. Effective nuclear charge decreases such that the outer most electrons become less strongly attracted hence less energy is required.

Or:

- On descending a group, both nuclear charge and screening effect increases but the increase in shielding effect is as a result of an extra shell of electrons added that outweighs that of the nuclear charge.
- Therefore, effective nuclear charge decreases so that electrons are less strongly held down the group and is easy to remove hence decrease in ionization energy.

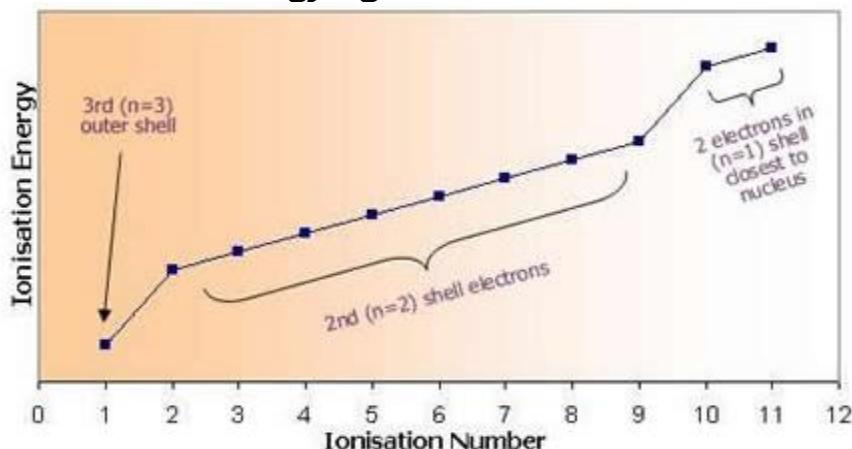
## IMPORTANCE OF IONIZATION ENERGY IN THE DETERMINATION OF THE CHEMISTRY OF AN ELEMENT:

Ionization energy provides the following information about the chemistry of an element i.e. atomic number, valency, group number, period, number of energy levels, metallic and non-metallic characters.

The values of ionization energy can be used to deduce:

- ❖ Atomic number of an element. The number of successive ionization energy indicates the number of electrons present. *E.g. Mg has 12 successive ionization energies.*
- ❖ Arrangement of electrons and distribution of energy levels
- ❖ Metallic character. *Elements which easily lose electrons have low values of ionization energy and are electropositive. The 1<sup>st</sup> ionization energy is usually below 800KJmol<sup>-1</sup>.*

### Graph of ionization energy against number of electrons removed



It should be noted that;

- ❖ The graph shows that there are two electrons in the outermost shell which are easily lost in the  $3s^2$  sub energy level with low energy. Therefore the electron in energy level [ $n = 3$  or ( $3^{rd}$ )] is the outermost shell.
- ❖ The third ionization energy is much greater than the 1<sup>st</sup> 2 electrons because the 3<sup>rd</sup> electron is being removed from a full new inner energy level (shell) which is very stable i.e.  $[2s^22p^6]$ .
- ❖ There is a gradual rise (increase) in ionization energy from the 3<sup>rd</sup> to 10<sup>th</sup> ionization energy because the ion has acquired stability after the removal of the 1st two electrons hence requiring high energy to remove the electrons.
- ❖ The 11th ionization energy is far much higher than the 10th ionization energy. In this case, the electron is being removed from a stable  $1s^2$  energy level is being very close to the nucleus with two electrons.

### 3) Electronegativity

**Electronegativity** is the tendency of an atom to become negatively charged in its covalent compounds.

**Electronegativity** is the relative attraction of an atom for the electrons of a covalent bond formed with an atom of another element.

**Electronegativity** is the tendency of an atom in a molecule to attract bonding electrons to itself in a covalent bond.

#### **Golden tips:**

Most nonmetals are electronegativity because they gain electrons to form negative ions.

Consider hydrogen chloride molecules, (HCl) Chlorine atom being more electronegativity than hydrogen in (H-Cl), it attracts the bonding electrons to itself, causing the chlorine atom to acquire a partial negative charge (-ve) and hydrogen acquire a partial positive charge (+ve).

## Electronegativity

**Definition:** A measure of the ability of an atom in a chemical compound to attract electrons

- Electronegativity tends to increase across a period
  - As radius decreases, electrons get closer to the bonding atom's nucleus
- Electronegativity tends to decrease down a group or remain the same
  - As radius increases, electrons are farther from the bonding atom's nucleus

### Factors affecting electro negativity:

19. State and explain the factors affecting electro negativity.

- ↗ Effective nuclear charge.
- ↗ Atomic radius (covalent radius).
- ↗ Screening effect of the inner electrons.

#### Explanation:

##### Effective nuclear charge.

Electronegativity value increases with increase in effective nuclear charge.  
For a low nuclear charge, the bonding electrons experience a low nuclear attraction leading to a low electronegativity value.  
For a high nuclear charge, the bonding electrons experience a high nuclear attraction leading to a high electronegativity value.

##### Atomic radius (covalent radius).

Electronegativity value increases with a decrease in atomic radius.  
For a small atomic radius, the bonding electrons are nearer to the nucleus hence they experience a greater attraction.  
For a large atomic radius, the bonding electrons are far away from the nucleus hence they experience less attraction.

##### Screening (shielding) effect of inner electrons.

For low screening effect the bonding electrons have high nuclear attraction leading to high electronegativity values.  
The greater the screening effects the less attracted are the bonding electrons hence lower values of electronegativity.  
Or:  
Electronegativity values increases with decrease in shielding effect.  
A low screening effect implies that the bonding electrons are less effectively shielded from the nuclear charge hence experience higher nuclear attraction.

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

### Trend in electronegativity:

#### \* Across the period:

##### Explanation:

Across the period, electronegativity increases because the atoms become smaller and the effective nuclear charge increases therefore the electron attractive power increases.

Or:

Across the period, the nuclear charge increases while the screening effect is almost constant. The effective nuclear charge increases for the electrons leading to increase in electronegativity value.

Or:

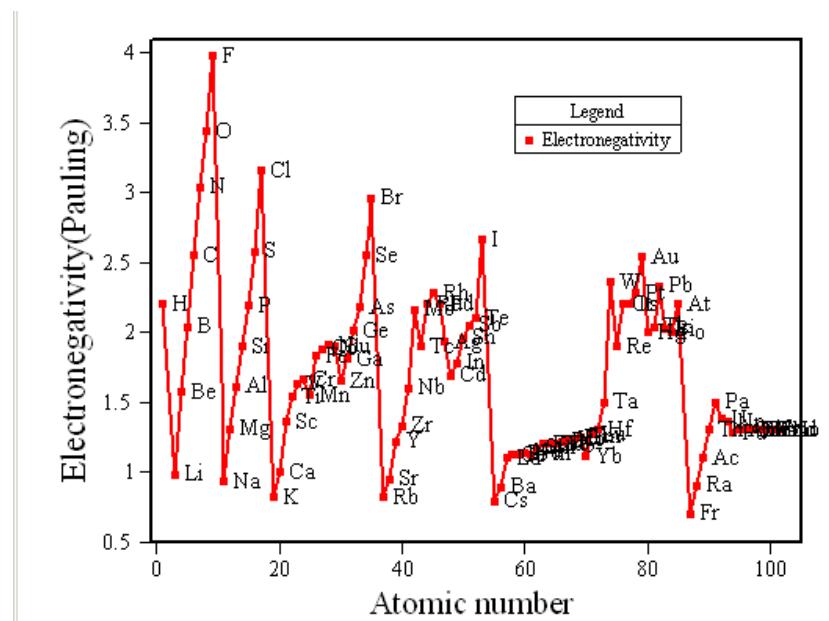
In moving from left to right across a period, from one element to the next, the nuclear charge increases by almost one unit and an electron is added to the outer shell. As the nuclear charge increases across, the atoms have an increasing electron attracting power and therefore an increase in electronegativity values.

##### Period 2:

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

##### Period 3:

Elements	Na	Mg	Si	P	S	Cl
electronegativity	0.9	1.2	1.8	2.1	2.5	3.0



#### \* Down the group:

Elements	F	Cl	Br	I
Electronegativity	4.0	3.0	2.8	2.5

##### Explanation:

Down the group, electronegativity values decreases due to increasing atomic radius and decrease in effective nuclear charge since an extra shell of electrons are added by 1 unit therefore an increase in shielding effect outweighs that of the nuclear charge.

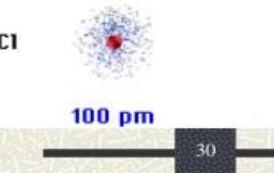
Or:

Electronegativity values decreases down the group. This is because down the group, new energy levels are being formed which increases the screening effect. The effective nuclear charge decreases hence leading to a decrease in nucleus to attract electrons.

#### 4). ELECTRON AFFINITY (EA.)

## Electron Affinity

- # Electron affinity is the amount of energy **absorbed** when an electron is added to an isolated gaseous atom to form an ion with a 1- charge.
- # Sign conventions for electron affinity.
  - If electron affinity > 0 energy is absorbed.
  - If electron affinity < 0 energy is released.
- # Electron affinity is a measure of an atom's ability to form negative ions.
- # Symbolically:
$$\text{atom(g)} + \text{e}^- + \text{EA} \rightarrow \text{ion}^-(\text{g})$$



### Electron Affinity

**Definition - the energy change associated with the addition of an electron**

- Affinity tends to increase across a period
- Affinity tends to decrease as you go down in a period

Electrons farther from the nucleus experience less nuclear attraction

Some irregularities due to repulsive forces in the relatively small p orbitals



1. What is electron affinity?

- ↗ This is the energy released when an electron is gained by one mole of an isolated neutral gaseous atom to form a uninegative gaseous ion.
- ↗ This is energy change that occurs when one mole of electron (s) combine with one mole of gaseous atom to form one mole of gaseous negatively charged ions.
- ↗ This is the energy change that occurs when one mole of electron (s) is/are added to one mole of gaseous atoms to form one mole of negative gaseous ions.
- ↗ This is enthalpy which occurs when one mole of electrons combine with one mole of gaseous atoms to form one mole of gaseous anions.

**Golden tip:**

- ✓ The 1<sup>st</sup> electron affinity is exothermic (negative) because an electron is being added to a neutral atom even for highly electropositive elements the more exothermic the E.A, the easier an atom gains electron hence the more stable the ion is.
- ✓ The 2<sup>nd</sup> electron affinity is endothermic (positive) because the negative ion produced repel further electron to be added so energy must be applied to overcome the repulsive force.
- ✓ The 2<sup>nd</sup> E.A is accompanied by absorption of energy i.e. endothermic. This is because the incoming electron experiences greater repulsion from both outermost electron and the negative ion. In addition, the increased radius of the ion decreases the nuclear attraction for the incoming electron.

2. State and explain the factors affecting electron affinity?

a) Atomic radius.

Electron affinity increases with decrease in atomic radius. Atoms with small atomic radius have high effective nuclear charge, hence the nucleus have strong nuclear attraction for the incoming electrons.

Atoms with larger atomic radius have low effective nuclear charge, hence the nucleus have low nuclear attraction for the incoming electrons therefore low electron affinity value.

b) Net charge on atom.

Electron affinity increases with increase in negative charge on the ion. Why? This is because, the stronger is the repulsion on the incoming electron and the higher is the amount of energy required to add the electron.

Consequently, the magnitude of electron affinity increases in the order of 2<sup>nd</sup>< 3<sup>rd</sup><4<sup>th</sup> etc.

c) Effective nuclear charge.

Electron affinity increases with increase in effective nuclear charge, Increase in effective nuclear charge causes the nucleus to strongly attract the incoming electrons.

Or:

The greater the nuclear, the more strongly the incoming electron is attracted and the greater the electron affinity is.

The smaller the nuclear charge the less strongly electron is attracted hence lower electron affinity.



d) Screening (or shielding) effect.

Electron affinity increases with decrease in screening effect. Decrease in screening effect implies the effective nuclear charge is high; hence the incoming electron is strongly attracted by the nucleus.

Or:

Shielding (or screening) of outer electrons by inner electrons reduces the attraction of outer electrons by the nucleus.

Therefore, increase in effective nuclear charge hence decrease in electron affinity. Within a given shell, the screening efficiency of the inner electrons decreases in the order of s>p>d>f. therefore s-electrons are more screening than p-electron and so on.

Or:

The greater the screening shielding effect, the electron is less strongly attracted hence lowering electron affinity.

The smaller the screening effect, the more strongly attracted is the incoming electron hence greater electron affinity.

e) Electronic structure of an atom.

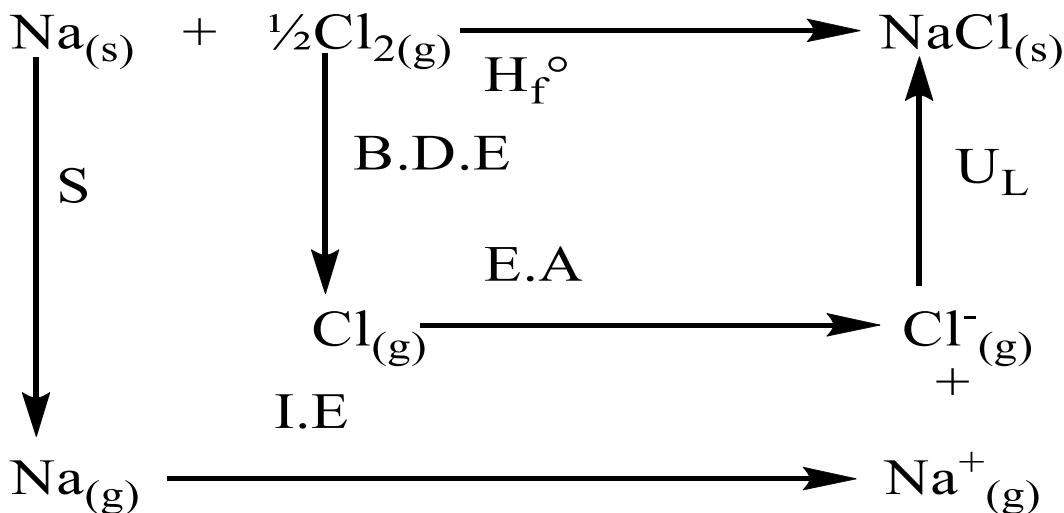
Electronic structure of an atom affects the value of electron affinity in that, atoms with filled or half-filled outer with outer electronic configuration are stable and resist addition of the electron leading

f) Penetrating power of valence electrons.

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

Consequently in a given shell, electron affinity increases in the orders of s>p>d>f. Golden tips:

- Electron affinity is estimated by an indirect method based on the Born Haber cycle. Consider the formation of sodium chloride, NaCl.



KEY:

U<sub>L</sub> = Lattice energy.

E.A = Electron affinity.

I.E = Ionization energy.

S = Sublimation energy.

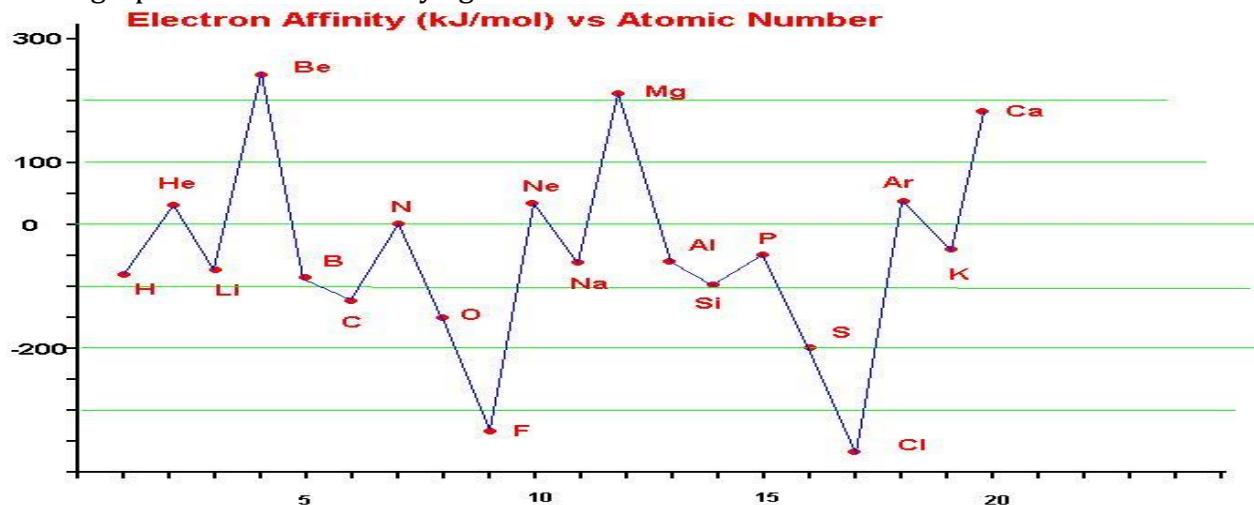
$\Delta H_f^\circ$  = Enthalpy of formation of Sodium Chloride. B.D.E = Bond dissociation energy. From Hess's law.  $\Delta H_f^\circ = S + B.D.E + E.A + I.E + U.L$ , E.A =  $\Delta H_f^\circ - S + B.D.E + I.E + U.L$

### **VARIATION OF ELECTRON AFFINITY ACROSS A PERIOD:**

3. Explain the variation of electron affinity across period 3 elements.

Elements	11Na	12Mg	13Al	14Si	15P	16S	17Cl
Electron Affinity (kJ/Mol)	-20	+67	-30	-135	-60	-200	-364

4. Plot a graph of Electron Affinity against atomic number.



5. Explain the shape of the graph.

Trend: Generally, Electron affinity increases across a period.

Explanation:

Effective nuclear charge increases across a period so that the nuclear attractions for the incoming electron increase.

However, Magnesium and Phosphorus shows abnormal values of electron affinity. This is due to decrease in atomic radius and increase in nuclear charge while screening effect remains almost constant. The effective nuclear increases leading to an increase in the nuclear attraction for the incoming electron.

Magnesium, the electron is being added to a 3s-subshell which is full and stable, therefore energy is required for the electron to be added.

Phosphorus, the value is less negative because an electron is being added to a 3p-subshell which is half filled and relatively thermodynamically stable hence energy is required to add the electron.

Or:

Effective nuclear charge increases across a period so that the nuclear attraction for the incoming electron increases.

Electron affinity of magnesium is more positive than expected because magnesium it's electron is being added to full 3s-subshell according to its electron configuration:

$^{12}\text{Mg}$ :  $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2$ , which is thermodynamically stable and resists the addition of electrons hence more energy is required or resists the addition of electron hence energy should be put in to effect it.

Similarly:

Electron affinity of phosphorous is less negative than expected because in phosphorous, the electron is being added to half full 3p-subshell which is also very stable and resists the addition of electron hence less energy is released.

$^{15}\text{P}$ :  $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^3$ .

### **Golden tips**

- ☞ There is a general increase in electron affinity with increase in atomic number. As atomic number increases, both nuclear charge and shielding effect increases. But since electrons are added to the same main energy level, increased nuclear charge outweighs that of shielding effect hence electron affinity increases.
- ☞ Elements with atomic number 12 and 15 respectively bear abnormally low electron affinity.

Why?

- ☞  $^{12}\text{Mg}$ :  $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2$                                      $^{15}\text{P}$ :  $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^3$
- ☞ The element with atomic number 12, the element has full 3s-subenergy level while element with atomic number 15, its 3p-subenergy level is half filled.
- ☞ Therefore, these two elements resists addition of an electron hence energy released is low.

### **Points to notes**

- ☞ Moving from one element to the next across a period, electrons are added to the same shell. At the same time; protons are added to the nucleus. The electrons are therefore, attracted and pulled towards the nucleus by increasing positive charges.
- ☞ So the radius of the atom decreases. However, the rate of decrease in the radius becomes smaller as more protons are added.
- ☞ The addition of one more proton example to the 11 already present in sodium in this case, causes a greater proportional increase in the attractive power of the nucleus. Than the addition of one more proton to the already 16 present in sulphur, hence the atomic radius falls by 0.026nm from sodium to magnesium but by **ONLY** 0.005nm from sulphur to chlorine.

### **VARIATION OF ELECTRON AFFINITY DOWN THE GROUP:**

Elements	F	Cl	Br	I
Electron affinity	-323	-364	-324	-295

6. Explain the variation of electron affinity down group.

Generally: Electron affinity decreases down the group.

Explanation:

Down the group, there is a decrease in effective nuclear charge and an increase in screening effect which outweighs the nuclear charge as a result of new energy level added.

This leads to decrease in the nuclear attraction for the incoming electrons leading to low energy.

Fluorine has low value of electron affinity than expected due to its small atomic radius which creates a strong repulsive force for the incoming electrons. The incoming electron has to be forced in to the outermost shell against the repulsive force hence some energy is used up reducing the energy released.

Or:

Down the group because of addition of an extra shell of electrons, the increase in screening effect outweighs that of nuclear charge so that effective nuclear charge decreases. Therefore, there is a decreasing ability to attract electrons hence decrease in electron affinity.

Or:

Down the group, Electron affinity decreases due to decrease in effective nuclear charge caused by addition of an extra energy level of electrons. The nuclear charge decreases and ability of the nucleus to attract electrons is reduced hence less energy is given out.

### **ELECTROPOSITIVITY:**

7. What is electropositivity?

☞ **Electropositivity** is the tendency of an atom to lose electron(s) to become positively charged.

Or:

☞ **Electropositivity** is the ability to lose outermost electrons to form a positively charged ion. This is basically a property of metallic elements because they have few electrons in the outermost energy level with low ionization energy.

8. State and explain the factors affecting electropositivity.

- ☞ Atomic radius: Electropositivity increases with increase in atomic radius. The bigger the atomic radius, the further away the outer electrons from the nucleus and the less the nuclear attraction the electrons experience.
- ☞ Ionization energy: Electropositivity increases with decrease in ionization energy. Decrease in ionization energy means little amount of energy required for an atom to lose electron.
- ☞ Effective nuclear charge: Electropositivity increases with decrease in nuclear charge because the outer shell electron is less attracted by the nucleus.
- ☞ Screening (shielding) effect: Electropositivity increases with increase in screening effect which reduces the effective nuclear attraction on the outer shell electrons.

## **VARIATION OF ELECTROPOSITIVITY**

9. Discuss the variation of electropositivity across the period.

Across the period, electropositivity decreases because electrons are added to the same energy level, therefore, they screen each other poorly hence nuclear charge increases and outweighs that of screening effect leading to increase in effective nuclear charge. Atomic radius decrease, Ionization energy increases, hence electropositivity increases.

10. Discuss the variation of electropositivity down the group.

Down the group, Electro positivity increases because the shielding of outer most electrons from nuclear attraction increases as more completed energy levels are added. The atomic radius increases and ionization energy decreases hence the tendency to lose electron increases hence increase in electropositivity.

Or:

Down the group, electropositivity increase because the effective nuclear increases and shielding effect also increases due to the formation of new energy levels hence the screening effect outweighs that of effective nuclear charge. Atomic radius increases, ionization energy decreases thus increase in electropositivity.

## **MELTING AND BOILING POINT**

11. What is melting point?

- ☞ **Melting point:** is a constant temperature at which pure solid is in equilibrium with the pure liquid at atmospheric pressure.
- ☞ **Melting point:** is the constant temperature at which a pure substance turns from solid to liquid state at a given pressure when the two states are at equilibrium.

12. State the factors affecting melting points of:

- a) Metals.

- ☞ Atomic radius of the metals.
- ☞ Type of crystal structure formed by the metals.
- ☞ The number of electrons each atom contribute to the electron cloud or charge of the metallic ion.

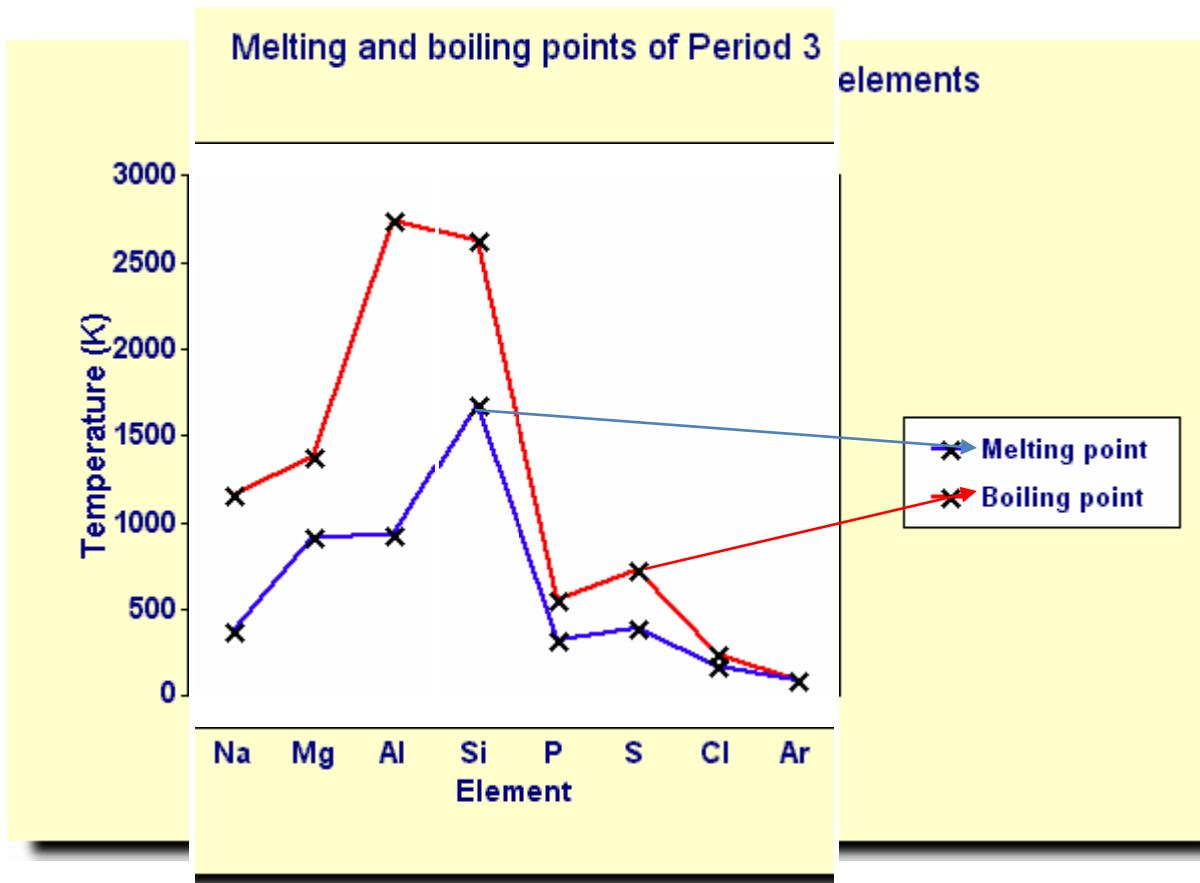
- b) Molecular substances (Non-metals)

- ☞ Molecular mass of the substance.
- ☞ Type of intermolecular forces of attraction.
- ☞ Type of close packing of the molecules in the solid.

Table of physical data:

Element	Metallic character	Proton No:	Atomic radius	Oxidation States	I.E (KJ/Mol)	Mpt(°C)	Bpt(°C)
Sodium,Na	Metal	11	1.57	+1	502	98	883
Magnesium,Mg	"	12	1.36	+2	745	639	1090
Aluminium,Al	"	13	1.28	+3	587	660	2467
Silicon,Si	Metalloid	14	1.17	+4	792	1410	2680
Phosphorus,P	Non-metal	15	1.10	+3,+5	1020	44	280
Sulphur,S	"	16	1.04	-2,+4,+6	1000	113	445
Chlorine,Cl	"	17	0.09	-1,+1,+3,+7	1260	-101	-35
Argon,Ar	"	18	-	-	1530	-184	-187

The graph is often divided into three sections to make explanations easier. Mouse over the graph, then select to learn about a section, or [go directly to the explanations](#).



## Explanation of the trends

Melting points generally increase going from sodium to silicon, then decrease going to argon (with a “bump” at sulphur)

### Melting

When a substance melts, some of the attractive forces holding the particles together are broken or loosened so that the particles can move freely around each other but are still close together. The stronger these forces are, the more energy is needed to overcome them and the higher the melting temperature.

### Boiling

When a substance boils, most of the remaining attractive forces are broken so the particles can move freely and far apart. The stronger the attractive forces are, the more energy is needed to overcome them and the higher the boiling temperature.

### Sodium, magnesium and aluminium

Sodium, magnesium and aluminium are all **metals**. They have **metallic bonding**, in which positive metal ions are attracted to delocalized electrons. Going from sodium to aluminium:

- the charge on the metal ions increases from +1 to +3 (with magnesium at +2) ...
- the number of delocalized electrons increases ...
- so the strength of the metallic bonding increases and ...
- the melting points and boiling points increase.

### Silicon

Silicon is a **metalloid** (an element with some of the properties of metals and some of the properties of non-metals). Silicon has **giant covalent bonding**. It has a giant lattice structure similar to that of [diamond](#), in which each silicon atom is covalently-bonded to four other silicon atoms in a tetrahedral arrangement. This extends in three dimensions to form a giant molecule or macromolecule.

Silicon has a very high melting point and boiling point because:

- all the silicon atoms are held together by strong covalent bonds ...
- Which need a very large amount of energy to be broken.

### Phosphorus, sulphur, chlorine and argon

These are all **non-metals**, and they exist as small, separate molecules. Phosphorus, sulphur and chlorine exist as **simple molecules**, with strong covalent bonds between their atoms. Argon exists as separate atoms (it is **monatomic**).

Their melting and boiling points are very low because:

- when these four substances melt or boil, it is the van der Waals' forces between the molecules which are broken ...
- which are very weak bonds ...
- so little energy is needed to overcome them.

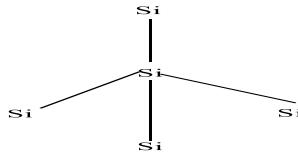
Sulphur has a higher melting point and boiling point than the other three because:

- phosphorus exists as P<sub>4</sub> molecules ...
- sulphur exists as S<sub>8</sub> molecules ...
- chlorine exists as Cl<sub>2</sub> molecules ...
- argon exists individual Ar atoms ...
- the strength of the van der Waals' forces decreases as the size of the molecule decreases .
- so the melting points and boiling points decrease in the order S<sub>8</sub> > P<sub>4</sub> > Cl<sub>2</sub> > Ar.

Summary:

- Metals form giant metallic structure which requires a lot of energy. Magnesium has higher melting point than sodium because it contributes 2 electrons per atom to the metallic bond while sodium only contributes 1 electron per atom. Hence magnesium forms a stronger metallic bond than sodium making it to have higher melting point.
- Aluminium doesn't donate all its 3 valence electrons to the electron cloud, hence not very high melting point.
- Silicon has a giant atomic structure with covalent bonds. Each silicon atom is bonded to four silicon atoms via strong covalent bonds. This results in 3 dimensional structures.

Diagram:



- There is a fall in melting point from silicon to phosphorus ( $P_4$ ) because phosphorus is held together by weak Van der Waal's forces which require less energy to break.  
The magnitude of Van der Waal's forces decreases across the period, thus decrease in melting point.
- Sulphur has the highest melting point because it forms rings of  $S_8$  atoms which are held by Van der Waal's forces. The strength of Van der Waal's forces depends on the molecular mass.  $S_8$  has the highest molecular mass that makes it have high melting point.
- Argon has the lowest melting point because it is mono atomic, hence very weak Van der Waal's forces while chlorine is diatomic.

### **VARIATION OF MELTING POINT AMONGST GROUP (I) AND (II) METALS:**

Melting point of the elements decreases down the group because of increase in atomic radius and the number of electrons donated to the electron cloud is the same. The ionic radius of the cations formed increases hence decreasing the charge density. The force of attraction between the bonding electrons and the positive ion (metallic bonds) decreases. This decreases the melting point.

### **VARIATION OF MELTING POINT AMONGST GROUP (VII) ELEMENTS:**

Melting point of group (VII) elements increases down the group due to increase in the magnitude of Van der Waal's forces of attraction as a result of increase in atomic size (molecular mass) down the group. That is why iodine is a solid, bromine is a liquid, and chlorine and fluorine are gases.

### **BOILING POINTS:**

**Boiling point:** is the constant temperature at which the pure liquid is in equilibrium with its vapour at atmospheric pressure.

### **Points to notes:**

- The magnitude of boiling point depends on the strength of the bonds which must be broken and in converting the liquid to vapour.
- For metals, most of the metallic bonds still exist in the liquid state; therefore a considerable amount of energy is needed to completely break the metallic bonds.

For this reasons, the boiling points of metals are much higher than their melting point.

- ☛ For silicon, most of the covalent bonds have been broken during melting and so the boiling point is not much higher than the melting point.
- ☛ For molecules such as phosphorus, sulphur and chlorine, it involves breaking the Van der Waal's forces which is much easier therefore melting point is lower than boiling point.

### **CHARGE DENSITY:**

13. What is charge density?

**Charge density:** is the charge per unit volume.

**Charge density:** is the ratio of charge of a given ion to its radius.

**Charge density:** is the ratio of the charge of a cation to the ionic radius. It's known as the polarizing power of a cation.

**Mathematically:**

$$\text{Charge density (Polarizing)} = \frac{\text{charge}}{\text{ionic radius}}$$

**Points to note:**

An ion (cation) with a high charge density will have a high polarizing power while that with low charge density will have low polarizing power.

### **EFFECT OF POLARIZATION ON THE IONIC PROPERTY OF A COMPOUND:**

According to Fajan, polarization is favoured by:

- ❖ High charge. Highly charged positive ions greatly polarize anions with large negative charge
- ❖ Small radius of the Cation
- ❖ Large anions. Anions with large radius are more polarisable

Polarization affects both the chemical and physical properties of ionic compounds and considers the table below.

Cations	Na <sup>+</sup>	Mg <sup>2+</sup>	Al <sup>3+</sup>
Ionic radius (nm)	0.095	0.065	0.050
Charge on the ion	+1	+2	+3
Charge density (Polarizing power)	$\frac{+1}{0.095} = 10.5$	$\frac{+2}{0.065} = 30.8$	$\frac{+3}{0.050} = 60.0$
Melting points of the chlorides (°C)	801	712	180 (Sublimes)

### **EXPLANATION:**

- ☛ The polarizing power increase from sodium to Aluminium via Magnesium ions. The Aluminium ion produces the greatest distortion (polarization) of the electrons on the chloride ions than both magnesium and sodium ions. Aluminium chloride has a greater covalent character than both chlorides of magnesium and sodium has the least covalent character with the highest ionic character while Aluminium chloride has the lowest ionic character. Because sodium chloride has the highest ionic character, it has the highest melting point, Aluminium chloride having the highest covalent character; it has the lowest melting point.
- ☛ Hence, Cations with high polarizing power their compounds tends to be more covalent and less ionic while cations with low polarizing power, their compounds tends to be more ionic and less covalent.

## SOLUBILITY OF IONIC COMPOUNDS IN WATER

For an ionic compound to dissolve in water, two energy changes must be overcome.

- (a) Lattice energy,(U<sub>L</sub>) (b) Hydration energy,(ΔH<sub>h</sub>)

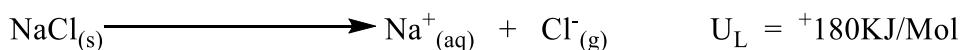
Mathematically:

$$\text{Enthalpy of solution} = \text{Lattice energy} + \text{Hydration energy}$$
$$\Delta H_{\text{sol.}} = U_L + \Delta H_h$$

### A. LATTICE ENERGY:

This is the enthalpy change which occurs when one mole of a crystal, Lattice is broken down in to its constituent gaseous ion.

Equation:



This is enthalpy change which occurs when one mole of ionic crystal lattice is formed for its constituent gaseous ions.

Equation:



### FACTORS THAT AFFECTS LATTICE ENERGY:

#### ✓ Charge on the ion ie, ionic charge:

Lattice energy increases with increase in ionic charge. This is because increased ionic charge increases the electrostatic attraction between the oppositely charged ions. Consider both chlorides of sodium and magnesium.

Magnesium chloride has higher lattice energy than sodium chloride because the electrostatic attraction between Mg<sup>2+</sup> and Cl<sup>-</sup> ions is higher than those sodium and magnesium ions.

#### ✓ Ionic radius:

Lattice energy increases with decrease in ionic radius. The smaller the ionic radius, the closer the ions of opposite charge to each other and the stronger the ionic bond.

Also charge density increases with decrease in ionic radius. The higher the charge density, the higher the electrostatic attraction between oppositely charged ion.

Example:

Sodium chloride has higher lattice energy than potassium because potassium ion has a bigger ionic radius than sodium ion.

Consider lattice energy of:

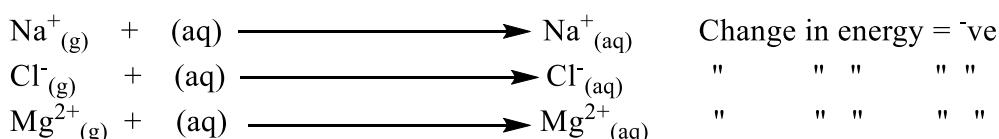
Sodium of:

Fluoride = - 915, Chloride = -775, Bromide = -742, Iodine = -699(KJ/Mol)

### B. HYDRATION ENERGY:

This is the enthalpy change which occurs when one mole of gaseous ions is surrounded by water molecules to form an infinitely dilute solution.

Equation:



Hydration energy is an exothermic process

## **FACTORS AFFECTING HYDRATION ENERGY:**

14. State and explain the factors affecting Hydration energy.

☛ Ionic radius.

An ion with a small ionic radius is highly hydrated than an ion with a big ionic radius, hence releasing more energy.

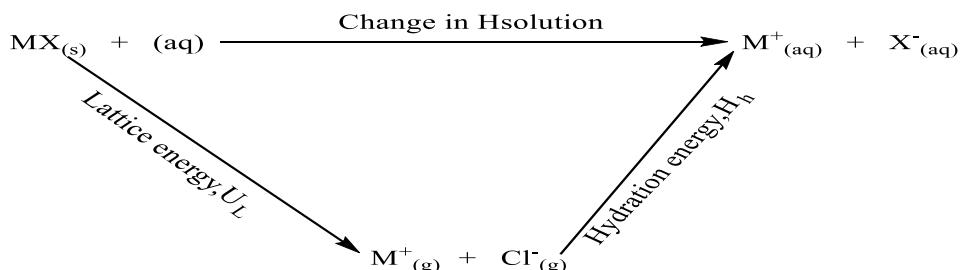
☛ Charge on the ion.

Hydration energy increases with an increase in the charge of the ion. Highly charged ions have high charge density and readily dissolve in water releasing a lot of energy hence higher hydration energy.

Example:  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$ .  $\text{Al}^{3+}$  have higher hydration energy than  $\text{Mg}^{2+}$ .

### **Points to note:**

Relationship between hydration energy, lattice energy and enthalpy of solution.



### **C. ENTHALPY OF SOLUTION:**

This is the enthalpy change that occurs when one mole of an ionic compound in the solid state is dissolved in water to form an infinitely dilute solution.

Mathematically:

$$\text{Enthalpy of solution, } H_{\text{SOL}} = \text{Lattice energy, } U_L + \text{ Hydration energy, } H_H$$

If a salt readily dissolves in water, the sign of Enthalpy of solution will be negative (-ve) but if the salt does not readily dissolve in water, the sign of Enthalpy of solution will be positive (+ve).

1. Given that the Lattice and hydration energies of salts AX and BX

Salts	Lattice energy (KJ/Mol <sup>1</sup> )	Hydration energy (KJ/Mol <sup>1</sup> )
AX	+880	-860
BX	+790	-800

a)

Calculate the enthalpy of solution of each salt.

▪ Salt AX.

$$\begin{aligned}\text{Enthalpy of solution, } H_{\text{SOL}} &= \text{Lattice energy, } U_L + \text{ Hydration energy, } H_H \\ &= +880 + -860 \\ &= +20 \text{ KJ/Mol}^1\end{aligned}$$

▪ Salt BX.

$$\begin{aligned}\text{Enthalpy of solution, } H_{\text{SOL}} &= \text{Lattice energy, } U_L + \text{ Hydration energy, } H_H \\ &= +790 + -800 \\ &= -10 \text{ KJ/Mol}^1\end{aligned}$$

b) Which of the two salts is more soluble in water?

- Salt BX is more soluble than salt AX because it's enthalpy of solution;  $H_{\text{sol}}$  is exothermic while salt AX is endothermic.

### **EFFECTS OF LATTICE ENERGY:**

✗ **Solubility of an ionic compound (salt).**

- Solubility of a salt decreases with increase in lattice energy. When the lattice energy is high, the salt will have very strong electrostatic force of attraction between the oppositely charged ions and vice versa.  
Consider calcium carbonate and calcium chloride.
- $\text{CaCO}_3$  is insoluble in water while  $\text{CaCl}_2$  is soluble.
- This is because the attraction between the double positive ion on  $\text{Ca}^{2+}$  ion and the double negative charge on  $\text{CO}_3^{2-}$  ion is much higher than between the  $\text{Ca}^{2+}$  ion and  $\text{Cl}^-$  ion, hence higher lattice energy.
- The higher the lattice energy, the harder it is to separate the ions in the crystal apart, the less likely it is to dissolve.

✗ **Melting point of a substance.**

- When the lattice energy is high, the melting point of an ionic compound is also high because it requires a lot of energy to separate the ions apart because of the strong electrostatic force of attraction between the oppositely charged ions.

2. The table below shows the melting point of some compounds.

Compounds	$\text{Al}_2\text{O}_3$	$\text{Al}_2\text{Cl}_3$	$\text{CaO}$	$\text{CaCl}_2$
Melting points(K)	2290	451	2850	1050

Explain why?

- a) The melting point of Aluminium chloride is abnormally low compared to Aluminium oxide.

The chloride ions have a larger ionic radius than the oxide ion. They are more polarized by the aluminium ion than the oxide ions. This makes aluminium chloride to become more covalent in character with low melting point as compared to aluminium oxide which is ionic in character with high melting point.

- b) The melting point of calcium oxide is much higher than that of calcium chloride.

The oxide ion is much smaller and highly charged than the chloride ion with a single charge. The ionic bond in calcium oxide is stronger than those in calcium chloride because of the doubly charged calcium ion and the doubly charged oxide ion, hence the lattice energy with high melting point.

Also because of the big ionic radius of the chloride ion, it is easily polarized making the bonding partly covalent with low melting point.

## GROUP (I) ELEMENTS (ALKALI METALS).

Group (I) elements			Atomic radius (Å)		Electron configurations
${}_{\text{3}}\text{Li}$	180	1330	0.15	0.06	[He] $2s^1$ (2:1) $1s^2, 2s^1$
${}_{\text{11}}\text{Na}$	98	892	0.19	0.10	[Ne] $3s^1$ (2:8:1) $1s^2, 2s^2, 2p^6, 3s^1$
${}_{\text{19}}\text{K}$	63	760	0.23	0.13	[Ar] $4s^1$ (2:8:8:1) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$
${}_{\text{37}}\text{Rb}$	39	688	0.24	0.15	[Kr] $5s^1$ (2:8:18:8:1) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 5s^1$
${}_{\text{55}}\text{Cs}$	29	690	0.26	0.17	[Xe] $6s^1$ (2:8:18:18:8:1) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 5s^2, 5p^6, 6s^1$
${}_{\text{87}}\text{Fr}$	T <sub>m</sub> /°C	T <sub>b</sub> /°C	AR/nm	IR/nm	[Rn] $7s^1$ (2:8:18:32:18:8:1) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 4f^{14}, 5s^2, 5p^6, 5d^{10}, 6s^2, 6p^6, 7s^1$
Radioactive elements artificially made					

Elements	Li	Na	Rb	Cs	Fr	KEY:
1 <sup>st</sup> IE/KJmol <sup>-1</sup>	519	494	418	402	376	T <sub>m</sub> = melting temperature T <sub>b</sub> = boiling temperature AR = Atomic radius 1 <sup>st</sup> I.E = 1 <sup>st</sup> Ionization energy 2 <sup>nd</sup> I.E = 2 <sup>nd</sup> Ionization energy
2 <sup>nd</sup> IE/KJmol <sup>-1</sup>	7300	4600	3100	2700	2440	
Density/gcm <sup>-3</sup>	0.53	0.97	0.86	1.53	1.90	
Standard electrode potential, E <sup>o</sup> /V M <sup>+</sup> <sub>(aq)</sub> /M <sub>(s)</sub> /Volts	-3.05	-2.71	-2.93	-2.92	-2.92	

Notes:

Francium is a radioactive element.

- ✓ **S-block elements (or elements in Group 1):** these are elements which have got their outer most electrons in s-sub energy level & **only** Helium in Group 0.

Generally, the outer electronic configuration is ns<sup>1</sup>; they are the S-block elements. Where n is principal quantum number.

- ✓ They are the most reactive metal elements and their reactivity increases down the group because of decrease in 1st ionization energy down the group.

- ✓ They are the most electropositive elements in the periodic table.
- ✓ They have low densities since they have relatively bigger atomic radius.
- ✓ There melting points decreases down the group because their atomic radius increases down the group, the bond length increases and the strength of the metallic bonds decrease.

### **Physical properties of Group (I) elements:**

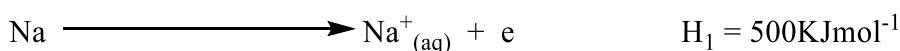
- ✓ As one might expect, the atomic radii increase with increase in atomic number down the groups. Each succeeding element has electrons in one more shell than the previous element.
- ✓ The outermost s-electrons in these metals are held very weakly by nucleus. Hence, the outer electrons can drift further from the nucleus than in most other atoms. So, the elements in Groups (I) have larger atomic radii than those elements which follow them in their respect periods.  
The large atomic size results in weaker forces between neighboring atoms because there is a reduced attraction of the nuclear charge for the shared mobile electrons.
- ✓ Consequently, the elements in Groups (I) have lower melting and boiling and points than we normally associate with metals. All Group (I) metals melt below 200°C. In contrast, most of the transition metals melt at temperature above 1000°C.
- ✓ The reduced interatomic forces in these metals make them relatively soft. As we have seen, s-block elements have larger atomic radii than transition metals of approximately the same relative atomic mass. This results in lower densities and larger molar volumes.
- ✓ The members of Groups (I) are silvery coloured and tarnish rapidly in air. They show relatively weak metallic bonding because they have only single valence electrons. They differ in a number of ways from metals later in the periodic table:
- ✓ **Oxidation state:**

This is the net charge that can be created on an atom when all other atoms bonded to it have been removed as ions with a noble gas configuration.

The elements easily lose their valence electron to form positively charged ions therefore the oxidation state of group (I) is +1.

Summary:

- ☞ They form a constant oxidation state of +1.
- ☞ They are soft, they can be cut be a penknife.
- ☞ Their melting and boiling temperatures are low.
- ☞ They have low densities. (Li, Na, P are less dense than water.)
- ☞ They have low standard enthalpies (heats) of melting and vaporization.
- ✓ The outer electron or electrons can be excited to a higher energy level. When they fall to a lower energy level, energy is emitted. For these metals, the energy is sufficiently low to have a wavelength in the visible spectrum. These elements therefore colour flames: Li-red, Na-yellow, K-lilac, Rb-red and Cs-blue.
- ✓ **Ionization energy:**



The ionization energy required for the process is low. The s-electrons are shielded from the attraction of the nucleus by the noble gas core and are easily removed. As the size of the atoms increases down the groups, the electrons to be removed

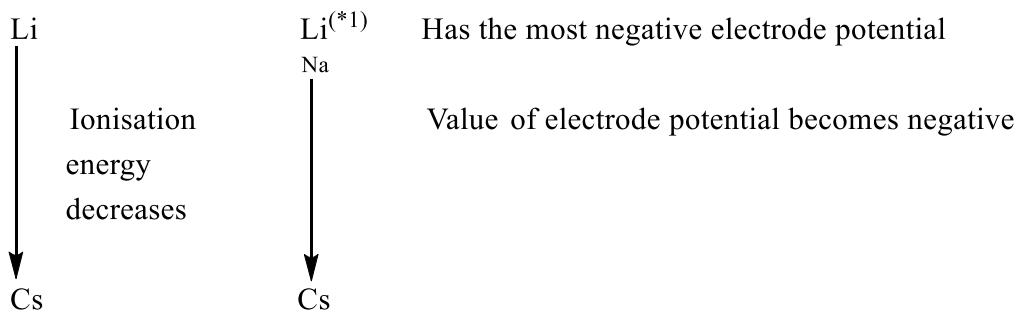
become more distant from the nuclear charge, and the ionization energy decreases.

### CHEMICAL REACTIVITY OF THE S-BLOCK METAL ELEMENTS:

- ♣ The metals in Group (I) elements exist in fixed oxidation states of +1 in their compounds.
- ♣ The metals in Group (I) elements are readily oxidized to monovalent ions,  $\text{Na}^+$  for example. High 2<sup>nd</sup> I.E of Group (I) elements prohibits the formation of other ions such as  $\text{Na}^{2+}$ .
- ♣ The ease of oxidation of Group (I) elements is relatively reflected by high redox potentials of those elements.
- ♣ The negative values show that the metals are electropositive and tend to be oxidized. Hence the reverse reactions in the half reaction below takes place.
- ♣ Because they are readily oxidized and hence readily produce electrons, all the metals in Group (I) are strong reducing agents.
- ♣ However, the metals cannot be used as reducing agents in aqueous solutions, because they reduce the water instead in vigorous and violent reactions. In non-aqueous conditions they reduce non-metals and some compounds such as ammonia.

### STANDARD REDOX POTENTIALS OF GROUP (I) METAL ELEMENTS:

Half - reaction	Electrode potential/Volts
$\text{Li}^+_{(\text{aq})} + \text{e} \rightleftharpoons \text{Li}_{(\text{s})}$	-3.04
$\text{Na}^+_{(\text{aq})} + \text{e} \rightleftharpoons \text{Na}_{(\text{s})}$	-2.71
$\text{K}^+_{(\text{aq})} + \text{e} \rightleftharpoons \text{K}_{(\text{s})}$	-2.93
$\text{Rb}^+_{(\text{aq})} + \text{e} \rightleftharpoons \text{Rb}_{(\text{s})}$	-2.99
$\text{Cs}^+_{(\text{aq})} + \text{e} \rightleftharpoons \text{Cs}_{(\text{s})}$	-3.02



(\*)1) The small size of  $\text{Li}^+$  gives it a high standard enthalpy of hydration. This is why  $\text{Li}^+$  has the most negative value of electrode potential in the group. The small size of  $\text{Li}^+$  enables it to polarize anions, and its compounds have some covalent character.

#### **Points to note:**

- ✗ Because of the shielding of this outer electron from attraction of the nucleus by completed shell of electrons, the 1<sup>st</sup> ionization energies of these elements are very low, decrease with increasing number of shielding shells. Hence the elements are very reactive as metals, and reactivity increase down the group.
- ✗ In general, the hydroxides, carbonates and sulphates of Group (I) elements are more stable to heat than other metals, and their nitrates do not decompose in the usual way.

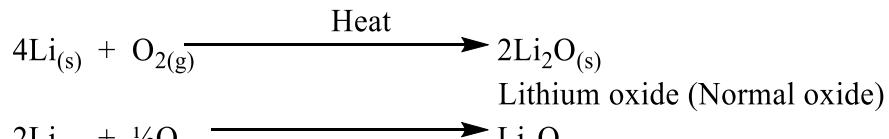
### **REACTIONS WITH NON METALS:**

1. Li, Na, K, Rb and Cs belong to group (I) metal elements of the periodic table. Describe the reactions of the elements with;

(i) Air.

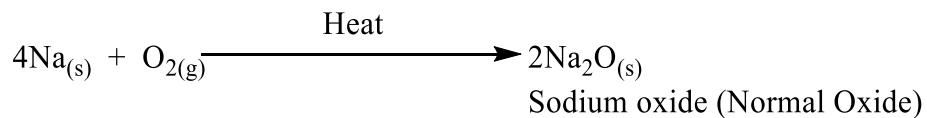
- ☞ Lithium burn in air (oxygen) gas readily with a red (scarlet) flame to form normal oxide of lithium oxide.

Equation:



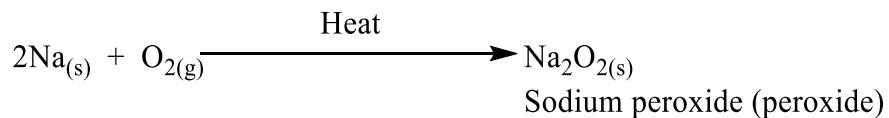
- ☞ Sodium burn in limited supply of air (oxygen) gas readily with a bright, golden yellow flame to form normal oxide of sodium monoxide.

Equation:



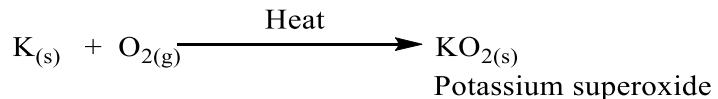
- ☞ Sodium also burn in excess supply of air (oxygen) gas readily with a bright, golden yellow flame to form a pale solid of sodium peroxide a temperature of about 600K.

Equation:



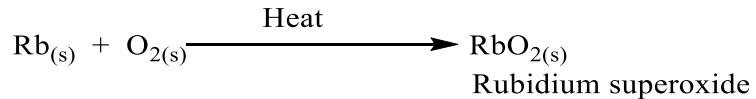
- ☞ Potassium burns in air (oxygen) gas readily with a lilac flame to form potassium superoxide.

Equation:



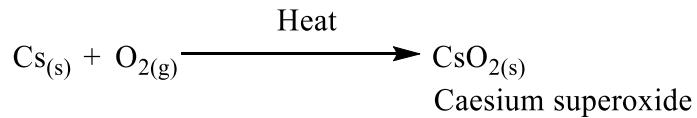
- ☞ Rubidium burns in excess air (oxygen) gas with a red flame to form rubidium superoxide.

Equation:



- ☞ Caesium also burns in excess air (oxygen) gas with a blue flame to form Caesium superoxide.

Equation:



Notes:

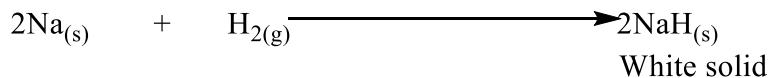
The reactions with oxygen (air) gas occur rapidly. When the metals are exposed to air they begin to tarnish after a few seconds, becoming coated

with oxides. To prevent this, lithium, sodium and potassium are normally stored under oil. Rubidium and Caesium are even more reactive and are normally stored in sealed containers.

2. Explain why Lithium doesn't form peroxide or superoxide when burn in oxygen.
  - ✓ The reason is that the sizes of ions:  $O_2^-$  is larger than  $O_2^{2-}$ , which is larger than  $O_2^2-$ . Therefore,  $Li^+$  ion is too small to either peroxide or superoxide ions to cluster round it to form a stable crystal lattice.
3. Discuss the action of water on oxides of element of Group (I) metals of the periodic table.
  - Lithium oxide  
Lithium oxide reacts violently with water to form lithium hydroxide solution.  
Equation:  
$$Li_2O_{(s)} + H_2O_{(l)} \longrightarrow 2LiOH_{(aq)}$$
  - Sodium oxide  
Sodium oxide reacts violently with water to form sodium hydroxide solution.  
Equation:  
$$Na_2O_{(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(aq)}$$
  - Sodium peroxide  
Sodium peroxide reacts violently with water to form solutions of sodium hydroxide and hydrogen peroxide.  
Equation:  
$$Na_2O_2(s) + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_2O_2(aq)$$
  - Potassium peroxide dissolves in water to form both solution of potassium hydroxide and hydrogen peroxide.  
Equation:  
$$K_2O_2(s) + 2H_2O_{(l)} \longrightarrow 2KOH_{(aq)} + H_2O_2(aq)$$
  - Potassium superoxide  
Potassium superoxide dissolves in water to form solution of potassium hydroxide, hydrogen peroxide solution and oxygen gas.  
Equation:  
$$2K_2O_2(s) + 2H_2O_{(l)} \longrightarrow 2KOH_{(aq)} + H_2O_2(aq) + O_2(g)$$
  - Caesium superoxide  
Caesium superoxide dissolves in water to form caesium hydroxide solution.  
Equation:  
$$Cs_2O_{(s)} + H_2O_{(l)} \longrightarrow 2CsOH_{(aq)}$$
  
(ii) Hydrogen gas.  
☞ Lithium reacts with heated dry hydrogen gas to form a white solid of lithium hydride i.e. ionic hydride.  
Equation:  
$$2Li_{(s)} + H_{2(g)} \longrightarrow 2LiH_{(s)}$$
  
White solid

- ☞ Sodium reacts with heated dry hydrogen gas to form a white solid of sodium hydride.

Equation:



- ☞ Potassium reacts with heated dry hydrogen gas to form a white solid resembling that of sodium hydride in chemical behavior.

Equation:



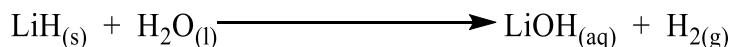
Note:

Since the metals are electropositive, the oxidation state of hydrogen in the hydrides is -1.

4. Discuss the action of water on the hydrides of element of Group (I) metals of the periodic table.

- Lithium hydride.

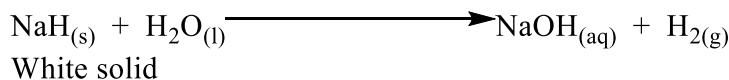
Equation:



- Sodium hydride.

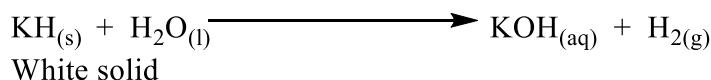
A white solid of Sodium hydride yields hydrogen gas and sodium hydroxide solution when acted upon by cold water.

Equation:



- Potassium hydride.

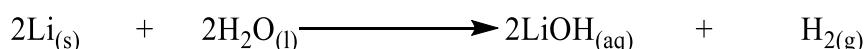
Equation:



(iii) Water.

- ☞ Lithium reacts with cold with water comparatively slowly to form lithium hydroxide solution and a colourless gas that's hydrogen gas.

Equation:



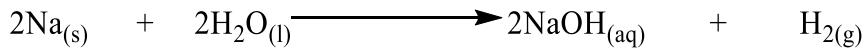
Note:

Lithium is not a completely typical metal of Group (I), because of the small size of its atom and consequent comparative lack of electropositive character. It shows general resemblance to other metals of this Group in its oxidation state of +1, general chemical activity, reaction with water and

physical characteristics. But, in some respect, it resembles the elements of Group (II). It can be said to have 'diagonal relationship' with magnesium.

- ☞ Sodium attacks cold water rapidly with evolution of hydrogen and formation of sodium hydroxide solution.

Equation:

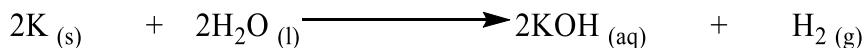


Note:

The hydrogen gas does not burn unless the movement of sodium is restricted.

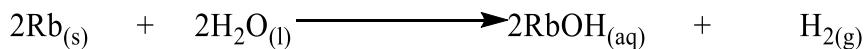
- ☞ Potassium reacts violently with water in cold. Hydrogen gas is liberated and a burn with the lilac flame characteristic of the presence of potassium compounds. Potassium hydroxide solution is left in solution.

Equation:



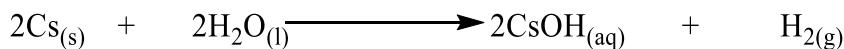
- ☞ Rubidium reacts with water more violently in cold liberating hydrogen gas and rubidium hydroxide solution.

Equation:



Caesium also reacts with water explosively in cold forming caesium hydroxide solution and hydrogen gas.

Equation:



Note:

- ☞ Because of shielding of outermost electron from the attraction of the nucleus by completed shells of electrons, the 1st ionization energies of these metals are very low and decreases with increasing number of shielding shells. Hence the elements are all reactive as a metals and reactivity increases down the group.

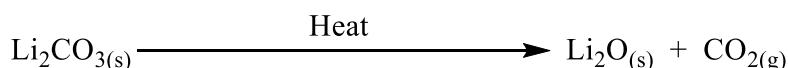
### CARBONATES AND HYDROGEN CARBONATES:

- In general, the hydroxides, carbonates and sulphates of group (I) metal elements are more stable to heat than those of other metals and their nitrates don't decompose in the usual way.
- All the carbonates are ionic except lithium carbonate which is covalent. Lithium carbonate is covalent because of the small ionic radius of lithium ion which makes it easily to greatly polarize the carbonate ion leading to the formation of covalent bond.

Because of being covalent:

- ☞ Lithium carbonate is easily decomposed to form lithium oxide and carbon dioxide gas while the other carbonates are not easily decomposed by heat.

Equation:

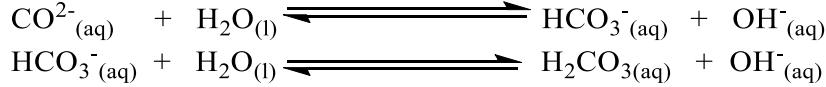


- ☞ Lithium carbonate is only sparingly soluble in water and can be precipitated.
5. Explain why Lithium carbonate decomposes while other carbonates of group I do not.

- ☞ It is because the Lithium ions have a high charge density hence easily polarize the carbonate ions to form a covalent compound which is held by weak Vander Waals forces which makes it easily decompose.
- Or:
- ☞ Lithium ion has the smallest ionic radius while ionic radius of the group (I) metal cations increases down the group. This makes lithium ion to have the highest polarizing power than the rest of the group (I) metals cations. Lithium ions therefore polarizes the carbonate ion making the bonding in lithium carbonate covalent, hence making it less stable than the rest whose bonding is ionic.

6. (a). Explain why Sodium carbonate is used as a base in acid-base titration.  
 (b). (i) State and Explain what is observed when sodium carbonate solution is added to aluminium chloride solution.  
 (ii) Write the equation of reaction in b (i).
- The aqueous solution of the other carbonates is alkaline due to hydrolysis.

Equation:

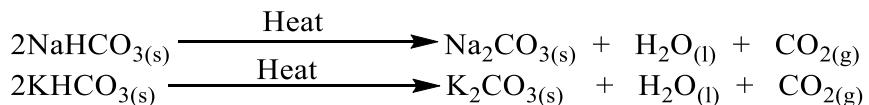


- ☞ The carbonate ion is highly negatively charged; it readily withdraws a proton from water releasing high concentration of hydroxyl ions.
- ☞ The weak carbonic acid partially ionizes in water; the concentration of hydrogen ion is less than the concentration of hydroxyl ion making the solution alkaline.

### HYDROGEN CARBONATES:

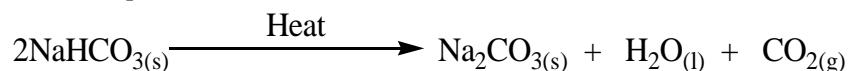
- Hydrogen carbonates are the most stable and exist as solids except lithium hydrogen carbonate which is unstable and only exists in solution.
- Hydrogen carbonates are easily decomposed to form carbonates, carbon dioxide gas and water:

Equation:



3. Explain why sodium hydrogen carbonate decomposes on heating.

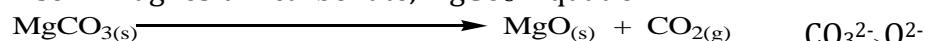
Decomposition is likely to occur when a compound with a small cation and a large anion is covalent to one with the same cation but a smaller or highly charged anion. Equation:



Therefore, because  $\text{HCO}_3^-$  has charge, it is therefore, decomposes.



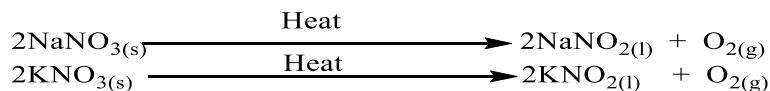
Also in Magnesium carbonate,  $\text{MgCO}_3$ . Equation:



### NITRATES:

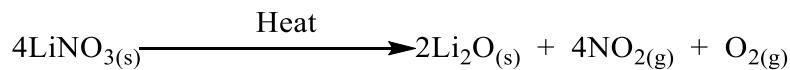
- The nitrate decomposes when heated to form the respective metal nitrite and oxygen gas.

Equation:



- However, Lithium nitrate is unstable; it decomposes completely when heated to form lithium oxide, nitrogen dioxide and oxygen gas.

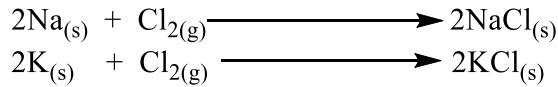
Equation:



### HALIDES:

- They form ionic halides which are soluble in water except lithium halide.

Equation:



4. Explain why sodium chloride is soluble in water but insoluble in diethyl ether.  
When sodium chloride is put in water, its crystals lattice is broken hence setting free sodium,  $\text{Na}^+$  and chloride,  $\text{Cl}^-$  ions which are then surrounded by the polar water molecules. These ions-solvent interaction are stronger than the ion-ion  $[\text{Na}^+ \cdot \text{Cl}^-]$  and solvent-solvent (water-water) interactions. Because of this, sodium chloride dissolves in water.

The insolubility of sodium chloride in a non-polar solvent like diethyl ether is because the attraction between the sodium,  $\text{Na}^+$  and chloride,  $\text{Cl}^-$  ions are stronger than those between the ions and non-polar diethyl ether molecules and also between the molecules of the diethyl ether.

- Lithium halides are covalent because of the small ionic radius of lithium ion, making it to have high polarizing power. It highly polarizes the halide ion forming a covalent bond. Hence; the lithium halides are insoluble in water but soluble in organic solvents.

### ANOMALOUS PROPERTIES OF LITHIUM:

- Lithium shows anomalous properties from the rest of group (I) A metals and tends to resemble magnesium, a group (II) A metal in most of its chemical properties. Reasons:

- ☞ Lithium has a small atomic radius.
- ☞ Lithium forms a cation with a small ionic radius giving the ion a high charge density and high polarizing power.
- ☞ Lithium resembles magnesium because both form ions with similar charge density and have similar polarizing power.
- ☞ Lithium and magnesium atoms have similar electronegativity and electrode potential hence lithium and magnesium exhibit diagonal relationship.

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- ☞ Lithium and magnesium atoms have similar electronegativity and electrode potential hence lithium and magnesium exhibit diagonal relationship.

### **DIAGONAL RELATIONSHIP:**

- 7. What is diagonal relationship?

**Diagonal relationship:** refers to elements adjacent to one another and right angle to each other in the periodic table having similar chemical properties.

Or:

This is the similarity in chemical properties between elements in period two to their diagonal neighbors in period three and adjacent groups.

Moving across the period, electronegativity increases and the ionic radius of cations decreases.

Down the group, electronegativity decreases and the ionic radius of the cations increase. But moving diagonally elements have similar electronegativities, similar atomic/ionic radius and hence resemble each. Pair of elements that shows diagonal relationship are:

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

### **The similarity in chemical properties is due to following reasons:**

- Similar electronegativity
- Similar electropositivity
- Similar electrode potential
- Similar polarizing power or charge density

## SIMILARITIES BETWEEN LITHIUM AND MAGNESIUM, BERYLLIUM & ALUMINIUM AND BORON AND SILICON.

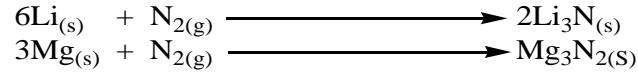
<b>Li and Mg</b>	<b>Be and Al</b>	<b>B and Si</b>
Both react with nitrogen on heating to form nitrides.	Oxides and hydroxides are amphoteric. $\text{Be(OH)}_2(s) + 2\text{OH}^-(aq) \rightarrow \text{Be(OH)}_4^{2-}(aq)$ $\text{Al(OH)}_3(s) + \text{OH}^-(aq) \rightarrow \text{Al(OH)}_4^-(aq)$	Both form acidic oxide as $\text{B}_2\text{O}_3$ and $\text{SiO}_2$
Their hydrogen carbonates exist in solution	Both react with Conc. Sodium hydroxide solution to form a complex and hydrogen gas. $\text{Be}(s) + 2\text{OH}^-(aq) + 2\text{H}_2\text{O}(l) \rightarrow \text{Be(OH)}_4^{2-}(aq) + \text{H}_2(g)$ $2\text{Al}_{(s)} + 2\text{OH}^-(aq) + 6\text{H}_2\text{O}(l) \rightarrow 2\text{Al(OH)}_4^-(aq) + 3\text{H}_2(g)$	Both form series of covalent hydrides.
Both form normal oxides when heated in oxygen (air)	Their chlorides and bromides are covalent and dimerize in vapour phase as $\text{Be}_2\text{Cl}_4$ and $\text{Al}_2\text{Cl}_6$ . $2\text{AlCl}_3(s) \rightleftharpoons \text{Al}_2\text{Cl}_6(g)$	Both form chlorides which hydrolyze readily.
Their hydroxides and carbonates are sparingly soluble in water	Both form ionic carbides which hydrolyze to form methane. $\text{Be}_2\text{C}(s) + 4\text{H}_2\text{O}(l) \rightarrow \text{CH}_4(g) + 2\text{Be(OH)}_2(aq)$ $\text{Al}_4\text{C}_3(s) + 12\text{H}_2\text{O}(l) \rightarrow 3\text{CH}_4(g) + 4\text{Al(OH)}_3(aq)$	Form covalent compounds.
Carbonates, hydroxides, peroxide decompose on heating to give an oxide.	Both are rendered passive concentrated nitric acid.	Form borides and silicides with metals.
Nitrates decompose on heating to give an oxide, nitrogendioxide and oxygen.	Both form fluoro complexes.e.g. $\text{BeF}_4^{2-}$	
Halides (except fluorides) and chlorates (VII) are soluble in organic solvent.		

### SUMMARY:

#### Lithium and Magnesium.

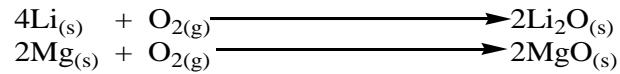
Both lithium and Magnesium combine directly with nitrogen gas forming nitrides other alkali metals do not reacts with nitrogen gas.

Equations:



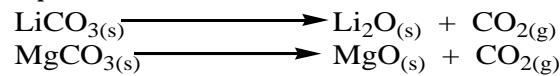
Both Lithium and Magnesium form normal oxides only, other alkali metals form normal oxides, peroxides & super oxides.

Equations:

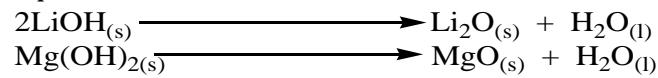


Carbonates, peroxides and hydroxides of Lithium and Magnesium are sparingly soluble in water and decompose on heating. Carbonates, peroxides and hydroxides of other alkali metals are soluble and (stable) do not decomposed by heat.

Equations:



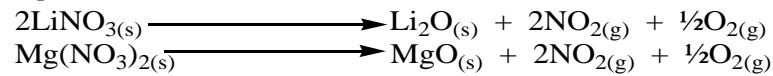
Equations:



Their hydrogen carbonates exists as a solution.

Nitrates of Lithium and Magnesium decomposes on heating to form oxides, nitrogen dioxides and oxygen gases when heated strongly.

Equations:



Hydroxides of both metals are deliquescent.

Fluorides of both metals are soluble in organic solvents.

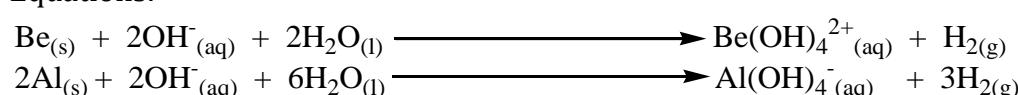
Both metals forms carbides when heated in carbon.

### Beryllium and Aluminium.

Both metals are rendered passive reaction by concentrated nitric acid because of formation of insoluble oxides.

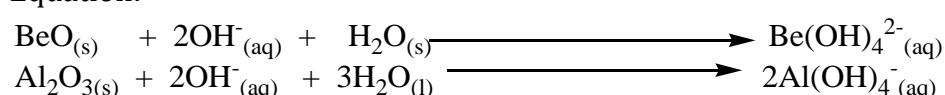
Both metals reacts with concentrated alkalis to give off hydrogen gas.

Equations:



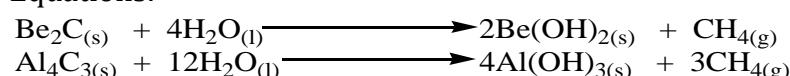
Both oxides are amphoteric and reacts with hot concentrated alkalis.

Equation:



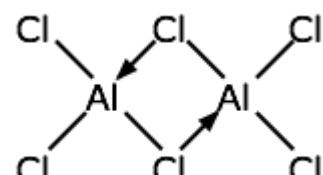
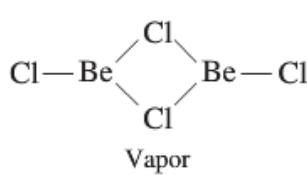
Carbides of both metals yields methane on hydrolysis.

Equations:



Chlorides of both metals are covalent and polymeric solids when anhydrous.

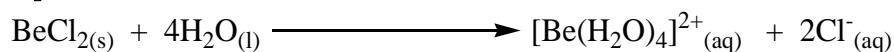
Equations:



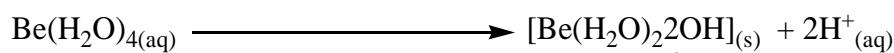
**Notes:** Remember to show the donating electron and in this case, chlorine atom donates electron to both beryllium and aluminium atoms respectively all the compounds Aluminium and Beryllium are covalent in nature.

Both beryllium and aluminium chlorides are covalent and are hydrolyzed in water to form acidic solution.

**Equations:**



Or:



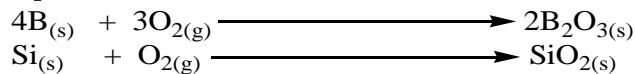
Or:



 **Boron and Silicon.**

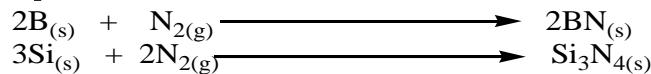
Both burns in air to form acidic oxides.

**Equations:**



Both burns in nitrogen gas to form nitrides.

**Equations:**



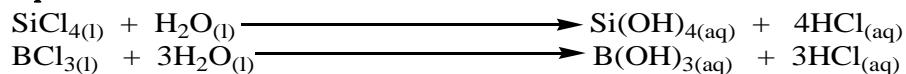
Both exist in amorphous and crystalline state and exhibit allotropy.

Both forms covalent compounds.

Their hydrides are simple molecular.

Their chlorides are liquids, fume in most air and are readily hydrolyzed by water.

**Equations:**

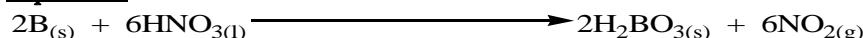


Both form weak acids like  $\text{H}_3\text{BO}_3$  and  $\text{H}_2\text{SiF}_6$  when reacted.

**Notes:**

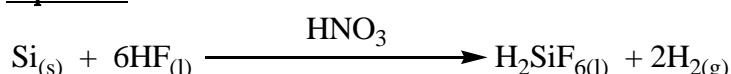
Boron reacts with only oxidizing acids, i.e. nitric and sulphuric acid, only when hot and concentrated. The product is trioxoboric acid.

**Equation:**



But silicon is very resistant to the action of acids. It is only attacked by hydrofluoric acid (more rapidly if nitric acid is present).

**Equation:**



Both the metals and their oxides are readily soluble in alkalis.

Their carbides are very hard and used as abrasives.

5. State three @ properties in which:

- ✓ Lithium differs from the rest of group (I) elements.
- ✓ Beryllium differs from the rest of group (II) elements.
- ✓ Boron differs from the rest of group (III) elements.

### **GROUP (II) ELEMENTS:**

- Alkaline earth metals and includes:
 

✓ Beryllium, Be	✓ Strontium, Sr
✓ Magnesium, Mg	✓ Barium, Ba
✓ Calcium, Ca	✓ Radium, Ra
- The outer general electronic configuration of Group (II) elements is  $ns^2$ .
- They have a fixed valency of 2 and oxidation state of +2.
- Radium is a radioactive element.

### **CHEMICAL TRENDS:**

Elements	Be	Mg	Ca	Sr	Ba
Atomic Radius	0.089	0.136	0.174	0.191	0.198
Ionic Radius	0.031	0.065	0.099	0.113	0.135
Melting point	1280	850	842	770	710

- Generally atomic radius increases down the group.
- 8. Explain why the atomic radius of Group (II) elements increases down the group?
- Also, ionic radius increases down the group with decrease in melting points down the group.
- 9. Explain why melting points of Group (II) elements decreases down the group?
  - ✓ Down the group, the ionic radius of the positive cations increases hence decreasing the charge density.
  - ✓ The bonding electrons becomes further away from the positive ion. The force of attraction between the bonding electrons and positive cations decreases (metallic bonding), hence decrease in melting point of group (II) elements.

#### **Notes:**

The exception is beryllium which forms covalent compounds due to the undesirable charge density on  $Be^{2+}$  (charge density is the charge per unit volume and the volume of the  $Be^{2+}$  ion is very small).

#### **Golden tips:**

Group 13 contains one non-metal, namely boron, and the other elements are metals. Boron is also the only element which does not form a stable trication ( $B^{3+}$  again will have too high a charge density to be stable).

10. Why do the other elements form trications?

Because they have the valence electronic configuration  $ns^2np^1$  and when three electrons are lost they have a full valence shell.

### **EFFECTS OF IONIC RADIUS OF GROUP (II) IONS AS COMPARED TO GROUP (I) IONS:**

- The atoms of group (II) A elements have smaller atomic radius than those of group (I)A similarly, their ions are smaller than those of group (I)A ions.
- Because of the small ionic radius of group (II)A ion and double charge, their polarizing powers are much greater than those of group (I)A metals ions hence it affects the following properties:

- ↗ Solubility.
  - ↗ Melting & boiling points.
  - ↗ Thermal stability.
- (a) Solubility.
- Group (II) salts are less soluble than group (I) salts. Their enthalpy of hydration are much large than those of group (I) A metal ions. Large enthalpies of hydration would lead to group (II) A salts being more soluble than group (I) A salts.
  - However, group (II) A salts have greater lattice energy which reduces their solubilities and the overall effect is that they becomes less soluble.
- (b) Thermal stability.
- The compounds of group (II) A are less stable to decomposition than group (I) A compounds example sodium carbonate is not decomposed by heat whereas magnesium carbonate decomposes.
  - This is because group (II)A cations are more highly charge with smaller ionic radius than group (I)A cations hence they have higher polarizing power than group (I)A cations.
  - Consequently, they highly polarize ...the to anions. This makes group (II) A compounds more covalent than those of group (I) A compounds hence easily decomposed.
- (c) Melting & boiling points.
- Salts of group (II) generally have lower melting and boiling points than those of group (I).this is because, group (II) cations are highly charged with a smaller ionic radius than those of group (I).
  - Their cations have higher polarizing power than those of group (I) cations making compounds of group (II) more covalent than those of group (I).the more covalent character, the lesser the melting and boiling points.

11. Explain the following.

- Magnesium carbonate is insoluble in water while sodium carbonate is soluble.
  - $Mg^{2+}$  ion has a smaller ionic radius than  $Na^+$  ion and also  $Mg^{2+}$  ion has a double charge while  $Na^+$  ion is a single charge. Because of the highly charge and small ionic radius of  $Mg^{2+}$  ion and the high charge on the  $CO_3^{2-}$  ions, Magnesium carbonate has a higher or lattice energy than sodium carbonate therefore sparingly soluble.  
Or
  - Because of the high charge and small ionic radius of  $Mg^{2+}$  than  $Na^+$ , it easily polarizes the carbonate ions, making magnesium carbonate more covalent while sodium carbonate is more ionic in character, therefore magnesium carbonate is insoluble in water while sodium carbonate is soluble in water.
- Magnesium carbonate is insoluble in water while magnesium chloride is soluble.

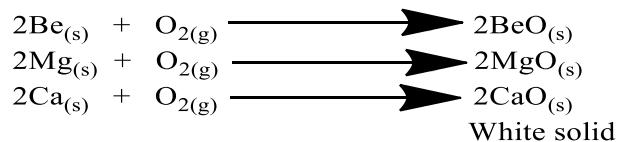
- The electrostatic attraction between the double positive charge on  $Mg^{2+}$  ion and the double negative charge on  $CO_3^{2-}$  ion is much higher than between  $Mg^{2+}$  and  $Cl^-$  ion, making magnesium carbonate to have high lattice energy than magnesium chloride.
  - The higher the lattice energy, the harder it is to separate the ions in crystal apart and the higher the hydration energy and the less likely it is for the salt to dissolve.
- Or
- The  $CO_3^{2-}$  ion is more polarized than the  $Cl^-$  ion making magnesium carbonate to have a higher covalent character than magnesium chloride this higher hydration energy make magnesium carbonate to be insoluble in water.

### **CHEMICAL PROPERTIES:**

#### A. Reaction with air:

The metals burns brightly in air when heated forming oxides which are white in colour.

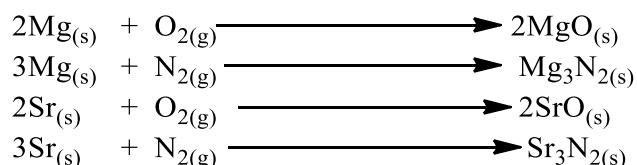
Equation:



Golden tips:

However, magnesium forms a mixture of the oxide and nitride when heated in air.

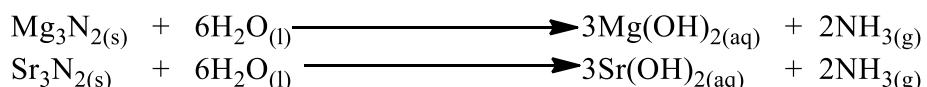
Equation:



Golden tips:

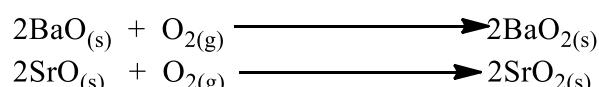
Magnesium and Strontium nitride reacts with water forming a white precipitate of magnesium hydroxide and ammonia gas liberated.

Equation:



Barium and strontium oxide form peroxides when further heated in air.

Equation:



Golden tips:

The reaction of the elements with air increases from Beryllium to Barium.

#### B. Reaction with water:

The mode of reaction increases from Beryllium to Barium because of:

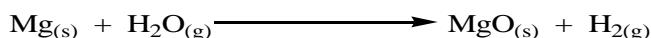
- ✗ Electronegativity increases down the group.
- ✗ Ionization energy decreases down the group.
- ✗ The solubility of the hydroxides increases down the group.

I. Beryllium.

It doesn't react with water whether cold, hot or steam because Beryllium hydroxide is insoluble.

II. Magnesium.

Magnesium burns with a dazzling white flame when heated in steam **NOT** water to form a white ash of magnesium oxide and hydrogen gas liberated.  
Equation:



III. Calcium, Strontium & Barium

Calcium reacts moderately with cold water followed by Strontium and Barium reacts vigorously with cold water. In also cases hydrogen gas is liberated and their respective metal hydroxides are formed.

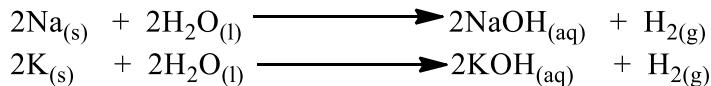
Equation:



**COMPARE WITH GROUP (I) ELEMENTS:**

All group (I) A elements reacts vigorously with cold water forming Hydroxides and hydrogen gas liberated.

Equation:



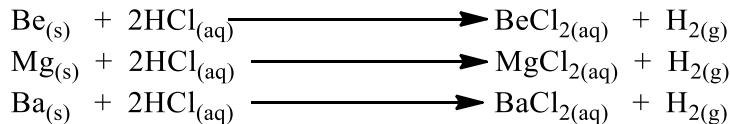
The reaction with cold water becomes more vigorously as you descend down the group.

C. Reaction with acids:

(a). Dilute acid.

All the elements reacts with dilute hydrochloric acid forming respective salts and hydrogen gas is liberated. The reaction increases down the group because the chlorides become more soluble.

Equation:

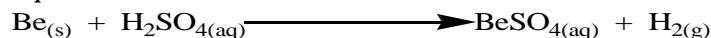


The reaction is more vigorous when the acid is concentrated.

✓ Dilute sulphuric acid.

Beryllium-Reacts with warm dilute sulphuric acid to give Beryllium sulphate and hydrogen gas.

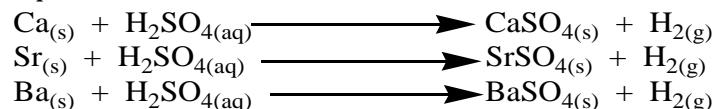
Equation:



Magnesium, Calcium, Strontium and Barium reacts with cold dilute sulphuric acid forming their respective metal sulphate and hydrogen gas.

The reaction decreases down the group because the stability of sulphates decrease forming insoluble sulphate that retard the reaction.

Equation:



Notes:

Magnesium oxide is said to react slowly with dilute Nitric acid to give some Hydrogen gas but when the Nitric acid is more concentrated, it yields oxides of nitrogen in the usual way.

Equation:



### **COMPARE WITH GROUP (1) A:**

All group 1A elements reacts explosively with dilute acids than group (II) A elements. This is because group (1) A elements are more electropositive and their salts are more soluble.

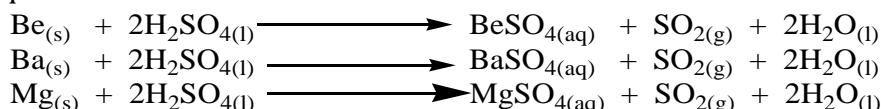
(b). with concentrated oxidizing acids:

- ✗ Hot concentrated sulphuric acid.

All the elements reacts with hot concentrated acid forming sulphur dioxide gas (reduced) and respective metal sulphate and water.

The reaction decreases down the group because the solubility of sulphates decreases, hence Barium has little effect on concentrated sulphuric acid because barium sulphate is insoluble and the reaction stops.

Equations:



- ✗ Concentrated nitric acid.

Beryllium doesn't react with concentrated nitric acid because it is rendered passive due to the formation of an insoluble oxide.

The rest react with concentrated nitric acid and are oxidized to  $\text{M}^{2+}$  (metal nitrate) and the acid is reduced to nitrogen dioxide gas.

Equation:



D. Reaction with aqueous alkali:

Beryllium reacts with hot concentrated alkalis forming a complex called Beryllate ion and hydrogen gas. Beryllium reacts with alkalis because it is amphoteric.

Equation:



Or

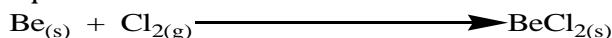


The rest of the elements do not react with alkalis because they are basic and highly electropositive.

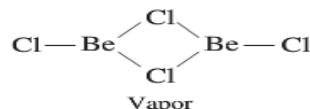
#### E. Reaction with non-metals:

Beryllium when heated in chlorine gas forms a covalent chloride which is insoluble in water.

Equation:



Beryllium chloride dimerises in vapour state (phase) and exist as beryllium chloride,  $\text{Be}_2\text{Cl}_4$ .

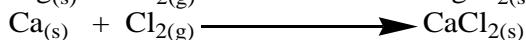


Formula:

Beryllium chloride is covalent because Beryllium forms a cation which is highly charged with smallest ionic radius. Beryllium ion has high polarizing power and it polarizes the chloride ion leading to the formation of covalent bond.

The other metals form chlorides when heated in chlorine gas. The chlorides are ionic and soluble in water.

Equations:



### COMPOUNDS OF GROUP (II) A:

All elements exhibit an oxidation state of +2 and smaller ionic radius than the corresponding group (1) elements. Group (II)A ions have high polarizing power.

Group (II)	Charge density	Hydration energy(KJ/Mol)	Group (I)	Charge density	Hydration energy(KJ/Mol)
$\text{Be}^{2+}$	$\frac{2}{0.031}=64.5$		$\text{Li}^+$	$\frac{1}{0.060}=16.7$	
$\text{Mg}^{2+}$	$\frac{2}{0.065}=30.8$	-1920	$\text{Na}^+$	$\frac{1}{0.095}=10.5$	-406
$\text{Ca}^{2+}$	$\frac{2}{0.099}=20.2$	-1650	$\text{K}^+$	$\frac{1}{0.133}=7.5$	-322
$\text{Sr}^{2+}$	$\frac{2}{0.191}=10.5$	-1440	$\text{Rb}^+$	$\frac{1}{0.152}=6.6$	-301

Notes:

Since the cations of group (II) elements have high polarizing power on the accompanying anions, it has the effect that:

- ↗ There compounds are less ionic than those of group (1) e.g. magnesium chloride is less ionic than sodium chloride.
- ↗ Their carbonates and hydrogen carbonates are insoluble in water.
- ↗ Their enthalpies of hydration are much higher than those of group of group (1), have higher lattice energies.
- ↗ There carbonates are less stable to heat i.e. they are easily decomposed.
- ↗ Their salts tend to be hydrated e.g. chlorides and sulphates.

6. Explain why Magnesium melts at **650°C** while sodium melts at **97.8°C**.

Both sodium and magnesium are metals which have metallic bonding. Magnesium has a higher melting point than sodium because magnesium contributes more electrons (two) to its charge cloud than sodium (one) and therefore magnesium forms a stronger metallic bond.

**Golden tips:**

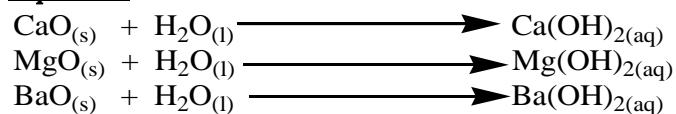
The melting points of metals depends on the number of electrons a metal contributes to its charge cloud. The greater the number of such electrons, the stronger the attraction between the cations formed and the delocalized electrons hence higher melting point.

- 1) Hydroxides.

The hydroxides can be prepared by either:

- (i).dissolving the oxides in water except beryllium oxide which is insoluble.

**Equation:**



- (ii).by adding aqueous sodium hydroxide or aqueous ammonia to a soluble salts of group (II).

**Equations:**



**SOLUBILITY OF THE HYDROXIDES:**

Hydroxides	Solubility at 25°C Mol <sup>-1</sup> /100g of water	
Be(OH) <sub>2</sub>	INSOLUBLE	Insoluble
Mg(OH) <sub>2</sub>	2.0 X 10 <sup>-5</sup>	0.002
Ca(OH) <sub>2</sub>	1.5 X 10 <sup>-3</sup>	0.150
Sr(OH) <sub>2</sub>	3.4 X 10 <sup>-3</sup>	0.400
Ba(OH) <sub>2</sub>	1.5 X 10 <sup>-2</sup>	4.000

12. State and explain the trend of the solubilities of the hydroxides of this group.

↙ Down the group, the solubility of group (II) hydroxides increases, this is due to decrease in lattice energy as the size of ionic radius of metal ion increase. Large ionic metal radius makes less overlap) holding force) of the ions reducing the lattice energy.

↙ This is (Lattice energy) overcome by the hydration energy, hence increased solubility down the group.

Or:

↙ The solubility of the hydroxides increases down the group. Why?

↙ This because both Lattice and hydration energy decreases down the group due to increase in ionic radius of the group (II) ions, but the Lattice energy decrease more rapidly than the hydration energy and the hydration energy overcomes the lattice energy leading to increase in the solubility of the hydroxide.

Or:

The solubility of the hydroxide increases down the group as a results of increase in ionic character.

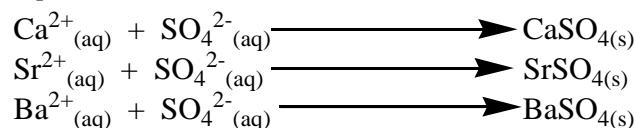
Down the group, the ionic radius of the cations increases, the polarizing power of the double charged cations decreases and the bonding becomes less covalent but more ionic in character. Water being an ionic solvent tends to dissolve the more ionic compounds leading to increase in solubility of the hydroxides down the group.

Notes: The solubility of the nitrates is similar to the hydroxides.

## 2) Sulphates

The sulphates are prepared by precipitation by adding a sulphate ions,  $\text{SO}_4^{2-}$  to any soluble salt except, Beryllium and Magnesium sulphates which are soluble.

Equations:



## SOLUBILITY OF THE SULPHATES.

Sulphates	$\text{BeSO}_4$	$\text{MgSO}_4$	$\text{CaSO}_4$	$\text{SrSO}_4$	$\text{BaSO}_4$
Solubility at 25°C in gm/100g of water	4.3000	8.6000	0.2000	0.1100	0.0024

### 13. State and explain the trend of the solubilities of the sulphates of this group.

The solubility of the sulphates decreases down the group.

- ↗ This is because both Lattice and hydration energy decreases but the hydration energy decreases more rapidly than Lattice energy. Since both cation and anion are double charged, this results in high Lattice energy hence decrease in solubility down the group.

Notes:

- ↗ The trend is the same with chromates and carbonates.

## 3) Chlorides

The chlorides are prepared by reacting dilute hydrochloric acid with excess metal hydroxide or carbonates.

Equation:



Chlorides	Conductivity ( $\Omega^{-1}\text{cm}^2/\text{Mol}$ )	Bonding	Melting point (°C)
$\text{BeCl}_2$	00.09	Covalent	405
$\text{MgCl}_2$	32.00	Ionic	714
$\text{CaCl}_2$	58.00	"	782
$\text{SrCl}_2$	63.00	"	872
$\text{BaCl}_2$	71.00	"	963

- ↗ The molar conductivity increases down the group because of increase in ionic character. Molar conductivity is very low because the salt is mainly covalent, it hardly forms ions for electric conductivity.

- ✗ Beryllium chloride is covalent because Beryllium ion has a small ionic radius which is double charged. Beryllium ion has high polarizing power which polarizes the chloride ion making the bonding covalent.
- ✗ Down the group, the ionic radius of the cations increases leading to decrease in polarizing power. The bonding becomes less covalent but more ionic.
- ✗ The melting point increases down the group due to increase in ionic bonding forces.
- ✗ The melting points generally increases down the group as shown above in the table.  
Why?  
✗ This is because down the group, ionic radius of the cation increases with constant charge. Which reduces charge density of the cation down the group hence polarizing power reduces therefore this increases the ionic character of the chlorides down the group hence increase in melting points.

### **HYDROLYSIS OF THE CHLORIDES OF GROUP (II) ELEMENTS:**

- ✗ Beryllium chloride is hydrolysed by water to form beryllium hydroxide and hydrogen chloride gas.
- ✗ Equation:  

$$\text{BeCl}_{2(s)} + 2\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{Be(OH)}_{2(s)} + 2\text{HCl}_{(g)}$$
- ✗ Magnesium chloride can only undergo partial hydrolysis by water.  
Equation:  

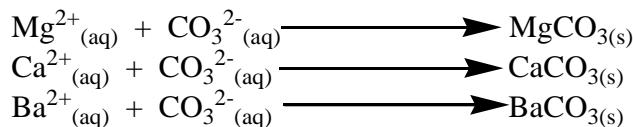
$$\text{MgCl}_{2(s)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{Mg(OH)Cl}_{(s)} + \text{HCl}_{(g)}$$
- ✗ When heated, hydrated magnesium chloride is hydrolysed by its water of crystallization. It is therefore not possible to obtain the anhydrous chloride by evaporation of its aqueous solution.  
Equation:  

$$\text{MgCl}_{2(s)} + \text{H}_2\text{O}_{(l)} \longrightarrow \text{MgO}_{(s)} + 2\text{HCl}_{(g)}$$
- ✗ Calcium chloride is only hydrolysed to a small extent to form calcium oxide or calcium hydroxide. Strontium and barium chlorides are not hydrolysed.

#### 4) Carbonates

They are prepared by precipitation by adding a soluble carbonate to a solution containing a soluble group (II) metal ions.

Equations:



### **THERMAL STABILITY OF THE CARBONATES:**

The thermal stability of an ionic salt depends on two factors:

-The ionic radius of the ions. — The charge on ion.

**The table below shows the decomposition temperatures for group II carbonates**

Carbonates	$\text{BeCO}_3$	$\text{MgCO}_3$	$\text{CaCO}_3$	$\text{SrCO}_3$	$\text{BaCO}_3$
Temperature ( $^{\circ}\text{C}$ )	100	350	900	1290	1350

### **EXPLANATION:**

- The smaller the ionic radius, the greater will be their degree of approaching each other in the crystal Lattice and more stable the salt.
  - The greater the charges, the stronger the electrostatics forces of attraction, the more strongly will the ions attract each other, the more stable will be the salt.
  - Moving down the group, the charge remain the same but the ionic radius increases, the charge on the carbonate ion is the same throughout. The polarizing power of the cations decreases the bonding in the metal carbonate becomes more ionic down the group, hence the compounds becomes more stable.
  - Hence the decomposition temperature increase in the order of:  
 $\text{BeCO}_3 < \text{MgCO}_3 < \text{CaCO}_3 < \text{SrCO}_3 < \text{BaCO}_3$   
 $\text{Be}(\text{NO}_3)_2 < \text{Mg}(\text{NO}_3)_2 < \text{Ca}(\text{NO}_3)_2 < \text{Sr}(\text{NO}_3)_2 < \text{Ba}(\text{NO}_3)_2$
- NOTES:
- The thermal stability increases due to increasing ionic character i.e. Lattice enthalpy. The larger the metal ion, the less the polarizing power thus the carbonates become ionic and the stronger the electrostatic forces of attraction.
  - Group I metal carbonates are more stable than group II metal carbonates. This is because  $\text{M}^{2+}$  ions have higher charge density than  $\text{M}^+$  ions therefore they polarize the large carbonates more than  $\text{M}^+$ .

14. Explain why magnesium carbonate decompose when heated while sodium carbonate does not.

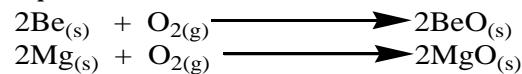
Magnesium ion,  $\text{Mg}^{2+}$  has a high charge, small ionic radius than sodium ion,  $\text{Na}^+$ .it therefore has high polarizing power which makes it easy to polarize the big carbonate ions, $\text{CO}_3^{2-}$  making the bonding in magnesium carbonate to have some covalent character while the bonding in sodium carbonate is ionic due to the low polarizing power of  $\text{Na}^+$ , hence magnesium carbonate easily decomposes.

5) Oxides

The oxides can be prepared by:

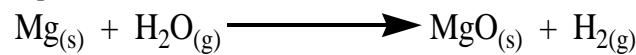
- Heating the metals in oxygen.

Equation:



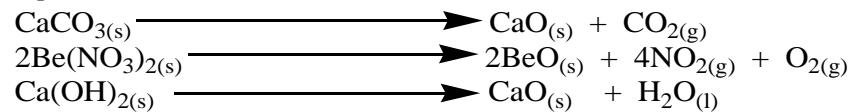
- Passing steam over heated metals.

Equations:



- Heating the carbonates, nitrates or hydroxides of group (II) elements.

Equations:



**Notes:**

All the oxides are white crystalline solid with high melting points.

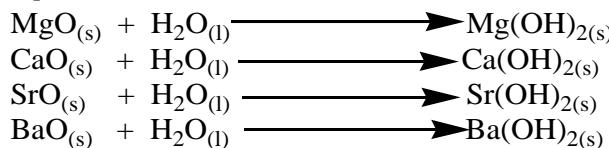
Beryllium oxide is amphoteric and the bonding is covalent while the rest of the oxides are basic and the bonding is ionic.

Oxides	Types of oxides	Types of bonding	Melting points (°C)
BeO	Amphoteric	Covalent	2530
MgO	Basic	Ionic	2800
CaO	"	"	2570
SrO	"	"	2000
BaO	"	"	1920

- ☞ Generally, the melting point decreases down the group. This is because of the decrease in the ionic bond force caused by increase in the ionic radius of the cations down the group.
- ☞ Magnesium oxide has a higher melting point than beryllium oxide because it is ionic and beryllium oxide is covalent due to its small ionic radius and making it to have polarizing power to polarize the oxide ion making the bonding covalent.
- 6) Reactions with water:

Beryllium oxide does not react with water because it forms an insoluble beryllium hydroxide while the rest of the metal oxides do react readily with water liberating heat and metal hydroxides. The metal oxides become more soluble down the group.

Equations:



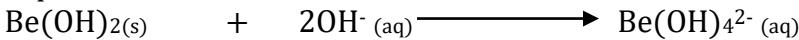
15. Explain why beryllium oxide does not react with water?

Beryllium oxide is covalent in nature, forms insoluble hydroxide and therefore it does not react with water while the other members react with water because the oxides are largely ionic in nature and sparingly dissolves in water.

16. Explain why beryllium hydroxide cannot be prepared by precipitation method.

Because Beryllium hydroxide is amphoteric and therefore it forms complex.

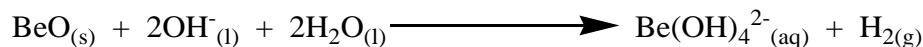
Equation:



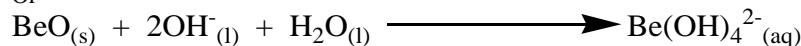
- 7) Reactions with alkalis:

With the exception of beryllium, the elements do not react with alkalis. Beryllium oxide reacts with alkalis to form complex salt (Beryllate ions).

Equation:



Or



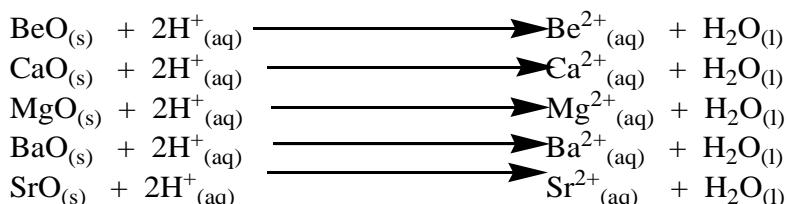
Reasons why the rest do not react with alkalis under any conditions:

This is because the oxides of Magnesium, Calcium, Strontium and Barium are basic in nature while Beryllium oxide is amphoteric oxide.

### 8) Reactions with dilute acids:

All the metal oxides reacts with dilute acids to form corresponding salts and water.

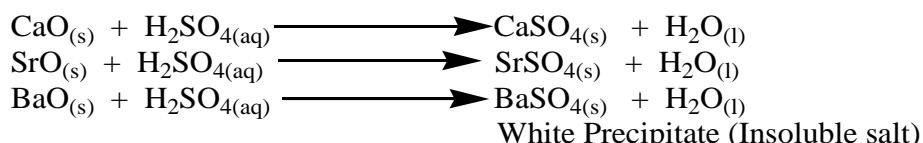
## Equations:



## Notes:

Calcium, strontium & Barium oxides reacts slightly with dilute sulphuric acid forming an insoluble sulphates which stops the reaction because the solubility of the sulphates decreases down the group.

Equation:



#### **CALCIUM OXIDE, CaO (QUICK LIME):**

17. Describe how ethyne gas can be prepared in the laboratory.

### **Procedures:**

It is obtained by heating calcium carbonate.

### Equation:



This oxide has a high affinity for water and it is normally used as a drying agent for alcohol and gas.

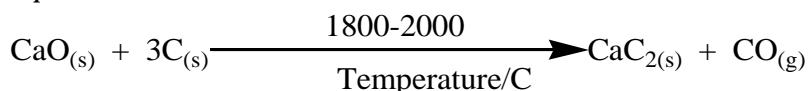
When cold water is added to calcium oxide, it swells with a hissing sound, then cracks and eventually crumbles to a white powder called slaked lime.

### Equation:



A saturated solution of calcium hydroxide is called lime water. Calcium oxide reacts with heated carbon to form calcium carbide.

### Equation:



When cold water is added to calcium carbide, it is hydrolyzed to form ethyne gas.

### Equation:



All carbides of Group (II) elements except Beryllium carbide when hydrolyzed with cold water, they form ethyne gas while beryllium carbide forms methane.

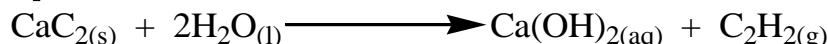
Magnesium carbide (Contains  $C_3^{4-}$ ) on hydrolysis gives propyne.

### **Equation:**



Calcium carbide (Contains  $\text{C}\equiv\text{C}^{2+}$  ions) gives ethyne on hydrolysis.

Equation:



18. Describe how methane gas can be prepared in the laboratory.

Beryllium carbide is prepared by heating the elements of beryllium and carbon at a temperature of above  $900^{\circ}\text{C}$ .

Beryllium carbide can also be prepared by reduction of beryllium oxide with carbon at a temperature above  $1500^{\circ}\text{C}$ .

Equation:



Beryllium carbide obtained is hydrolyzed or decomposes slowly in water.

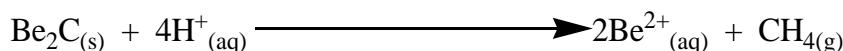
Equation:



Or:

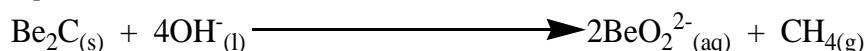
The rate of decomposition is fastest in mineral acids with evolution of methane gas.

Equation:



However, in hot concentrated alkali the reaction is very rapid, forming the alkali metal beryllates and methane gas.

Equation:



### **HYDROLYSIS OF GROUP (II) SALTS:**

19. What is Hydrolysis?

**Hydrolysis:** is a reaction between water molecules and highly charged cations and anions ( $\text{CO}_3^{2-}$ ) which disturbs the water equilibrium hence producing more hydroxide ions ( $\text{OH}^-$ ) or hydrogen ions giving a solution of  $\text{P}^{\text{H}}$  greater or less than 7. Salts of beryllium are highly hydrolyzed and show acidic properties.

Although most salts of beryllium are covalent, Beryllium ion in solution exist as hydrated beryllium ion.

Equation:

Because of the high charge density on beryllium ion, it strongly attracts water molecules towards itself than  $\text{Mg}^{2+}$  with a lower charge density hence Beryllium salts shows more acidic properties than magnesium salts.

The acidity or degree of hydrolysis decreases down the group due decrease in charge density of the cations.

Equation:



### **COMPLEX FORMATION:**

20. What is complex ion?

**Complex ion:** is a negative or positive ion in which group of atoms with lone pairs of electrons (Ligands) or negative charges co-ordination with a central metal atom.

**Complex ion:** is an ion that contains a central ion or atom linked to other atoms, ions or molecules via co-ordination bonds.

### **FACTORS FAVOURING FORMATION OF COMPLEX IONS:**

21. State two factors favouring formation of complex ions.

A complex formation is favoured by:

- ↗ A small and highly charged cation, i.e small and highly charged cations easily attract the lone pair of electrons in the ligand (donor atom).
- ↗ Presence of a suitable empty (vacant) d-orbital to accommodate the lone pairs of electrons from ligand to form a dative bond.

22. Explain why formation of complex ions decreases down the group (II) elements.

The tendency of group (II) elements to form complexes decreases down the group is due to decreasing charge density of the cation as the ionic radius increases.

This tends to a decrease in the nuclear charge attraction for the lone pair of electron down the group, hence decrease in the ability to form complexes.

Beryllium is able to form complexes because it forms cation with the smallest ionic radius with high charge density. The nucleus can strongly attract lone pairs from ligands, hence forming complexes.

Examples:

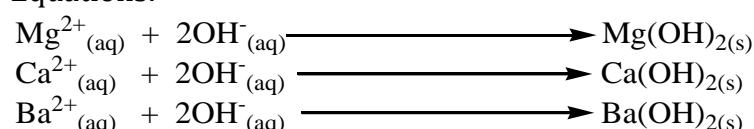


### **IDENTIFICATIONS OF $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ and $\text{Ba}^{2+}$ :**

#### **Dilute Sodium hydroxide Solution until in excess:**

A white precipitate insoluble in excess is observed by  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Ba}^{2+}$

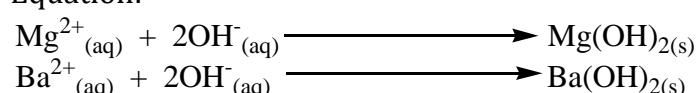
Equations:



#### **Dilute Ammonia solution until in excess**

$\text{Ba}^{2+}$  and  $\text{Mg}^{2+}$  - White precipitate insoluble in excess.

Equation:

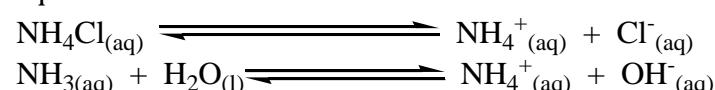


The white precipitate of magnesium hydroxide dissolves in the presence of ammonium chloride.

Why?

This is because ammonium chloride is a strong electrolyte which dissociates completely to form ammonium ion,  $\text{NH}_4^+$  which suppresses the ionization of aqueous ammonia due to common ion effect. Therefore the concentration of Hydroxyl ion is low.

Equations:



$\text{Ca}^{2+}$ - No observable change.

Notes:

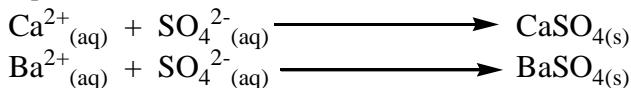
Calcium ions,  $\text{Ca}^{2+}$  do not form white precipitate because aqueous ammonia solution is a weak base, it cannot provide hydroxyl ions in sufficient quantity to exceed the solubility product of calcium hydroxide which is quite high and the hydroxides being very soluble.

**Dilute Sulphuric acid / Sodium Sulphate solution**

$\text{Mg}^{2+}$  - No observable change

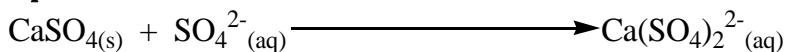
$\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  - White precipitate

Equations:



However, Calcium sulphate is soluble in excess acid due to complex formation.

Equation:



Dilute Sulphuric acid does not precipitate magnesium sulphate hence it's used to differentiate  $\text{Mg}^{2+}$  ion from  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  ions.

**Potassium Chromate (VI) solution and sodium hydroxide.**

Potassium chromate (VI) solution forms a yellow precipitate when added to a solution containing both Calcium,  $\text{Ca}^{2+}$  and Barium,  $\text{Ba}^{2+}$ .

Notes:

Calcium chromate its yellow precipitate is soluble in excess sodium hydroxide solution while the yellow precipitate of Barium chromate is not soluble in excess sodium hydroxide.

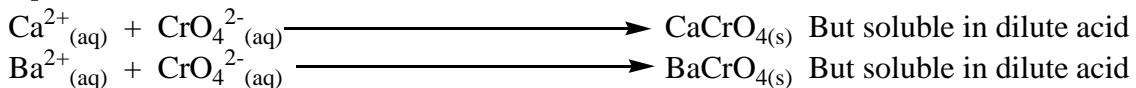
**Potassium Chromate (VI) solution and ethanoic acid**

$\text{Ba}^{2+}$  - Yellow precipitate insoluble in Ethanoic acid

$\text{Ca}^{2+}$  - Yellow precipitate soluble in Ethanoic acid

$\text{Mg}^{2+}$ -No observable change.

Equations:

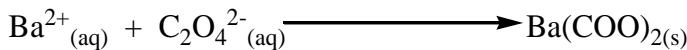


**Ammonium Oxalate (Ethandiote) and Ethanoic acid**

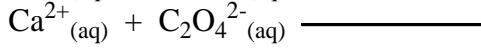
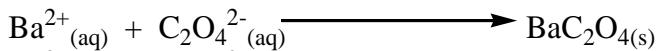
$\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$  - white precipitate

$\text{Mg}^{2+}$ - No observable change

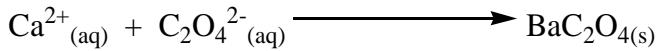
Equations:



Or:



Or:



Notes:

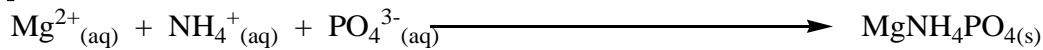
Calcium oxalate is insoluble in hot ethanoic acid but Barium oxalate is soluble (dissolves) in hot ethanoic acid.

This is a test used to differentiate  $\text{Ba}^{2+}$  from  $\text{Ca}^{2+}$  ions.

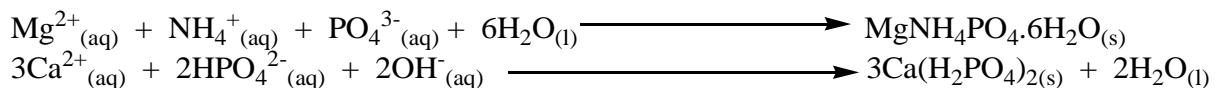
**Disodium Hydrogen Phosphate or sodium phosphate/sodium dihydrogen phosphate**

$\text{Ca}^{2+}, \text{Ba}^{2+}, \text{Mg}^{2+}$  - A white precipitate insoluble in excess Ammonia solution.

Equations:



Or:



Notes:

Calcium phosphate can be converted to super phosphate by treatment with 70% of dilute sulphuric acid.

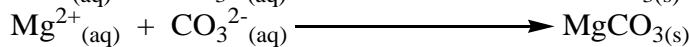
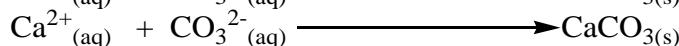
Equation:



### Ammonium carbonate solution

$\text{Ba}^{2+}, \text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions when treated with ammonium carbonate solution, they all reacts to liberate a white precipitate.

Equations:



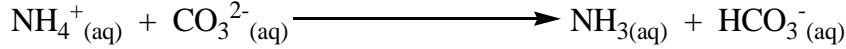
Notes:

In the presence of ammonium chloride, Only Barium,  $\text{Ba}^{2+}$  and Calcium,  $\text{Ca}^{2+}$  ions forms white precipitate and No observable change occurs with Magnesium,  $\text{Mg}^{2+}$ .

Reasons:

Magnesium ions will not form white precipitate with ammonium chloride. Why? This is because of the presence of ammonium chloride that reduces the concentration of carbonate ions below that necessary to exceed that of the solubility product of magnesium carbonate.

Equation:



N.B.  $\text{Zn}^{2+}$  - forms a white precipitate soluble in excess ammonia solution.

23. Name the reagents used to differentiate Magnesium,  $\text{Mg}^{2+}$  from Calcium,  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  ions.

24. Name the reagents used to differentiate Calcium,  $\text{Ca}^{2+}$  from Barium,  $\text{Ba}^{2+}$  ions.

### GROUP IV ELEMENTS:

Elements	<b>6C</b>	<b>14Si</b>	<b>32Ge</b>	<b>50Sn</b>	<b>82Pb</b>
Electronic configuration	$[\text{He}]2s^22p^2$ $1s^22s^22p^2$	$[\text{Ne}]3s^23p^2$ $1s^22s^22p^63s^23p^2$	$[\text{Ar}]4s^24p^2$	$[\text{Kr}]5s^25p^2$	$[\text{Xe}]6s^26p^2$
Atomic radius (nm)	0.077	0.117	0.122	0.141	0.154
Boiling points/°C	4830 <sup>d.</sup>	2680	2830	2270	1730
Melting points/°C	3730 <sup>d.</sup>	1410	937	232	327

Electronegativity	2.5	1.8	1.8	1.8	1.8
1 <sup>st</sup> I.E (KJ/Mol)	1086	787	760	707	715
Type of structure	Giant molecular	Giant molecular similar to diamond		Giant metallic	

### — Existence

Carbon exists as graphite, diamond and amorphous carbon. Silicon occurs as Silica ( $\text{SiO}_2$ ). Tin exist as grey tin and white tin. Lead occurs as an ore in form of galena ( $\text{PbS}$ ).

Notes:

Graphite is a good conductor of electricity because of the presence of mobile electrons along the layers.

It is used as a lubricant because the layers are held by weak Vander Waals forces that hold the layers to slide over each other.

Golden tips:

Carbon is a typical non-metal, silicon and germanium are metalloids while Tin and Lead are typical metals.

Consequently, the character in the bonding in their corresponding compounds shows a trend from covalent to ionic.

All the elements have similar ground state electronic configuration of  $\text{ns}^2\text{np}^2$  promoted to  $\text{ns}^1\text{np}^3$  i.e.,  $\text{sp}^3$  hybridization hence are able to form four covalent bonds with a tetrahedral structure.

### (a) Melting point.

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

Melting point: is a constant temperature at which pure solid is in equilibrium with the pure liquid at atmospheric pressure.

Graph:

Explanation:

The melting points of group IV elements depend on the structure. Carbon and Silicon have giant atomic structures which require a lot of energy to break. However the melting point of silicon is lower than that of carbon since the covalent bonds in silicon atoms are longer thus weaker. Germanium is a Metalloid with an intermediate giant atomic structure. Tin and Lead are weak metals with a metallic structure however lead is more metallic than tin hence has a higher melting point.

Golden tips:

Melting point decrease down the group. The very high melting point of carbon (diamond) is caused by the great energy needed to break the numerous short and strong covalent carbon-carbon bond (catenation). From carbon to Germanium, they adopt a giant atomic structure.

Tin and lead have a giant metallic structure. The strength of the metallic bond depends on the number of electrons donated to the electron cloud and the atomic radius. The strength of the metallic bond decreases with increase in atomic radius.

**(b) Oxidation states**

The elements exhibit both +2 and +4 oxidation states. The +4 oxidation state is attained by promoting one S- electron to an empty P-orbital to avail four electrons from  $ns^2$  &  $np^2$ . Down the group, the  $nS^2$  electrons become more reluctant to participate in bonding.

Golden tips:

The stability of the two possible oxidation states are not the same for all the elements. The +2 oxidation state become more stable down the group from carbon to lead while +4 O.S is more stable from lead to carbon.

This is due to inert pair effect. Therefore the stability of +2 oxidation state increases while that of +4 decreases.

**STABILITY OF GROUP (VI) ELEMENTS:**

Oxidation state:

Elements	+2 O.S		+4 O.S	
Carbon				
Silicon				
Germanium				
Tin				
Lead				
Lead				

25. What is inert pair effect?

Inert pair effect is the inability of the inner s-pair electron to take part in bonding as the atomic radius increases down the group.

**(c) Atomic radius.**

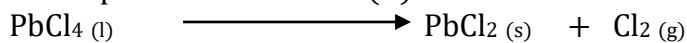
Atomic radius increases down the group because the screening effect outweighs the increased nuclear charge due to the formation of a new energy level. The effective nuclear charge decreases leading in the increase in atomic radius.

1. Explain the cause of inert pair effect.

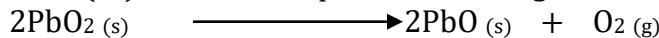
- ↗ AS the radius of the atoms increase down the group there is increasing tendency for the two bonding electrons in the S- Sub energy level to resist taking part in bonding.

**Examples of inert pair effect include:**

Carbon forms carbon tetrachloride while lead (IV) chloride readily decomposes to form Lead (II) chloride and Chlorine



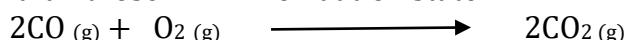
Lead (IV) oxide decomposes on heating to form lead (II) oxide and Oxygen



Lead forms stable compounds in +2 oxidation state. Compounds in +4 oxidation state are very unstable and decompose to compounds in +2 oxidation state.

Carbon monoxide is readily oxidized to carbon dioxide by air.

Carbon dioxide and silicon dioxide are more stable in +4 oxidation state than those in +2 oxidation state.



Carbon and silicon form stable compounds in the +4 oxidation state. Their compounds in +2 oxidation state are unstable and tends to be oxidized to +4 oxidation state.

Germanium both +2 & +4 oxidation states have equal stabilities, therefore, their compounds formed also have equal stabilities.

Tin and lead forms stable compounds in +2 oxidation state.

**CARBON BEHAVES DIFFERENTLY FROM THE REST OF THE GROUP MEMBERS DUE:**

2. State three reasons why carbon behaves differently from the rest of the group members?

- Small Atomic radius
- High electronegativity
- Lack of vacant d-orbital

**SOME OF THE PROPERTIES IN WHICH CARBON DIFFERS FROM THE REST OF THE MEMBERS INCLUDE:**

3. State some properties in carbon is different from the rest of the group members.

- The halides are stable to hydrolysis.
- It forms gaseous oxides unlike other members.
- It forms a stable multiple bonds with itself and with other non-metals.
- Carbon can form a number of hydrocarbons because it can catenate.

Catenation is the ability of the element to form bonds between atoms of the same element.

**UNIQUENESS OF CARBON:**

4. Mention some uniqueness of carbon that you know.

- ☛ Carbon does not shows inert pair effect.
- ☛ Compounds of carbon are inert to acid and alkalis.
- ☛ Carbon is much more electropositive than the rest of the group members.
- ☛ Carbon has only single oxidation state of +4 while the other members have both +2 and +4.
- ☛ All the oxides of carbon are gases at room temperature while the other oxides are solids.
- ☛ Carbon form multiple bonds with itself and other non-metals Examples: C-H, C=C, C=O, C≡N, C≡C.

- ↗ Carbon forms very stable bonds with other carbon atoms resulting in long chains and ring structures Examples: Benzene, Alkanes, Alkenes etc. This is known as catenation.
5. Explain why carbon dioxide exist as a gas at room temperature while other oxides like silicon dioxide exist as solids at room temperature.
- ↗ Because of the high electronegativity value and small atomic radius of carbon, it forms strong double bonds with oxygen that exist as discrete molecule which are held by weak Vander Waals forces of attraction which are easily broken at room temperature hence exist as a gas.
  - ↗ For silicon dioxide, the atomic radius of silicon is big, the molecules are closely packed together in a tetrahedral giant structure by several Si-O single covalent bonds. Hence exist as a solid and to break it, it requires a large amount of energy, hence a high melting points. Diagram:



### **REACTIONS OF GROUP (IV) ELEMENTS:**

6. Discuss the reactions of group (IV) elements with the followings.

**(a) Air:**

Graphite ignites at red heat (with some difficulty) and burns to form carbon dioxide gas.

**Equation:**



However in limited amount of air, Carbon forms carbon monoxide.

**Equation:**



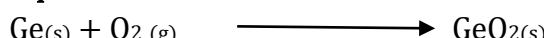
Amorphous silicon burns readily in oxygen at red heat but in air, oxidizes only superficially.

**Equation:**



Germanium burns strongly in air to form germanium oxide.

**Equation:**



Tin is not affected by air at room (ordinary) temperature but it burns in air at a temperature of about 1750K.

**Equation:**



Tin (IV) oxide is more stable than Tin (II) oxide.

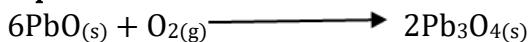
Lead burns in limited supply of air to form a yellow solid just above its melting point.

Equation:



However in excess supply of air, a mixture of lead (II) oxide and Tri-lead tetra oxide (or red lead) is formed.

Equation:



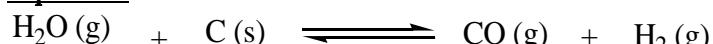
Notes:

All the oxides of the Group (IV) element are Covalent bond except Tin and lead oxide which are ionic character.

**(b) Water**

When heated to high temperature, coke (carbon) reacts with steam to form water gas.

Equation:



Amorphous silicon is unaffected by water, but attacks steam slowly at red heat.

Or

Hot silicon reacts with steam to form silicon dioxide and hydrogen gas or silicon reacts with boiling water or steam to form silicon dioxide.

Equation:



Germanium, Ge and Tin, Sn **DO NOT** react with water in any form.

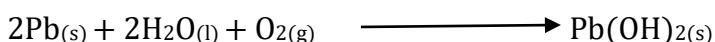
Tin reacts with steam slowly when heated to form Tin (IV) oxide and hydrogen gas.

Equation:



Pure water, free from air, does not attack Lead, the presence of air, however, produces the very sparingly soluble lead (II) hydroxide

Equation:



Notes:

Hard water containing  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$  ions reacts very slowly with lead due to the formation of an insoluble lead (II) carbonate and lead (II) sulphate respectively.

**(c) Acids**

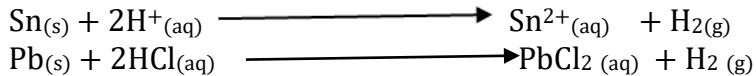
\* Dilute acids.

DILUTE HYDROCHLORIC ACID.

Carbon, Silicon & Germanium (non-metals) **DO NOT** react with dilute hydrochloric acid except Tin and Lead (metals) reacts slowly with cold dilute hydrochloric acid but very vigorously with hot dilute hydrochloric acid forming Tin (II) chloride, Lead (II) chloride and hydrogen gas. The reaction is more rapidly at higher concentrations.

Equations:





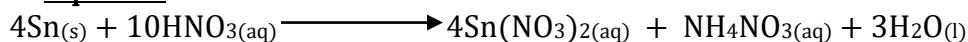
### DILUTE SULPHURIC ACID.

Carbon, Silicon & Germanium DO NOT reacts with dilute sulphuric acid even Tin and Lead DO NOT reacts with dilute sulphuric acid.

### DILUTE NITRIC ACID.

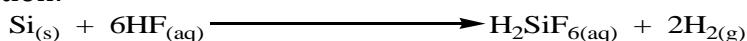
Carbon, Silicon & Germanium DO NOT reacts with dilute nitric acid. Except Tin reacts slowly with cold dilute nitric acid to form usual mixed products of tin (II) nitrate, ammonium nitrate & water.

### Equation:



Silicon only reacts with hydrofluoric acid, owing to the stability of hexafluorosilicate (IV) complex,  $\text{SiF}_6^{2-}$ , formed and NO reactions with any metal of Group (IV) elements.

### Equation:



Lead reacts with ethanoic acid in presence of air to form lead (II) ethanoate.

### Equation:

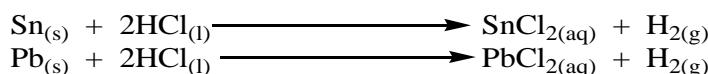


### \* Concentrated acids.

### CONCENTRATED HYDROCHLORIC ACID.

Hot concentrated hydrochloric acid reacts with Tin and Lead to form Tin (II) chloride and Lead (II) chloride respectively with evolution of a colourless gas i.e hydrogen gas.

### Equations:

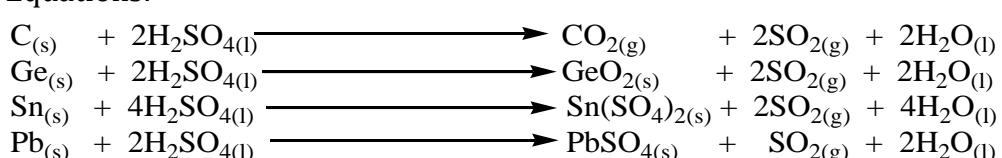


Carbon, Silicon and Germanium DONOT reacts with concentrated hydrochloric acid.

### CONCENTRATED SULPHURIC ACID.

Carbon, Germanium, Tin & lead reacts with hot concentrated sulphuric acid to form colourless gases and water respectively.

### Equations:



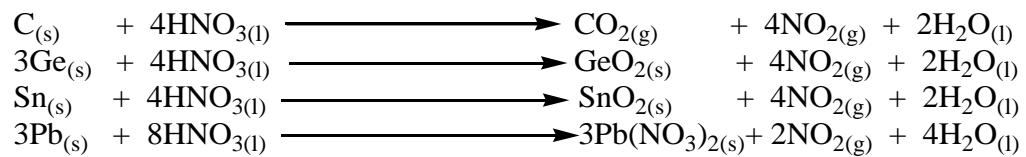
Silicon DOES NOT reacts with hot concentrated sulphuric acid.

### CONCENTRATED NITRIC ACID.

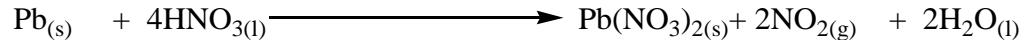
Hot (warm) concentrated nitric acid oxidizes both Tin and Germanium to their metal oxides while carbon to carbon dioxide gas and nitrogen dioxide gas respectively then oxidizes Lead to Lead (II) nitrate with evolution of nitrogen dioxide gas.

Silicon **DO NOT** reacts with hot concentrated nitric acid.

**Equations:**



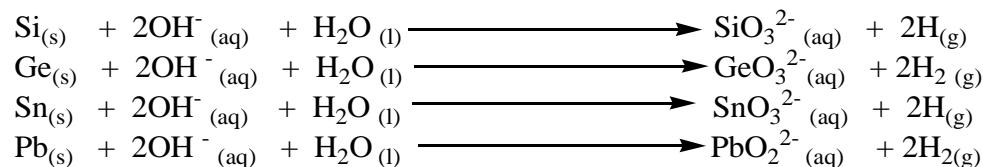
Or:



(d) **Alkalies**

Silicon, Germanium, Tin and lead reacts with hot concentrated alkalis to form Silicate, Germanate (IV), Stannate (II) and Plumbate (II) ions with evolution of a colourless gas respectively.

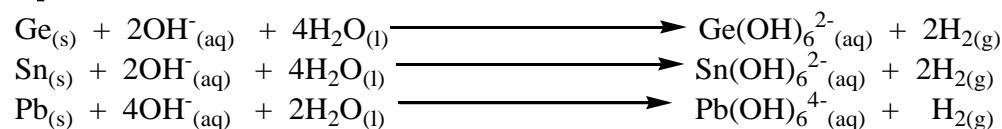
**Equations:**



**Notes:**

$\text{SiO}_3^{2-}$ ,  $\text{GeO}_3^{2-}$ ,  $\text{SnO}_3^{2-}$  &  $\text{PbO}_2^{2-}$  are often written in hydrated form as follows.

**Equations:**

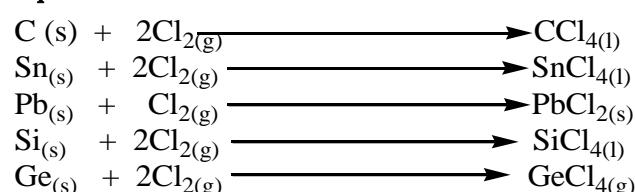


Carbon **DO NOT** reacts with alkalis.

(d) **Non metals**

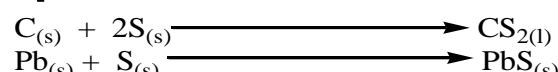
With the exception of lead, all the elements combine with chlorine gas when heated to form tetrachloride BUT lead forms lead (II) chloride & **NOT VERY SURE** about carbon and chlorine gas.

**Equations:**



With the exception of lead, all the elements combine with sulphur when heated to form disulphides BUT lead forms lead (II) sulphide.

**Equations:**



### COMPOUNDS OF GROUP (IV) ELEMENTS:

Elements	T <sub>m</sub> /K	T <sub>b</sub> /K	Electronic configuration
Carbon, <sub>6</sub> C	3930	Sublimes	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup> [He]2p <sup>2</sup>
Silicon, <sub>14</sub> Si	1683	2628	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>2</sup> [Ne] 3s <sup>2</sup> 3p <sup>2</sup>
Germanium, <sub>32</sub> Ge	1210	3103	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>2</sup> [Ar] 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>2</sup>
Tin, <sub>50</sub> Sn	505	2533	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>6</sup> 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>2</sup> [Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>2</sup>
Lead, <sub>82</sub> Pb	601	2013	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>6</sup> 4d <sup>10</sup> 4f <sup>14</sup> 5s <sup>2</sup> 5p <sup>6</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup> [Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>

Keys: T<sub>m</sub>/K = Melting points /Kelvin, T<sub>b</sub>/K = Boiling points /Kelvin, [] = Argon gas core

Elements	Carbon	Silicon	Germanium	Tin	Lead		
Monoxides (+2 O.S)	CO	-	GeO	SnO	PbO		
Physical states	Colourless gas	-	Black powder	Black powder	Brown (cold)		
Nature	Weakly acidic	-	Amphoteric				
Dioxides (+4 O.S)	CO <sub>2</sub>	SiO <sub>2</sub>	GeO <sub>2</sub>	SnO <sub>2</sub>	PbO <sub>2</sub>		
Physical states	Colourless gas	White solid	White solid	White solid	Brown solid		
M.pts(°C)	-56.5	1700	1116	1827	752(Decomposes)		
Nature	Acidic		Amphoteric				
Dichlorides	-		GeCl <sub>2</sub>	SnCl <sub>2</sub>	PbCl <sub>2</sub>		
Physical states	"		Pale yellow	White solid			
Nature	"		Ionic bond		Ionic bond		
Tetrachlorides	CCl <sub>4</sub>	SiCl <sub>4</sub>	GeCl <sub>4</sub>	SnCl <sub>4</sub>	PbCl <sub>4</sub>		
Physical states	Colourless liquid			Yellow liquid			
Nature	Covalent bonds			Ionic bonds			
Structures	Simple molecular	Giant molecular					
Bonding	Covalent	Ionic					

Hydrides	Methane, CH <sub>4</sub>	Silane, SiH <sub>4</sub>	Germanane GeH <sub>4</sub>	Stannane, SnH <sub>4</sub>	Plumbane, PbH <sub>4</sub>
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## A. OXIDES:

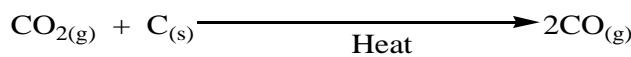
There are two forms of oxides namely:

(a) Monoxide, MO where the oxidation state of the elements is +2.

-Carbon monoxide, CO

It can be prepared by passing carbon dioxide gas over heated coke (carbon).

Equation:



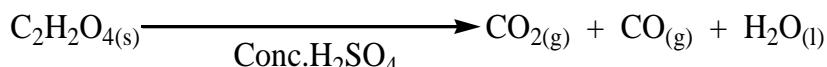
By dehydration of methanoic acid with concentrated sulphuric acid.

Equation:



By the action of concentrated sulphuric acid on oxalic acid.

Equation:



## PROPERTIES:

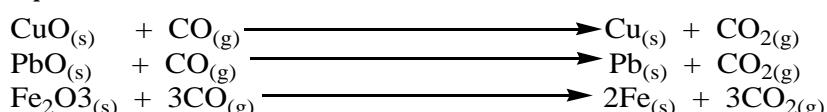
It has a linear shape and it's covalent.

It is a colourless, odourless & extremely poisonous gas.

It is a neutral oxide hence it does not react with acids, water & base.

It is a reducing agent, it reduces metallic oxides to respectively metals and is itself oxidized to carbon dioxide gas.

Equations:



It burns with a blue flame in air forming carbon dioxide gas.

Equation:



-Silicon (II) oxide, SiO

It is very unstable and known to exist in the vapour phase and it can be prepared by heating silicon in silica.

Equation:



-Germanium (II) oxide, GeO

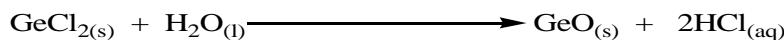
It is prepared by reducing Germanium (IV) oxide when heated with Germanium. It is amphoteric oxide.

Equation:



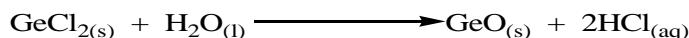
It can also be prepared by hydrolysis of Germanium (II) chloride.

Equation:



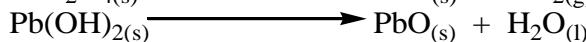
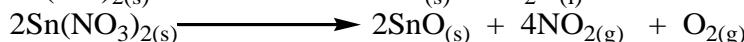
Germanium (II) oxide (Germanium monoxide), GeO can be prepared also by the action of water on Germanium (II) chloride.

Equation:



-Tin and Lead (II) oxides are prepared by the action of heat on their hydroxides, nitrates or oxalates.

Equations:



### **Golden tips on BASICITY OF THE MONOXIDES:**

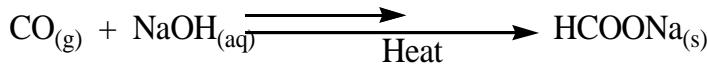
Carbon monoxide, CO and Silicon (II) Oxide, SiO are neutral oxide, simple molecular structures are Covalent bonds in nature while GeO, SnO and PbO are amphoteric oxides predominantly with giant ionic structures.

Notes:

Basic character increases down the group. For an individual element, basic character increases with decreasing oxidation state number e.g. CO is weakly acidic but CO<sub>2</sub> is acidic.

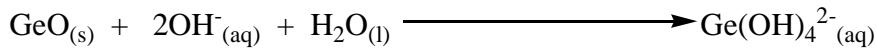
Carbon monoxide is slightly acidic and reacts with hot solution of sodium hydroxide to form sodium methanoate.

Equation:

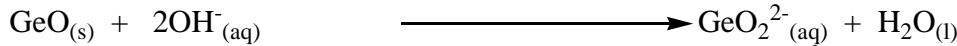


GeO, SnO & PbO are amphoteric through predominantly basic. They form salts with dilute acids and also reacts with hot concentrated alkalis to form complex salts of names Germanate, Stannate, & Plumbate (II) ions respectively.

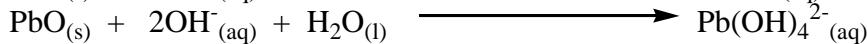
Equations:



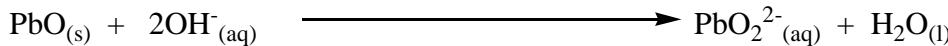
Or:



Or:

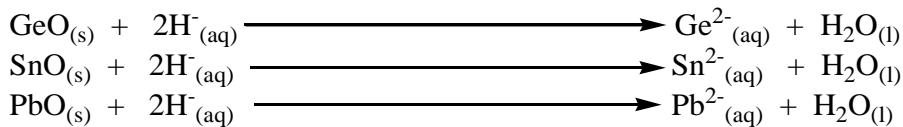


Or:



They also reacts with dilute mineral acids to form salts and water respectively.

**Equations:**



(b) Dioxides,  $\text{MO}_2$  where the oxidation state of the elements is +4.

Oxides	$\text{CO}_2$	$\text{SiO}_2$	$\text{GeO}_2$	$\text{SnO}_2$	$\text{PbO}_2$
M.pts( $^{\circ}\text{C}$ )	-56.5	2590	1116	1827	752 (Sublimes)

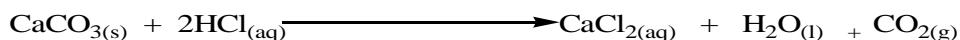
**Explanations:**

Carbon dioxide gas is a simple molecular hence low melting points. Silicon dioxide forms a giant molecular structure with many covalent bonds that have to be broken before melting occurs. This explains its high melting points. The rest of the oxides adopt intermediate molecular and ionic structures.

-Carbon dioxide,  $\text{CO}_2$ .

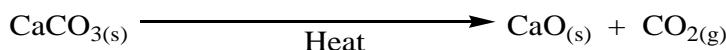
It is prepared by the action of dilute hydrochloric acid on calcium carbonate.

Equation:



On large scale, it is prepared by heating calcium carbonate.

Equation:



### **PROPERTIES:**

Carbon dioxide gas is an acidic oxide.

Carbon dioxide gas is a colourless, it is moderately soluble in water forming weak carbonic acid.

Equation:



7. Explain briefly the following observations below:

- a) Carbon dioxide gas is a gas at room temperature whereas silicon (IV) oxide is a solid with a high temperature.

The **atomic radius of carbon atom is smaller than that of silicon**. Carbon and Oxygen atoms approach each other's closely, their p-orbitals overlap leading to formation of stable multiple bonds between carbon and oxygen atoms.

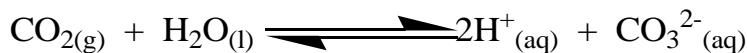
Consequently, only discrete molecules of carbon dioxide are formed, held together by only weak Van der Waal's forces.

There's no overlap of p-orbitals in silicon dioxide because of the large size of the silicon atom. Silicon forms only single very strong covalent bonds with four other oxygen atoms. This gives silicon dioxide a 3-dimensional giant structure which is a solid.

b) A solution of sodium thiosulphate becomes cloudy with the formation of a yellow precipitate when left standing in air.

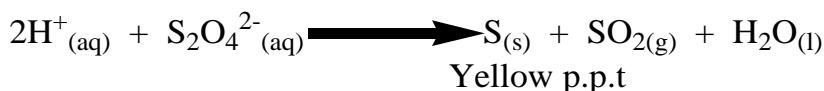
**Carbon dioxide gas from air dissolves in solution to form weak carbonic acid.**

**Equation:**



The **hydrogen, H<sup>+</sup> ions** formed reacts with the **thiosulphate, S<sub>2</sub>O<sub>4</sub><sup>2-</sup> ions** to form **yellow insoluble precipitate**.

**Equation:**



-Silicon (IV) oxide, SiO<sub>2</sub>.

It is prepared by hydrolysis of silane.

**Equation:**



-Germanium (IV) oxide, GeO<sub>2</sub>.

It is prepared by hydrolysis of Germanium (II) or (IV) chloride.

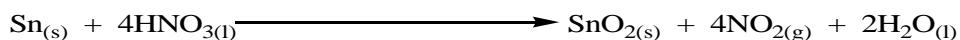
**Equation:**



-Tin (IV) oxide, SnO<sub>2</sub>.

It is prepared by the action of concentrated nitric acid on tin metal. This amphoteric oxide.

**Equation:**



-Lead (IV) oxide, PbO<sub>2</sub>.

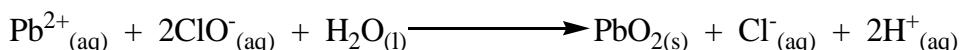
Lead (IV) oxide is prepared by the action of concentrated nitric acid on Tri lead tetra oxide.

**Equation:**



It can be also be prepared by oxidizing lead (II) salt using warm sodium chlorate (I).

**Equation:**



### **Golden tips on BASICITY OF THE DIOXIDES:**

(a). Reaction with alkalis.

8. Discuss reactions of the oxides of each element with dilute sodium hydroxide solution.

CO, CO<sub>2</sub>, SiO<sub>2</sub>, GeO<sub>2</sub>, SnO, SnO<sub>2</sub> & PbO, PbO<sub>2</sub> are amphoteric oxides though acidic character predominates. They reacts with hot concentrated alkalis to form complex soluble salts.

But carbon dioxide gas is more acidic than other dioxides hence it can react with cold dilute alkalis to form sodium carbonate.

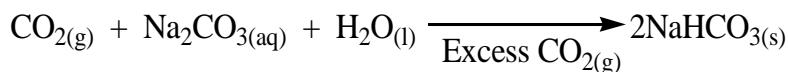
Equation:



Note:

When carbon dioxide gas is in excess, a white precipitate of sodium hydrogen carbonate is formed.

Equation:



Burning magnesium reduces carbon dioxide gas to a black mass of carbon and a white ash of magnesium oxide.

Equation:



Carbon monoxide gas reacts with hot dilute sodium hydroxide solution to form sodium methanoate.

Equation:



Silicon dioxide [silicon (IV) oxide] reacts with dilute sodium hydroxide solution forming sodium silicate and water.

Equation:



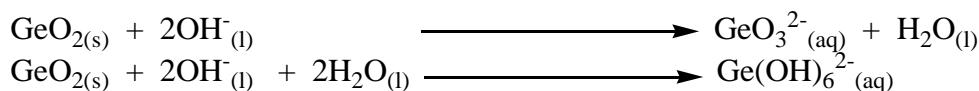
Burning magnesium reduces silicon dioxide or silicon dioxide gas to silicon and a white ash of magnesium oxide.

Equation:



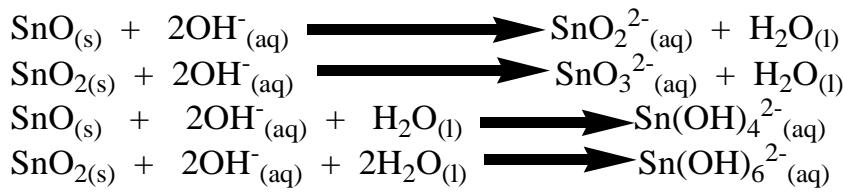
Germium dioxide [germium (IV) oxide reacts with dilute sodium hydroxide forming germinate (IV) oxide.

Equation:

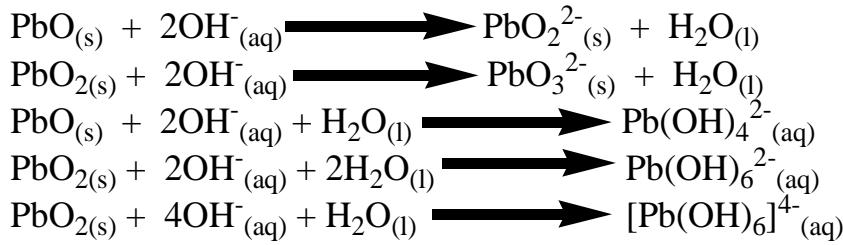


Tin (II) oxide and Tin (IV) oxide reacts with dilute sodium hydroxide solution to form stannate (IV) oxide.

Equation:



Lead (II) oxide and Lead (IV) oxide reacts with dilute sodium hydroxide solution to form plumbate (IV) oxide.

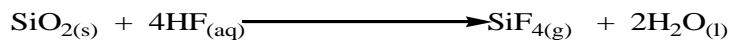


(a). Reaction with acids.

Both Carbon dioxide & Silicon (IV) oxide are acidic in nature and therefore, they DON'T react with any dilute non-oxidizing acids.

Silicon dioxide (Silicon (IV) oxide) reacts ONLY with dilute hydrofluoric acid to form silicon tetraflouride.

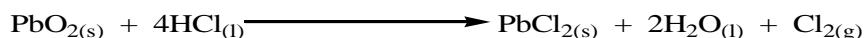
Equation:



Lead (IV) oxide reacts with warm (hot) concentrated hydrochloric acid.

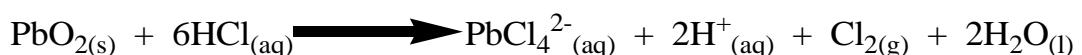
Which it oxidizes the acid to chlorine gas and leaves a white precipitate of lead (II) chloride.

Equation:



Or:

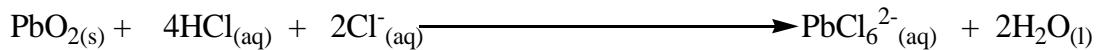
Equation:



Notes:

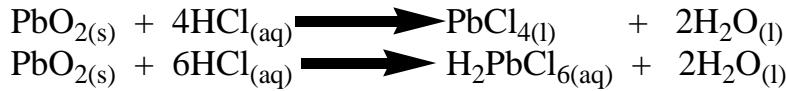
When excess concentrated hydrochloric acid is reacted with lead (IV) oxide at  $0^\circ\text{C}$  (Cold), it forms a complex ion.

Equation:



Lead (IV) oxide reacts with cold concentrated hydrochloric acid to form lead (IV) chloride and water.

Equation:



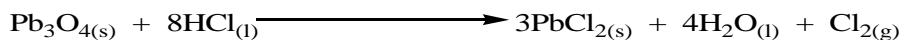
Addition of concentrated ammonium chloride to the complex produces a yellow precipitate. i.e.

Equation:



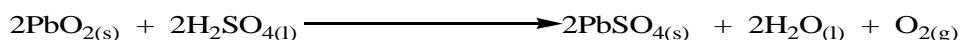
Red lead oxide (Tri Lead tetra oxide) also gives a similar reactions.

Equation:



Lead (IV) oxide reacts with heated concentrated sulphuric acid to form a white solid of lead (II) sulphate with evolution of a colourless gas.

Equation:



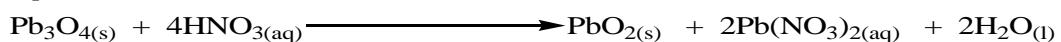
Red lead (Tri Lead tetra oxide) reacts with heated concentrated sulphuric acid to form a white solid of lead (II) sulphate with evolution of a colourless gas.

Equation:

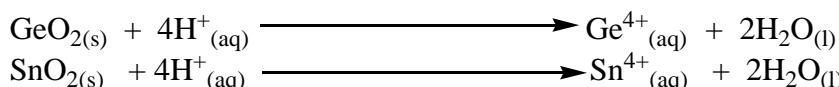


Red lead (Tri Lead tetra oxide) reacts with hot concentrated nitric acid to form a white solid of lead (IV) oxide and lead (II) nitrate respectively.

Equation:



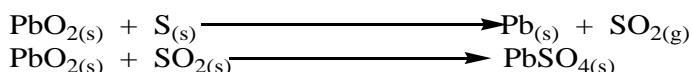
Germanium & Tin (IV) oxides reacts with dilute acids to form salts and water respectively. Equations:



### Golden tips:

-lead (IV) oxide oxidizes sulphur to sulphur dioxide gas, the sulphur dioxide gas formed reacts with excess lead (IV) oxide to form a white solid of lead (II) sulphate.

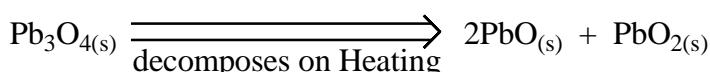
Equations



Red lead (Tri lead tetra oxides,  $\text{Pb}_3\text{O}_4$ ).

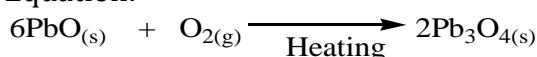
This is a mixed oxide. It contains both lead (II) and (IV) oxides.

Equation:



It can be prepared by heating lead (II) oxide in oxygen gas at a temperature of about  $400^\circ\text{C}$ .

Equation:



### Acidic nature of the oxides:

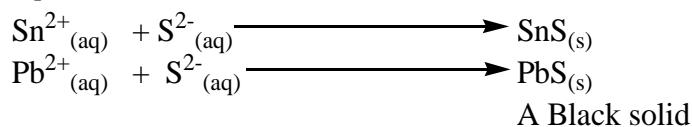
☞ The dioxides are more acidic than the monoxides (monoxides are more basic than dioxides). For example

Carbon monoxide is neutral but carbon dioxide is acidic and it reacts with alkalis to form carbonates.

- Germanium (II) oxide is amphoteric and reacts with both acids and alkalis to form salts while germanium (IV) oxide is acidic, only reacting with alkalis to form salts and not acids.
  - The acidity of the oxides decreases down the group as the metallic nature of the elements increases. For example
  - Carbon dioxide, silicon dioxide and germanium dioxide are acidic and react with alkalis to form the corresponding salts
  - Tin (IV) oxide and lead (IV) oxide are amphoteric, and react with both acids and alkalis to form salts
- A solution containing tin (II) ions and lead (II) ions react with hydrogen sulphide gas to precipitate the metal sulphide. State what is observed and write an equation for the reaction in both case.

A black solid of both tin and lead (II) sulphide are formed.

Equations:



## B. CHLORIDES:

They form two types of chlorides. Namely: Dichlorides,  $\text{MCl}_2$  and Tetrachlorides,  $\text{MCl}_4$ . However, carbon and silicon **DO NOT** form chlorides in the +2 oxidation state.

Elements	Carbon	Silicon	Germanium	Tin	Lead
Dichlorides	-	-	Pale yellow	White solid	
Compounds	-	-	$\text{GeCl}_2$	$\text{SnCl}_2$	$\text{PbCl}_2$
Tetrachlorides	Colourless liquid				Yellow liquid
Compounds	$\text{CCl}_4$	$\text{SiCl}_4$	$\text{GeCl}_4$	$\text{SnCl}_4$	$\text{PbCl}_4$
Bonding	Covalent			Ionic	
B.pt $(^{\circ}\text{C})$	78	58	83	114	Decomposes

The dichlorides are solids while the tetrachlorides are volatile liquids. Lead (IV) chloride exists but lead (IV) bromide and iodide do not exist. This is because bromine and iodine are not sufficiently strong oxidizing agents to convert  $\text{Pb}^{2+}$  to  $\text{Pb}^{4+}$ .

The increase in boiling point of the tetrachloride is due to increase in the molecular size (mass) leading to increase in the magnitude of the Vander Waals force of attraction.

- Briefly explain each of the following in terms of types of chemical bonding involved.
  - The melting points of tetrahalides of group (IV) elements increases from carbon to tin.  
All tetrahalides of group (IV) are covalent compounds which are held together by weak Van der Waal's forces. The increase in boiling points from the

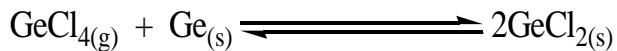
tetrahalides of carbon to tin is because of increasing magnitude of the Van der Waal's forces that increases as the size of the tetrahalides increases.

b) Carbon dioxide is a gas whereas silicon dioxide is a solid of high melting point. Both carbon dioxide and silicon dioxide are covalent compounds. Silicon dioxide has a giant three-dimensional network of very many strong covalent bonds which is responsible for its very high melting point while carbon dioxide molecules are held together by weak Van der Waal's forces which are easily overcome.

### **PREPARATIONS DICHLORIDES, MCl<sub>2</sub>:**

-Germanium (II) chloride is a pale yellow solid made by passing a vapour of germanium (IV) over hot germanium.

Equation:



-Tin (II) chloride is a white crystalline solid prepared by heating Tin with moderately concentrated hydrochloric acid, and crystallizes as the dehydrate, of chemical formula of SnCl<sub>2</sub>.2H<sub>2</sub>O, Known as tin salt.

Equation:



-Tin (II) chloride is also obtained by heating Tin in dry hydrogen chloride gas.

Equation:



-Lead (II) chloride is a white precipitate obtained by the action of cold dilute hydrochloric acid on lead salts or a solution containing Pb<sup>2+</sup> ion.

Equation:



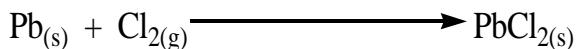
-Lead (II) chloride is also prepared by the action of hot concentrated hydrochloric acid on lead metal.

Equation:



-Lead (II) chloride is also prepared by passing dry chlorine gas over heated lead metal.

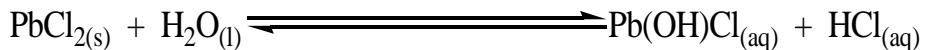
Equation:



Notes:

Lead (II) chloride is insoluble in cold water and it does not undergo hydrolysis but soluble in hot water and it undergo hydrolysis forming basic salt which is soluble.

Equation:



Lead (II) Chloride is sparingly soluble in water and does not undergo hydrolysis. However it dissolves on heating since solubility increases with temperature.

Equation:



Lead (II) chloride is also soluble (dissolves) in concentrated hydrochloric acid due to the formation of a soluble complex known as Tetra chloro plumbate (II) ions.

Equation:



### **REACTION WITH WATER (HYDROLYSIS) OF DICHLORIDES:**

General, the dichlorides hydrolyses to give monoxides (or hydroxides) and hydrogen chloride gas. And only formed by Germanium, Tin & Lead but those of Germanium & Tin are less stable than that of lead (II) chloride.

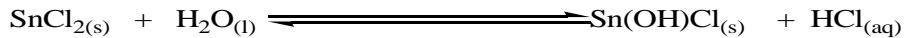
-Germanium (II) chloride hydrolyses in water to form Germanium (II) oxide and hydrochloride gas.

Equation:



-Tin (II) chloride in cold water undergoes partial hydrolysis to form a (cloudy solution) or white basic hydroxide and hydrochloric acid.

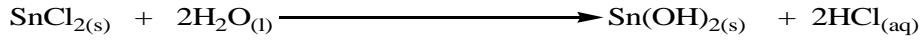
Equation:



Note:

However, Tin (II) chloride undergoes complete hydrolysis in hot excess water to form Tin (II) hydroxide and hydrochloric acid.

Equation:



The hydrolysis is partial because the charge density of  $\text{Sn}^{2+}$  ion is not high enough in order for it to undergo complete hydrolysis.

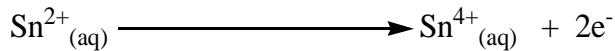
### **REDUCING PROPERTIES OF TIN (II) CHLORIDE:**

3. Explain the reducing properties of Tin (II) chloride.

A solution of Tin (II) chloride in moderately concentrated hydrochloric acid is a reducing agent.

The Tin (II) ion,  $\text{Sn}^{2+}$  donates two electrons to form Tin (IV) ion,  $\text{Sn}^{4+}$ .

Equation:

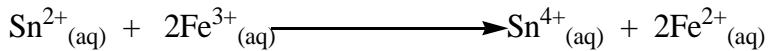


4. Explain the reducing properties of Tin (II) chloride with the followings and state what is observed & write an equation for the reaction in each case.

- a) Iron (III) salt.

Tin (II) chloride reduces an iron (III) salt in solution to the corresponding Iron (II) salt, the solution turns from yellow (or brown) to pale green (or dirty green).

Equations:



b) Iodine.

Tin (II) chloride reduces iodine, usually dissolved in potassium iodide solution, to the iodine ion, the solution turns from dark brown to colourless.

Equation:



c) Potassium manganite (VII).

Tin (II) chloride decolorized acidified potassium manganite (VII) solution rapidly producing manganese (II) ion as the principal product. I.e the purple colour turns colourless.

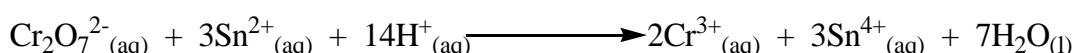
Equation:



d) Potassium dichromate (VI).

Tin (II) chloride reduces acidified potassium dichromate (VI) from golden yellow solution to a green solution containing the chromium (II) ion.

Equation:

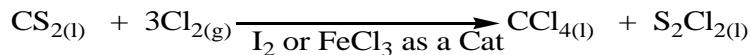


### **PREPARATIONS TETRACHLORIDES, MCL<sub>4</sub>:**

-Carbon tetrachloride, CCl<sub>4</sub>.

Carbon tetrachloride is prepared by passing chlorine gas through Carbon disulphide solution in the presence of iron (III) chloride as a catalyst at a temperature of about 30°C or boiling under reflux, in the presence of iodine as a catalyst.

Equation:



5. Explain why the bonds in Carbon tetrachloride are polar but the whole Carbon tetrachloride molecules is non-polar.

Chlorine atom is more electronegative than carbon atom, it attracts the bonding electrons towards itself which gives rise to a dipole moment towards chlorine atom.

The chlorine atom acquire a partial negative charge while carbon atom acquire a partial positive charge.

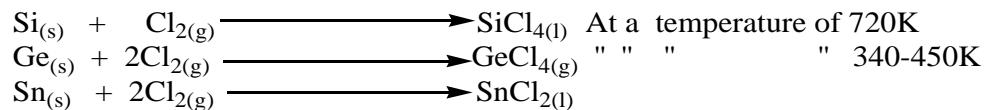
This unequal distribution of the bonds in electrons is responsible for the bond polarity in carbon tetrachloride.

However, the carbon –chloride bonds are symmetrically arranged in the carbon tetrachloride because the chlorine atom is tetrahedrally arranged around the carbon atom.

The bond polarity effect cancels each other so that the net-dipole moment is zero, hence the molecule is non-polar.

-Silicon,  $\text{SiCl}_4$ , Germanium,  $\text{GeCl}_4$  & Tin tetrachloride,  $\text{SnCl}_4$  are prepared by direct synthesis (passing dry chlorine gas).

**Equations:**



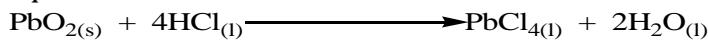
-Silicon tetrachloride,  $\text{SiCl}_4$  can also be prepared by passing dry heated chlorine gas over a mixture of silica and carbon.

**Equation:**



-Lead tetrachloride,  $\text{PbCl}_4$  can be prepared by the action of cold concentrated hydrochloric acid on lead (IV) oxide and it's obtained as a yellow liquid.

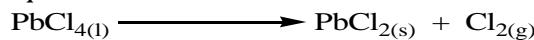
**Equation:**



**Note:**

Lead (IV) chloride is an oily yellow liquid. It decomposes on heating to form a white crystals of lead (IV) chloride and a greenish yellow gas (i.e. chlorine gas) is evolved.

**Equation:**



### **THERMAL STABILITY OF THE TETRACHLORIDE:**

The tetrachlorides of carbon, silicon & germanium are stable to heat, but those of Tin & Lead decomposes on heating to form dichlorides.

6. The thermal stability of the tetrachlorides are in the order of  $\text{CCl}_4 > \text{SiCl}_4 > \text{GeCl}_4 > \text{SnCl}_4 > \text{PbCl}_4$ . Explain the observation.  
Down the group, the atomic radius of the group (IV) elements increases down the group, the bond length between the elements and chlorine atoms increases, the bonds strength decreases, therefore the energy required to break the bonds decrease.
7. State what would be observed and write equations for the reaction that would take place, if any, when the followings are treated with water.

(i)  $\text{CCl}_4$

**Observation:**

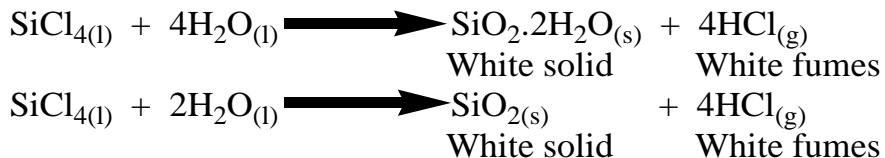
No observable change.

**Equation:**

No reaction

(ii)  $\text{SiCl}_4$

**Equations:**

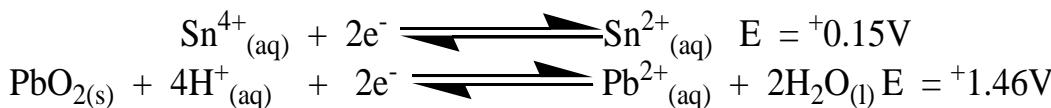


(iii)  $\text{SiCl}_4$

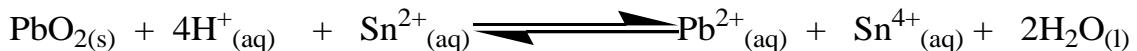
Equation:



8. Equations for some half-cell reactions are shown below:



Write the overall cell equation for the spontaneously feasible reaction.



Calculate the  $E^\circ$  above.

$$E_{\text{cell}} = E_R - E_L$$

$$E_{\text{cell}} = +1.46 - +0.15$$

$$E_{\text{cell}} = +1.31\text{V}$$

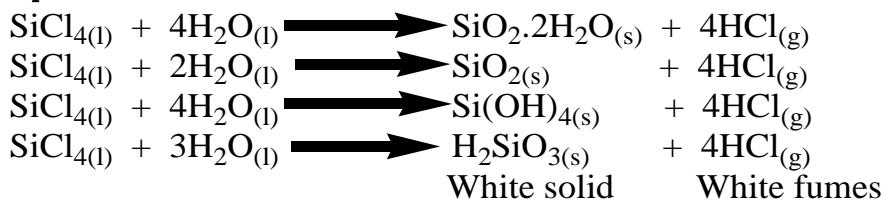
9. Carbon, Silicon, Tin and Lead are elements of group (IV) of the periodic table, discuss the reactions of each chlorides with water.

- ↗ Carbon tetrachloride **DOES NOT** hydrolyze in water it is inert. [The carbon atom lacks d-orbitals to accept electrons].
- ↗ Silicon tetrachloride hydrolyzes in water to form silicic acid and hydrogen chloride gas.

Notes:

It dissolves in water forming a white solid and a white fumes.

Equations:



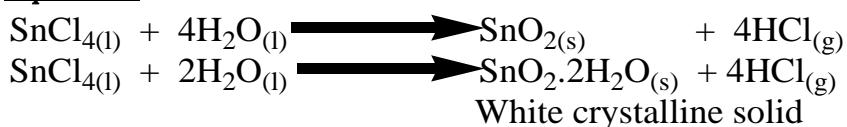
A white fumes [Hydrogen chloride gas] is formed when in contact with ammonia gas forming a dense white fume of ammonium chloride.

Equation:



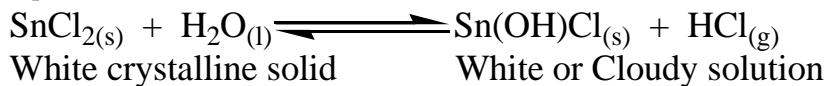
- ↗ Tin (IV) chloride hydrolyzes in water to give hydrated Tin (IV) oxide and hydrogen chloride gas.

Equations:



- ✓ However, Tin (II) chloride [a white crystalline solid] undergoes ONLY partial hydrolysis to form a basic chloride or white basic hydroxide or cloudy solution and hydrogen chloride gas.

Equation:



A white fumes [Hydrogen chloride gas] is formed when in contact with ammonia gas forming a dense white fume of ammonium chloride.

Equation:



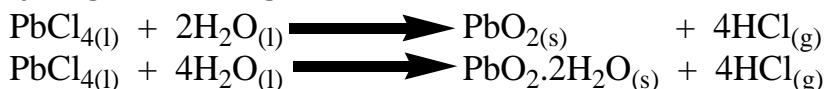
- ✓ But in HOT and EXCESS, Tin (II) chloride forms Tin (II) hydroxide.

Equation:



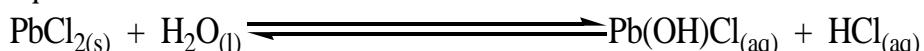
The hydrolysis is partial because the charge density of  $\text{Sn}^{2+}$  ion is not high enough in order for it to undergo complete hydrolysis.

- ✗ Lead (IV) chloride hydrolyzes to form hydrated lead (IV) oxide and hydrogen chloride gas.



- ✗ Lead (II) chloride is insoluble in cold water and it does not undergo hydrolysis but soluble in hot water and it undergo hydrolysis forming basic salt which is soluble.

Equation:



Lead (II) Chloride is sparingly soluble in water and does not undergo hydrolysis. However it dissolves on heating since solubility increases with temperature.

Equation:



Lead (II) chloride is also soluble (dissolves) in concentrated hydrochloric acid due to the formation of a soluble complex known as Tetra chloro plumbate (II) ions.

Equation:

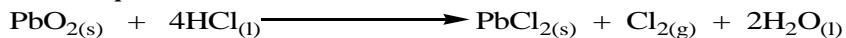


10. A sample of lead (IV) oxide was treated with warm concentrated hydrochloric acid.

- (a) State what was observed.

A white precipitate is formed and greenish-yellow gas is evolved.

- (b) Write equation for the reaction.

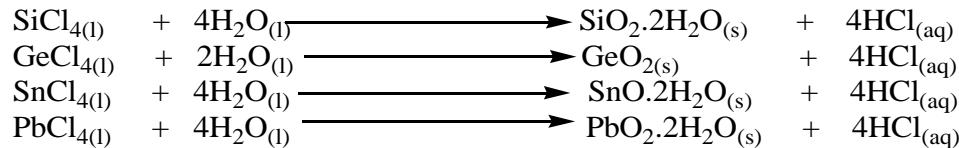


### REACTION OF TETRACHLORIDES WITH WATER (HYDROLYSIS):

11. Discuss the reaction of tetrachlorides of group (IV) elements with water.

- Carbon tetrachloride does not undergo hydrolysis with water because carbon lacks empty d-orbital to accept lone pair of electrons from water.
- The rest of the tetrachlorides are hydrolyzed by water because their central atoms have empty d-orbitals to accept lone pair of electrons from water molecules forming a white (misty) fumes of hydrogen chloride gas.
- The tendency to undergo hydrolysis in water is in the order of  $\text{SiCl}_4 > \text{GeCl}_4 > \text{SnCl}_4 > \text{PbCl}_4$ .
- $\text{SiCl}_4$  is highly hydrolysed even in damp air because  $\text{Si}^{4+}$  ion has the highest charge density. It strongly attract the lone pair of electron from water while  $\text{Pb}^{4+}$  ion has the least charge density and  $\text{PbCl}_4$  is least hydrolyzed.

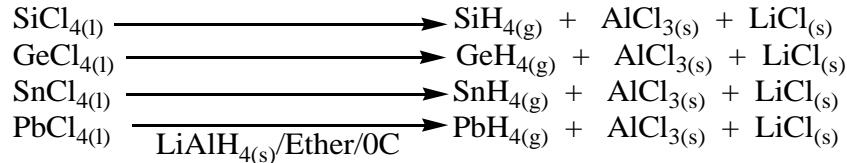
Equations:



### C. HYDRIDES:

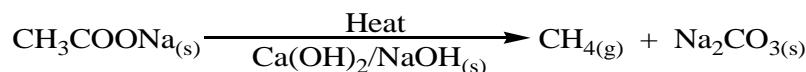
Carbon forms the largest number of hydrides followed by silicon. The striking stability of hydrides of carbon compared with hydrides of other group (IV) elements is attributed to the relatively high C-C bond energy, high C-H bond energy and the fact that carbon does not have easily accessible d-orbitals. Apart from methane, other hydrides are made by reduction of corresponding tetrachloride using lithium aluminium tetra hydride at  $0^\circ\text{C}$  in the presence of dry ether.

Equations:



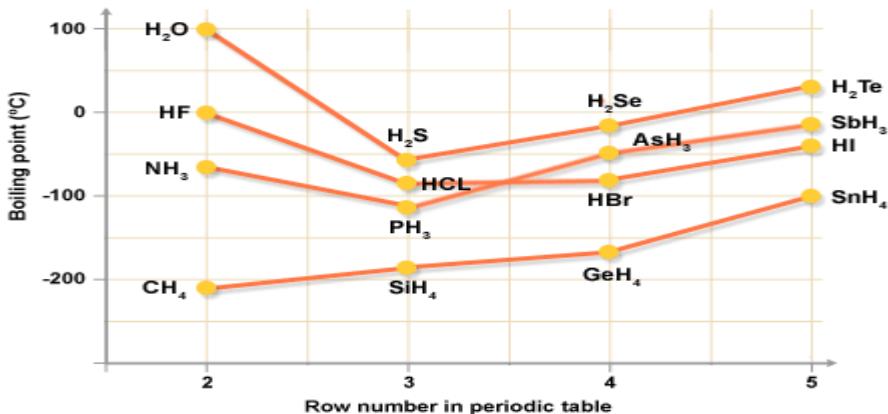
Methane is made by decarboxylation of sodium ethanoate,

Equation:



### PHYSICAL PROPERTIES:

- ☛ They are all colourless gases at room temperature.
- ☛ They are all covalent compounds with tetrahedral shape.
- ☛ They have low melting & boiling points because they have simple molecular structure with weak Van der Waals force of attraction between the molecules.
- ☛ The boiling point increases down the group in the order of  $\text{CH}_4 < \text{SiH}_4 < \text{GeH}_4 < \text{SnH}_4 < \text{PbH}_4$ . This is because the magnitude of the Vander Waals forces of attraction increases down the group with increase in molecular mass (molecular size).

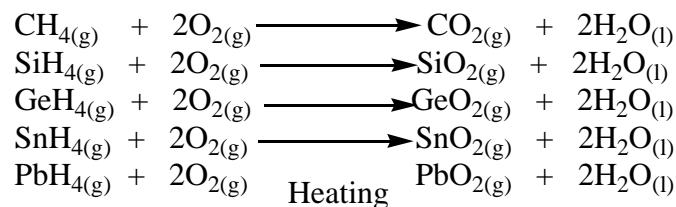


☞ The thermal stability decreases down the group. Down the group, atomic radius increases bond length increases and the bond strength decreases. When heated, they tend to easily decompose down the group because of decrease in bond strength. Methane is very stable but plumbane is least stable due to changing character as +2 oxidation state becoming more stable and decrease in electronegativity down the group.

☞ Reactions with air.

They all burns in air (oxygen gas) to produce dioxides and water.

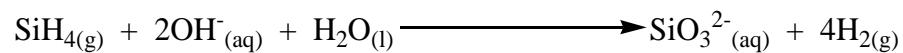
Equations:



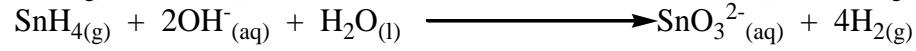
☞ Reaction with water (Hydrolysis).

Only Silane and stannane are hydrolysed but the rest do not undergo hydrolysis. The hydrolysis of both silane and stannane is in the presence of alkali.

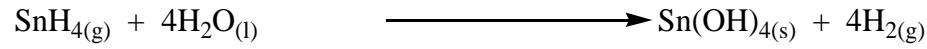
Equations:



Or



Or



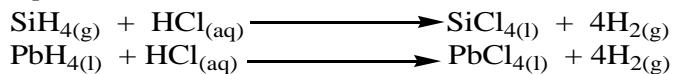
The trend in hydrolysis is in accordance with their electronegativity values.

The greater the greater the electronegativity, the less the hydrolysis.

☞ Reaction with dilute hydrochloric acid.

Except methane, all the hydrides reacts with dilute hydrochloric acid to form tetrachlorides and hydrogen gas.

Equations:

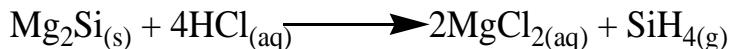


12. Both magnesium and Sulphur reacts with silicon to form silicides of the formulae  $\text{Mg}_2\text{Si}$  and  $\text{SiS}_2$  respectively.

Write equation for the reaction between:

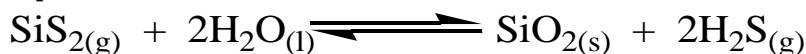
Magnesium silicide ( $\text{Mg}_2\text{Si}$ ) with dilute hydrochloric acid.

Equation:



Silicon disulphide ( $\text{SiS}_2$ ) with cold water.

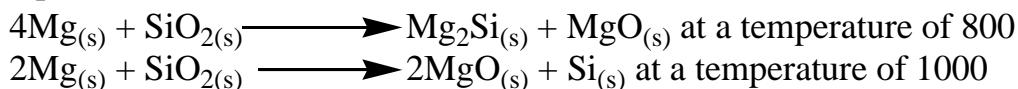
Equation:



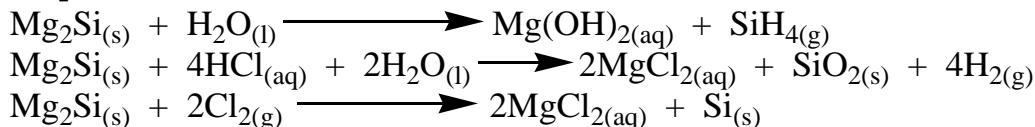
Note:

Magnesium silicide ( $\text{Mg}_2\text{Si}$ ) does not react with alkali and ammonium hydroxide solution, is hydrolyzed by water decomposed by acid and halogens.

Equations:



Golden tips:

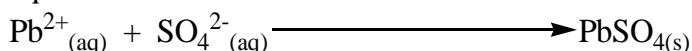


### IDENTIFICATIONS OF $\text{Pb}^{2+}$ , $\text{Sn}^{2+}$ and $\text{Sn}^{4+}$ :

Sodium sulphate/dilute sulphuric acid.

A white precipitate insoluble on warming.

Equation:

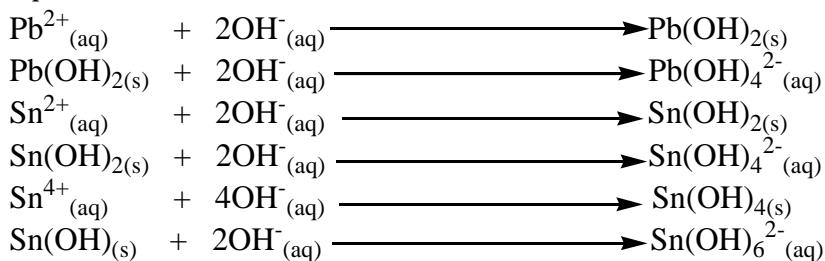


No observable change occurs with both  $\text{Sn}^{2+}$  &  $\text{Sn}^{4+}$ .

**Dilute sodium hydroxide solution until in excess:**

A white precipitate soluble in excess forming colourless solution.

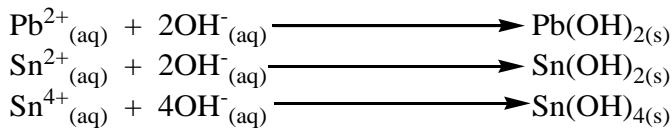
Equations:



**Dilute ammonium hydroxide solution until in excess:**

A white precipitate insoluble in excess.

Equations:



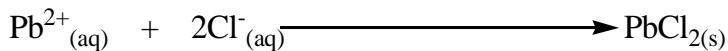
Note:

Ammonia solution is a weaker base than sodium hydroxide solution therefore, it does not produce enough hydroxyl ions to enable complex formation as in the case of sodium hydroxide.

#### Dilute hydrochloric acid /sodium chloride solution.

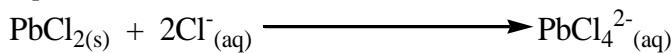
A white precipitate, soluble on warming (hot water).

Equation:



A white precipitate dissolves on warming and reappears on cooling, the precipitate dissolves in concentrated hydrochloric acid forming a complexes.

Equation:

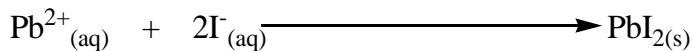


No observable change occurs with both  $\text{Sn}^{2+}$  &  $\text{Sn}^{4+}$ .

#### Potassium iodide solution.

A yellow precipitate, soluble on heating to form a colourless solution.

Equation:



#### Potassium chromate solution.

A yellow precipitate insoluble in ethanoic acid.

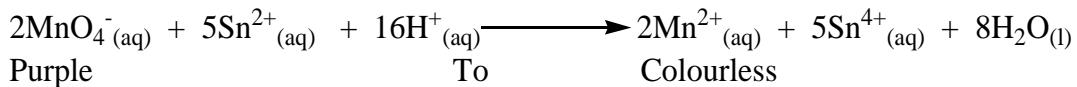
Equation:



#### Acidified potassium permanganate (VII) solution.

The purple colour of acidified potassium permanganate (VII) solution turns from purple to colourless.

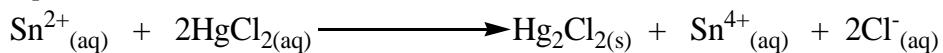
Equation:



#### Mercury (II) chloride solution.

A white precipitate that slowly turns grey.

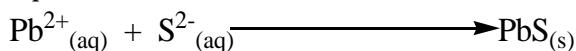
Equation:



#### Ammonium sulphide/Hydrogen sulphide solution.

A black precipitate, soluble in dilute nitric acid.

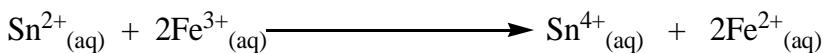
Equation:



13. Explain the following observations.

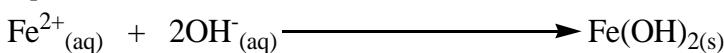
- (a) When Tin (II) chloride solution was added to Iron (III) chloride solution followed by sodium hydroxide solution, a green precipitate is formed. Iron (III) in the solution is reduced by Tin (II) to Iron (II) and Tin (II) is oxidized to Tin (IV) ion.

Equation:



The Iron (II) in solution reacts with the sodium hydroxide to form Iron (II) hydroxide.

Equation:



(b) When tri lead tetra oxide dissolves in dilute nitric acid, a colourless solution and a brown solid is formed.

Tri lead tetra oxide dissolves (reacts) with nitric acid to form a brown solid of lead (IV) oxide and a colourless solution.

Equation:

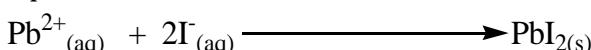


14. The resultant mixture in 14 (b) above is filtered to obtain the residue and the filtrate.

(a) To the 1<sup>st</sup> portion of the filtrate is added potassium iodide. State what was observed and write ionic equation for the reaction.

A yellow precipitate is observed.

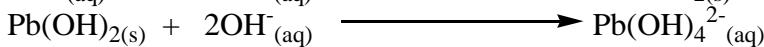
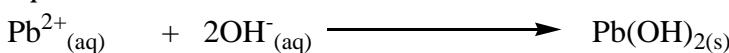
Equation:



(b) To the 2<sup>nd</sup> portion of the filtrate, excess sodium hydroxide solution is added. State what is observed and write ionic equation for the reaction.

A white precipitate is observed, soluble in excess forming a colourless solution.

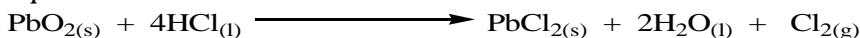
Equations:



(c) To the residue, hot concentrated hydrochloric acid is added. State what was observed and write an ionic equation for the reaction.

A white precipitate & a greenish-yellow gas is evolved.

Equation:



15. Describe how you would determine the percentage of Tin in its alloys in the laboratory.

Procedures:

- Measure a known mass of the alloy and dissolves it in dilute hydrochloric acid.
- Make the solution up to 250cm<sup>3</sup> of volumetric flask using distilled water.
- Pipette a known volume of the solution in to a conical flask and titrate it with a standard potassium permanganate (VII) solution.

Treatment of results:

## GROUP VII ELEMENTS (HALOGENS):

Elements	Nature at R.T	Boiling point	Bond energy	Electron Affinity	Electron egativity
Fluorine	Pale yellow gas	-188	158	-322.6	4.0
Chlorine	Pale Greenish-Yellow gas	-34	242	-364	3.0
Bromine	Red brown liquid	58	193	-342	2.8
Iodine	Black solid	183	151	-295.4	2.5
Astatine	<b>RADIOACTIVE ELEMENT</b>				
Elements	Fluorine, $_9F$	Chlorine, $^{17}Cl$	Bromine, $^{35}Br$	Iodine, $^{53}I$	Astatine
Outer shell	$2s^22p^5$	$3s^23p^5$	$4s^24p^5$	$5s^25p^5$	
Melting Pt	-220	-101	-7	113	/°C
Boiling point	-188	-35	59	183	/°C
O.S	-1	-1,+1,+3,+5,+7	-1,+1,+5	-1,+1,+3,5,+7	
Electrode potential/V	+2.87	+1.36	+1.09	+0.54	
Bond length/nm	0.142	0.200	0.229	0.266	-

### **GENERAL PROPERTIES:**

All the elements exists as diatomic molecules i.e.,  $F_2$ ,  $Cl_2$ ,  $Br_2$ , &  $I_2$ , the two atoms in each atomic molecule are being joined by covalent bond. All exists as non-polar diatomic molecule. They are coloured and highly electronegative and very reactive.

Reasons why the elements are very reactive:

- Low bond dissociation energy of the molecules which allows formation of atoms.  
i.e,  $Cl_2 \longrightarrow 2Cl(g)$ .
- High values of both electronegativity and electron affinity of the individual atoms which allows easy formation of ions.
- The elements all have 7 electrons on their outer shell with one electron less than those of inert gases. The outermost general electronic configuration is  $ns^2np^5$ .they attain stable octet of noble gases by either:
  - Sharing of electrons (covalency) between themselves ( $Cl_2$ ) or other atoms.
  - Accepting an electron (electrovalency) to form univalent ion.

Equation:



- Melting (and also Boiling) points:

Melting (and also Boiling) points of the halogens increases down the group with increasing molecular mass down the group.

This is because the molecules are held by weak Van der Waals forces. As molecular mass increases, the magnitude of the Van der Waals also increases consequently increasing both melting & boiling points.

Fluorine & chlorine are gases at room temperature. Bromine is a liquid while Van der Waals forces in iodine are strong enough to hold its molecules in a solid state.

- Bond energy: is the amount of energy required to break one mole of a covalent bond in to its constituent gaseous atoms.

Equation:



Bond energy usually decreases with increase in bond length.

Bond energy generally decreases down the group. This is because down the group, atomic radius increases hence causing an increase in bond length of (X-X). The longer the bond, the weaker it is. Fluorine has an abnormally low bond enthalpy because of its very small atomic radius. Due to small atomic radius of fluorine, the non-bonding electron pairs on the fluorine atoms are very close to each other causing a strong repulsion. This weakens the F-F bond.

Notes:

Bond energy (or Bond dissociation enthalpy)

- Electrode potentials decrease (become less positive) down the group. Down the group, there is a decrease in bond dissociation energy and electron affinity. Both these two factors favour electrode potential to become less positive.

However, although fluorine has a lower electron affinity than chlorine. Its low bond dissociation enthalpy enables it to have higher electrode potential than chlorine. Electrode potential gives a measure of oxidizing power –the higher (more positive) the electrode potential, the stronger is the oxidizing power.

Therefore oxidizing power of the halogens decrease down the group.

**Note.** Fluorine shows strict differences in its properties from the rest of Group (VII) elements.

**Explanation:** Fluorine has an extremely small atomic radius compared to any other halogen. This gives rise to very high electronegativity, unexpectedly low bond dissociation energy, high lattice energy in fluorides, and very high electrode potential and forms very strong covalent bonds with other elements. Fluorine lacks empty orbitals and as such it has only one oxidation state of -1

#### Explanation for the variation of the physical properties of the halogens

##### Physical state

The physical state of the halogen molecules depend on the strength of the Van der Waals forces of attraction between the halogen molecules which also depends on the size of the atoms of the elements.

As the size of the atoms of the elements increases down the group, the strength of the Van der Waals forces of attraction increases leading to a decrease in volatility with increasing relative molecular mass of the resultant halogen molecule. In fluorine and chlorine molecules, because of the smaller sizes of fluorine and chlorine atoms, the Van der Waals forces of attraction between respective fluorine and chlorine molecules are so weak that they can easily be broken down even at room temperature hence fluorine and chlorine molecules exit as gases at room temperature. In bromine and iodine molecules due to subsequent increase in the sizes of the bromine and iodine molecules, the Van der Waals forces of attraction become stronger enough to keep them as liquid and solid respectively.

2

##### Atomic radius

**Atomic radius generally increases down the group from fluorine to iodine.**

Down the group, both nuclear charge and screening effect increase.

The increase in screening effect outweighs increase in nuclear charge due to addition of an extra inner fully filled sub-energy level from one element to the next.

This leads to a decrease in the effective nuclear charge and hence nuclear attraction for the outermost electrons subsequently decreases.

As a result, the outermost electrons are less strongly attracted by the nucleus leading to an increase in the size of the atoms from fluorine to iodine.

**Boiling point/melting point.**

**Boiling points of halogen molecules increase down the group with increasing molecular weight of the molecules.**

This is because the simple molecules are held by weak Van der Waals forces whose magnitude increases with increase in magnitude of molecular mass.

Fluorine being the smallest atom forms the smallest molecule with the lowest molecular mass, has the weakest

Van der Waals forces of attraction hence has the lowest boiling point.

Iodine being the biggest atom forms the largest molecule with the biggest molecular mass, has the strongest Van der Waals forces of attraction hence has the highest boiling point.

**First Ionization energy**

**First ionization energy of the halogens decreases down the group from fluorine to iodine.**

Down the group, both nuclear charge and screening effect increase from one element to the next.

The increase in screening effect outweighs increase in nuclear charge due to addition of an extra inner fully filled sub-energy level from one element to the next.

This leads to a decrease in the effective nuclear charge and hence nuclear attraction for the outermost electrons subsequently decreases.

As a result, the outermost electrons are less strongly attracted by the nucleus and can thus be easily removed.

**Bond Dissociation Energy (BDE)**

**The bond dissociation energy decreases down the group. However, fluorine has unexpectedly low bond dissociation energy.**

Bond dissociation energy is determined by the size the atoms. The smaller the atoms, the greater the forces of attraction and hence the stronger the bond between the atoms, and consequently the higher the bond dissociation energy.

The bigger the atoms, the weaker the forces of attraction and hence the weaker the bond between the atoms and, consequently the lower the bond dissociation energy.

In the above respect, chlorine forms the strongest covalent bonds hence the highest bond dissociation energy while iodine forms the weakest covalent bonds resulting into the lowest bond dissociation energy.

Fluorine has abnormally low bond dissociation energy. This is because fluorine atom being the smallest atom, there is stronger repulsion between the bonding electrons and the lone pairs of electrons which weakens the fluorine-fluorine bond.

3

**First Electron affinity**

**Electron affinity of halogens generally decreases down the group.**

Down the group, both nuclear charge and screening effect increase from one element to the next.

The increase in screening effect outweighs increase in nuclear charge due to addition of an extra inner fully filled sub-energy level from one element to the next.

This leads to a decrease in the effective nuclear charge and hence nuclear attraction for the incoming electrons subsequently decreases.

Therefore, the incoming electron successively experiences greater repulsion hence less energy is evolved from chlorine to iodine.

However, the electron affinity of fluorine is lower than expected. Due to its smallest atomic radius, electrons in the outermost shell strongly repel each other and also repel the incoming electron leading to release of lower energy.

### **Electrode Potential**

**Electrode Potential is the measure of the reducing power of an element.**

The more reducing an element is, the more negative is its Electrode Potential.

The more oxidizing the element is, the more positive is its Electrode Potential.

The most negative electrode potential represents the strongest reducing agent and the most positive electrode potential represents the strongest oxidizing agent. The reduction potential becomes less positive down the group therefore fluorine is the most powerful oxidizing agent.

The reducing power of the halogens is in the order of

iodine>bromine>chlorine>fluorine. The reducing power of the halogens increases down the group with increasing atomic size.

Fluorine is the least reducing element. This is because fluorine has the smallest atomic size. As a result, electrons in the outermost shell repel each other strongly and the incoming electron. This reduces the ability of fluorine to accept electrons. Iodine is the most reducing halogen. . This is because iodine has the largest atomic size. As a result, electrons in the outermost shell repel each other minimally and the incoming electron. This increases the ability of iodine to accept electrons.

### **Electronegativity**

**Electronegativity of the halogens decreases down the group from fluorine to iodine.**

Down the group, both nuclear charge and screening effect increase from one element to the next.

The increase in screening effect outweighs the increase in nuclear charge due to addition of an extra inner fully filled sub-energy level from one element to the next.

This leads to a decrease in the effective nuclear charge and hence nuclear attraction for the outermost electrons subsequently decreases. As a result, the bonding electrons are less strongly attracted by the nucleus.

### **OXIDATION STATES OF THE HALOGENS**

Halogens except fluorine exhibit a number of positive oxidation states.

Fluorine being the smallest atom of the halogens lacks vacant d-orbitals. The other halogens are large and have empty d-orbitals.

As a result, electrons can be easily transferred or promoted from the p-orbitals to the vacant d-orbitals.

E.g. Consider chlorine; electronic configuration  ${}_{17}\text{Cl} \ 1s^2 2s^2 2p^6 3s^2 3p^5$

	3s	3p	3d
Cl(I)			
Cl(III)			
Cl(V)			
Cl(VII)			

Examples

Compounds	HCl	HOCl	HClO <sub>2</sub>	HClO <sub>3</sub>	HClO <sub>4</sub>
Oxidation states of Cl	-1	+1	+3	+5	+7

Note: The oxidation state of -1 exists in ionic compounds while all other oxidation states exist only in the oxyanions of the halogens.

### **PREPARATIONS OF HALOGENS IN THE LABORATORY:**

16. Describe briefly how fluorine, Bromine and chlorine can be prepared in the laboratory.

Golden tips:

The reduction potential becomes less positive down the group therefore fluorine is the most powerful oxidizing agent.

The most negative electrode potential represents the strongest reducing agent and the most positive electrode represents the strongest oxidizing agent.

17. State some reasons why fluorine is the most powerful oxidizing agent.

- Low bond dissociation energy
- High enthalpy of hydration
- Absence of enthalpy of fusion and vaporization

18. State reasons why Fluorine behaves differently from the rest of the members due.

- |   |   |
|---|---|
| <ul style="list-style-type: none"> <li>• Low bond energy</li> <li>• High electronegativity</li> </ul> | <ul style="list-style-type: none"> <li>• Small atomic radius</li> <li>• High electrode potential</li> </ul> |
|---|---|

19. State some Special properties in which fluorine behaves differently.

- Fluorine does not form oxo-acids.
- Fluorine has only one oxidation state.
- Hydrofluoric acid is the weakest acid compared to other halogen acid.
- Oxides of fluorine are not acidic while those of other halogens are acidic.
- It combines directly with carbon at room temperature to form carbon teta fluoride.
- Hydrogen fluoride has a very high boiling point due to formation hydrogen bonding.
- Calcium, Lithium & magnesium fluoride is insoluble in water while the other halides are soluble in water.

- Silver fluoride is soluble in water while silver chloride, bromide and iodide are insoluble in water. This is because the small fluoride ions have high hydration energy which exceeds lattice energy hence the enthalpy of solution is negative.

## **REACTIONS OF HALOGENS:**

20. Discuss the reaction of halogens with the followings:

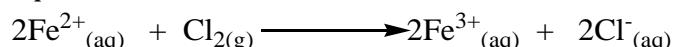
- Nonmetals:

### **OXIDATION REACTIONS:**

- Iron (II) to Iron (III).

Fluorine, Chlorine, Bromine & Iodine are shaken with a solution of iron (II) sulphate, it oxidizes  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  ions.

Equation:



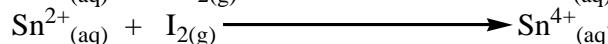
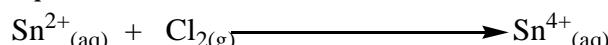
Or:



- Tin (II) to Tin (IV).

Fluorine, Chlorine, Bromine & Iodine oxidizes Tin (II) to Tin (IV) ion.

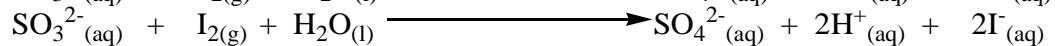
Equations:



- Sulphite ions (saturated solution of sulphur dioxide)

They all oxidizes sulphites ion to sulphates ions.

Equations:



Sodium thiosulphate

Chlorine reacts with sodium thiosulphate to form sulphate ion with a deposit of yellow solid.

Equation:



When chlorine and bromine is in excess, being a stronger oxidizing agent than iodine, it oxidizes the thiosulphate ion to sulphate ion.

Equations:



Iodine oxidizes thiosulphate ion to tetrathionate ion.

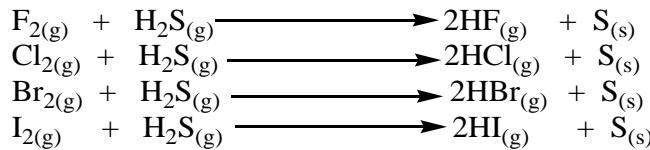
Equation:



- Hydrogen sulphide

They all oxidizes hydrogen sulphide gas to a yellow solid of sulphur.

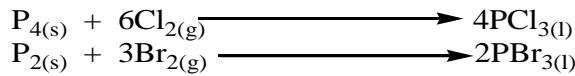
Equations:



(v) Phosphorous.

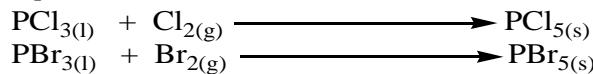
Heated phosphorous reacts with dry both bromine and chlorine gas to form phosphorous trichloride.

Equations:



If more chlorine gas is passed over heated phosphorous, both phosphorous tri bromide or chloride and pentabromide or chloride are formed respectively.

Equations:



But Iodine forms only phosphorous triiodine.

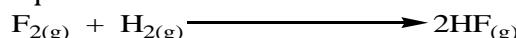
Equation:



(vi) Hydrogen gas.

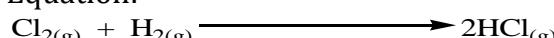
Fluorine gas explodes in hydrogen gas to form hydrogen fluoride.

Equation:



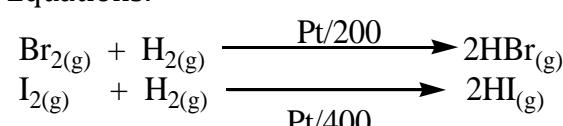
Reaction with Chlorine gas is slow in diffuse light but explosive in sunlight or ultra violet light but very slow in darkness.

Equation:



Both bromine and iodine only reacts with hydrogen gas in the presence of a catalyst at high temperature (Heat).

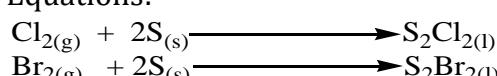
Equations:



(vii) Sulphur.

Both Bromine & Chlorine gases reacts with molten sulphur to give disulphur dichloride, which is a yellow liquid.

Equations:

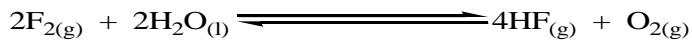


Both Fluorine and iodine gases **DONOT** reacts with molten sulphur.

(viii) Water

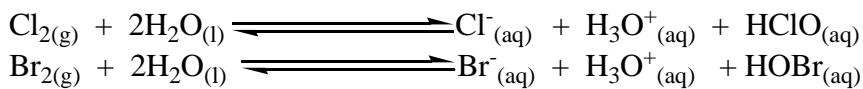
Fluorine reacts with cold water, forming hydrogen fluoride and oxygen gas.

Equation:

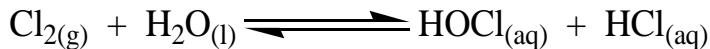


Both chlorine, Bromine & Iodine dissolves slowly in water forming chlorine water. Chlorine water is slightly acidic due to disproportionation of chlorine to form hydrochloric acid and chloric (I) acid.

Equation:



Or:



Iodine is very sparingly soluble in water and the reaction is reversible in which oxygen gas oxidizes the iodide ion back to iodine.

21. Define the term Disproportionation?

Disproportionation is a reaction in which the same species undergoes simultaneous oxidation and reduction.

22. Explain briefly the observations below:

Iodine is much more soluble in potassium iodide than in water.

Iodine molecules are non-polar whereas water molecules are polar. This reduces the solubility of iodine in water.

In potassium iodide however, iodine reacts with iodide,  $\text{I}^-$  ions to form a soluble complex called tri-iodide,  $\text{I}_3^-$  ions.

Equation:



Or:

Iodine is sparingly soluble in water but readily dissolves in aqueous solution of potassium iodide.

Iodine molecules do not react with water and do not form bonds with water molecules hence sparingly soluble.

Iodine reacts with iodide,  $\text{I}^-$  ions from potassium iodide to form tri-iodide,  $\text{I}_3^-$  ions which is soluble in water.

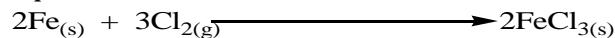
Equation:



b) Metals

Fluorine combines readily and directly with metals. Chlorine gas, the metal has to be heated in dry gas. Iodine reacts slowly with metals at high temperature.

Equations:

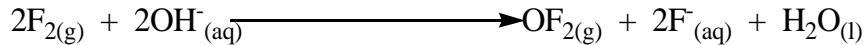


c) Alkalies

(i) Cold dilute alkalies

Fluorine reacts with cold dilute alkalies to form the following products in the equation below.

Equation:

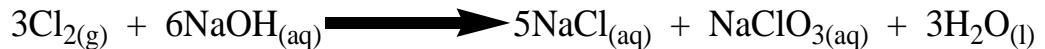


Or:

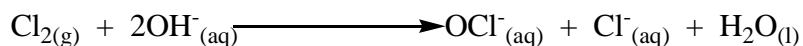


Both Chlorine and Bromine produces a pale yellow solution of alkalis chlorate & bromate (I), alkalis chloride & bromide and water respectively.

Equations:



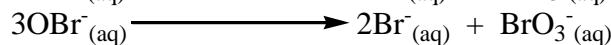
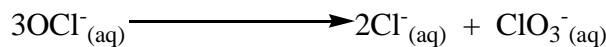
Or:



Notes:

The sodium chlorate (I) and sodium bromate (I) formed above disproportionate at temperature above 70°C. i.e,

Equations:



(ii) Hot concentrated alkalis

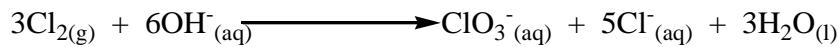
Fluorine reacts with hot concentrated sodium hydroxide solution.

Equation:



Chlorine, Bromine & Iodine reacts with hot concentrated alkalis the products below.

Equations:



23. Discuss how the followings are prepared in the laboratory.

- Potassium chlorate (V) or Potassium bromate (V) & Potassium iodate (V).
- Sodium chlorate (V) or Sodium bromate (V) & Sodium iodate (V).

Golden tips:

Chlorine is more soluble in sodium hydroxide solution than in water. This is because chlorine is non-polar and sparingly dissolves in water to equilibrium below.

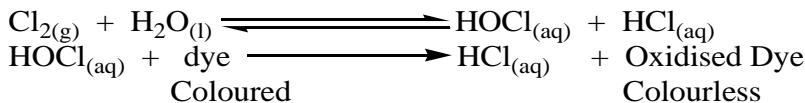
Equation:



24. Describe the bleaching action of chlorine.

The bleaching action of chlorine is brought about by the chlorate (I) ion, which is an oxidizing agent. Chlorine bleaches by oxidizing the dye. Therefore dry chlorine gas does not bleach.

Equation:



The oxidized dye is colourless. Loss of colour is caused by structural changes in the organic molecule. Bromine has a similar action but much less vigorous. Iodine does not react with water and therefore does not bleach.

### COMPOUNDS OF GROUP (VII) ELEMENTS:

#### A. Hydrides:

##### PREPARATIONS OF HALO ACIDS (HYDRIDES):

-Hydrogen Fluoride, HF.

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

Equation:



-Hydrogen Chloride, HCl.

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

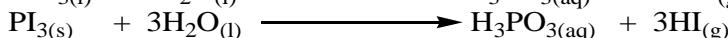
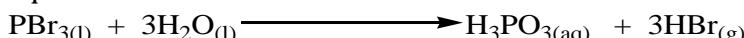
Equation:



-Hydrogen Bromide, HBr.

Both hydrogen bromide and hydrogen iodide are prepared by hydrolysis of phosphorous tribromide and triiodide respectively.

Equations:



Notes:

Both hydrogen bromide and hydrogen iodide cannot be prepared by action of concentrated sulphuric acid on any halides why?

Since they are both strong reducing agent, they can be oxidized by concentrated sulphuric acid to bromine and iodine respectively.

Or:

Hydrogen bromide and iodide cannot be made by the action of concentrated sulphuric acid because concentrated sulphuric acid oxidizes them to halogens. They are instead made by hydrolysis of phosphorous tri bromide or phosphorous tri iodide.

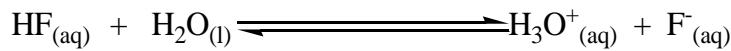
Hydrides	HF	HCl	HBr	HI
B.E (KJ/Mol)	+560	+430	+370	+290
B.pt(°C)	+19.9	-85.0	-66.7	-35.4
p <sup>Ka</sup>	3.25	-7.4	-9.5	-10

Explanation:

- ↗ Bond energy decreases down the group. This is due to an increase in atomic radius of the halogen down the group. Increase in atomic radius causes an increase in H-X bond length. The longer the bond, the weaker it is.

Or:

- ↗ Bond energy decreases down the group. This is because down the group, Electronegativity decrease. Fluorine being the most electronegative than the others, it forms the strongest H-F bond while iodine is the least electronegative, it forms the weakest H-I bond.
- ↗ Boiling point, generally boiling point increases down the group with hydrogen fluoride having an abnormally high boiling point. This is because molecules of the hydrides are held by weak Van der Waals forces whose magnitude depend on the increase with increasing molecular mass.
- ↗ Fluorine is highly electronegative than the rest hence hydrogen fluoride molecules associate through strong hydrogen bonds this gives hydrogen fluoride an abnormally high boiling point.
- ↗ Acidic strength, Halogen hydrides dissolves in water to form acidic solutions. The  $pK_a$  values of the acids can be used as a measure of acidic strength-the lower the values, the stronger is the acid.
- ↗ Acidic strength of the hydrides increases down the group. This is because atomic radius increases down the group in the order of F<Cl<Br<Consequently the H-X bond length increases down the group. The longer the bond, the weaker it is. The weaker the bond the stronger is the acid. Hydrofluoric acid is a weaker acid which is slightly ionized in aqueous solution. Equation:



Moist hydrogen fluoride and aqueous solution of the acid attack silica and glass, so the solution is stored in polythene containers.

Equation:



Increases across		
N-H	O-H	F-H
391	464	568
		↑ Increases up
Cl-H		432
Br-H		366
I-H		298

25. Explain these trends in bond energies in KJ/mol in terms of nuclear charge and size.  
From left to right across the periodic table, nuclear charge increases, attracting the shared electrons in the bond more strongly and making the bond stronger.

As we descend a group in the periodic table, the shared electrons get further away from the nucleus [as the atoms get larger] and are less strongly attracted to the nucleus, making the bond weaker.

26. Why fluorine is the most electronegative atom?

The outer electron 'feel' a greater nuclear charge of 7 [the greatest possible]. This is true of the outer electrons in all the halogens but those in fluorine are closest to the nucleus.

27. What do you expect to be the most electropositive atom [the one that will give away electrons most readily]?

Francium.

28. For each of the following atoms, calculate the approximate shielded nuclear charge felt by one of the outer electrons.

Mg, Ca, F, Cl, N, O, H

2, 2, 7, 7, 5, 6, 1

29. Use your answer to explain why H-F is a polar molecule.

The shared electrons 'feel' a greater nuclear charge from fluorine than hydrogen.

#### B. Oxides

Chlorine forms six oxides, but only the following three have any considerable importance. All six oxides are unstable and the oxides are acidic in nature.

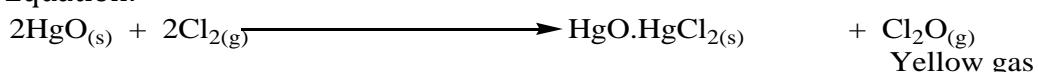
Oxides of bromine have not been extensively studied since they are unstable. While the best known oxide of iodine is iodine pent oxide.

#### PREPARATION OF OXIDES OF CHLORINE:

(i) Chlorine monoxide (Dichlorine oxide),  $\text{Cl}_2\text{O}$

- ☛ Dichlorine oxide or chlorine monoxide is prepared by passing dry chlorine gas over freshly precipitated mercury (II) oxide which has been dried at a temperature of 670K.
- ☛ The reaction tube should be cooled by water. Dichlorine oxide can be condensed in a U-tube immersed in ice-salt.

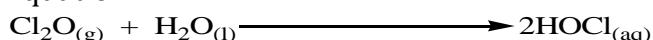
Equation:



Note:

The yellow gas reacts with water forming chloric (I) acid (Hypochlorous acid), so acting as the anhydride of this acid.

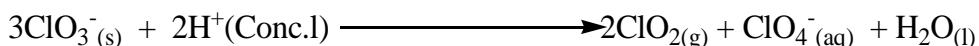
Equation:



(ii) Chlorine dioxide,  $\text{ClO}_2$

- ☛ Chlorine dioxide is prepared by the action of concentrated sulphuric acid on potassium chlorate (V) in the present of heat.

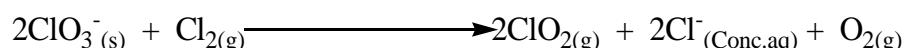
Equation:



Or:

- ☛ Chlorine dioxide is prepared also by the action of dry chlorine gas on silver chlorate (V) at a temperature of about 360K.

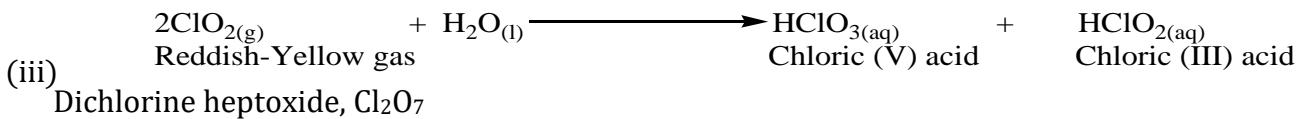
Equation:



Note:

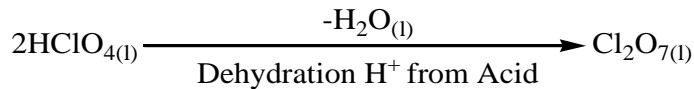
Chlorine dioxide gas reacts with water as a mixed acidic anhydride, forming chloric acid (III) acid (Chlorous acid) and chloric (V) acid (Chloric acid).

Equation:



☞ Dichlorine heptoxide is prepared by dehydration of chloric (VII) acid, whereby acid is gradually phosphorous (V) oxide cooled in ice-salt. After an interval in which dehydration occurs, dichlorine heptoxide can be distilled off.

Equation:



Note:

Dichlorine heptoxide reacts with water to form chloric (VII) acid.

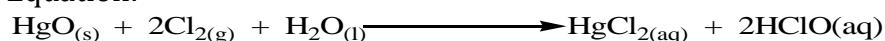
Equation:



(iv) Chloric (I) acid (Hypochlorous acid), HClO

☞ Chloric (I) acid (Hypochlorous acid) is prepared by passing chlorine gas via a suspension of freshly yellow prepared mercury (II) oxide in water.

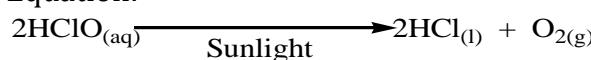
Equation:



Note:

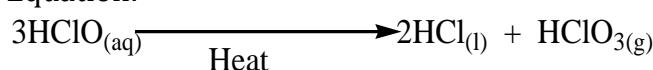
Chloric acid is a weak acid and it liberates oxygen gas under the action of sunlight exposure.

Equation:



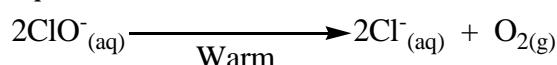
Hypochlorous acid is also decomposed by heat.

Equation:



The acid liberate oxygen gas when warmed with cobalt (II) salt present as a catalyst.

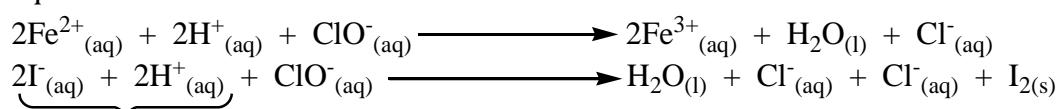
Equation:



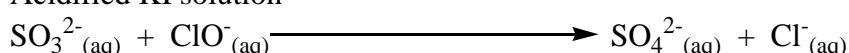
Both the acid and its salts have powerful oxidizing properties and are used as a bleaching agents and antiseptics.

Examples of their oxidizing action in solution are:

Equations:



Acidified KI solution



(iii) Chloric (V) acid, HClO<sub>3</sub>.

Chloric (V) acid is prepared in aqueous solution by the action of barium chlorate (V) with an equimolar proportion of sulphuric acid in dilute solution.

Equation:



Note:

If heated, Chloric (V) acid decompose to some useful products.

Equation:



Note:

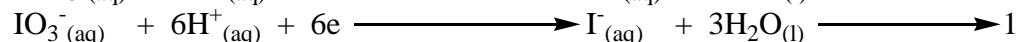
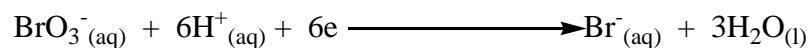
Chloric acid and its salts like sodium chlorate are powerful oxidizing agents in solution.

Equation:



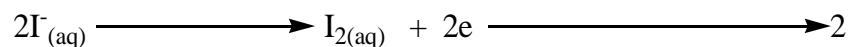
Similarly, bromates (V) and iodates (V) ions are powerful oxidizing agents.

Equations:

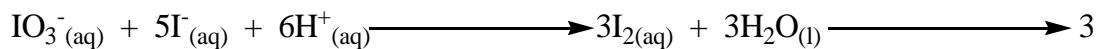


The iodate (V) ion oxidizes iodide ions then to iodine.

Equation:



The overall reaction equation between iodate (V) ions and iodide ion is:



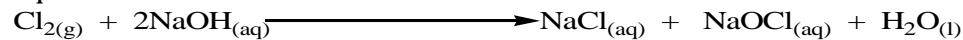
This is obtained by multiplying equation 2 by 3 then summing up together with equation 1. This is done to balance the number of electrons in either equation.

(iv) Chloric (VII) acid (Perchloric acid),  $\text{HClO}_4^-$ .

**Question: Explain why chlorine is more soluble in sodium hydroxide solution than in water.**

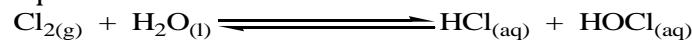
In sodium hydroxide solution, chlorine reacts irreversibly to form sodium chloride solution, sodium chlorate (I) solution and water.

Equation:



However, in water chlorine reacts reversibly to form hydrochloric acid and chloric (I) acid.

Equation:

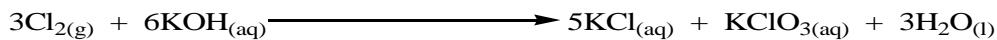


**Question: Describe briefly how chlorine can be converted to potassium chlorate (V)**

Chlorine gas is passed through a hot concentrated solution of potassium hydroxide to form a pale yellow solution which is a mixture of potassium chloride and potassium chlorate (V).

Equation:

HClO	Chloric (I) acid
HClO <sub>2</sub>	Chloric (III) acid
HClO <sub>3</sub>	Chloric (V) acid
HClO <sub>4</sub>	Chloric (VII) acid



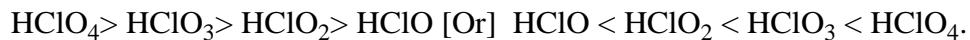
The solution is allowed to cool. In the process of cooling, potassium chlorate (V) crystallizes out with some little potassium chloride. The resultant is again dissolved in hot water and cooled to recrystallize potassium chlorate (V). This process is repeated several times until the final product are pure crystals of potassium chlorate (V).

### C. Oxo acids.

Chlorine gas forms several oxy acids which includes:

HClO	Chloric (I) acid	↓	Thermal stability increases
HClO <sub>2</sub>	Chloric (III) acid		Acid strength increases
HClO <sub>3</sub>	Chloric (V) acid		Oxidizing power increases
HClO <sub>4</sub>	Chloric (VII) acid		

Oxidation States	Acid			Anion	
	Formula	Systematic name	Traditional name	Formula	Systematic name
+1	HOCl	Chloric (I) acid	Hypochlorous	ClO <sup>-</sup>	Chlorate (I)
+3	HClO <sub>2</sub>	Chloric (III) acid	Chlorous	ClO <sub>2</sub> <sup>-</sup>	Chlorate (III)
+5	HClO <sub>3</sub>	Chloric (V) acid	Chloric	ClO <sub>3</sub> <sup>-</sup>	Chlorate (V)
+7	HClO <sub>4</sub>	Chloric (VII) acid	Perchloric	ClO <sub>4</sub> <sup>-</sup>	Chlorate (VII)



As the oxidation states (numbers) of chlorine increases, both the thermal stability and the acid strength of the Oxo acids increases. While the oxidizing power of the acids decreases with increasing oxidation states (numbers) of the order of:  
 $\text{HClO or HOCl} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$ .

### Binary Acids:

Two factors are related to the acid strengths of nonmetals hydrides.

Namely:

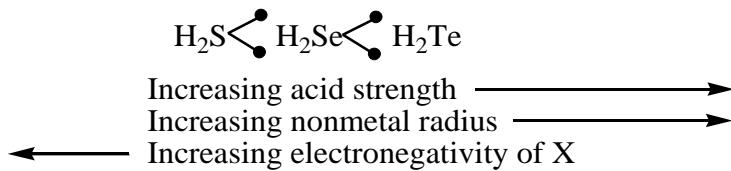
- 1) The polarity of the X-H bond.
- 2) The strength of the X-H bond. (X stands for a nonmetal atom).

Explanation:

- ☛ The polarity of a X-H bond increases with the electronegativity of the nonmetal atom. The greater the electronegativity of the nonmetal atom, the more it withdraw electrons from the hydrogen atom. This facilitates the release of H<sup>+</sup> as a proton. Hence acid strength increases as the electronegativity of the nonmetal atom increases.
- ☛ The strength of the X-H bond decreases as the atomic radius of X increases. A hydrogen ion is more easily broken away from a larger atom than a smaller one. This happens because the electron cloud in a large atom is more diffuse. The smaller the nonmetal atom, the denser the electron cloud. This greater electron density results in a greater attraction for the proton. Hence acid strength increases as the atomic radius of the nonmetal atom increases.

- When comparing acid strengths of the hydrides in a group of the periodic table versus those within a period, one must consider both the electronegativity of the nonmetal atom and bond energy. Within a series of hydrides of the elements in a group the acid strength increases with increasing atomic radius of the nonmetal.

Examples:



- In this series, the electronegativity of X varies only slightly, and so is outweighed by the more significant increases in atomic radius, as shown below in the table.

	H <sub>2</sub> S	H <sub>2</sub> Se	H <sub>2</sub> Te
Radius of X (pm)	104	117	137
Electronegativity of X	2.5	2.4	2.1

- When reading across a row of the periodic table the situation is reversed. The importance of bond polarity in determining acid strength outweighs that of atomic radius. For instance, the hydrides of the elements phosphorus, Sulphur, and Chlorine show increasing acid strength as shown below. Increasing acid strength parallels the increasing electronegativity on the nonmetal.

	PH <sub>3</sub>	H <sub>2</sub> S	HCl
Increasing acid strength	→		
Increasing nonmetal radius	←		
Increasing electronegativity of X		→	
Radius of X (pm)	110	104	99
Electronegativity of X	2.1	2.5	3.0

- The smaller decrease in atomic radius is insignificant in comparison to the larger change in electronegativity. The trend in acid strength results from significant increases in bond polarity when going across the row.

- Oxoacids. I.e. HClO > HBrO > HIO or HOI < HOBr < HOCl. Oxoacids with the same structure, but with different central atoms whose elements are in the same group, acids strength increases with increasing electronegativity values of the central atom. Hence, acid strength increases in the following series where the central atom is a halogen element as shown above.

- In each molecule, the O-H bond strength is approximately the same. In this series the ability of the halogen atom to withdraw electron density from the O-H bond increases

with increasing electronegativity. As the O-H bond in a series of acids becomes more polar, the acid strength increases.

- ☛ For Oxo acids that have the same central atom, but differing numbers of attached oxygen atoms, the acid strength increases with increasing oxidation number of the central atom. Therefore,  $\text{HNO}_3$  is stronger than the  $\text{HNO}_2$ ,
- ☛ The oxygen atoms draw electrons away from the nitrogen atom, making it more positive. The more positive the nitrogen atom, the more effective it is in withdrawing from the O-H bond. This increases the polarity of the O-H bond.

### **RELATIVE ACID STRENGTH:**

1. Which one of the following pairs is the stronger acids?
  - ☛ HCl or HBr
    - These acids are nonmetal hydrides of elements within Group (6A) of the periodic table. Variations in atomic radius are more important within a group than electronegativity variations.
    - The stronger acid is the one with the greater radius of its nonmetal atom. HBr is the stronger acid than HCl.
  - ☛ HCl or  $\text{H}_2\text{S}$ 
    - These acids are nonmetal hydrides of the elements within the third row of the period table. The electronegativity values changes more significantly going across a row than does the atomic radius. HCl with its more polar bond is the stronger acid than  $\text{H}_2\text{S}$ .
  - ☛  $\text{HClO}_3$  or  $\text{HBrO}_3$ 
    - Within this group the strengths of the acids increases with increasing electronegativity of the central atom. The electronegativity values of  $\text{Cl}^-$  ion is greater than that of  $\text{Br}^-$  ion.
  - ☛  $\text{H}_3\text{PO}_3$  or  $\text{H}_3\text{PO}_4$ 
    - $\text{H}_3\text{PO}_3$  &  $\text{H}_3\text{PO}_4$  are oxoacids of the same element. The acid strength increases as the number of oxygen atoms increase.  $\text{H}_3\text{PO}_4$  is the stronger acid because of the greater number of oxygen atoms bonded to the phosphorus atom. In  $\text{H}_3\text{PO}_4$ , phosphorus has a higher oxidation number than  $\text{H}_3\text{PO}_3$ .

**Oxidizing power and thermal stability:** The oxidizing power of these acids decreases as the oxidation number increases in the order of  $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$ . Stability of Oxo acids of chlorine in the increasing order is,  $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$  and the increasing stability order of anions of Oxo acids of chlorine is,  $\text{ClO}^- < \text{ClO}_2^- < \text{ClO}_3^- < \text{ClO}_4^-$ . As the number of oxygen atoms in an ion increases there will be a greater dispersal of negative charge and thus greater will be the stability of ion formed. For different halogen having the same oxidation number, the thermal stability decreases with increase in atomic number i.e., it is in the order  $\text{HClO} > \text{HBrO} > \text{HIO}$  and  $\text{ClO}^- > \text{BrO}^- > \text{IO}^-$ . However, in  $\text{HXO}_3$  is most stable. The stability order being  $\text{HClO}_3 < \text{HBrO}_3 < \text{HIO}_3$ .

The acidity of Oxo acids of different halogens having the same oxidation number decreases with increase in the atomic size of the halogen i.e.  $\text{HClO}_4 > \text{HBrO}_4 > \text{HIO}_4$ .

Reasons why different halogen having the same oxidation states decreases in the order of:  $\text{HClO}_3 < \text{HBrO}_3 < \text{HIO}_3$  or  $\text{HClO}_4 > \text{HBrO}_4 > \text{HIO}_4$ .

In any series of oxo acids of halogens, the first member possesses high acidic strength. This is due to high electronegativity and small size of the respective halogens.

Example:

Among perhalic acids, perchloric acid has high acidic strength. As chlorine is more electronegative than bromine or iodine, the shared electron pair lies relatively nearer to chlorine in a Cl-O bond than in a Br-O or I-O bond. As a consequence, the O-H bond becomes much weaker in case of perchloric acid, thereby facilitating the release of proton readily and easily.

Oxoacids of chlorine	
Halogen oxoacid series	Cl
Hypohalous acids	$\text{HOCl}$
Halous acids	$\text{HOCIO}$
Halic acids	$\text{HOClO}_2$
Perhalic acids	$\text{HOClO}_3$



#### **ACIDIC STRENGTH:**

Acidic strength of the acids decreases in the order of:  $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$  and increases in the order of:  $\text{HClO}$  or  $\text{HOCl} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$ .

### Explanation:

Acidic strength increases with increase in the number of oxygen atoms attached to the chlorine atom. Oxygen atom is more electronegative than chlorine atom.

The oxygen atom withdraw electrons from the O-H bond through the chlorine atom hence this increases the partial positive charge on the hydrogen atom therefore weakening the O-H bond. The weaker the O-H bond, the stronger is the acid.

### Illustrations:

Increase in the number of oxygen atoms causes an increase in partial positive charge on the hydrogen atom thus weakening the O-H bond. This increases the ease with which a proton is lost.

Or:

The acidic strength depends on the number of oxygen atoms in the acid molecule. Since oxygen is more electronegative than chlorine, it pulls the bonding electrons

towards itself and this negative inductive effect is transmitted to the O-H bond weakening it thus hydrogen ions are released in solution. The greater the number of the oxygen atom, the greater the effect and the weaker the O-H bond. Thus the strength of the acid is  $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$ .

Or:

The greater the number of oxygen atoms the acid has, the greater the acidity. Therefore Perhalic acid,  $\text{HClO}_4$  is the most acidic. This is because the greater the number of oxygen atoms the greater is the electron displacement towards the oxygen atom and the weaker will be the H-Cl bond.

The acidic strength of Oxo acids of chlorine increases with increase in the number of oxygen atoms and the order is:  $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$ .

**Notes:**

This is due to oxygen atom being more electronegative than chlorine atom and this pulls electrons more strongly away from the chlorine atom and effect weakens the H-Cl bond such that  $\text{H}^+$  ion is easily lost to the solution. The greater the number of oxygen atoms the greater the effect and the greater the acidity.

Or:

Strong acids are those which dissociate to a great extent in solution.

When the central atom remains constant but the number of oxygen atoms surrounding that central atom increase, the added oxygen atoms draw electrons away from the central atom. This makes the central atom more positive. Thus, the central atom can more effectively draw electrons away from the O—H bond. As electron density of the O—H bond decreases, the bond becomes more polar.

As the O—H becomes more polar, the Oxo acid more readily dissolves in water (dissociates to a greater extent). Therefore, acid strength increases as the number of oxygen attached to the central atom increases.

Or:

Strength of acid depends on the bond strength of the O-H bond in the acid and the stability of the conjugate base. As the number of oxygen atoms increase in Oxo acids, there will be more electronegative oxygen atoms to pull electron density away from the O-H bond, weakening it and causing it to break more easily. Also, such inductive effect can pull charge density from the conjugate base, stabilizing it further. Thus, Oxo acids become stronger when there are more oxygen atoms in the acid. However, this is not applicable if the Oxo acids are not all monoprotic or all diprotic.

Or:

Oxo acids have oxygen and at least one O-H group attached to central metal atom. The determining factor for an oxyacid's relative strength has to do with the central atom's oxidation state (positive character), as well as the number of O atoms around that central atom.

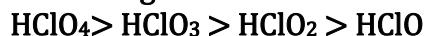
As the number of oxygen increases

1. Oxidation state of metal increases.
2. Oxygen is electronegative, it withdraws electron density developing more delta positive on metal.

Thus metal attracts more electron density from O-H, making it acidic. Now as the number of oxygen increases, acidity increases. You can now take some examples and work on it.

Or:

**Acid strength of the Oxo acids of chlorine increases in the order of:**



The acidic strength depends on the number of oxygen atoms in the acid molecule. Since oxygen is more electronegative than chlorine, it pulls the bonding electrons towards itself and this negative inductive effect is transmitted to the O-H bond weakening it thus hydrogen ions are released in solution.

The greater the number of the oxygen atom, the greater the negative inductive effect and the weaker the O-H bond and hence the stronger the acid. The lower the number of the oxygen atom, the lesser the negative inductive effect and the stronger the O-H bond and hence the weaker the acid.

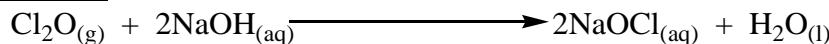
#### Oxo acids of halogens

Fluorine does not form any Oxo acid since it is the strongest oxidizing agent. Chlorine, bromine and iodine mainly form four series of Oxo acids namely hypohalous acid ( $\text{HXO}$ ), halous acid ( $\text{HXO}_2$ ) halic acid ( $\text{HXO}_3$ ) and perhalic acid ( $\text{HXO}_4$ ).

### **REACTIONS OF OXIDES OF CHLORINE WITH SODIUM HYDROXIDE**

#### **SOLUTION:**

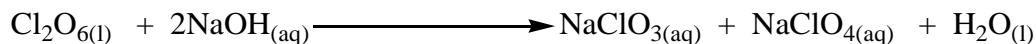
#### **EQUATIONS:**



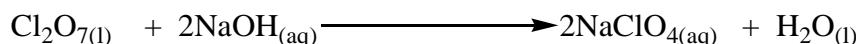
Orange



Yellow



Red



Colourless

### **TEST OR ANALYSIS OF CHLORIDE, BROMIDE AND IODIDE IONS:**

- (i) Using concentrated sulphuric acid.

Procedure:

- ✓ To the unknown solid substance, add a little of concentrated sulphuric acid and warm the mixture.

Observations:

- ↙ Evolution of a colourless gas, with a sharp smell, which forms dens white fumes with ammonia gas shows the presence of chloride,  $\text{Cl}^-$  ion.

Note:

Sulphuric acid displaces hydrogen chloride gas (the colourless gas) from chloride.

Equation:

Observations:

- ↙ Evolution of a brown gas (bromine) shows the presence of bromide ion.

Observations:

- ↙ Formation of a purple vapour (iodine vapour) shows the presence of an iodide ion.

(ii) Using dilute nitric acid and silver nitrate solution.

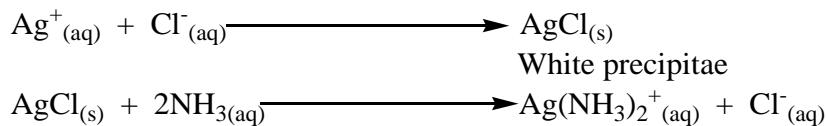
Procedure:

- ✓ To the solution of the unknown, add dilute nitric acid followed by silver nitrate solution.

Observations:

↗ Formation of white precipitate indicates the presence of chloride,  $\text{Cl}^-$  ion. The precipitate dissolves in excess ammonia due to formation of complex ion.

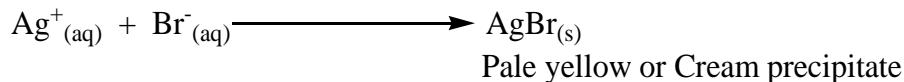
Equation:



Observation:

↗ Formation of a cream precipitate (or pale yellow) indicates the presence of bromide,  $\text{Br}^-$  ion.

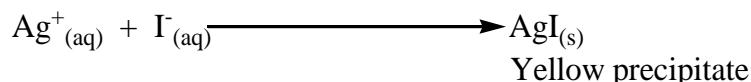
Equation:



Observation:

↗ Formation of a yellow precipitate indicates the presence of iodide ion,  $\text{I}^-$  ion.

Equation:



(iii) Using concentrated sulphuric acid and manganese (IV) oxide.

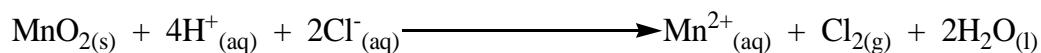
Procedure:

- ✓ To the unknown solid sample, add manganese (IV) oxide followed by concentrated sulphuric acid and warm the mixture.

Observations:

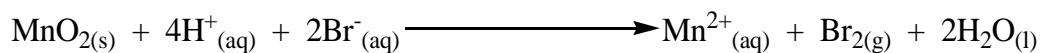
↗ Evolution of a greenish yellow gas that turns moist blue litmus paper red shows the presence of chloride,  $\text{Cl}^-$  ion.

Equation:



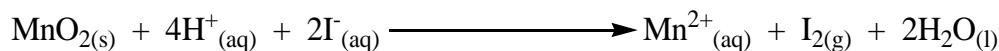
↗ Evolution of brown fumes (reddish) shows the presence of bromide,  $\text{Br}^-$  ion.

Equation:



↗ Evolution of a purple vapour (or dark solution) shows the presence of iodide,  $\text{I}^-$  ion.

Equation:



Notes:

A mixture of manganese (IV) oxide and concentrated sulphuric acid are very powerful oxidizing agent which oxidizes chloride,  $\text{Cl}^-$ , bromide,  $\text{Br}^-$ , & iodide,  $\text{I}^-$  ions to chlorine, bromine & iodine gases respectively.

(iv) Using lead (II) ethanoate or lead (II) nitrate solution.

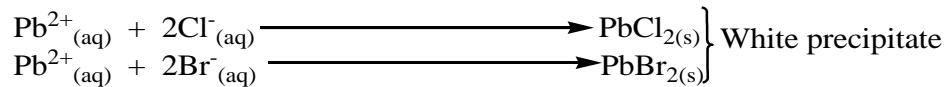
Procedure:

- ✓ To the solution of the unknown, add a few drops of lead (II) nitrate solution.

Observations:

- ☛ Formation of a white precipitate that dissolves on warming shows presence of either chloride,  $\text{Cl}^-$  or bromide,  $\text{Br}^-$  ions.

Equations:

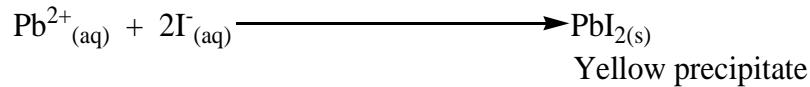


☛ Note:

white precipitate of Bromide,  $\text{Br}^-$  ion soluble in hot water.

- ☛ Formation of a yellow precipitate soluble on heating shows the presence of iodide,  $\text{I}^-$  ion.

Equation:



Note:

- ☛ Yellow precipitate dissolves in hot water to give a colourless solution.

(v) Using chlorine water (or slightly acidified sodium hypochloride) and carbon tetrachloride.

Procedure:

- ✓ To the solution of the unknown, add 1 to 2 drops of chlorine water followed by 3cm<sup>3</sup> of carbon tetrachloride. Shake well and allow to settle.

Observations:

- ☛ A brown (or red) carbon tetrachloride layer shows the presence of bromide,  $\text{Br}^-$  ion.

Reason:

- ☛ This is because the reagent oxidizes bromide,  $\text{Br}^-$  ion to bromine which is dissolved in carbon tetrachloride layer turning to brown.
- ☛ A purple (or violet) carbon tetrachloride layer shows the presence of iodide,  $\text{I}^-$  ion.

### **PHYSICAL PROPERTIES OF THE HYDROGEN HALIDES.**

Compounds	HF	HCl	HBr	HI
B.E (KJ/Mol)	544	431	366	299
B.p.t (°C)	+19.9	-85.0	-67.0	-36.0
M.p.t (°C)	-8.31	-144.2	-56.9	-56.8
Acid strength (Ka)	$5.6 \times 10^{-4}$	$1.0 \times 10^7$	$1.0 \times 10^9$	$1.0 \times 10^{11}$

Explanations for the variations in the physical properties of the hydrogen halides

**Boiling point**

The boiling points increase with increase in molecular mass from HCl to HI.

The boiling points of molecular compounds depend on the strength of the intermolecular forces of attraction between the molecules.

The stronger the intermolecular forces of attraction between the molecules, the higher the boiling point and the weaker the intermolecular forces of attraction between the molecules, the lower the boiling point.

HCl, HBr, and HI are simple molecules held by weak Van der Waals forces of attraction whose magnitude increases with increase in molecular mass.

Thus as molecular mass increases from HCl to HI down the group, the strength of the Van der Waals forces of attraction increases hence leading to an increase in boiling point from HCl to HI.

However, HF has an extremely higher boiling point because its molecules associate through hydrogen bonding. Fluorine atom is very small and highly electronegative. This causes a big electron displacement in the hydrogen-fluorine (H-F) bond. Due to this, hydrogen fluoride molecules associate through strong hydrogen bonding. These strong hydrogen bonds require very high amounts of energy to be broken down hence a very high boiling point of hydrogen fluoride.

**Note.** The boiling point of the hydrogen halides decrease in the order of HF>HI>Br>HCl  
**Bond energy**

**The bond energy of the hydrogen halides decreases down the group from HF to HI due to:**

Increased atomic radius which increases the bond length and Decrease in electronegativity down the group thus the bonds become less polar.

Down the group, as electronegativity of the halogens decreases from fluorine to iodine, the strength of the hydrogen-halide (H-X) bond decreases.

Fluorine atom being very small and highly electronegative, it greatly polarizes the H-F bond thus hydrogen fluoride molecules associate through very strong hydrogen bonds which are extremely hard to break leading to the highest bond energy and thermal stability of the HF molecule.

Iodine atom being the biggest and least electronegative, the hydrogen-iodide (H-I) bond is the weakest thus the easiest to break leading to the lowest bond energy and thermal stability of the HI molecule.

### 3. Acid Strength (Ka)

**The acid strength of group (VII) hydrides increase in the order of HF<HCl<HBr< HI i.e. it increases from HF to HI down the group.**

The acid strength depends on the degree of dissociation of the acid thus the concentration of the hydrogen ion in aqueous solution. I.e. it depends on the ease with which a hydrogen ion is lost into solution which primarily depends on the strength of the hydrogen-halide (H-X) bond.

As electronegativity decreases down the group due to increase in atomic radius, the strength of the H-X bond decreases is in the order HF> HCl> HBr> HI

The weaker the H-X bond, the more easily the proton is lost and the stronger the acid is; the stronger the H-X bond, the least easily the proton is lost and the weaker the acid is.

Thus in HF, the H-F bond is not easily broken hence it does not easily release a proton in aqueous solution hence it is the weakest acid. The H-I bond is the weakest bond therefore in aqueous solution it easily release a proton hence making HI the strongest acid among halogen acids.

#### **Note.**

HF slightly ionizes in dilute solution as:



**N.B.** When concentrated, HF is a weaker acid than in dilute solution due to hydrogen bonding which reduces the concentration of hydrogen ions. I.e.



**Question:** *Hydrogen fluoride has a higher boiling point and it is a weaker acid than hydrogen chloride. Explain. (10 marks)*

Fluorine atom is smaller and highly electronegative than chlorine atom. This causes a big electron displacement in the hydrogen-fluorine (H-F) bond. Due to this, hydrogen fluoride molecules associate through strong hydrogen bonding while hydrogen chloride molecules are held by weak Van der Waals forces of attraction.

Therefore to break down the strong hydrogen bonds in hydrogen fluoride molecules requires very high amounts of energy than breaking down the weak Van der Waals forces of attraction in hydrogen chloride hence a very high boiling point of hydrogen fluoride than hydrogen chloride. HF is a weaker acid than HCl. The acid strength of the hydrogen halides depends on the strength of the H-X bond. It thus follows that the stronger the H-X bond, the weaker the acid and the weaker the H-X bond the stronger the acid. Fluorine atom being smaller and highly electronegative than chlorine atom, the H-F bond is stronger than the H-Cl bond. Thus, in HF, the H-F bond is not easily broken hence it does not easily release a proton in aqueous solution hence it is a weaker acid compared to HCl.

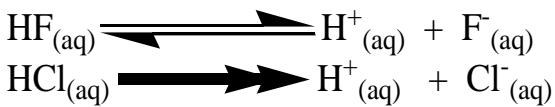
OR:

Fluorine atom is smaller and highly electronegative compared to the chlorine atom. Therefore the H-F bond is highly polarized compared to the H-Cl bond. This leads to stronger intermolecular hydrogen bonds in hydrogen fluoride.

Hydrogen chloride molecules instead have weaker Van der Waal's forces among themselves. Therefore, the boiling point of HF is higher than that of HCl since Vander Waal's forces are weaker than hydrogen bonds.

The covalent bond in hydrogen fluoride is much stronger than in hydrogen chloride due to the small size of fluorine compared to chlorine. The H-F bond is thus more difficult to break than the H-Cl bond thus fewer HF moles ionizes to form hydrogen, H<sup>+</sup> ions.

Equations:



Hydrogen fluoride is thus a weaker acid than hydrochloric acid.

**Question:** *State two factors which affect the acid strength of the hydrogen halides down the group*

- (i) The bond energy of the H-X bond; down the group the bond strength of the H-X bond decreases and therefore, the tendency to form H<sup>+</sup> ions increases.
- (ii) Electronegativity of the halogens; as electronegativity of the halogens decreases down the group due to increase in atomic radius, the strength of the H-X bond decreases is in the order HF > HCl > HBr > HI.

### PERIOD 3 ELEMENTS:

The period runs from sodium to Argon. The table below shows some physical parameters of the elements involved.

Elements	Na	Mg	Al	Si	P	S	Cl	Ar
M.pt.(°C)	98	651	660	1410	44	114	-101	-189
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0	
Ionization energy	502	745	587	792	1020	1000	1260	1530
Atomic radius	1.57	1.36	1.28	1.17	1.10	1.04	0.99	
Electron Affinity	2.0	-6.7	3.0	13.5	6.0	20.0	36.4	
Oxidation states	+1	+2	+3	+4	+3, +5	-2, +4, +6,	+1, +3, -1, +5, +7	
Structure	← Close packed →			Giant molecular	← Discrete molecular structure →			
Chlorides	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>	Cl <sub>2</sub>	
B.pt.(°C)	1465	1418	423	57	74,164	138	-35	
Bonds	Ionic		← Covalent →					
Structure	Giant ionic		← Simple molecular structure →					
Oxides	Na <sub>2</sub> O Na <sub>2</sub> O <sub>2</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>2</sub> , SO <sub>3</sub>	Cl <sub>2</sub> O, Cl <sub>2</sub> O <sub>7</sub>	
Bonds	← Ionic →			← Covalent →				
Nature	Basic		Amphoteric		Acidic			
Structure	← Giant ionic →			Giant molecular	← simple molecular →			
Hydrides	NaH	MgH <sub>2</sub>	AlH <sub>3</sub>	SiH <sub>4</sub>	PH <sub>3</sub>	H <sub>2</sub> S	HCl	
Bonds & structures	Ionic bonds & Giant ionic structures				Covalent bonds & Simple molecular structures			

- ✓ The changing properties across a period 3 elements are related to the change in the nuclear charge and size of the atoms with the increasing number of outer-shell electrons.
  - ✓ The major properties which change across a period are:
    - ☒ Redox properties.
    - ☒ Structure and bonding.
    - ☒ Solubility and complexing properties.
  - ✓ The third period starts with sodium in Group (I) and continues through magnesium, aluminium, silicon, phosphorus, sulphur, chlorine and ends with argon in Group (0) of the periodic table.
  - ✓ Sodium, magnesium, & aluminium adopt metallic bonding with strong force of attraction between the cation and the delocalized mobile electron.
  - ✓ The strength of the metallic bonds depends on the number of electron each atom contribute to the electron cloud.
  - ✓ Silicon is a metalloid which has a giant molecular structure with strong covalent bonds between the atoms of the silicon.
  - ✓ Phosphorus, sulphur, chlorine and argon are non-metals which consist of discrete molecules of  $S_8$ ,  $P_4$ ,  $Cl_2$  and  $Ar$ . Vander Waal's forces of attraction hold the molecules together. The strength or magnitude of Van der Waal forces depends on the molecular size or molecular mass.

## **GENERAL PROPERTIES:**

## A. PHYSICAL PROPERTIES OF PERIOD THREE ELEMENTS:

**(a) Standard electrode potential (V).**

Very weak reducing agent

Powerful oxidizing agent

Na	Mg	Al	Si	P	S	Cl
-2.71	-2.37	-1.66	-	-	-0.48	+1.36

Powerful reducing agents      Weak reducing agents and weak oxidizing agents

Melting & boiling points, Electronegativity, Electronaffinity, Atomic radius, Electropositivity & Ionization energy explanation refers to the properties of periodic table in the introduction part of the inorganic chemistry.

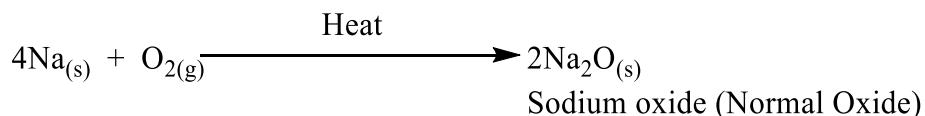
## B. CHEMICAL PROPERTIES OF PERIOD THREE ELEMENTS:

(a) Reaction with air (oxygen gas).

Vigour or reaction with oxygen gas.

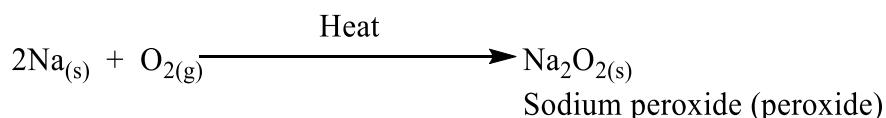
 Sodium burn in limited supply of air (oxygen) gas readily with a bright, golden yellow flame to form normal oxide of sodium monoxide.

Equation:



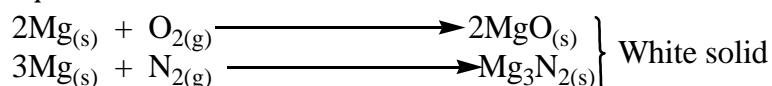
- ☞ Sodium also burn in excess supply of air (oxygen) gas readily with a bright, golden yellow flame to form a pale solid of sodium peroxide at a temperature of about **600K**.

Equation:



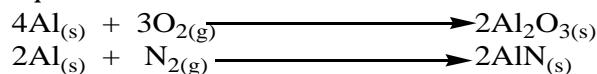
- ☞ Magnesium burns with a brilliant bluish-white flame in air when heated forming oxides which are white in colour.

Equations:



- ☞ When heated in air, powdered Aluminium burns to form a white oxide and a smaller amount of nitride.

Equations:



- ☞ Amorphous Silicon burns readily in oxygen at red-heat, but, in air, oxidizes. Silicon dioxide is produced.

Equation:



- ☞ White phosphorus catches fire spontaneously in air, burning with a white flame and producing clouds of white smoke-a mixture of phosphorus (III) oxide and phosphorus (V) oxide.

Equations:



Notes:

The proportions of these depend on the amount of oxygen gas available. In an excess of oxygen gas, the product will be almost entirely phosphorus (V) oxide.

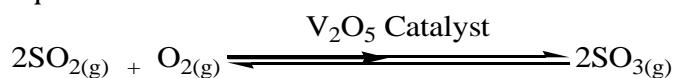
- ☞ Sulphur burns in air (oxygen gas) on gentle heating with a pale blue flame. It produces colourless sulphur dioxide gas.

Equation:



- ☞ Traces of sulphur trioxide gas is also formed, which gives a misty appearance to the gas.

Equation:



Note:

The sulphur trioxide gas formed is by combination of sulphur dioxide gas formed with oxygen gas in the presence of Vanadium (V) oxide as a catalyst.

☛ Both Chlorine and Argon DONOT react with air in any condition.

(b) Reaction with hydrogen gas.

☛ Sodium reacts with heated dry hydrogen gas to form a white solid of sodium hydride.

Equation:



☛ Magnesium reacts with heated dry hydrogen gas to form a white solid of magnesium hydride at a temperature of about **350°C**.

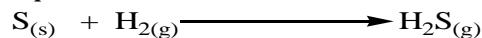
Equation:



☛ Aluminium, Silicon and Phosphorous DO NOT react with hydrogen gas.

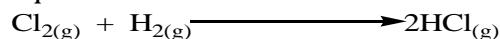
☛ Sulphur combined directly with hydrogen gas to form hydrogen sulphide.

Equation:



☛ Chlorine combined directly with hydrogen gas in the presence of activated charcoal with absorption of hydrogen chloride in water.

Equation:

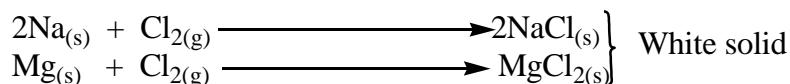


(c) Reaction with chlorine gas.

☛ The chlorides of both sodium and magnesium are formed by heating the metal in air until it burns, and lowering it in to the vessel containing chlorine gas.

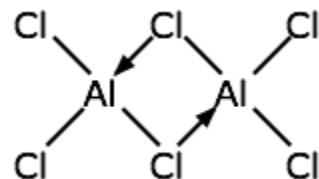
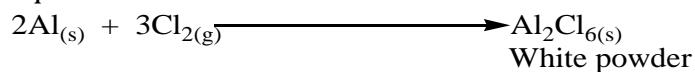
Both sodium and magnesium continues to burn in chlorine gas to form a white products coating the walls of the reaction vessel.

Equations:



☛ A stream of dry chlorine (or hydrogen chloride) gas is passed over heated aluminium. It sublimes at a temperature of about 456K and exist as  $\text{Al}_2\text{Cl}_6$ .and aluminium chloride condenses as a white powder.

Equation:

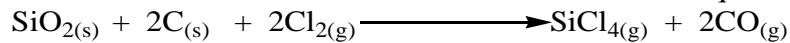
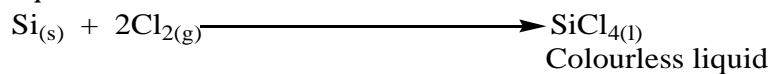


Note:

The structure of  $\text{Al}_2\text{Cl}_6$ . This anhydrous form of results from  $\text{AlCl}_3$  molecules forming dimers: Chlorine atom donate lone pairs of electrons in to the vacant orbital in the valence shell not the aluminium atoms.

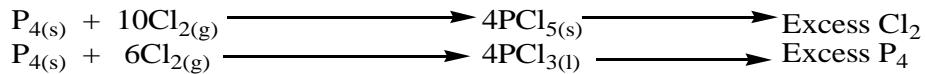
- ☛ Amorphous silicon ignites spontaneously in chlorine to form a colourless liquid of silicon tetrachloride.  
It can also be prepared by heating a mixture of silicon (IV) oxide and carbon in a dry current of chlorine gas.

Equations:



- ☛ Heating phosphorus in excess chlorine gas forms phosphorus pentachloride, excess phosphorus forms trichloride.

Equations:

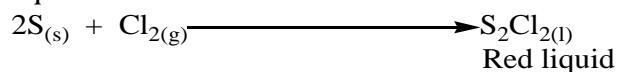


Note:

Phosphorus pentachloride and trichloride is a liquid at room temperature and 1 bar.

- ☛ Sulphur combined directly with dry chlorine gas when heated to form a red liquid of disulphur dichloride.

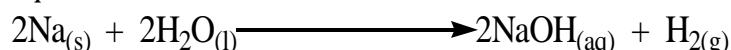
Equation:



- (d) Reaction with water (steam).

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

Equation:

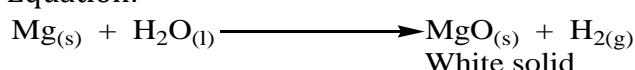


Note:

A lot of heat is liberated, the heat causes sodium to melt but doesn't burn in flame. The resultant solution is alkaline when tested.

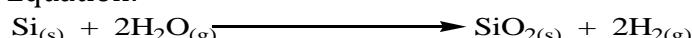
- ☛ Magnesium hardly reacts with cold water but instead burns brilliantly in steam to form magnesium oxide and hydrogen gas.

Equation:



- ☛ Aluminium **DOES NOT** react with water because of the formation of a protective layer of the oxide which prevents the reaction.
- ☛ Silicon reacts with steam when heated strongly to form silicon (IV) oxide and hydrogen gas is also liberated.

Equation:



- Red phosphorus is insoluble in water while white phosphorus is soluble but does not react with water, meaning that red phosphorus reacts with water when vaporized to form phosphorus (III) oxide and hydrogen gas.

Equation:



- Sulphur does not react with water.

- Chlorine gas reacts with cold water to form chloric (I) and hydrochloric acid.

Equation:

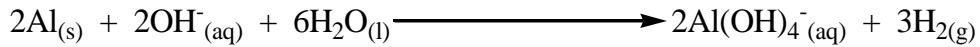


- Reaction with alkalis (sodium hydroxide solution).

- Both sodium and magnesium **DO NOT** react with alkalis because they are basic and electropositive.

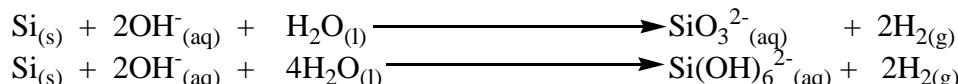
- Aluminium is amphoteric and reacts with concentrated sodium hydroxide solution to form sodium tetrahydroxo aluminate (III) and hydrogen gas.

Equation:



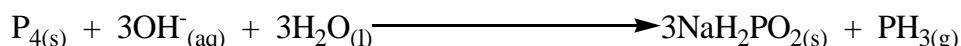
- Silicon reacts with hot concentrated sodium hydroxide solution to form sodium silicate and hydrogen gas.

Equation:



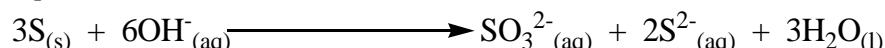
- Phosphorus reacts with hot concentrated sodium hydroxide solution to form sodium hypophosphate and phosphine gas.

Equation:



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

Equation:



Note:

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

Equation:



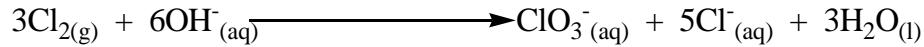
- Chlorine gas reacts with cold concentrated sodium hydroxide solution to form sodium chloride, sodium chlorate (I) and water.

Equation:



- Chlorine gas also reacts with hot concentrated sodium hydroxide solution to form sodium chloride, sodium chlorate (V) and water.

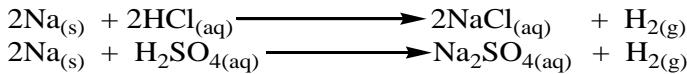
Equation:



(f) Reaction with acids.

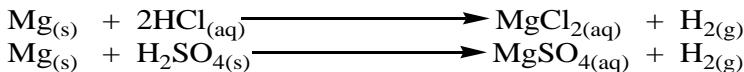
(i) Dilute mineral acid (Dilute non-oxidizing acids).

- ☞ Sodium reacts with both dilute hydrochloric and sulphuric acid to form hydrogen gas, chloride,  $\text{Cl}^-$  and sulphate,  $\text{SO}_4^{2-}$  ions respectively.
- Equations:



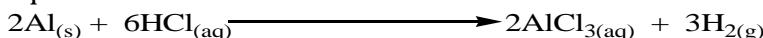
- ☞ Magnesium reaction with both dilute hydrochloric and sulphuric acid to form salts and hydrogen gas.

Equation:



- ☞ Aluminium reacts rapidly with hot dilute hydrochloric acid **BUT** do not react with dilute sulphuric acid perhaps because of the insolubility of the oxide layer in the acid.

Equation:



- ☞ Silicon, phosphorus, sulphur **do not** react with any dilute mineral acids **BUT** silicon is attacked **ONLY** by hydrofluoric acid.

Equation:



**Reason:**

Silicon, Phosphorus & Chlorine **DONOT** react with acid because they are acidic in nature.

**Golden tips:**

- ☞ Nitric acid is an oxidizing acid so Magnesium is the **ONLY** metal that reacts with dilute nitric acid the rest of the period members **DONOT** react with oxidizing nitric acid.

Equation:



(ii) Concentrated mineral acid.

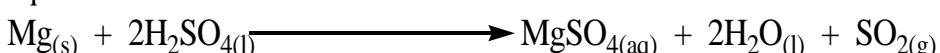
- ☞ Magnesium reacts with hot concentrated nitric acid while oxidizes metals to nitrates and is itself reduced to nitrogen monoxide (or nitrogen dioxide gas).

Equation:



Magnesium also reacts with hot concentrated sulphuric acid to yield sulphur dioxide gas and other useful products.

Equation:



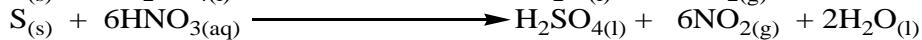
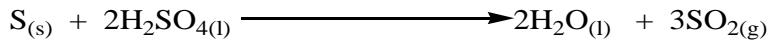
- ☞ Aluminium reacts with hot concentrated sulphuric acid to form sulphate,  $\text{SO}_4^{2-}$  ion, water and sulphur dioxide gas.

Equation:



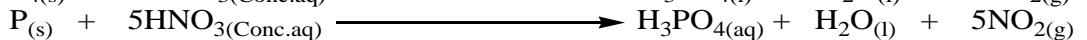
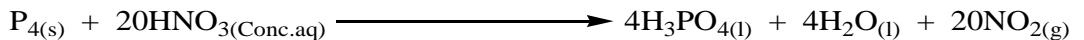
Sulphur is oxidized by both hot concentrated sulphuric and nitric acid to useful products.

Equations:



Phosphorus is oxidized by hot concentrated nitric acid to useful products and is itself reduced to nitrogen dioxide gas.

Equations:



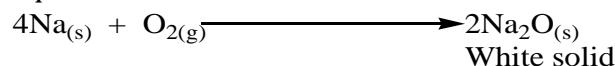
### **PREPARATIONS OF COMPOUNDS OF PERIOD (III)**

#### **ELEMENTS:**

##### **A. PREPARATION OF PERIOD (III) OXIDES.**

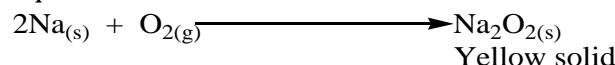
— Sodium oxide (sodium monoxide) is prepared by heating sodium in limited supply of air (oxygen gas).

Equation:



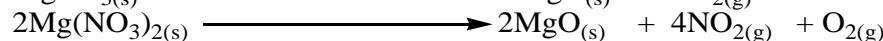
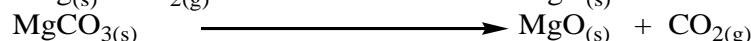
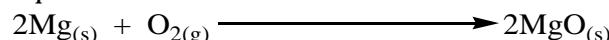
— Sodium peroxide is manufactured by heating sodium metal in excess supply of air (oxygen gas) at a temperature of about 600K.

Equation:



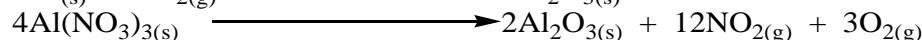
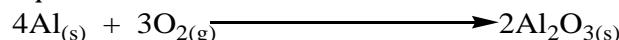
— Magnesium oxide is prepared by burning either magnesium metal in air (oxygen gas) or by decomposition of either magnesium carbonate or nitrate.

Equations:



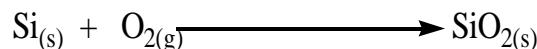
— Aluminium (III) oxide is prepared by burning aluminium metal in excess supply of air (oxygen gas) or thermal decomposition of either aluminium (III) nitrate or hydroxide by heat.

Equations:



— Silicon (IV) oxide is prepared by burning silicon in oxygen gas (air).

Equation:



— Silicon (IV) oxide is also prepared by burning silicon over steam at red heat.

Equation:



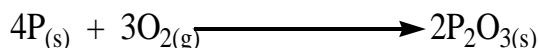
— Silicon (IV) oxide is prepared by burning silane over air (oxygen gas).

Equation:



— Phosphorus (III) oxide is prepared by burning phosphorus in limited supply in air (oxygen gas).

Equation:



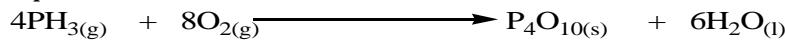
— Phosphorus (V) oxide is prepared by burning phosphorus in excess supply in air (oxygen gas).

Equation:



— Phosphorus (V) oxide is prepared by burning phosphine in air (oxygen gas).

Equation:



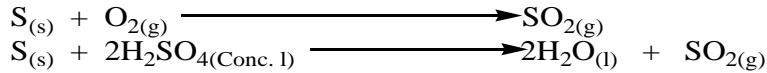
— Phosphorus (V) oxide is prepared by burning calcium phosphate (V) and silica at a higher temperature.

Equation:



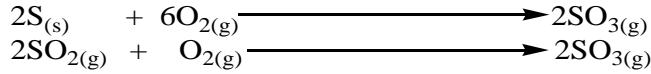
— Sulphur dioxide gas is prepared by burning sulphur in limited supply of air (oxygen gas).

Equation:



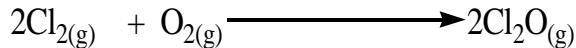
— Sulphur trioxide gas is prepared by burning sulphur in excess supply of air (oxygen gas).

Equation:



— Dichlorine oxide is prepared by burning chlorine gas in limited supply oxygen gas.

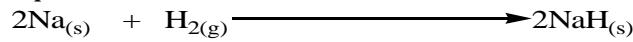
Equation;



## B. PREPARATION OF PERIOD (III) HYDRIDES.

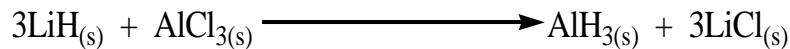
— Sodium hydride is a white crystalline solid prepared by heating sodium in a stream of dry hydrogen gas.

Equation:



— Aluminium hydride is a white solid precipitated when lithium hydride is treated with excess aluminium chloride in a solution of ether.

Equation:



- Silane is obtained by fractional distillation from a mixture of silicon hydrides formed when magnesium silicide is treated with hydrochloric acid.

Equation:



- However, a more convenient way of preparing silane is by reduction of silicon tetrachloride with lithium aluminium hydride.

Equation:



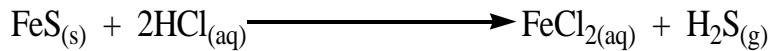
- Phosphorus trihydride (phosphine) is prepared by heating concentrated sodium hydroxide solution with white phosphorus.

Equation:



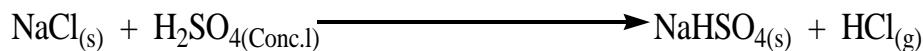
- Hydrogen sulphide gas is prepared by action of dilute hydrochloric acid on iron (II) sulphide.

Equation:



- Hydrogen chloride gas is prepared by the action of concentrated sulphuric acid on sodium chloride.

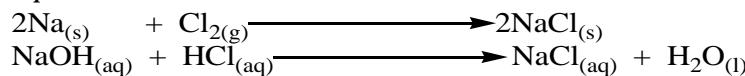
Equation:



### C. PREPARATION OF PERIOD (III) CHLORIDES.

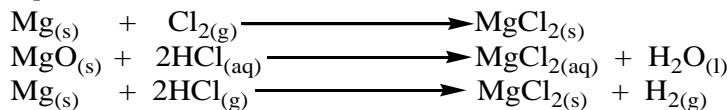
- Sodium chloride is prepared by neutralization method involving sodium hydroxide and hydrochloric acid. NaCl is an ionic chloride. This is a very vigorous reaction.

Equations:



- Magnesium chloride is prepared by reacting its carbonate, oxide or hydroxide with dilute hydrochloric acid. MgCl<sub>2</sub> is also an ionic chloride. Vigorous reaction when the elements are heated.

Equations:



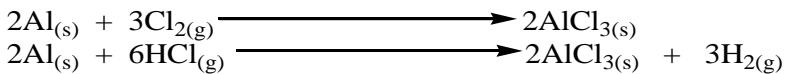
- Aluminium (III) chloride is a white solid prepared by passing dry chlorine gas (or hydrogen chloride gas) over the heated aluminium. It sublimes at 456K and at temperature above 456K, it exists as Al<sub>2</sub>Cl<sub>6</sub>.

Equation:



- Aluminium (III) chloride is prepared by heating aluminium metal in either dry chlorine or hydrogen chloride gas.

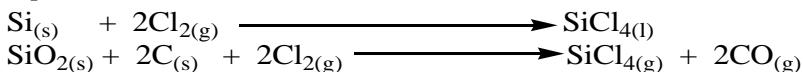
Equation:



Note:

- Anhydrous magnesium chloride is prepared by direct synthesis since any attempt to obtain it from the hydrated magnesium chloride or by evaporation of its aqueous solution to yields a basic chloride due to hydrolysis.
- Silicon (IV) chloride is prepared by directly combination of dry chlorine gas with silicon.

Equations:

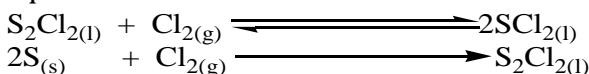


Notes:

Silicon (IV) chloride is conveniently prepared by heating a mixture of silicon (IV) oxide and carbon in a dry current of chlorine gas.

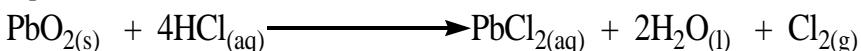
- Sulphur dichloride or disulphur dichloride combined directly to form chlorides  
Sulphur dichloride reacts with chlorine gas at 0°C and dry chlorine gas is passed over molten sulphur to form disulphur dichloride.

Equations:



- Chlorine gas is prepared by heating lead (IV) oxide with concentrated hydrochloric acid.

Equation:



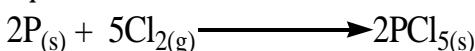
- Phosphorus trichloride is a colourless liquid prepared by passing dry chlorine gas over heated white phosphorus.

Equation:



- Phosphorus pentachloride is prepared by passing excess dry chlorine gas over phosphorus.

Equation:



### Physical properties of chlorides:

$\text{NaCl}$  and  $\text{MgCl}_2$  are ionic chlorides. Since a large amount of energy is required to separate the ions, the melting point is high.

$\text{AlCl}_3$  and  $\text{SiCl}_4$  are molecular covalent chlorides, and so only intermolecular forces exist between the molecules. The melting points are thus much lower than the ionic chlorides.  $\text{AlCl}_3$  actually exists in polymeric form in the solid state, which is converted to a dimeric form in the gas phase. This is because the aluminium atom is electron deficient – it has only 3 of its four valence orbitals occupied, so it has an empty orbital with which it can accept a lone pair of electrons from a Cl atom on an adjacent monomer. At high temperatures, it reverts to a simple molecular structure.

PCl<sub>5</sub> is ionic so its melting point is thus high. On heating, however, it reverts to a simple covalent structure and sublimes.

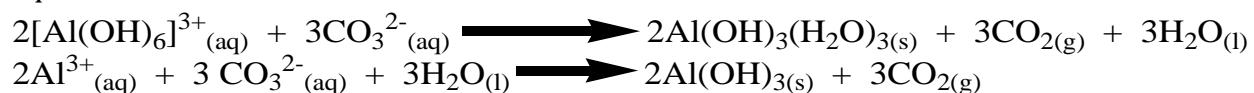
**Notes:**

The metals however can also form covalent compounds with non-metals depending on the difference in electronegativity. AlF<sub>3</sub> for instance is ionic ( $\Delta EN = 2.5$ ) but AlCl<sub>3</sub> is covalent ( $\Delta EN = 1.5$ ).

1. Briefly explain the following observations below:

- Sodium chloride melts at 800°C whereas Aluminum chloride sublimes at 180°C.  
Sodium, Na<sup>+</sup> ions has a smaller charge density compared to the Aluminum, Al<sup>3+</sup> ions. Sodium chloride therefore forms a giant ionic structure with strong ionic bonds between the ions hence higher melting point.  
Aluminum chloride has a covalent layered structure with weak Van der Waal's forces between the layers which can be easily broken giving it a lower melting point.
- When sodium carbonate solution was added to a solution of aluminum chloride, a white precipitate was formed and a colourless gas evolved.  
Aluminum chloride solution produces hydrogen, H<sup>+</sup> ions [is acidic] due to hydrolysis, the hydrogen, H<sup>+</sup> ions [is acidic] reacts with carbonate, CO<sub>3</sub><sup>2-</sup> ions to form carbon dioxide gas and a white precipitate of insoluble aluminum hydroxide solution.

Equations:



**PREPARATION OF PERIOD (III) HYDROXIDES.**

**(ATTENTION BOYS 'READ ABOUT PREAPARATION OF HYDROXIDE')**

**COMPOUNDS OF PERIOD (III):**

Period (III) elements forms several compounds including:

- Oxides.

**BONDING AND STRUCTURES OF PERIOD (III) OXIDES:**

Sodium, Magnesium & Aluminium oxides forms giant ionic structures hence forming ionic bonds, Ionic character of these oxides decreases with increasing charge density of the cation. Silicon (IV) oxide forms a giant covalent structure.

The rest of the oxides form simple molecular structures.

**MELTING POINTS OF PERIOD (III) OXIDES:**

Sodium, Magnesium & Aluminium oxides have giant ionic structures hence form ionic bonds.

They have high melting and boiling points. The melting points increases from sodium via magnesium to aluminium (III) oxides. This is because ionic radius decreases from sodium to aluminium ions and the charges on the cations increases from Na<sup>+</sup> to Al<sup>3+</sup>.

The oppositely charged ions approach each other closely in Al<sub>2</sub>O<sub>3</sub> and strongly attracts themselves because of the high charge on Al<sup>3+</sup> hence stronger ionic bond in Al<sub>2</sub>O<sub>3</sub> and high melting and boiling point.

Silicon dioxide has a giant molecular structure with three dimensional network of covalent bonds. It has high melting point because of the strong bonding structure.

$P_2O_3$ ,  $P_2O_5$ ,  $SO_2$ ,  $SO_3$ ,  $Cl_2O$ ,  $Cl_2O_7$ , These consist of small discrete molecules with simple molecular structure. They have low melting and boiling point because of the weak Van der Waal's forces of attraction holding the molecules.

Or:

The melting point increases from sodium via magnesium to aluminium oxide then reducing up to dichlorine heptoxide.

Sodium, magnesium and aluminium oxides have giant ionic structures. The ions are held together by strong ionic bonds.

The melting point increases from sodium oxide to magnesium oxide due to increase in charge density of the cation, from magnesium oxide to aluminium oxide it decreases due to very high charge density of aluminium ion which makes aluminium oxide partly covalent (less ionic).

Silicon dioxide has a giant covalent structure. Its atoms are held by strong covalent bonds, the rest of the oxides have simple molecular structures.

Molecules are held by weak Van der Waal's forces of attraction whose strength decreases with decrease in polarity of the molecules as a result of decrease in difference of electronegativity of the bonding atoms.

### **REACTIONS OF PERIOD (III) OXIDES WITH:**

1) Water.

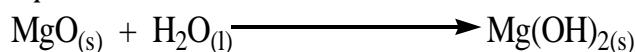
☞ Sodium oxide is a white solid that reacts with water to give strongly (or violent) basic aqueous sodium hydroxide solution.

Equation:



☞ Magnesium oxide is a white powder which is only slightly (sparingly) soluble in water to form weak basic aqueous solution.

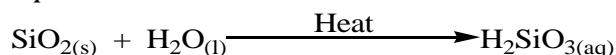
Equation:



☞ Aluminium (III) oxide is a white solid and DONOT react with water because it is very insoluble in water.

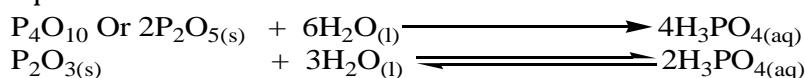
☞ Silicon (IV) oxide is highly insoluble in water and DONOT react with water except under high temperature.

Equation:



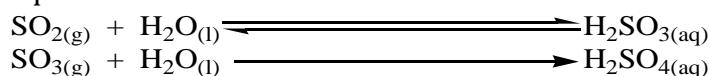
☞ Phosphorus (V) and phosphorus (III) oxide reacts with water to form aqueous solution.

Equations:



☞ Sulphur dioxide and sulphur trioxide gas reacts with water to form an acidic solution because of its moderate solubility in water.

Equations:

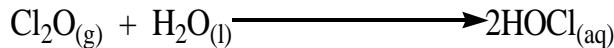


Note:

Sulphur trioxide gas reacts violently with a hissing sound and much heat is evolved.

☞ Dichlorine oxide (chlorine monoxide) reacts (dissolves) with water to form aqueous hypochlorous acid.

Equation:



☞ Chlorine dioxide reacts with water to form mixed acidic anhydride of chloric (III) and chloric (V) acid (chloric acid).

Equation:



☞ Dichlorine heptoxide reacts with water to form aqueous perchloric acid.

Equation:

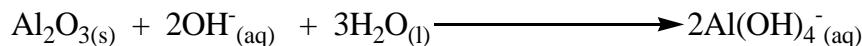


## 2) Alkalies (i.e. sodium hydroxide solution).

☞ Sodium and magnesium oxides are basic in nature and therefore DONOT reacts with alkalies in any condition.

☞ Aluminium (III) oxide reacts with concentrated alkalies to form a complex salts (aluminate).

Equation:

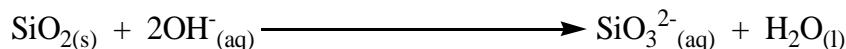


Or:



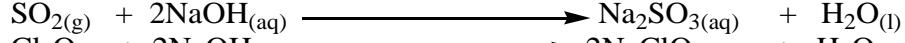
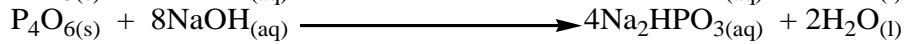
☞ Silicon (IV) oxide reacts with concentrated alkalies to form silicate (complex salts).

Equation:



☞ The rest of the peroxide (III) oxide's members reacts with alkalies to form salts and water.

Equations:



## 3) Acids.

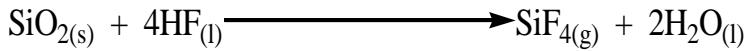
☞ Sodium, magnesium & aluminium oxides reacts with dilute mineral acids to form their respective salts and water.

Equations:



☞ Silicon (IV) oxide doesn't reacts with any mineral acids except hydrofluoric acid.

Equation:



☞ And the rest of the remaining period (III) oxides **DONOT** reacts with any mineral acids.

## B. Hydrides.

### Bonding and structures:

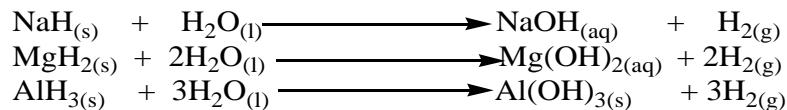
Sodium is highly electropositive and the hydride is ionic while those of magnesium and aluminium are ionic too but moving towards the rest of the other remaining period (III) elements which are predominantly covalent hence the covalent character attribute to the small ionic radius and high charge density of the cations. And the other members of the period (III) hydrides are covalent and simple molecular held by weak Van der Waal's forces of attraction hence the acidity of the hydrides increases across the period from left to right.

### REACTIONS OF PERIOD (III) HYDRIDES WITH:

#### 1) Water.

☞ Sodium, magnesium & aluminium hydrides reacts with cold water to form aqueous sodium hydroxide (alkaline) solution and hydrogen gas.

Equations:

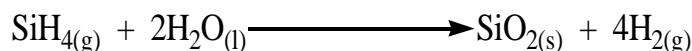


Notes:

The reaction indicates that the hydroxyl,  $\text{OH}^-$ , ions are being removed from solution, so the solution becomes less basic from sodium hydride to aluminium hydride via magnesium hydride but the acidity increases.

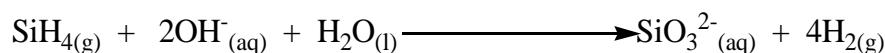
☞ Silane is hydrolysed by cold water to form silicon (IV) oxide and hydrogen gas.

Equation:



☞ Silane is also hydrolysed by cold water in presence of an alkali to form sodium silicate and hydrogen gas.

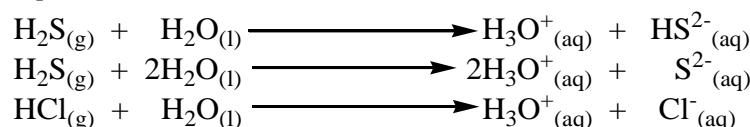
Equation:



☞ Phosphine **DONOT** reacts with water because it's almost insoluble in water and it is non-polar since both P and H have almost equal electronegativity values.

☞ Hydrogen sulphide and hydrogen chloride gas does not hydrolysed in water but instead ionizes to form acidic solution.

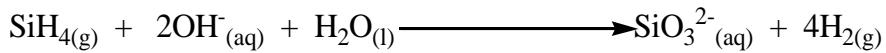
Equations:



#### 2) Alkalies.

☞ Silane is hydrolysed by water in the presence of an alkalis to form silicate and hydrogen gas.

Equation:



☞ Hydrogen sulphide reacts with sodium hydroxide solution to form sodium hydrogen sulphide and water.

Equation:



☞ Aqueous hydrogen chloride reacts with sodium hydroxide solution to form sodium chloride solution and water.

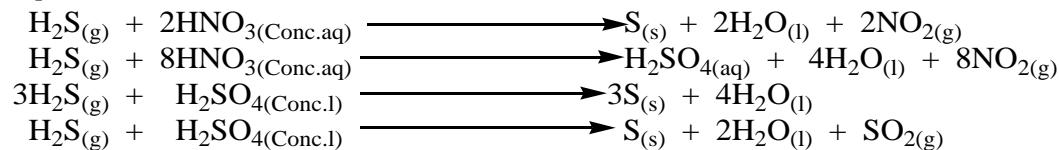
Equation:



### 3) Acids

☞ Hydrogen sulphide gas reduces both concentrated sulphuric and nitric acid to very useful products.

Equations:



### C. Chlorides.

#### **BONDING AND STRUCTURES OF PERIOD (III) CHLORIDES:**

Electropositive metals form mainly ionic compounds but the degree of ionic character reduces as electropositivity decreases across the period. Magnesium and aluminium chlorides are ionic with some considerable degree of covalent character. The rest of the chlorides on the right are covalent through the bonds possess some polarity. Bond type and structure have a big consequence on melting point of the chlorides.

#### **MELTING POINTS OF PERIOD (III) CHLORIDES:**

- Sodium and magnesium chloride have giant ionic structures with strong electrostatic force of attraction between the appositively charged ions, hence they have high melting and boiling points.
- Melting and boiling points decreases from sodium to aluminium chlorides. This is because the ionic radius of the cations decreases from sodium,  $\text{Na}^+$  to aluminium,  $\text{Al}^{3+}$  ion. The charge on the cations increases for sodium,  $\text{Na}^+$  to aluminium,  $\text{Al}^{3+}$  ions. This results in aluminium,  $\text{Al}^{3+}$  ion having the greatest polarizing power.

Table:

Ions	Ionic radius	Charge	Polarizing power
$\text{Na}^+$	0.095	1	$\frac{1}{0.095} = 10.5$
$\text{Mg}^{2+}$	0.065	2	$\frac{2}{0.065} = 30.7$
$\text{Al}^{3+}$	0.050	3	$\frac{3}{0.050} = 60.0$

- Aluminium,  $\text{Al}^{3+}$  ion greatly polarizes the chloride,  $\text{Cl}^-$  ion than both magnesium,  $\text{Mg}^{2+}$  and sodium,  $\text{Na}^+$  ions. Aluminium (III) chloride is more covalent than both magnesium and sodium chlorides hence low melting points.
  - The other chlorides of silicon, phosphorus, sulphur and chlorine adopt simple molecular structures with weak Van der Waal's forces of attraction holding them hence low melting and boiling points.
- Or:
- Melting point of chlorides generally decreases as the period is traversed from left to right.
  - Sodium and magnesium chlorides form giant ionic lattices though the degree of ionic character decreases with increase in charge density in the same direction. Therefore, magnesium chloride has a lower melting point than sodium chloride.
  - Aluminium,  $\text{Al}^{3+}$  ion have a very high charge density which induces a very high covalent character in aluminium (III) chloride hence low melting point.
  - Silicon tetrachloride is covalent consisting of molecules held by weak Van der Wall's forces of attraction holding them hence low melting point.
  - Phosphorus trichloride is also simple molecular hence low melting points
  - Phosphorus pentachloride has abnormal high melting point because at ordinary temperature it's known to consist of  $\text{PCl}_4^-$  and  $\text{PCl}_6^-$  ions though in vapour state it consists of  $\text{PCl}_5$  molecules.
  - It is this ionic character that is responsible for its abnormally high melting points.
  - The chlorides of sulphur are simple molecular held by weak Van der Waal's forces of attraction. Magnitude of the Van der Waals force decrease with decreasing molecular mass.
2. Briefly explain each of the following observations in terms of the types of chemical bonding involved.
- a) Sodium chloride melts at  $800^\circ\text{C}$  whereas Aluminium chloride sublimes at  $180^\circ\text{C}$ .  
Both sodium and aluminium chloride have ionic bonding. But because of small size and large charge of the  $\text{Al}^{3+}$  ion which gives it a high polarizing power, the electrons on the outermost shell of the chloride,  $\text{Cl}^-$  ion is greatly polarized (displaced) towards the  $\text{Al}^{3+}$  ion such that  $\text{AlCl}_3$  develops some covalent character which makes it have a low melting point just like most covalent compounds. Sodium chloride is pure ionic hence very high melting point.
  - b) Nitrogen is gaseous at room temperature whereas phosphorous can exist in several solid forms at room temperature.  
The molecules of both nitrogen and phosphorus are held together by weak Van der Waal's forces. Because phosphorus has a bigger size than nitrogen, the Van der Waal's forces in phosphorus are stronger and are capable of holding the molecules of phosphorus as a solid while in nitrogen because of small size the forces are so weak that they are even overcome at room temperature so that nitrogen is a gas.
  - c) Sulphur melts at  $119^\circ\text{C}$  whereas phosphorus melts at  $118^\circ\text{C}$ .

Both sulphur and phosphorous molecules are held together by Van der Waal's forces of attraction. Because sulphur has a bigger size, S<sub>8</sub> than phosphorous, P<sub>4</sub>, The forces are in greater magnitude hence sulphur has a higher melting point than phosphorus.

**Golden tips:**

The magnitude of Van der Waal's forces is dependent on the size of the molecules. The greater the size, the greater the Van der Waal's forces and the higher the melting points.

### **REACTIONS OF PERIOD (III) CHLORIDES WITH:**

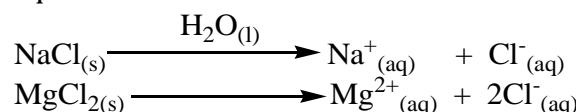
1) Water

- ☞ Sodium chloride and Magnesium chloride dissociate to form neutral aqueous solution since they are ionic and a lot of energy is required to separate it. The chlorides of sodium and magnesium are predominantly ionic and are white solid with high melting points, which dissolves in water.

Note:

Meaning that purely ionic chlorides do not react with water but instead dissolves in water to form ions

Equations:



- ☞ However magnesium chloride dissociates in cold water and the resultant solution is slightly acidic because it undergoes hydrolysis due to higher charge density on magnesium, Mg<sup>2+</sup> ion.

Note:

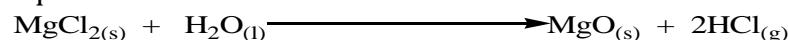
Magnesium chloride undergo partial hydrolysis in cold water to form a basic chloride.

Equations:



However, if heated magnesium chloride undergo hydrolysis to form magnesium oxide which is a white solid.

Equation:

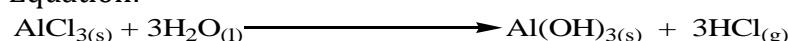


**Golden tips:**

All the other chlorides of (III) elements have significantly covalent character and reacts with water. These reactions called **Hydrolysis** reactions.

- ☞ Anhydrous aluminium (III) chloride undergoes hydrolysis liberating hydrogen chloride gas.

Equation:



**Golden tip:**

Aluminium (III) chloride fumes in moist air by hydrolysis liberating hydrogen chloride gas and this explains why its solution is acidic.

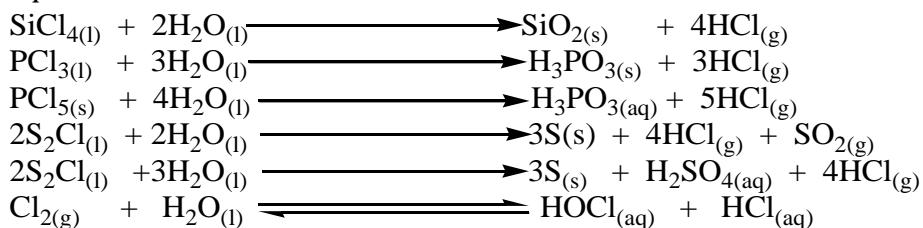
- ☞ Hydrated aluminium (III) chloride dissolves in water to form an acidic solution.

Equation:



The chlorides of silicon, phosphorus, disulphur dichloride and chlorine gas are predominantly covalent. They all react with water (are hydrolysed) rather than simply dissolving in water, hence fume in air to form acidic solutions.

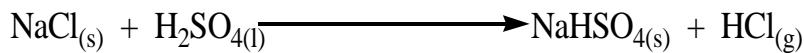
Equations:



## 2) Acids.

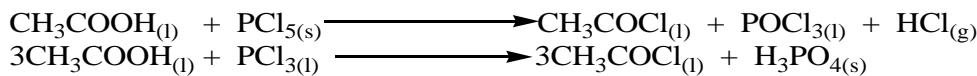
Sodium chloride reacts with concentrated sulphuric acid to yield hydrogen chloride gas.

Equation:



Chlorides of phosphorus react with carboxylic acids to yield corresponding acyl chlorides.

Equations:



## D. Hydroxides.

Based on the normal valency of the elements, we would expect the following hydroxides:

Elements	Na	Mg	Al	Si	P	S	Cl		
Valency	1	2	3	4	5	6	7		
Expected hydroxide	NaOH	Mg(OH) <sub>2</sub>	Al(OH) <sub>3</sub>	Si(OH) <sub>4</sub>	P(OH) <sub>5</sub>	S(OH) <sub>6</sub>	Cl(OH) <sub>7</sub>		
Hydroxide formed	"	"	"	H <sub>2</sub> SiO <sub>3</sub>	H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub>	HClO <sub>4</sub>		
Character	Strong Base	Weak base	amphoteric	Weak acid		Strong acid			
Expected hydroxide	Water molecule (s) lost			Hydroxide formed					
Si(OH) <sub>4</sub>	-H <sub>2</sub> O			H <sub>2</sub> SiO <sub>3</sub>					
P(OH) <sub>5</sub>	-H <sub>2</sub> O			H <sub>3</sub> PO <sub>4</sub>					
S(OH) <sub>6</sub>	-2H <sub>2</sub> O			H <sub>2</sub> SO <sub>4</sub>					
Cl(OH) <sub>7</sub>	-3H <sub>2</sub> O			HClO <sub>4</sub>					

### Explanation:

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

### Acid-base character of the hydroxides:

For metallic hydroxides, basic strength increases with increase in ease of loss of the hydroxyl group in form of OH<sup>-</sup> ions. The less electronegative the metal, the weaker is the M-OH bond and consequently the stronger is base.

Electronegativity of the metal atoms increases in the order  $\text{Na} < \text{Mg} < \text{Al}$  hence basic strength reduces in the order of  $\text{NaOH} > \text{Mg(OH)}_2 > \text{Al(OH)}_3$ .

The non-metallic hydroxides (known as oxy-acids) are acidic. Their acidic strength increases with increase in the ease of loss of a proton.

The acidic strength increases in the order of:  $\text{H}_2\text{SiO}_3 < \text{H}_3\text{PO}_4 < \text{H}_2\text{SO}_4 < \text{HClO}_4$ . This trend can be explained by considering the structures of the acids (not drawn to scale) below.

Oxygen atoms attached to the central atom withdraw electrons from the central atom which in turn withdraws electrons from hydroxyl groups bonded to it, this increases the partial positive charge on the hydrogen atom making it more easily lost.

The greater the effect of withdrawing electrons, the stronger the acid. This effect increases with increase in number of oxygen atoms attached to the central atom and also with increase in the electronegativity of the central atom.

Electronegativity of the central atom increases in the order of:  $\text{Si} < \text{P} < \text{S} < \text{Cl}$  hence acidic strength also increases in the same order.

## **EXTRACTION OF ALUMINIUM, CHLORINE, SODIUM & SODIUM HYDROXIDE SOLUTION:**

### **• ALUMINIUM**

Ores of aluminium:

- Bauxite or Gibbsite (impure hydrate aluminium oxide),  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ .
- Cryolite (Sodium hexafluoroaluminate (III)),  $\text{Na}_3\text{AlF}_6$ .

### **EXTRACTION PROCESS:**

- During extraction process of aluminium, there are two major processes involved. And the general method's name of extraction of aluminium is known is as Hall and Herout.

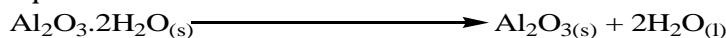
Namely:

- ☞ 1<sup>st</sup> stage is purification of bauxite by Bayer process to produce anhydrous aluminium oxide (Alumina).
- ☞ 2<sup>nd</sup> stage is reduction of Alumina (anhydrous aluminium oxide) by electrolysis.

Stage 01: purification of bauxite by Bayer process to produce anhydrous aluminium oxide (Alumina).

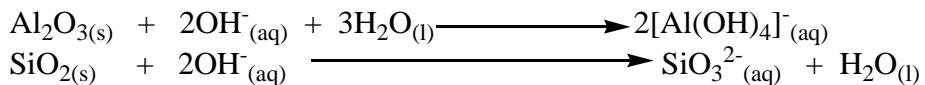
- The crude bauxite contains iron (III) oxide, silicon (IV) oxide (silica) and other impurities. But silica is an acidic and iron (III) oxide is basic impurities.
- The crude bauxite is roasted over (in) air (oxygen gas) to convert iron (II) in to iron (III) oxide and then to remove the water of crystallization since the bauxite contains some water molecule (impure hydrated aluminium (III) oxide).

Equation:



- The roasted bauxite ore is crushed in to powder is heated with excess concentrated sodium hydroxide solution under high pressure.

Equations:

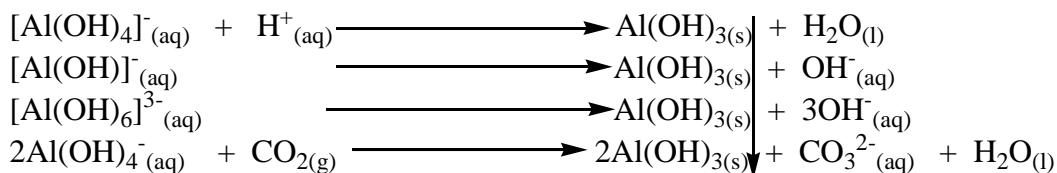


Note:

Aluminium oxide since it is an amphoteric oxide, it will dissolve to form aluminate while silicon dioxide is an acidic, also dissolves in to form silicate. But both iron (III) oxide and titanium (IV) oxide remains undissolved, and it is removed by filtration process since both are basic oxide. And they are removed from the mixture by allowing them to settle out.

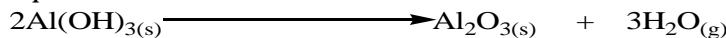
- The solution is then filtered off and transferred to a precipitation tank where it is seeded with crystals of aluminium hydroxide. On seeding, the aqueous sodium tetrahydroxoaluminate (III) solution decomposes, forming aluminium hydroxide. Or the solution is then treated with weak acid (e.g. carbon dioxide gas to produce carbonic acid) in order to produce aluminium hydroxide.

Equations:



- The aluminium hydroxide crystals are filtered, washed, dried and then heated (roasted) at a temperature of about 1000°C strongly to form pure aluminium oxide.

Equation:



- This method of purification involves chemical methods of concentrating the ore which includes:

### 1) Leaching

By this, ore is treated with a suitable aqueous reagent that dissolves the ore leaving behind the impurities.

#### Example:

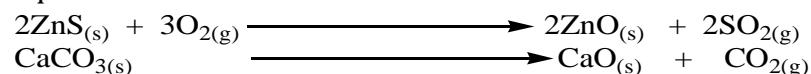
Pure aluminium oxide is obtained from bauxite using concentrated sodium hydroxide solution. Aluminium oxide dissolves (since it is amphoteric oxide) together with silicon (IV) oxide (since it is acidic oxide) but some impurities do not dissolve.

### 2) Roasting

During roasting, the ore is heated (roasted) (over) in air (oxygen gas). Roasting may cause oxidation or reduction and may be accompanied by calcination. Calcination is the heating of the ore to bring about decomposition with elimination of volatile products.

The volatile products can be carbon dioxide, sulphur dioxide and steam in case of sulphites.

#### Equations:



### 3) Smelting.

This is the method of concentrating the ore by melting it. Two layers are formed, after melting, which include the molten metal layer and slag. Slag, being less dense, floats on the metal layer.

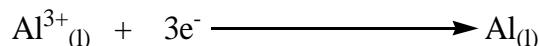
Stage 02: reduction of Alumina (anhydrous aluminium oxide) by electrolysis.

- During electrolysis process to reduce the alumina (anhydrous aluminium oxide), a solvent must be used, since the melting point of anhydrous aluminium oxide is so high, a molten mixture of the ore cryolite, sodium hexafluoroaluminate,  $\text{Na}_3\text{AlF}_6$ , with calcium fluoride and aluminium fluoride is added to lower its melting point (temperature).
- Aluminium collects at the bottom of the steel tank as shown in the diagram below and is tapped off at regular intervals since aluminium oxide is dissolved in the melting process, and electrolyzed at a temperature of about  $850^\circ\text{C}$  to give aluminium at the cathode and oxygen gas at the anode respectively.

Equation:

- $\text{Al}_2\text{O}_{3(s)} \rightleftharpoons \text{Al}^{3+}_{(aq)} + \text{AlO}_3^{3-}_{(aq)}$  Gives rise to the electrode processes  
Aluminium is discharged at the graphite lining of the cell which acts as the cathode.

Equation at the cathode:



- The molten aluminium collects at the bottom of the cell and is tapped off periodically. Oxygen gas is evolved at the anode.

Equation at the anode:



Note:

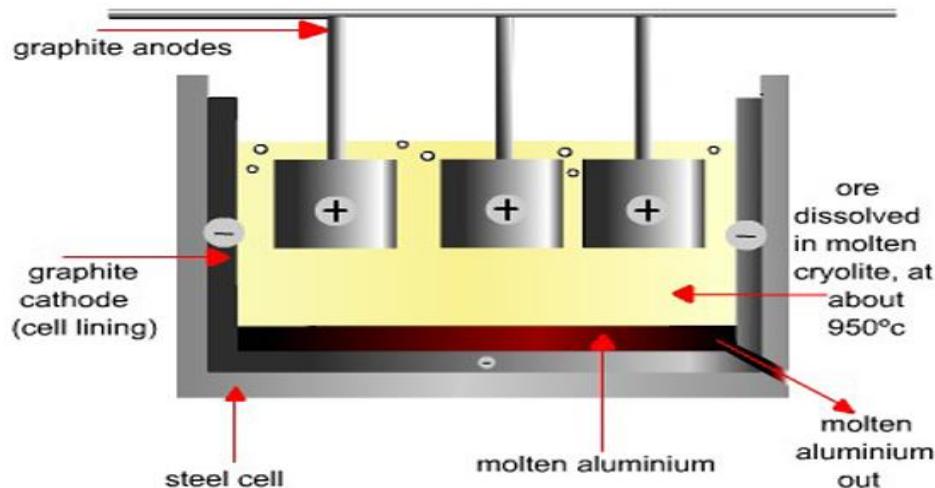
A high voltage is used to avoid decomposition of solvent, cryolite.

The process required a large amount of energy, thus it is uneconomical.

The anode burns in oxygen, thus it has to be replaced from time to time.

The purpose of sodium hydroxide added is to remove aluminium oxide from its impurities.

### **DIAGRAM FOR EXTRACTION:**



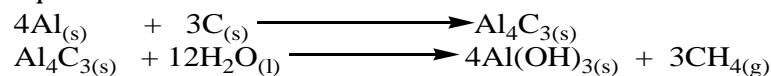
## **USES OF ALUMINIUM:**

- ✓ Since it is a good conductor of heat, it is used to make saucepans.
  - ✓ Since it has ability to reflect heat and light, it is used for wrapping food.
  - ✓ Because of its low density and strength, it is used for making bodies of aircrafts.

## **REACTIONS OF ALUMINIUM:**

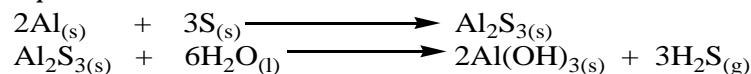
- ✓ Aluminium halides are  $\text{AlF}_3$ ,  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ , and  $\text{AlI}_3$ . Explains the observations:
  - ✓ The above halides are largely covalent because of the high polarizing power of the aluminium,  $\text{Al}^{3+}$  ion character increases from  $\text{AlF}_3$  to  $\text{AlI}_3$ . Iodide,  $\text{I}^-$  ion is the most polarized because of the big ionic radius of the iodide,  $\text{I}^-$  ion.
  - ✓ Aluminium fluoride is ionic because of the small ionic radius of the fluoride,  $\text{F}^-$  ion that makes it to experience negligible polarization.
  - ✓ Aluminium reacts with carbon to form aluminium carbide which is then hydrolysed by water to aluminium (III) hydroxide and methane gas.

Equation:



- ✓ Aluminium reacts with sulphur at a high temperature to form aluminium (III) sulphide which is then hydrolysed by water to form aluminium (III) hydroxide and hydrogen sulphide gas.

**Equation:**



## **IDENTIFICATION OF ALUMINIUM, $\text{Al}^{3+}$ .**

- 1) Using aqueous sodium hydroxide solution.

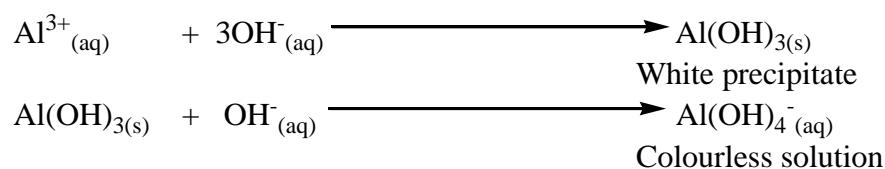
#### **Procedure:**

- ✓ To a solution, add sodium hydroxide solution.

#### Observation:

White precipitate, soluble in excess sodium hydroxide solution forming a colourless solution.

### Equations:



- 2) Using aqueous ammonia solution.

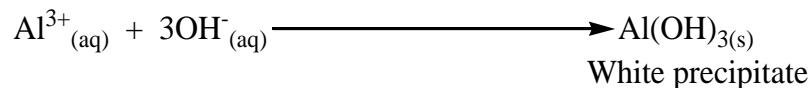
## Procedure:

- ✓ To a solution, add aqueous ammonia hydroxide solution.

## Observation:

White precipitate insoluble in excess aqueous ammonia solution.

### Equation:



3) Using sodium carbonate solution.

Procedure:

- ✓ To a solution, add sodium carbonate solution.

Observation:

White precipitate, bubbles of a colourless gas is given off.

The white precipitate dissolves in gradually in excess sodium carbonate to form a colourless solution.

Equations:

4) Using aluminium reagents.

Procedure:

- ✓ To a solution suspected of  $\text{Al}^{3+}$  ion, acidify the solution with dilute hydrochloric acid the add 4 drops of aluminium reagent followed by aqueous sodium hydroxide solution dropwise.

Observation:

A pink lake is formed.

5) To the solution suspected of  $\text{Al}^{3+}$  ion, add alizarin solution or litmus paper solution followed by ammonia solution.

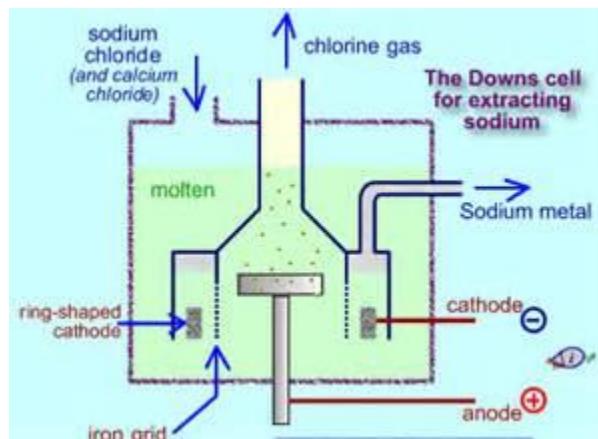
Observation:

Pink solution (Pink lake) is formed.

## • SODIUM AND CHLORINE GAS:

- Sodium is extracted commercially from sodium chloride using the Downs cell as shown below in the diagram. This a cylindrical steel cell, in which molten sodium chloride is electrolyzed between a central graphite (carbon) anode and a circular steel (iron) cathode.

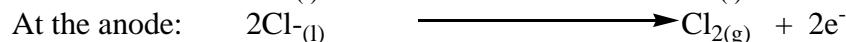
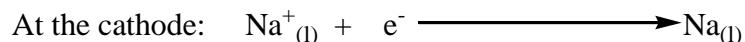
Diagram:



- Sodium chloride melts at a temperature of about  $800^{\circ}\text{C}$  and the steel cell corrodes rapidly while some sodium is produced by electrolysis process.

- Calcium chloride is then added to the molten sodium chloride to lowers the melting points since the melting point of sodium chloride is high. Hence during electrolysis, the sodium,  $\text{Na}^{+}$  ions migrate to the cathode and are discharged while chloride,  $\text{Cl}^{-}$  ions migrate to the anode and are oxidized by electron loss to form liquid chlorine gas.

Equations at the cathode and anode respectively:



Or

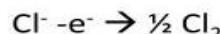
## Electrolysis of Sodium from molten Sodium Chloride(Downs cell)

The Downs cell consists of a graphite anode (doesn't react with chlorine) surmounted by a hood to remove chlorine gas, and a circular steel cathode. Added to the Sodium Chloride is **Calcium Chloride** which *helps to reduce* the melting point.

Cathode reaction:



Anode Reaction:



- **SODIUM HYDROXIDE SOLUTION AND CHLORINE GAS:**

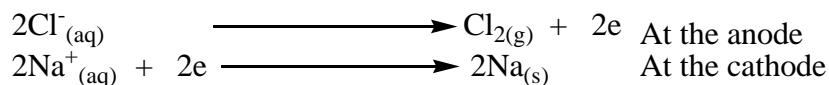
(a) During manufacture of sodium hydroxide solution by electrolysis of brine (concentrated sodium chloride solution), chlorine and hydrogen gases are vital by-products.

(b) Manufacture of sodium hydroxide solution, chlorine and hydrogen gases, there are three stages involved.

A. 1<sup>st</sup> stage is electrolysis of concentrated brine.

During electrolysis process concentrated sodium chloride solution is electrolyzed. Mercury cathode is used to enable sodium ions to be discharged in preference to hydrogen ions while chloride ion is discharged at the anode.

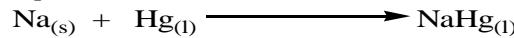
Equations:



B. 2<sup>nd</sup> stage is formation of amalgam.

Sodium formed at the cathode dissolves in the mercury, forming sodium amalgam.

Equation:



C. 3<sup>rd</sup> stage is the reaction of amalgam with water.

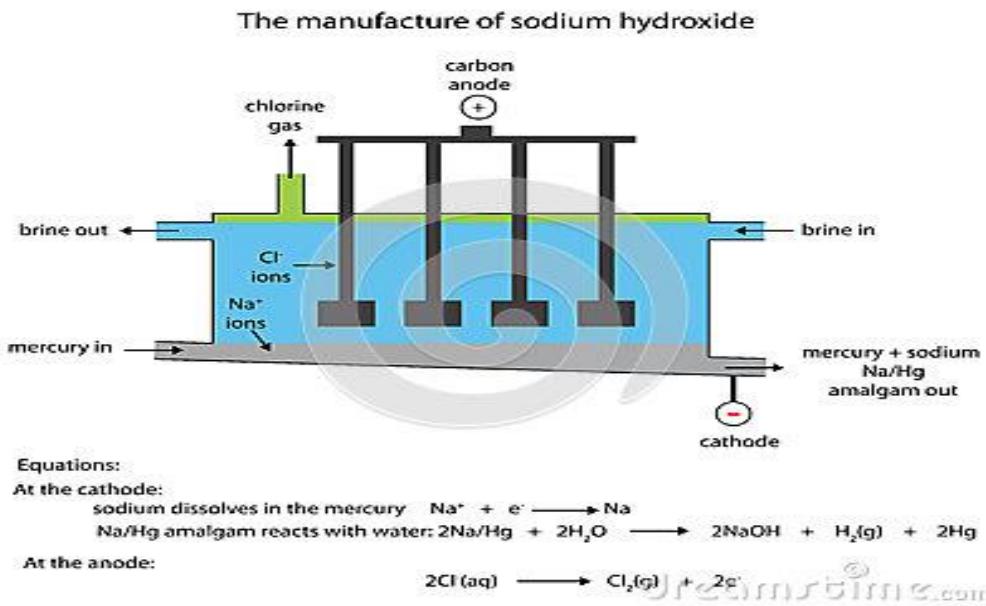
The sodium amalgam formed will flow into a separate chamber called soda cell (not shown in the diagram).

In this cell, sodium amalgam is mixed with water producing hydrogen gas and a liquor sodium hydroxide solution about 50% and a pure mercury is regenerated during this process.

Equation:



### DIAGRAM:



## PERIOD 4 (TRANSITIONAL METALS) ELEMENTS:

### — What is transition metals (d-block elements)?

- ✓ Transition metals: is a d-block element forming at least one stable ion that has a partially filled d-subshell.
- ✓ Transition elements: is an element that occurs in either d-or f-blocks elements.
- ✓ Transition metals: is an element that forms at least one ion with partially filled d-sub energy level.
- ✓ Transition elements: is an element which forms some compounds in which there is an incomplete sub-level of d-electrons.

Note:

From the above definition, scandium and zinc are excluded from the transition elements.

### Sub-topic:

#### **1. Properties of transition metals.**

Electron configuration of atoms and ions.

Electron configuration describes the distribution of electrons among different orbitals (including shells and subshells) within atoms and molecules.

Introduction:

There are four principle orbitals (**s**, **p**, **d**, and **f**) which are filled according to the energy level and valence electrons of the element. All four orbitals can hold different number of electrons.

The s-orbital can hold 2 electrons, and the other three orbitals can hold up to 6, 10, and 14 electrons, respectively. The s-orbital primarily denotes group (I) or group

(II) elements, the p-orbital denotes group 13, 14, 15, 16, 17, or 18 elements, and f-orbital denotes Lanthanides and Actinides group.

The main focus of this module however will be on the electron configuration of transition metals, which are found in the d-orbitals (d-block).

The electron configuration of transition metals is special in the sense that they can be found in numerous oxidation states.

### **FILLING TRANSITION METAL ORBITALS:**

The electron configuration for the first row transition metals consists of 4s and 3d subshells with an argon (noble gas) core. This only applies to the first row transition metals, adjustments will be necessary when writing the electron configuration for the first row of transition metals.

The noble gas core before the first row of transition metals would be the core written with brackets around the element symbol (i.e. [Ar] would be used for the first row transition metals).

And the electron configuration would follow a [Ar]  $ns^x$   $nd^x$  format. In the case of the first row transition metals.

The electron configuration would simply be [Ar]  $4s^x$   $3d^x$ . The energy level, "n" can be determined based on the periodic table, simply by looking at the row number in which the element is in. However, there is an exception for the d-block and f-block, in which the energy level, "n" for the d block is "n-1" ("n" minus 1) and for the f block is "n-2" (See following periodic table for clarification).

In this case, the "x" in  $ns^x$  and  $nd^x$  is the number of electrons in a specific orbital (i.e. s-orbitals can hold up to a maximum of 2 electrons, p-orbitals can hold up to 6 electrons, d-orbitals can hold up to 10 electrons, and f-orbitals can hold up to 14 electrons).

To determine what "x" is, simply count the number of boxes that you come across before reaching the number you are attempting to determine the electron configuration for.

### **Example of Determining Energy Levels (n):**

For example, if we want to determine the electron configuration for cobalt (Co) at group state, we would first look at the row number, which is 4 according to the periodic table below, meaning **n = 4 for the s-orbital**. In the addition, since we know that the energy level for the d block is "n-1", therefore **n = 3 for the d-orbital** in this case. Thus, the electron configuration for cobalt at ground state would simply be Co: [Ar]  $4s^2$   $3d^7$ .

### **Reason why $3d^7$ (contains 7 electrons):**

As stated, you could simply count the number of boxes on the periodic table, and since Cobalt is the 7<sup>th</sup> element of the first row transition metals, we get Cobalt Co: [Ar]  $4s^2$   $3d^7$ .

### **Transition Metals with an Oxidation State.**

In the ground state, the electron configuration of the transition metals follows the format,  $ns^x$   $nd^x$ . As for the electron configuration for transition metals that are charged (i.e. Cu<sup>+</sup>), the electrons from the s orbital will be moved to the d-orbital to form either  $ns^0$   $nd^x$  or  $ns^1$   $nd^x$

Golden tips:

It is helpful to 1<sup>st</sup> write down the electron configuration of an element at its ground state before attempting to determine the electron configuration of an element with an oxidation state.

**Examples:**

Vanadium at Ground state (Neutral):  $_{23}\text{V}:1\text{s}^22\text{s}^22\text{p}^63\text{s}^23\text{p}^64\text{s}^23\text{d}^3$  or [Ar] 4s<sup>2</sup>3d<sup>3</sup>

Vanadium with an oxidation state of +4,  $\text{V}^{4+}:1\text{s}^22\text{s}^22\text{p}^63\text{s}^23\text{p}^64\text{s}^03\text{d}^1$  or [Ar] 4s<sup>0</sup>3d<sup>1</sup>. or you can also write it as  $\text{V}^{4+}$ : [Ar] 3d<sup>1</sup>.

Nickel at Ground state (Neutral):  $_{28}\text{Ni}:1\text{s}^22\text{s}^22\text{p}^63\text{s}^23\text{p}^64\text{s}^23\text{d}^8$  or [Ar] 4s<sup>2</sup>3d<sup>8</sup>

Nickel with an oxidation state of +2,  $\text{Ni}^{2+}:1\text{s}^22\text{s}^22\text{p}^63\text{s}^23\text{p}^64\text{s}^03\text{d}^8$  or [Ar] 4s<sup>0</sup>3d<sup>8</sup>. or you can also write it as  $\text{Ni}^{2+}$ : [Ar] 3d<sup>8</sup>.

**NOTES:**

In this example, the electron configuration for  $\text{Ni}^{2+}$  still kept its 3d<sup>8</sup>, but lost the 4s<sup>2</sup> (became 4s<sup>0</sup>) because the s-orbital has the highest energy level of n = 4 in this case. Therefore, the s-orbital will lose its electron first, before the d-orbital, and so  $\text{Ni}^{2+}$  can be written as [Ar] 4s<sup>0</sup>3d<sup>8</sup> or [Ar] 3d<sup>8</sup>.

[Only the 3d and 4s sub-levels are shown in the table; all these elements possess the

argon gas core:  $1\text{s}^22\text{s}^22\text{p}^63\text{s}^23\text{p}^6$ .]

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Configuration	$3\text{d}^14\text{s}^2$		$3\text{d}^34\text{s}^2$		$3\text{d}^54\text{s}^2$		$3\text{d}^74\text{s}^2$		$+3\text{d}^{10}4\text{s}^1$	
(4 unexcited atoms)			$3\text{d}^24\text{s}^2$	$+3\text{d}^54\text{s}^1$		$3\text{d}^64\text{s}^2$		$3\text{d}^84\text{s}^2$		$3\text{d}^{10}4\text{s}^2$

Notice the anomalous behavior of chromium and copper.

**Reason:**

This is caused by the extra stability of the 3d sub-level (with its five orbitals) when it is either exactly half full or when it is completely full.

**Golden tips:**

The 4s-orbital is lower in energy than 3d-orbital. The 3d-orbitals begin to fill only after the 4s-orbital is complete.

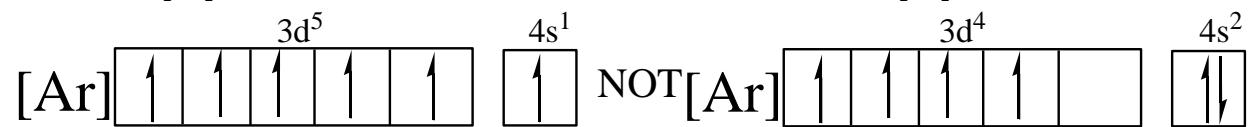
For elements after calcium, Ca [Ar] 4s<sup>2</sup>, electrons are added one at a time to the 3d-subshell beginning with scandium, the 1<sup>st</sup> transition element.

The electron configurations are given below in the table.

The electron configurations of chromium and copper in the ground state (i.e, when the atom is unexcited) is:

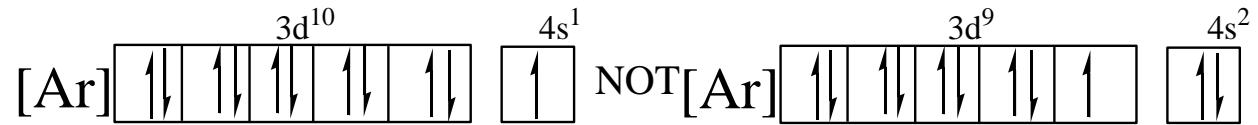
Chromium [Ar] 3d<sup>5</sup>4s<sup>1</sup>

NOT [Ar] 3d<sup>4</sup>4s<sup>2</sup>



Copper [Ar] 3d<sup>10</sup>4s<sup>1</sup>

NOT [Ar] 3d<sup>9</sup>4s<sup>2</sup>



The basis for these exception (abnormality) is that the energies of a 3d-orbital and a 4s-orbital are close for these two elements.

Hence, for chromium, the 4s and 3d-orbitals are almost identical in energy, and so the electrons enter all six of the available orbitals singly in accordance to Hund's rule.

In the case of copper, the abnormality shows the importance of extra stability associated with a completely filled 3d-subshell.

#### Electron configurations of Atoms and Ions:

Elements	Symbols	Atoms	+2 ion	+3 ion
Electron configurations of the elements				
Scandium	Sc	4s <sup>2</sup> 3d <sup>1</sup>	3d <sup>1</sup>	[Ne]
Titanium	Ti	4s <sup>2</sup> 3d <sup>2</sup>	3d <sup>2</sup>	3d <sup>1</sup>
Vanadium	V	4s <sup>2</sup> 3d <sup>3</sup>	3d <sup>3</sup>	3d <sup>2</sup>
Chromium	Cr	4s <sup>1</sup> 3d <sup>5</sup>	3d <sup>4</sup>	3d <sup>3</sup>
Manganese	Mn	4s <sup>2</sup> 3d <sup>5</sup>	3d <sup>5</sup>	3d <sup>4</sup>
Iron	Fe	4s <sup>2</sup> 3d <sup>6</sup>	3d <sup>6</sup>	3d <sup>5</sup>
Cobalt	Co	4s <sup>2</sup> 3d <sup>7</sup>	3d <sup>7</sup>	3d <sup>6</sup>
Nickel	Ni	4s <sup>2</sup> 3d <sup>8</sup>	3d <sup>8</sup>	---
Copper	Cu	4s <sup>1</sup> 3d <sup>10</sup>	3d <sup>9</sup>	---

#### Note:

To understand the electron configurations of the ions shown in the table above, it helps to recall that electrons are removed from the 4s-orbital before they are lost (taken) out of the 3d-orbital.

The energies of the 3d & 4s-orbitals are not as close together in the ions of the transition metals as they are in the neutral atoms.

In fact, for the ions of the transition elements the 3d-orbitals are lower in energy than the 4s-orbitals.

Therefore, the electrons most easily lost are those in the outermost principal energy level, the ns. Additional electrons may then be lost from the (n-1) d-orbital.

#### CHARACTERISTICS PROPERTIES OF TRANSITION METALS AND THEIR COMPOUNDS:

##### — State and explain the main features (characteristics) of a transition elements.

Main features of the transition metals are and explanation:

- The variable oxidation states.

Typical d-block elements shows more than one oxidation states in their compounds.

This is in contrast with s-block elements with only fixed oxidation state.

This is because, during ionization, the electrons are removed 1<sup>st</sup> from the 4s-orbital then followed by the 3d-orbital due to the energy difference between the 3d & 4s- orbitals which is very small hence transition elements can easily lose electrons from both 3d & 4s-orbitals.

Tables:

Common oxides	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	Sc <sub>2</sub> O <sub>3</sub>	Ti <sub>2</sub> O <sub>3</sub> TiO <sub>2</sub>	V <sub>2</sub> O <sub>3</sub> V <sub>2</sub> O <sub>5</sub>	Cr <sub>2</sub> O <sub>3</sub> CrO <sub>3</sub>	MnO MnO <sub>2</sub> Mn <sub>2</sub> O <sub>7</sub>	FeO Fe <sub>2</sub> O <sub>3</sub>	CoO Co <sub>2</sub> O <sub>3</sub>	NiO	Cu <sub>2</sub> O CuO	ZnO
Common chlorides	ScCl <sub>3</sub>	TiCl <sub>3</sub> TiCl <sub>4</sub>	VCl <sub>3</sub>	CrCl <sub>2</sub> CrCl <sub>3</sub>	MnCl <sub>2</sub> MnCl <sub>3</sub>	FeCl <sub>2</sub> Fe <sub>2</sub> Cl <sub>6</sub>	CoCl <sub>2</sub>	NiCl <sub>2</sub>	CuCl CuCl <sub>2</sub>	ZnCl <sub>2</sub>
Oxidation numbers that occur in compounds	3	4 3 2 1	5 4 3 2 1	6 5 4 3 2 1	7 6 5 4 3 2 1	6 5 4 3 2 1	5 4 3 2 1	4 3 2 1	3 2 1	2 1

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
≤0			0	0	0	0	0	0	0	
+1			0	0	0	0	0	0	0	O
+2		0	O	0	O	O	O	O	O	O
+3	O	0	0	O	0	O	O	0	0	
+4		O	0	0	O	0	0	0		
+5			O	0	0	△	0			
+6				O	0	0				
+7					O					

O : most common

Notes:

The most important oxidation states are emphasized by bold print. Notice that both scandium and zinc have only one common oxide, chloride and one oxidation state in their compounds. Notice also, how closely the oxidation states of the elements in their common oxides and chlorides compare with the more important oxidation states of the elements.

### Transition element oxides, fluorides & chlorides:

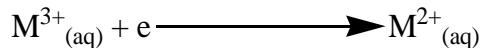
+II	+III	+IV	Oxidation states				Other compounds
			+V	+VI	+VII	+VIII	
TiO	Sc <sub>2</sub> O <sub>3</sub>						
	ScCl <sub>3</sub>						
	ScF <sub>3</sub>						
	Ti <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>					
	TiF <sub>3</sub>	TiF <sub>4</sub>					
	TiCl <sub>3</sub>	TiCl <sub>4</sub>					
VO	V <sub>2</sub> O <sub>3</sub>	VO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>				
	VF <sub>2</sub>	VF <sub>4</sub>	VF <sub>5</sub>				
	VCl <sub>3</sub>						
CrO	Cr <sub>2</sub> O <sub>3</sub>	CrO <sub>2</sub>		CrO <sub>3</sub>			
	CrF <sub>2</sub>	CrF <sub>3</sub>	CrF <sub>4</sub>	CrF <sub>5</sub>	(CrF <sub>6</sub> )		
	CrCl <sub>2</sub>	CrCl <sub>3</sub>					
MnO	Mn <sub>2</sub> O <sub>3</sub>				Mn <sub>2</sub> O <sub>7</sub>		Mn <sub>3</sub> O <sub>4</sub>
MnF <sub>2</sub>	MnF <sub>3</sub>		MnF <sub>4</sub>				
MnCl <sub>2</sub>	MnCl <sub>3</sub>						
FeO	Fe <sub>2</sub> O <sub>3</sub>						
	FeF <sub>2</sub>	FeF <sub>3</sub>					Fe <sub>3</sub> O <sub>4</sub>
	FeCl <sub>2</sub>			Fe <sub>2</sub> Cl <sub>6</sub>			
CoO	Co <sub>2</sub> O <sub>3</sub>						
	CoF <sub>2</sub>	CoF <sub>3</sub>					
	CoCl <sub>2</sub>						
NiO	Ni <sub>2</sub> O <sub>3</sub>	NiO <sub>2</sub>					
NiF <sub>2</sub>							
NiCl							
CuO						Cu <sub>2</sub> O	
CuF <sub>2</sub>							

- Their use as a catalysts (ability to catalyze the reactions).  
Many transition metals and their compounds shows catalytic activity.  
During heterogeneous catalysis, transition elements uses both of their 4s & 3d electrons for bonding.  
This enables the transition element to form temporary bonds with the reactant molecules.  
Hence, this increases the concentration of the reactants at the surface of the transition metals (catalyst) and weakens the bonds in the reacting molecules, therefore lowering activation energy.  
Examples which involves heterogeneous catalysis:

Golden tips:

The +2 & +3 oxidation states are shown by most elements from Ti to Cu. The relative stability of these two oxidation states are governed by the electrode potential for the reaction:

Equation:



Examples:

	Electrode Potential, E <sup>0</sup>
Ti <sup>3+</sup> /Ti <sup>2+</sup>	-0.125
V <sup>3+</sup> /V <sup>2+</sup>	-0.250
Cr <sup>3+</sup> /Cr <sup>2+</sup>	-0.120
Mn <sup>3+</sup> /Mn <sup>2+</sup>	-0.150
Fe <sup>3+</sup> /Fe <sup>2+</sup>	+0.250
Co <sup>3+</sup> /Co <sup>2+</sup>	+1.750

Notes:

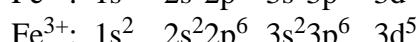
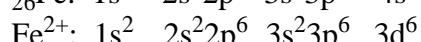
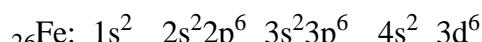
The value for M<sup>3+</sup> / M<sup>2+</sup> increases from Ti to Co but M<sup>3+</sup> / M<sup>2+</sup> is unexpectedly high and that of Fe<sup>3+</sup>/Fe<sup>2+</sup> is unexpectedly low.

The more positive the value of E<sup>0</sup>, the greater the ability for M<sup>3+</sup> to be converted to M<sup>2+</sup>.

Therefore, Mn<sup>3+</sup> is easily converted to Mn<sup>2+</sup> but Fe<sup>3+</sup> is not converted to Fe<sup>2+</sup>. Explain why Fe<sup>3+</sup> is not converted to Fe<sup>2+</sup>.

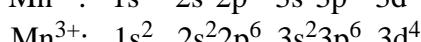
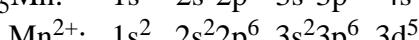
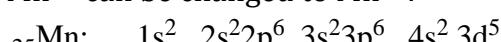
Iron (III) salt is not easily converted to Iron (II) salt is because Fe<sup>3+</sup> is more stable than Fe<sup>2+</sup>.and the paramount reason is because of it's electronic configuration whose 3d-subshell is half-full hence Fe<sup>3+</sup> is stable.

i.e:



SIMILARLY

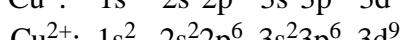
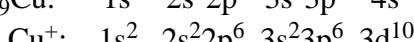
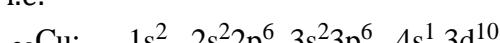
Mn<sup>2+</sup> can be changed to Mn<sup>3+</sup>.



SIMILARLY:

Cu<sup>2+</sup> is more stable than Cu<sup>+</sup> because of its electronic configuration whose 3d sub energy level is half filed and the heat change for Cu<sup>+(aq) / Cu<sup>2+(aq)</sup> is less exothermic than Cu<sup>2+(aq) / Cu<sup>+(aq)</sup>.</sup></sup>

i.e:

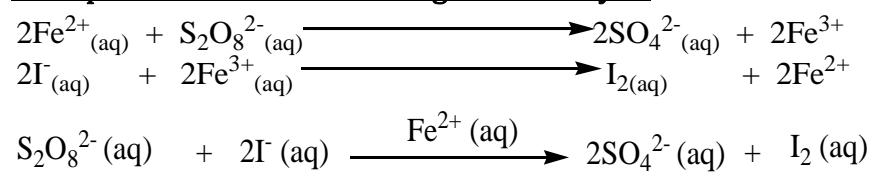


Notes:

Heterogeneous catalysis involves a catalyst that is not in the same phase as the reactant.

In homogenous catalysis, which is usually found in reactions in solution, in a sequence of the reaction stages and emerge unchanged at the end of the reaction.

**Examples which involves homogenous catalysis:**



**Notes:**

Homogenous catalysis involves a catalyst that is in the same phase as the reactant.

**Summary:**

Homogeneous catalysis (where the catalyst are in the same phase with the reactants), due to variable oxidation state transition metals/ ions form with the activated complex thus providing an alternative reaction path way of lower reaction energy

- Paramagnetism.

Paramagnetic substances are weakly attracted by a magnetic field. Any species with unpaired 3d electron is paramagnetic because there is a magnetic moment associated with the spinning electron.

Hence, transition metals ions that have unpaired electrons, the more paramagnetic is the ion. Therefore paramagnetic strength increases with increase in the number of unpaired 3d electrons.

- The formation of complex ions.

Transition metal elements have the ability to form complex ions.

Complex ion is formed when one or more molecules or negatively charged ions that becomes attached to the central atom.

Reasons why transition elements are able to form complexes:

- A. Small and highly charged ions.
- B. Presence of vacant 3d-orbitals to accommodate lone pairs of electrons from the ligands.

Transition metals form complexes or coordination compounds. Such complexes are formed by the coordination of lone pairs of electrons from a donor atom (called ligand) to an atom or cation (called acceptor) which has empty 3d-orbitals to accommodate them.

The central atom or ion must possess empty or partially filled 3d-orbital to accommodate the lone pair.

**Summary:**

Transition elements are able to form complexes because they possess partially filled 3d-orbitals which can accommodate lone pairs of electrons from ligands.

Ligand (s) is (are) neutral molecule or ion capable of coordinating a lone pair of electrons in to empty orbitals of a central atom or ion.

- The formation of coloured ions.

Compounds and ions of the d-block elements tend to be coloured.

Transition elements tend to be coloured this is because of absorption of light which is due to the presence of unpaired 3d-orbital (electrons) in the ions.

Aqueous solutions Scandium,  $\text{Sc}^{3+}$  & Zinc,  $\text{Zn}^{2+}$  ions are colourless because they do not contain unpaired 3d-orbitals.

Unpaired 3d-orbitals (electrons) absorb light energy by becoming promoted from their ground state and excited state.

- The formation of interstitial compounds.

## 2. **CO-ORDINATION COMPOUNDS & OXIDATION STATES:**

**A metal complex or co-ordination compound** is a chemical system composed of electron donor and electron acceptor.

**Oxidation states:** is the charge left on the central atom when all the atoms of the compound have been removed as ions.

**Oxidation states:** is the charge remaining on the central atom or ion when the ligands are removed together with their lone pairs.

**Coordination number:** is the number of coordinate bonds a central atom or ion is able to form.

**Coordination number:** is the number of atoms forming coordinate bonds with the central atom or ion.

**Coordination number:** is the number of **ligands** attached to the central atom.

### **Notes:**

The most common coordination numbers are: 2, 4 & 6.

**Ligands:** is (are) molecule or ion capable of coordinating a lone pair of electrons in to empty orbitals of a central atom or ion.

**A ligand** is anion or molecule with lone pairs of electrons linked to the central metal ion by a dative bond.

Ligands are classified on basing on the number of atoms directly bonded to the metal centre (Denticity). i.e.

#### **Monodentate / Unidentate ligands.**

These are ligands with one donor atom per ligand molecule.

Or

This is a ligand that can form only one bond to a central atom or ion i.e. has single tooth.

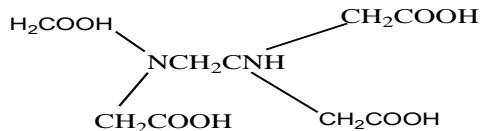
#### **Multidentate/ Chelating / Polydentate ligands**

This is a ligands that can form more than one bond i.e. have many tooth.

Or

These are ligands with two or more donor atoms per ligand molecule.

Example:



### Examples of ligands:

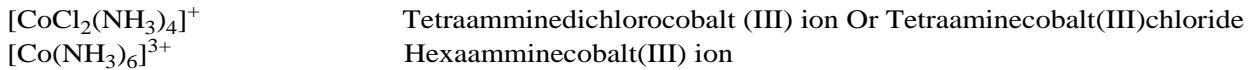
Ligands	Types of complex
Water	Aqua-
Ammonia	Ammine-
Hydroxide ion	Hydroxo-
Chloride ion	Chloro-
Cyanide ion	Cyano-
Nitrite ion	Nitro-
Carbon monoxide	Carbonyl-
Ethane-1,2-diamine	Ethane-1,2-diamine
Bromine ion	Bromo-
Sulphate ion	Sulphato-

### Nomenclatures of complex:

The IUPAC developed a systematic nomenclature for complex compounds. The rules may be summarized as followed:

- The cation is always named before the anion.
- The names of ligands precede the name of the central ion or atom
- The oxidation state of the central ion or atom is shown in Roman numerals in brackets immediately after its name.
- Metals forming complex anions are given the word ending **-ate**, whereas complex cations and neutral molecules are given their **usual** names.
- The order of naming ligands is anion, neutral molecules, cations. Within each category, if there is more than one type of ligand, they are named in alphabetical order following the prefixes of: di, tri, tetra, penta, hexa etc.
- In the formula of a complex ion, the symbol for the central atom appears 1<sup>st</sup> and followed by the anionic ligands and then neutral ligands.
- The formula for the complex ion may be enclosed in square brackets.

Examples:



### NOTE:

Neutral ligands usually possess their normal names except for water-aqua, ammonia-ammine, carbonmonoxide- carbonyl, nitrogen monoxide-nitrosyl, cationic ligands end in -ium' are hydrozinium  $[\text{H}_2\text{N}-\text{NH}_3^+]$

Ligands	Names of complex	Ligands	Names of complex
$\text{F}^-$	Fluoro-	$\text{SCN}^-$	Thiocyanato-
$\text{Cl}^-$	Chloro-	$\text{S}_2\text{O}_3^{2-}$	Thiosulphato-
$\text{Br}^-$	Bromo-	$\text{CH}_3\text{COO}^-$	Acetato-
$\text{I}^-$	Iodo-		
$\text{O}^{2-}$	Oxo-		
$\text{CN}^-$	Cyano-		
$\text{C}_2\text{O}_4^{2-}$	Oxalate-		

$\text{OH}^-$	Hydroxo-		
$\text{SO}_4^{2-}$	Sulphato-		
$\text{NO}_2^-$	Nitrito-		
$\text{NO}_3^-$	Nitrato-		
$\text{CO}_3^{2-}$	Carbonato-		

— Hydrated Chromium (III) chloride forms three isomers which form a white precipitate with silver nitrate solution. Write the formula and I.U.P.A.C name of each isomer.

- a.  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  Hexaaqua chromium(III)chloride  
 $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2\cdot\text{H}_2\text{O}$  Chloropenta aqua chromium(III)chloride  
 $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$  Dichlorotetra aqua chromium(III)chloride

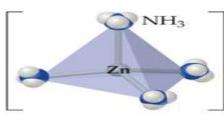
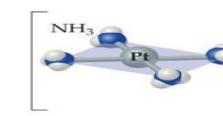
### SHAPES OF COMPLEXES:

The shapes of complex ions/ compounds are determined by the coordination number. The electron pairs around the central metal ion are repelled as far as possible from each other. In complexes with a coordination number of 6 [6 pairs of electrons donated by ligands], the ligands usually occupy octahedral positions. In complexes with a coordination number of 4, the ligands usually occupy tetrahedral positions although a few with a coordinated complexes have a square planar structure and complexes with a coordinated number of 2 usually have a linear arrangement of ligands.

Coordination NO:	Shape of complex	Examples
2	Linear	$[\text{Cu}(\text{NH}_3)_2]^+$ , $[\text{Au}(\text{CN})_2]^-$ , $[\text{Ag}(\text{NH}_3)_2]^+$ , $[\text{Ag}(\text{CN})_2]^-$ , $[\text{CuCl}_2]^-$ , $[\text{AuCl}_2]^-$
4	Tetrahedral	$\text{Ni}(\text{CO})_4$ , $\text{MnO}_4^-$ , $[\text{Zn}(\text{NH}_3)_4]^{2+}$ , $[\text{NiCl}_4]^{2-}$ , $[\text{MnCl}_4]^{2-}$ , $[\text{CdCl}_4]^{2-}$ , $[\text{Cu}(\text{CN})_4]^{3-}$
4	Square planar	$[\text{CuCl}_4]^{2-}$ , $[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ , $[\text{Pt}(\text{NH}_3)_4]^{2+}$ , $[\text{Pt}(\text{NH}_3)_4]^{2+}$ , $[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , $[\text{PdCl}_4]^{2-}$
6	Octahedral	$[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ , $[\text{Fe}(\text{CN})_6]^{4-}$ , $[\text{Fe}(\text{CN})_6]^{3-}$ , $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , $[\text{Co}(\text{NH}_3)_6]^{3+}$ , $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ , $[\text{Cu}(\text{NH}_3)_4\text{Cl}_2]^+$ , $[\text{Cu}(\text{H}_2\text{O})_6]^{3+}$ , $[\text{V}(\text{CN})_6]^{4+}$ , $[\text{Co}(\text{en})_3]^{3+}$
6	Distorted Octahedral	$[\text{Zn}(\text{OH})_2(\text{H}_2\text{O})_4]$ , $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$

### STRUCTURE OF SHAPES:

Coordination number	Shape	Hybridization	Examples
2	Linear	$\text{sp}$	$[\text{CuCl}_2]^-$
4	Tetrahedral	$\text{sp}^3$	$[\text{CuCl}_4]^-$
4	Square planar	$\text{dsp}^2$	$[\text{Ni}(\text{CN})_4]^{2-}$
6	Octahedral	$\text{sp}^3\text{d}^2$	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$



Co-ordination number	Shape	Example:
6	Octahedral	
4	Tetrahedral	
4	Square Planar	
2	Linear	

### ISOMERISM IN METAL COMPLEXES:

Isomerism occurs when the same molecular formula can represent more than one compound. Isomerism is a phenomenon whereby compounds having the same number of atoms have atoms differently arranged either spatially or sequentially.

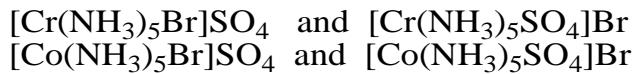
#### TYPES OF ISOMERISM IN METAL COMPLEXES:

##### A. Ionization isomerism:

Ionization isomers are as a result of exchange of anionic ligands inside and outside the coordination sphere.

This is common in chromium and cobalt.

#### Examples:

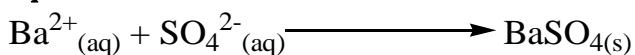


Distinguish between the two isomers:

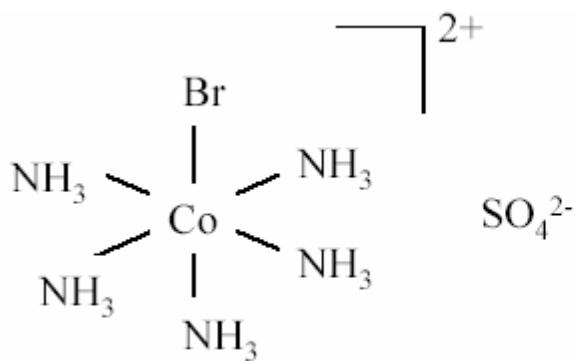


In X, the bromine atom is directly bonded to cobalt (III) ion while the sulphate is free and can therefore be precipitated by addition of a solution of barium nitrate or barium chloride solution to form a white precipitate of barium sulphate.

#### Equation:



The structure of X is:



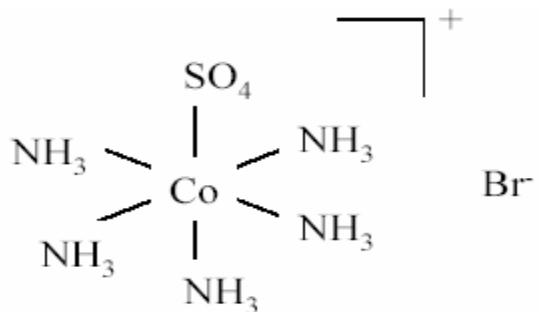
Or:

Addition of silver nitrate solution to X does not produce a yellow precipitate of silver bromide because the bromide,  $\text{Br}^-$  ion is not free unlike the sulphate,  $\text{SO}_4^{2-}$  ion. In Y, the sulphate,  $\text{SO}_4^{2-}$  ion is directly bonded to the cobalt (III) ion and not free but the bromide,  $\text{Br}^-$  ion is free and therefore addition of silver nitrate solution produces a yellow precipitate of silver bromide.

**Equation:**



The **structure of Y** is:



1. Complex ions can sometimes exhibit isomerism.
  - a) The compound  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  is isomeric with  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ .
    - (i) What type of isomerism is shown between the two complexes?
    - (ii) What ions will these two isomers yield in solution?
    - (iii) How would you confirm which isomer was which?  
(Use equations where possible to illustrate your answer)
  - b) What is the:
    - (i) Oxidation state.
    - (ii) Coordination number of cobalt in each complex ion.
  - c) Draw the structure of the complex ion  $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ , indicating its shape.

B. Hydrate isomerism:

Hydrate isomers are as a result of exchange of water molecules inside and outside the coordination sphere. The usual example is the crystalline isomers of chromium (III) chloride hexahydrate,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ .

Possible isomers:

$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  – hexaaquachromium (III) chloride- Violet.

$[\text{Cr}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$  – Penta aquachlorochromium (III) chloride – Green

$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$  – Tetraaquadichlorochromium (III) chloride – Green  
Although all the three salts correspond to the same formula, they differ in their properties.

The violet salt will give, when excess silver nitrate solution is added, three moles of silver chloride is precipitated for each mole of the salt. The salt therefore acts as  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} + 3\text{Cl}^-$ .

C. Geometrical isomerism:

2. Complete the table below.

(04 marks)

Formula of complex	Name of complex	Coordination Number	
$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$	Dithiosulphatoargentate (I) ion	2	
$[\text{VO}(\text{H}_2\text{O})_5]^{2+}$	Oxopentaaquavanadium (IV) ion	6	
$[\text{Zn}(\text{OH})_4(\text{H}_2\text{O})_2]^{2-}$	Tetrahudroxodiaquazincate (ii)	6	
$\text{FeO}_4^{2-}$	Tetraoxoferrate (VI) ion	4	
$\text{BH}_4^-$	Tetrahydridoborate (III) ion	4	

Dilute nitric acid was added drop-wise to the complex of Tetrahydroxodiaquazincate (II) ion until the solution was just acidic.

- i. State what was observed. (01 mark)
- ii. Write equations for the reaction that took place. (02½ marks)
- a) Using equations, show how the complex of dithiosulphatoargentate (I) ion is formed from silver chloride. (01½ marks)

## **CHEMISTRY OF INDIVIDUAL ELEMENTS & EXTRACTION OF METALS:**

### **(a)      The chemistry of chromium**

Chromium is a hard bluish-white metal. It has atomic number 24 with its outer electronic configuration of  $_{24}\text{Cr}:1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 4\text{s}^1 3\text{d}^5$  or: [Ar]  $4\text{s}^1 3\text{d}^5$ .

#### **Note:**

Chromium has got three possible oxidation states namely: +2, +3 & +6. But oxidation state of +3 is the most stable one. +2 oxidation state is not stable hence can be converted to +3. +2 oxidation state is a reducing agent while +6 oxidation state is oxidizing agent.

The two most important oxidation states of chromium are chromium (VI) and chromium (III).

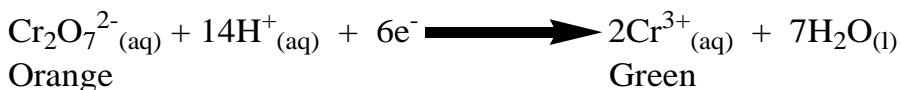
- Chromium (VI) compounds.  $\text{Cr}^{6+}$ :  $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6$ .

As you should expect, chromium (VI) compounds show oxidizing properties.

Especially, dichromate (VI) ions,  $\text{Cr}_2\text{O}_7^{2-}$ , are used to oxidize other compounds. The ion reacts best in acid medium (conditions) as shown below.

The colour turns from orange to green is a sure sign of the reaction taking place? The half-equation for the process is.

**Equation:**



## Notes:

Acidified sodium dichromate (VI) solution is used in organic chemistry to oxidize alcohols to aldehydes and acids.

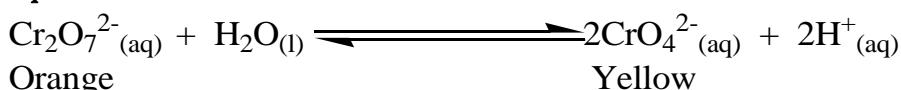
**Reason:**

Sodium dichromate (VI) solution,  $\text{Na}_2\text{Cr}_2\text{O}_7$  is used rather than potassium dichromate (VI) solution,  $\text{K}_2\text{Cr}_2\text{O}_7$  owing to its greater solubility in the reaction mixture.

— Explain why dichromate (VI)  $\text{Cr}_2\text{O}_7^{2-}$  ions reacts best in acidic condition.

The redox potential is highly dependent on the concentration of acid. However, this is due to the fact that if the solution is not acidified, the number of  $\text{Cr}_2\text{O}_7^{2-}$  ions decreases markedly. This is due to equilibrium especially if the alkali is added, all the orange dichromate (VI) ions are converted to yellow chromate (VI)  $\text{CrO}_4^{2-}$  ions.

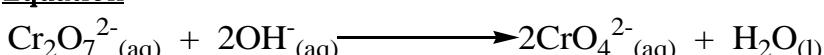
**Equation:**



Or

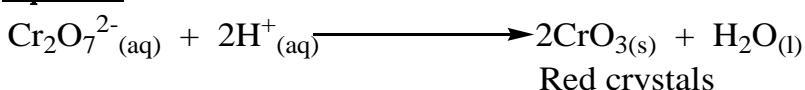
In aqueous solution a low pH favours the orange dichromate (VI) ion, and a high pH the yellow chromate (VI) ion.

### **Equation:**



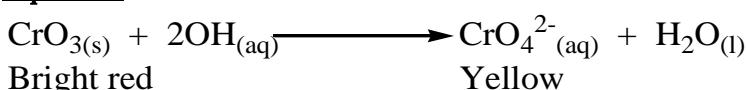
Chromium (VI) oxide,  $\text{CrO}_3$  is made by reacting sodium dichromate (VI) with concentrated sulphuric acid:

### Equation:



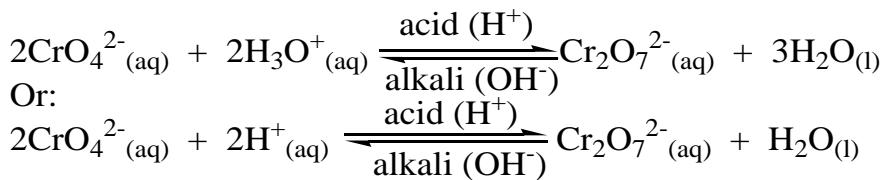
Chromium (VI) oxide is an acidic oxide. It reacts with alkalis forming chromate (VI) ions.

### **Equation:**



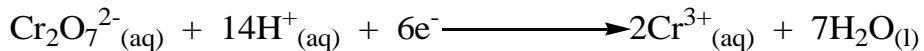
Under acidic conditions the chromate (VI) ions is converted to the dichromate (VI) ion. The reaction is reversed under alkaline conditions.

(v) Form E



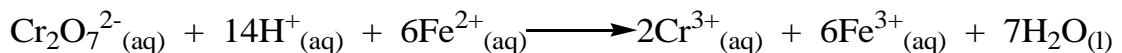
Dichromate (VI) is reduced to chromium (III) under acidic conditions:

Equation:



The positive value of standard redox potential (+1.33V), shows that dichromate (VI) is an oxidizing agent. It is used in volumetric analysis to determine the concentration of iron (II) in acidic solution.

Equation:



Observation:

The green turns to yellow colour of iron (III) ion.

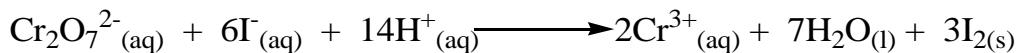
Note:

The acidified iron (II) solution is pipetted in to a conical flask and the dichromate (VI) solution added from a burette. A redox indicator such as barium diphenylamine sulphonate is used.

The 1<sup>st</sup> drop of excess dichromate (VI) solution converts this colourless substance to a deep blue colour. Potassium dichromate (VI) can be obtained in a high degree of purity and thus be used as a primary standard.

Liberation of iodine from acidified potassium iodide solution.

Equation:



Observation:

Oxidation of sulphite ion to sulphate ion.

Equation:

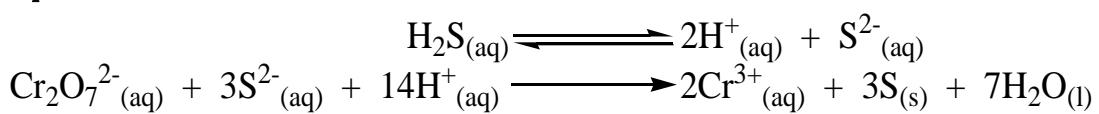


Observation:

The solution is rapidly turned **from orange-yellow to green colour**. The green colour is caused by the hydrated chromium (III) ion.

Oxidation of hydrogen sulphide to sulphur, which precipitates.

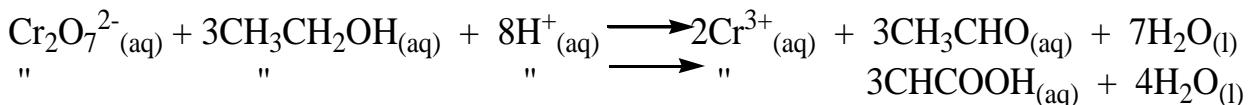
Equations:



Observation:

Oxidation of ethanol to ethanol and ethanoic acid.

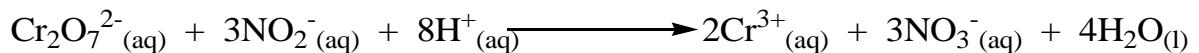
Equation:



Observation:

Oxidation of nitrite ion to nitrate ion.

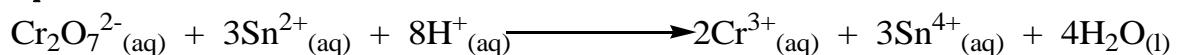
Equation:



Observation:

Oxidation of tin (II) ion to tin (IV) ion.

Equation:

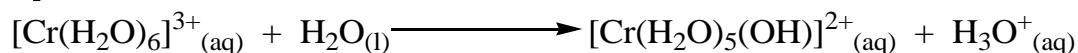


Observation:

- Chromium (III) compounds,  $\text{Cr}^{3+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

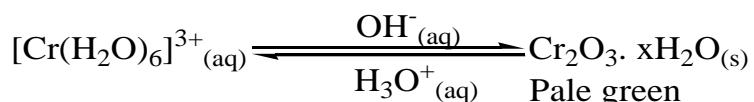
This is the most common and most stable form of chromium. In solution, chromium (III) exists as hexaaquachromium (III) ion,  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ . This ion is violet in colour when pure but usually appears green due to impurities. It undergoes hydrolysis, losing protons as follows:

Equation:



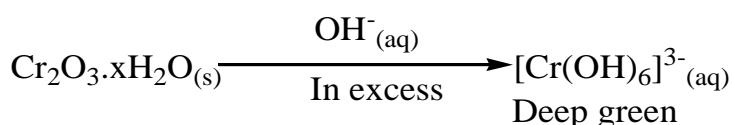
The hydrated chromium (III) ion is thus stable in acid conditions. Acid shifts this equilibrium to the left. The addition of alkalis such as sodium hydroxide solution to hydrated chromium (III) ions produces pale green precipitate of hydrated chromium (III) oxide,  $\text{Cr}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ .

Equation:



The oxide dissolves in excess alkali forming a deep green solution.

Equation:



Reactions of chromium:

✓ With air.

Chromium does not react with air (oxygen gas) at ordinary temperature (conditions) but on heating, it oxidizes to form green chromium (III) oxide.

Equation:



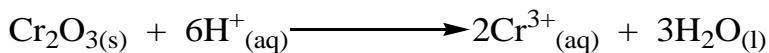
Notes:

(i) Chromium (III) oxide is amphoteric oxide, with a basic character predominating which is shown by the reaction of oxide with acids forming chromium (III) salts, though, after heating, the oxide dissolves only slowly in dilute acids.

Equation:

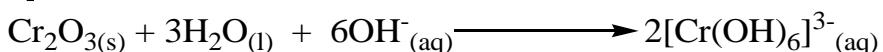


Or:



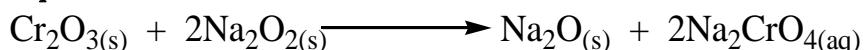
(ii) Acidic character is shown when the oxide forms chromates (VI) with excess caustic alkali.

Equation:



(iii) Fusion with sodium peroxide oxidizes chromium (III) oxide to sodium chromate (VI) solution.

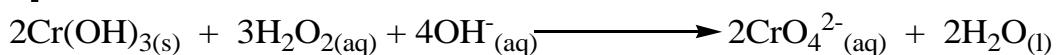
Equation:



Observation:

(iv) Chromium (III) hydroxide, like oxide, it is amphoteric hydroxide, and can be oxidized to chromate (VI) by heating with hydrogen peroxide in alkaline solution.

Equation:



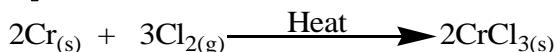
Observation:

A green solid **dissolves** in hydrogen peroxide in presence of an alkali forming a **yellow solution** of chromate (VI) solution.

✓ With halogen (chlorine).

Chromium with chlorine on heating or over heated chromium forming chromium (III) chloride.

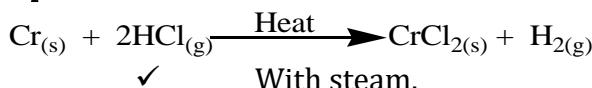
Equation:



Note:

When hydrogen chloride gas is used instead of chlorine gas, chromium (II) chloride and hydrogen gas is formed respectively.

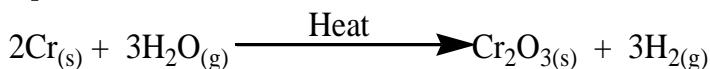
Equation:



✓ With steam.

Chromium is unaffected by cold or hot water but reacts with steam at red heat forming chromium (III) oxide.

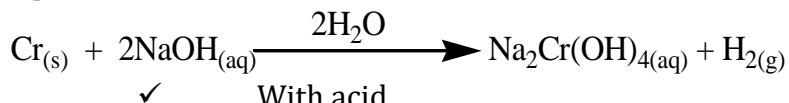
Equation:



✓ With alkalis.

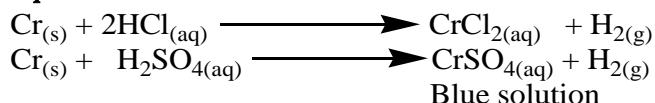
Chromium reacts slowly with alkalis (i.e. sodium hydroxide solution) forming a complex of

Equation:



Chromium reacts with both dilute hydrochloric & sulphuric acid forming a blue solution of chromium (II) chloride & sulphate respectively.

Equations:



Note:

Chromium reacts with hot concentrated sulphuric acid forming chromium (III) sulphate & sulphur dioxide gas respectively.

Equation:

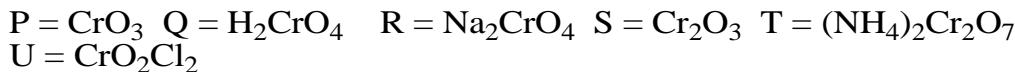


Chromium does not react with both dilute & concentrated nitric acid. Why? A thin layer of Chromium (III) oxide is formed which renders it inactive.

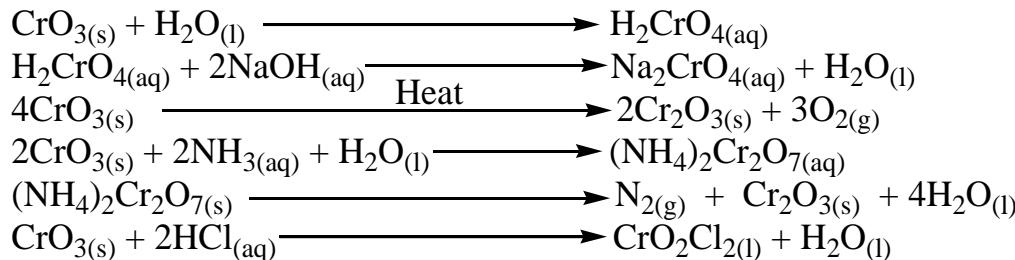
Golden tips: Compound in +2 oxidation state:

- a) Chromium (II) compounds,  $\text{Cr}^{2+}$  ion are unstable & readily oxidized to chromium (III),  $\text{Cr}^{3+}$  ion state. Therefore the most stable important oxidation states are +3 & +6.
3. When concentrated ammonia solution is added drop-wise to a solution of a metal cation, **A**, a green precipitate, **B** forms. **B** dissolves slowly in an excess ammonia solution to give a purple solution, **C**. **B** also dissolves in aqueous sodium hydroxide solution to give a green solution, **D**. Addition of hydrogen peroxide solution to **D** gives a yellow solution, **E**. When **E** is treated with dilute sulphuric acid, an orange solution **F** is formed.
  - (a) Identify **A** to **F**. (03 marks)
  - (b) Write equations of reactions for:
    - i. **D** from **B** (01 mark)
    - ii. **E** from **D** (01½ marks)
    - iii. **F** to **E** (01½ marks)
  - (c) State one practical application of:
    - i. **E** (01 mark)
    - ii. **F** (01 mark)
4. A bright red solid **P** dissolves in water to give a highly acidic solution **Q**. When treated with sodium hydroxide solution, **Q** forms a yellow solution **R**. On heating **P**, a green powder **S** was formed together with a colourless gas that rekindles a glowing splint. **P** dissolves in aqueous ammonia solution to form an orange solid **T**. On heating, **T** produces an inert gas, steam and **S**. **U**, a dark red-brown oil is formed when **P** is dissolved in cold, concentrated hydrochloric and sulphuric acid added gradually.

a) Identify the compounds. (03 marks)



b) Write the equations for all the reactions involved. (06 marks)



5. A pale green chloride of chromium, X was investigated with the following results:  
When 1.00g of X was heated in air to constant mass, water and hydrogen chloride were evolved and a residue of 0.286g of chromium (II) oxide remained.
6. When a pale green solid A is heated, it decomposed to a green solid B and a gas that turned lime water milky was evolved. B dissolved in dilute nitric acid to give a green solution C. On addition of aqueous sodium hydroxide solution to C, a green precipitate D insoluble in excess was obtained. D dissolve in aqueous ammonia to give a purple blue solution.

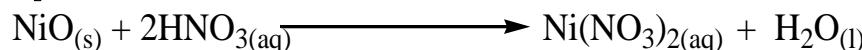
(a) Identify A, B, C and D.

- A. Nickel carbonate, NiCO<sub>3</sub>
- B. Nickel oxide, NiO
- C. Nickel nitrate, Ni(NO<sub>3</sub>)<sub>2</sub>
- D. Nickel (II) hydroxide, Ni(OH)<sub>2</sub>

(b) Write equation for the reaction between:

(i) B and dilute nitric acid.

Equation:



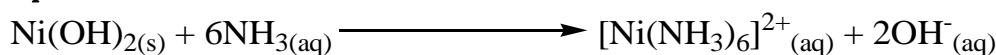
(ii) C and aqueous sodium hydroxide solution.

Equation:



(iii) D and aqueous ammonia solution.

Equation:



## (b) The chemistry of manganese

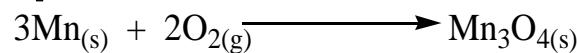
Electron configuration,  $^{25}Mn: 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$ .

### Chemical Properties of Manganese:

(i) With air.

Pure manganese is not attacked by air at room temperature but, if finely divided, burns when heated strongly.

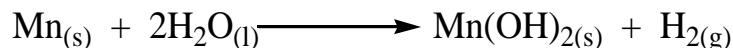
Equation:



(ii) With water.

Impure manganese reacts with hot water to form hydrogen gas.

Equation:



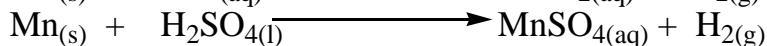
Notes:

Pure manganese **does not** attack water or steam.

- (iii) With dilute acids.

Manganese readily reacts with dilute acids (Hydrochloric or sulphuric acid) forming manganese (II) ions and hydrogen gas respectively.

Equations:



Notes:

- (v) Manganese also reacts with **hot concentrated** sulphuric acid to form manganese (II) sulphate and sulphur dioxide gas respectively.

Equation:



- (vi) Dilute nitric acid yields oxide of nitrogen gas.

Equation:

- (vii) Concentrated nitric acid gives mainly nitrogen dioxide gas.

Equation:

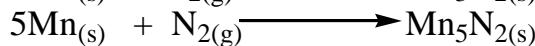
- (iv) With alkalis.

Manganese **DOESN'T** react with alkali.

- (v) With non-metals.

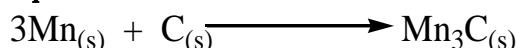
Manganese reacts with nitrogen gas at white heat to form nitrides.

Equations:



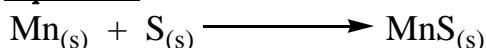
Manganese also reacts with carbon at electric furnace temperatures, to form carbide.

Equation:



Manganese also combine with both sulphur and chlorine gas forming manganese sulphide and chloride respectively.

Equations:



### Compounds of manganese:

Manganese can exist in the +2, +3, +4, +5, +6 & +7 oxidation states. In the +2 oxidation state, the 4s<sup>2</sup> electrons are lost, leaving the half-filled 3d sub-

shell. This half-filled arrangement possesses some stability, so that Mn<sup>2+</sup> ion is more stable than Ti, V, or Cr in the +2 oxidation state.

As usual, as the oxidation number of manganese increases, there's an increase in the covalent nature of its compounds and the acidity of its oxides.

### **Oxidation states of manganese:**

Manganese can exist in the following oxidation states, the main ones being shown in bold type:

### Electronic configuration:

$_{25}^Mn$  ---  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$  or [Ar]  $4s^2 3d^5$ .

$\text{Mn}^{2+}$  --  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5$  or  $[\text{Ar}] 4s^0 3d^5$ .

Mn<sup>3+</sup> -- 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>4s<sup>0</sup>3d<sup>4</sup> or [Ar] 4s<sup>0</sup> 3d<sup>4</sup>.

$\text{Mn}^{4+}$  --  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^3$  or  $[\text{Ar}] 4s^0 3d^3$ .

Mn<sup>5+</sup> -- 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>4s<sup>0</sup>3d<sup>2</sup> or [Ar] 4s<sup>0</sup> 3d<sup>2</sup>.

$\text{Mn}^{6+} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^1$  or  $[\text{Ar}] 4s^0 3d^1$ .

Mn<sup>7+</sup> -- 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>4s<sup>0</sup>3d<sup>0</sup> or [Ar] 4s<sup>0</sup> 3d<sup>0</sup>.

### Golden tips:

<sup>+7</sup> Mn<sub>2</sub>O<sub>7</sub> (Manganese (VII) oxide) MnO<sub>4</sub><sup>-</sup> (Manganate (VII) ion)  
Purple

+6	$\text{MnO}_3$	(Manganese (VI) oxide	Purple
			$\text{MnO}_4^{2-}$ (Manganate (VI) ion)

## **†4 MnO<sub>2</sub> (Manganese (IV) oxide)**

# MnO<sub>2</sub> Black

<b>Black</b>	
+3	Mn <sub>2</sub> O <sub>3</sub> (Manganese (III) oxide) Mn <sup>3+</sup> (Manganese (III) ion) Red

+2	MnO	(Manganese (II) oxide)	$\text{Mn}^{2+}$ (Manganese (II) ion)
			Pale pink

Pale pink

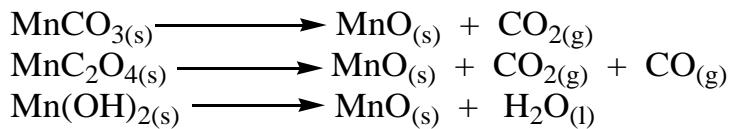
**Compounds of manganese in the +2 oxidation state.** As stated above, manganese (II) compounds are more resistant to oxidation than the corresponding compounds of the earlier transition elements.

than the corresponding compounds of the earlier transition elements. Manganese (II) is the most stable oxidation state of manganese under normal conditions. Powerful oxidizing agents [(e.g lead (IV) oxide, peroxodisulphate, sodium bismuthate (V)] in acidic solution may oxidize Mn (II) to Mn (VII) in the manganate (VII) or permanganate ion,  $MnO_4^{2-}$ .

## MANGANESE (II) OXIDE $\text{MnO}_2$

Manganese (II) oxide,  $\text{MnO}_2$ . Manganese (II) oxide is prepared or obtained as a grey-green solid by heating manganese (II) carbonate, ethanedioate (oxalate), or hydroxide in the absence of air.

Equations:



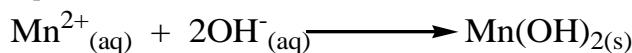
Notes:

Manganese (II) oxide is greenish powder. It is a strongly basic oxide indicating that manganese is acting as a metallic properties, and forms manganese (II) salts with dilute acids in a usual way.

Manganese (II) hydroxide, Mn(OH)<sub>2</sub>.

Manganese (II) hydroxide is precipitated by the addition of aqueous caustic alkali to a solution of any soluble manganese (II) salt. It's purely white in colour but rapidly turns dark brown by oxidation on exposure to air.

Equation:



Then:

Equations:



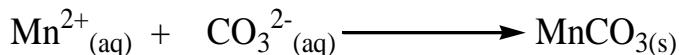
Or:



Manganese (II) carbonate, MnCO<sub>3</sub>.

Manganese (II) carbonate is prepared by precipitation of any soluble carbonate on a manganese (II) salt.

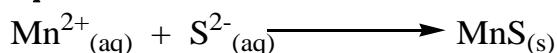
Equations:



Manganese (II) sulphide, MnS.

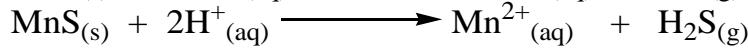
Manganese (II) sulphide is a pale pink solid formed when hydrogen sulphide gas is passed via an aqueous solution of manganese (II) ions in presence of aqueous ammonia and ammonium chloride.

Equation:



The manganese (II) sulphide is readily soluble in dilute hydrochloric acid.

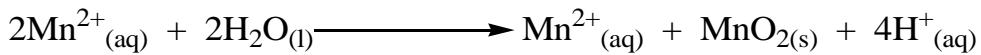
Equation:



**Compounds of manganese in the +3 oxidation state.**

Manganese (III) only occurs in complexes. It is unstable. Under acid conditions, manganese (III) **disproportionate in aqueous solution** to form manganese (II) and manganese (IV) ions respectively.

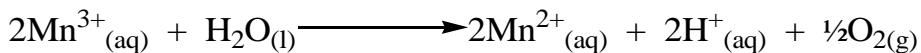
Equation:



**Notes:**

The Mn<sup>3+</sup> ion is, however, readily converted into Mn<sup>2+</sup>, by oxidation of water.

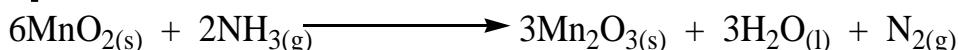
**Equation:**



**Manganese (III) oxide, Mn<sub>2</sub>O<sub>3</sub>.**

Manganese (III) oxide can be made by heating manganese (IV) oxide in ammonia gas. And it can also be made by aerial oxidation of manganese (II) hydroxide.

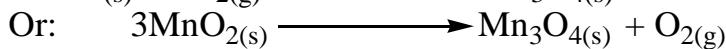
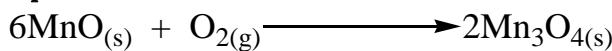
**Equation:**



**Trimanganese tetra oxide, Mn<sub>3</sub>O<sub>4</sub> or Manganese (II) dimanganese (III) oxide, Mn<sub>3</sub>O<sub>4</sub>.**

This red oxide of manganese is obtained by heating any other oxide of metal strongly in air.

**Equations:**



It is a mixed oxide of Pb<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>. For example, in cold concentrated sulphuric acid, it yields manganese (II) and manganese (III) sulphates.

**Equation:**



**Observation:**

Hot nitric acid, however, precipitates manganese (IV) oxide due to disproportionation of manganese (III) ion.

**Equation:**



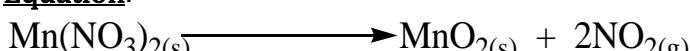
**Compounds of manganese in the +4 oxidation state.**

The most important of these compounds is manganese (IV) oxide.

**Manganese (IV) oxide, MnO<sub>2</sub>.**

Manganese (IV) oxide, MnO<sub>2</sub> is a black, insoluble powder in water. It is made by heating Manganese (II) nitrate at a temperature of 470K.

**Equation:**



Manganese (IV) oxide can also be got by reacting solid manganese (II) hydroxide with a solution of sodium chlorate (I).

**Equation:**



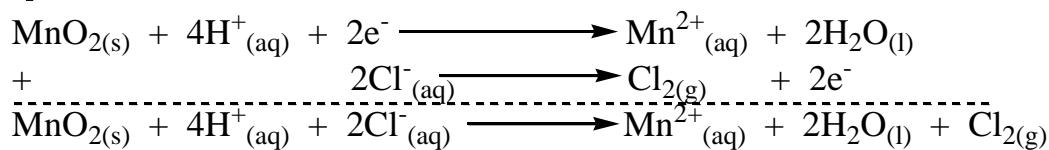
Manganese (IV) oxide is weakly amphoteric. It is a powerful oxidizing agent. Eg, it releases chlorine gas from concentrated hydrochloric acid.

Equation:



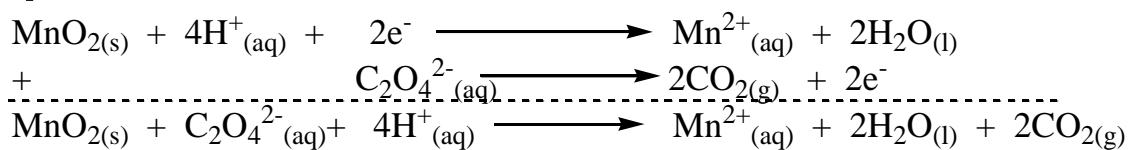
Manganese (IV) oxide is weakly amphoteric. It is a powerful oxidizing agent. Eg, it releases chlorine gas from concentrated hydrochloric acid.

Equations:



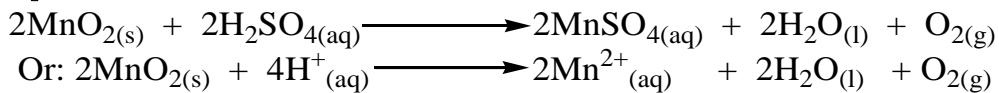
Manganese (IV) oxide is weakly amphoteric. It is a powerful oxidizing agent. Eg, it releases carbon dioxide gas from ethanedioic (oxalic) acid or oxalate.

Equations:



If warm with concentrated sulphuric acid, manganese (IV) oxide dissolves to yields oxygen gas and manganese (II) sulphate.

Equation:



7. State what will be observed and write an equation of reaction when manganese (IV) oxide reacts with sodium peroxide.

Observation:

A dark green solution of sodium manganate (VI) is formed.

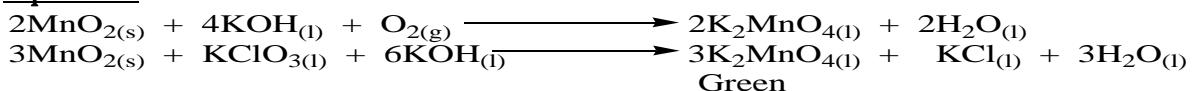
Equation:



**Compounds of manganese in the +6 oxidation state.**

This is an unstable oxidation state. Potassium manganate (VI) can be prepared by fusing manganese (IV) oxide with a strong oxidizing agent such as potassium chlorate (V) or potassium nitrate.

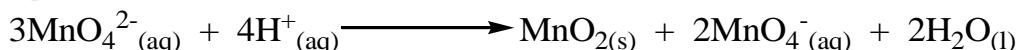
Equations:



Notes:

Potassium manganate (VI) is green in colour. It is only stable in alkaline solution. In acidic solution it disproportionate to manganese (IV) and manganese (VII) respectively.

Equation:



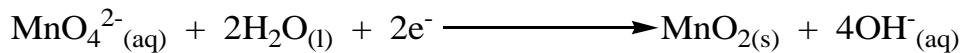
**Observations:**

A green solution turns to a black solid and black solution respectively.

Notes:

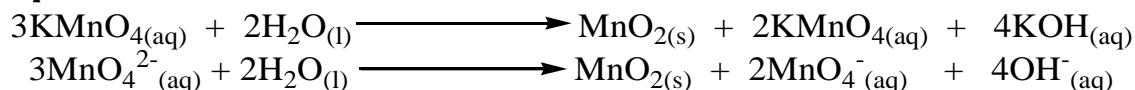
The manganate (VI) is quite powerful oxidizing agent, acting like all the oxidizing agents, as electron acceptors.

Equation:



Potassium manganate (VI) also undergoes disproportionation in a neutral condition forming a brown or black solid and a purple or black solution of manganese (IV) oxide and manganese (VI) respectively.

Equations:



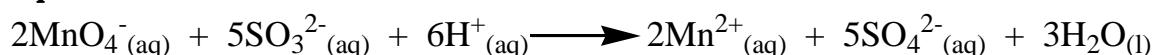
On bubbling carbon dioxide gas through the green solution, a purple solution [Potassium permanganate (VI) solution] and a brown solid is formed.

Equation:



When Sulphur dioxide gas is acidified by potassium manganate (VII) solution, hydrogen,  $\text{H}^+$  ion takes place in the reaction because Manganate (VII) ion is reduced [Loss of oxygen] by sulphite,  $\text{SO}_3^{2-}$  ion, The sulphite,  $\text{SO}_3^{2-}$  ion is oxidized to sulphate,  $\text{SO}_4^{2-}$  ion hence turns from purple to colourless solution.

Equation:



Or:



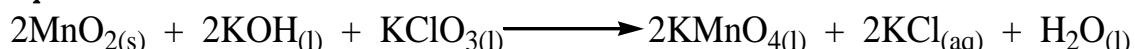
Purple solution

Colourless

## Compounds of manganese in the +7 oxidation state.

Preparation of potassium permanganate or managate (VII):

Equation:



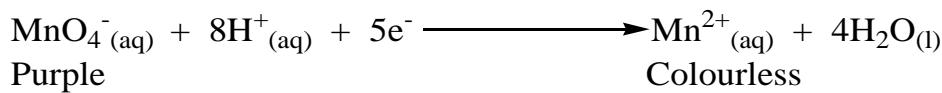
8. State the role of carbon dioxide gas during preparation of potassium managate (VII) (potassium permanganate (VII) solution) in the laboratory.

Carbon dioxide gas in **solution serves as an acid** that can convert any **manganate (VI)** formed during the reaction to **manganate (VII)**, by **disproportionation**.

Manganese exists in this oxidation state in the strongly acid  $\text{Mn}_2\text{O}_7$ . However, by far the most important compound containing manganese (VII) is potassium manganate (VII),  $\text{KMnO}_4$ . The solid is highly soluble in water, forming a deep purple solution. The ion manganate (VI),  $\text{MnO}_4^-$ , has a tetrahedral structure.

Potassium manganate (VII) is usually used in the presence of excess dilute sulphuric acid. Under these acidic conditions, it is reduced to  $\text{Mn}^{2+}$  ions, and the purple colour disappears.

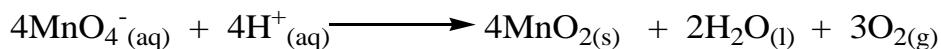
Equation:



Or:

Under slightly acidic conditions, Permanganate (VII) gradually decomposes forming manganese (IV) oxide also.

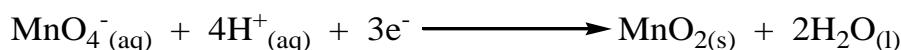
Equation:



Notes:

Under alkaline or neutral solution the manganate (VII) is reduced to manganese IV) oxide.

Equation:



Observations:

In neutral or alkaline solution, the colour changes **from purple to clear solution** and a **black precipitate** of manganese (IV) oxide is formed.

Properties of potassium manganate (VII).

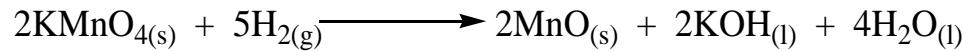
- ☛ Action of heat. When strongly heated, potassium manganate (VII) decomposes to give manganate (VI), manganese (IV), and oxygen gas.

Equation:



- ☛ Oxidizing action. The crystals burn if heated in hydrogen gas, giving potassium hydroxide and manganese (II) oxide.

Equation:



- ☛ Action on cold concentrated hydrochloric acid.

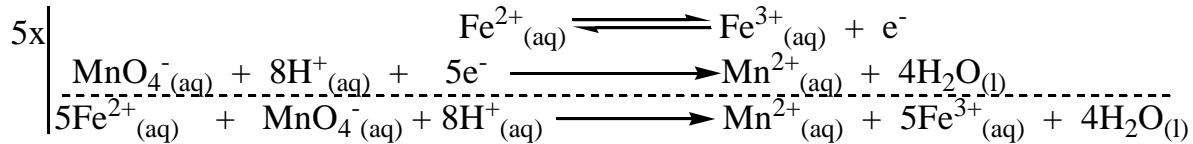
Equation:



EXAMPLES OF OXIDATIONS INVOLVING POTASSIUM MANGANATE (VII):

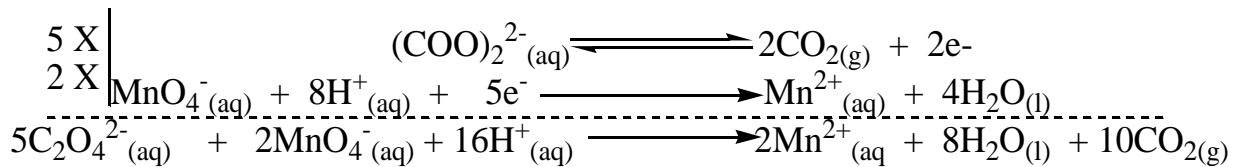
- (i) Iron (II) to iron (III).

Equations:



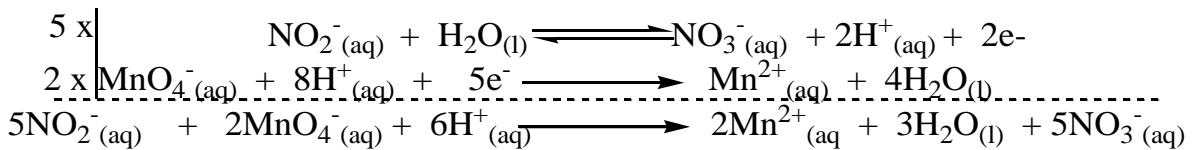
- (ii) Ethanedioic acid or an ethanedioate (in acidic solution) to carbon dioxide gas.

Equations:



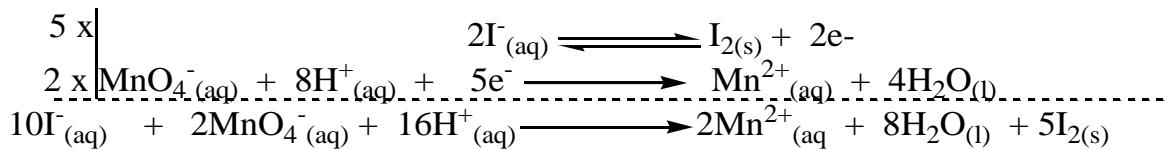
(iii) Nitrite (in acid solution) to nitrate.

Equations:



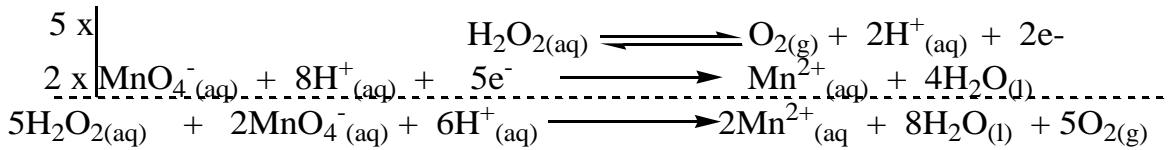
(iv) Iodide to iodine.

Equations:



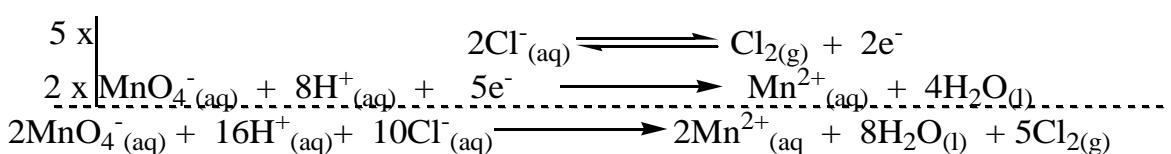
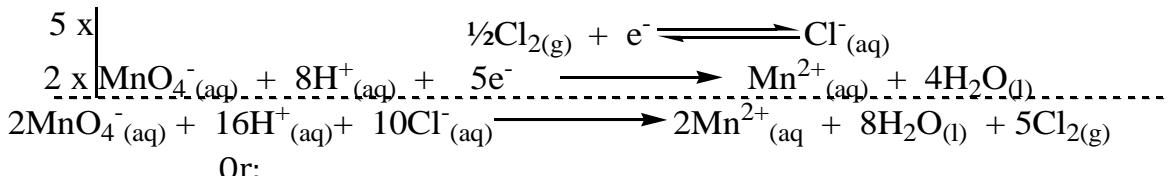
(v) Hydrogen peroxide to oxygen gas.

Equations:



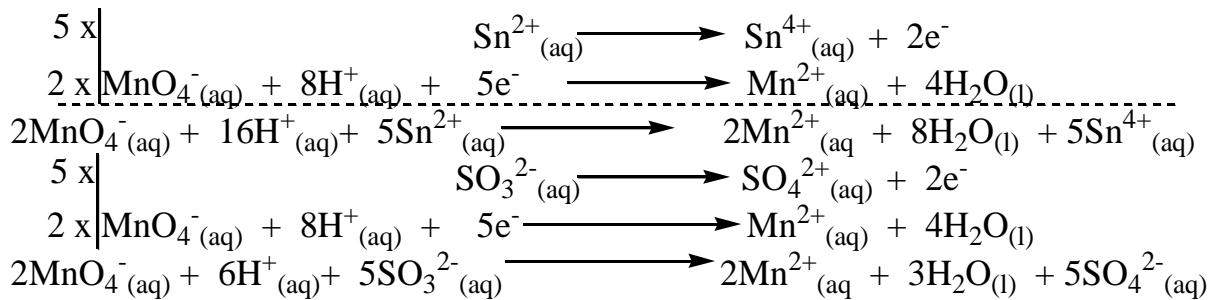
(vi) Potassium permanganate (VII) and hydrochloric acid to chlorine gas.

Equations:



(vii) Oxidation of tin (II) to tin (IV) ion and sulphite to sulphate ion respectively.

Equations:



3. A solution **A** contains a divalent metal ion and on addition of excess ethanedioic acid, a pale pink precipitate **B** is formed. On heating **B** in air, it decomposes 1<sup>st</sup> to a green solid **C** and on further heating to a black solid **D**. **C** is soluble in acid but **D** is not. When **D** is fused with solid potassium hydroxide and potassium chlorate, a green solid **E** is formed which forms a green solution in water. On acidifying the aqueous solution of **E**, the solution turns purple and **D** is also formed. The purple solution **F** reacts with acidified iron (II) sulphate solution to form a solution containing **A**.

- Identify **A** to **F**. (03 marks)
- Write equations for the respective reactions that took place. (6 mks)

### (c) The chemistry of iron

Electron configuration,  ${}_{26}\text{Fe}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ . Or Fe: [Ar]  $4s^2 3d^6$ .

$\text{Fe}^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^6$ . Or Fe: [Ar]  $4s^0 3d^6$ .

$\text{Fe}^{3+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5$ . Or Fe: [Ar]  $4s^0 3d^5$ .

### OCCURRENCE (ORES) OF IRON:

The commonest ores are:

- ✉ Iron pyrites ( $\text{FeS}_2$ ).
- ✉ Haematite or Iron (III) oxide ( $\text{Fe}_2\text{O}_3$ ).
- ✉ Magnetite or oxide of Iron ( $\text{Fe}_3\text{O}_4$ ).
- ✉ Siderite or Spathic Iron ore ( $\text{FeCO}_3$ ).
- ✉ Limonite or Brown Iron ore ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ).

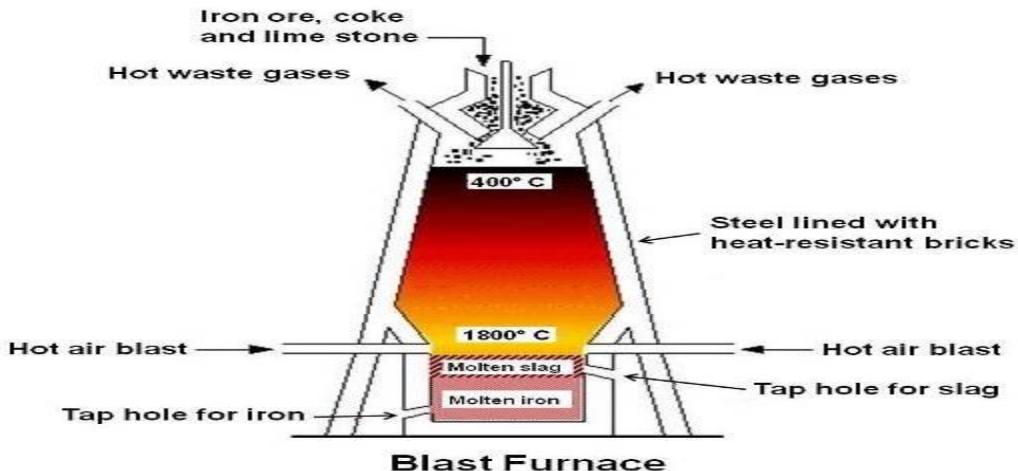
### THE MANUFACTURE OF IRON:

- Describe briefly how pure iron can be extracted or manufacture from haematite or brown iron ore.

The most vital raw materials from which iron is obtained are haematite ( $\text{Fe}_2\text{O}_3$ ) and brown iron ore ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ). In most parts of the world, there are still large quantities of high quality iron ores from which iron can be obtained.

The stages involves in extraction of iron.

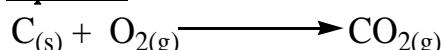
### DIAGRAM:



- (a) The first stage in the manufacture of iron involves preparing the ore for reduction in blast furnace.  
This involves crushing the ore to produce lumps size of one's fist. The lumps are pre-heated using hot gases from furnace that drives off water and other volatile impurities.  
The main impurities are silicon (IV) oxide (silica,  $\text{SiO}_2$ ) and aluminium oxide (alumina,  $\text{Al}_2\text{O}_3$ ).

- (b) The second stage in the manufacture of iron involves reducing the iron oxides.  
This is done using carbon (coke) in the presence of limestone (calcium carbonate) in the blast furnace.  
As the air enters the blast furnace, it reacts with coke. A highly exothermic reaction occurs forming carbon dioxide gas.

**Equation:**



This rises the temperature at the bottom of the furnace to about **2000K**. As the carbon dioxide gas rises up the furnace, it reacts with more coke forming carbon monoxide gas.

**Equation:**



The carbon monoxide gas produced then reduces the iron oxides to iron in the upper parts of the furnace. Here the temperature is between **750K** and **1000K**.

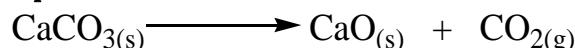
**Equation:**



In the blast furnace, limestone plays an essential part in the (removes) extraction of impurities from the iron.

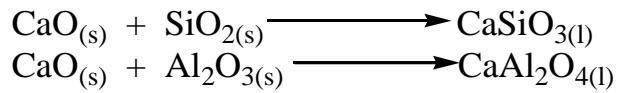
At the high temperature inside the furnace, the limestone decomposes into calcium oxide and carbon dioxide gas.

**Equation:**



The calcium oxide reacts with impurities in the iron such as sand (silicon (IV) oxide) and alumina (aluminium oxide). It forms calcium silicate and calcium aluminate, respectively.

Equations:



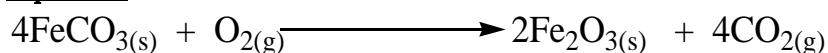
The mixture of calcium silicate and calcium aluminate which remains molten at the furnace temperature is known as **slag**. This flows to the bottom of the furnace where it floats on the molten iron. It is tapped off at a different level, separately from the iron.

Or:

Extraction of iron from spathic ore:

Roasting in air converts hydrated or spathic ore to anhydrous iron (III) oxide.

Equation:



Reduction in the blast furnace:

The furnace is charged with ore, coke, and limestone. The blast furnace process is very complex, but the principal reactions are following.

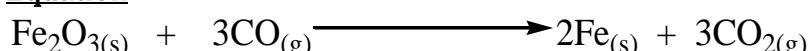
Near the base of furnace, coke burns in the air blast to produce carbon monoxide gas, probably the stages.

Equations:



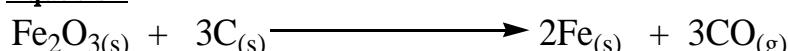
The first reaction is exothermic, and temperature is raised to **1800K**. Near the top of the furnace, at **900K**, the iron (III) oxide is reduced to iron as a solid.

Equation:



Some reduction can also takes place directly by carbon.

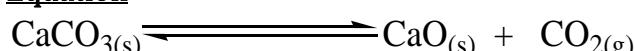
Equation:



Function of limestone:

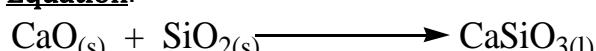
In the furnace, the limestone is decomposed by heat to quick lime.

Equation:



The lime reacts with siliceous earthy materials to form slag of silicates.

Equation:

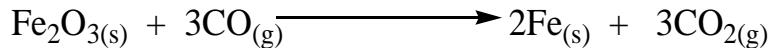


Or:

Extraction of iron from haematite ore:

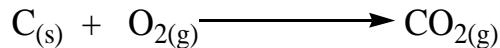
It is obtained by the reduction of the oxides by carbon monoxide gas.

Equation:



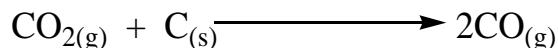
The blast furnace, in which this process takes place, is illustrated in the diagram. At the bottom of the furnace, coke is oxidized exothermically to carbon dioxide gas.

Equation:



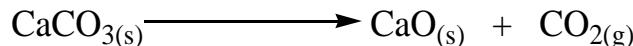
And the temperature of the furnace is about **1900°C** in this region. Higher up the furnace, carbon dioxide gas reacts with coke to form carbon monoxide gas.

Equation:



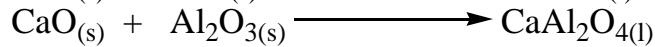
Iron oxides are reduced exothermically, and the iron produced falls to the bottom of the furnace, at the same, the limestone in the charge dissociates to form calcium oxide and carbon dioxide gas.

Equation:



Calcium oxide combines with silicon (IV) oxide and aluminium oxide, the impurities in the ore, to form a molten 'slag' of calcium silicate (IV) and calcium aluminate (III), which trickles down the stack.

Equations:



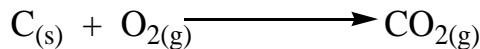
Summary:

Three solid raw materials are loaded in to the blast furnace:

- (c) Coke (C) This is a form of carbon made by heating coal in the absence of air. It is the fuel and the source of the reductant.
- (d) Iron ore ( $\text{Fe}_2\text{O}_3$ ) This is the source of the iron. It is usually crushed haematite or roasted carbonate.
- (e) Limestone ( $\text{CaCO}_3$ ) This combines with high-melting point impurities in the ore to form a liquid slag.
- (f) A high-pressure blast of heated air enters the furnace. A series of chemical reactions take place:

Equations:

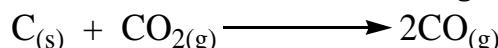
- ☛ Coke burns in the air.



- ☛ Limestone decomposes.



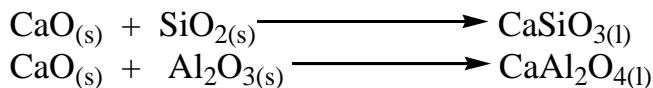
- ☛ Coke reduces the carbon dioxide gas.



- ☛ Carbon monoxide gas reduces the iron oxide ore.



- ☞ Impurities in the ore (mostly silica) react with calcium oxide to form a liquid slag.

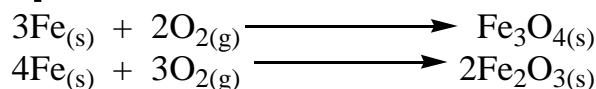


## **CHEMICAL PROPERTIES OF IRON:**

- ☞ With air or oxygen gas.

Iron is not affected with dry air or oxygen gas at room temperature. If heated, it combines with oxygen gas to give a black oxide of tri-iron tetra oxide (iron (II) diiron (III) oxide or triferric tetroxide) and iron (III) oxide respectively.

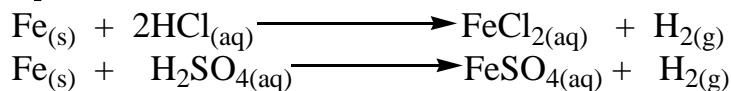
**Equations:**



- ☞ With acids.

Iron is above hydrogen gas in the electrochemical series. It liberates hydrogen gas & iron (II) salts in solution from warm dilute hydrochloric & sulphuric acid.

**Equations:**



Dilute nitric acid gives mixed products for which no definite equation could be written.

**Equation:**



Concentrated nitric acid renders iron passive, due to the formation of an impermeable oxide layer.

Concentrated sulphuric acid with heat, converts iron to iron (III) sulphate (not iron (II) sulphate)

**Reason:**

This is because hot concentrated sulphuric acid oxidizes iron to iron (III) sulphate.

**Equation:**



Iron also precipitate copper from solutions of its salts because of its strong electropositive character.

**Equation:**

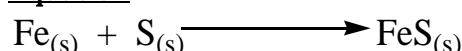


- ☞ With non-metals.

(a) Sulphur.

Iron when heated with powdered sulphur, a dark grey or black solid of iron (II) sulphide is formed.

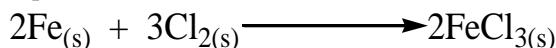
**Equation:**



(b) Chlorine gas.

Iron combines vigorously with dry chlorine gas, when heated to form a black sublimate of iron (III) chloride.

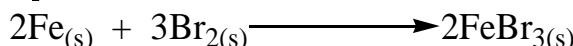
Equation:



(c) Bromine gas.

Bromine gas combines rapidly with damp moist iron filings at ordinary temperature to form iron (III) bromide.

Equation:



(d) Hydrogen chloride gas.

Iron when heated with hydrogen chloride gas, a white solid of iron (II) chloride is formed.

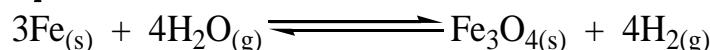
Equation:



☞ With water.

Iron reacts with steam NOT water when heated to form a black solid of iron (II) diiron (III) oxide or tri iron tetra oxide.

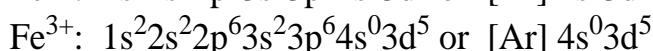
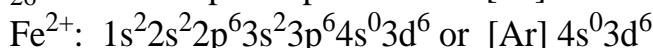
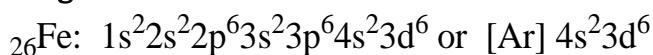
Equation:



## **THE COMPOUNDS OF IRON:**

Iron exhibit two most important oxidation states of +2 and +3 respectively. +3 is the most stable oxidation state.

Electronic configuration:



— Explain why iron (III) ion is more stable than iron (II) ion.

Iron (III) ion is more stable than iron (II) ion because of its **electronic configuration** which shows that **its five 3d-orbital (sub-energy level) is singly occupied by an electron or half-filled is stable than half-full 3d-orbital.**

— Iron (II)  $[1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^6]$  is unstable and is easily oxidized to iron (III)  $[1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5]$ . why?

## **COMPOUNDS OF IRON IN THE +2 & +3 OXIDATION STATE.**

Iron (II) compounds are readily oxidized by air or other oxidizing agents, particularly under neutral or alkaline conditions.

(a) Iron (II) oxide,  $\text{FeO}$ .

Iron (II) oxide can be made by heating iron (II) ethanedioate (ferrous oxalate) in the absence of air. Iron (III) oxide is a basic oxide.

Equation:

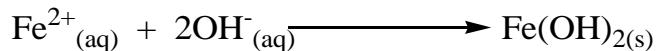


Observation:

A **yellow iron (II) oxalate** decompose on heating to form a **black solid** of iron (II) oxide and a **colourless gases** are given off.

Pure Iron (II) hydroxide is white, but, as usually precipitated by the action of aqueous alkali or ammonia on a solution of an iron (II) salt, that appear as a dark green gelatinous.

Equation:



Notes:

Both iron (II) oxide and iron (II) hydroxide, rapidly turns brown or yellow in colour on exposure to air by aerial oxidation to iron (III) oxide and iron (III) hydroxide respectively.

Iron (II) chloride is prepared by heating iron with hydrogen chloride gas, a white solid of iron (II) chloride is formed.

Equation:



Iron (II) sulphate is prepared by warming iron filings (or, better iron wire) with dilute sulphuric acid.

Excess dilute sulphuric acid should not be used because iron (III) sulphate will be formed instead of iron (II) sulphate.

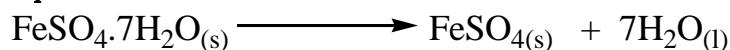
Equation:



The crystal are efflorescent and can be oxidized on exposure to air, with formation of brown patches of basic iron (III) sulphate.

It is also crystallized as iron (II) sulphate-7-water from solution when heated, a **pale green crystals** turns to **white anhydrous iron (II) sulphate**.

Equation:



Pale green crystall White powder

Notes:

The **white anhydrous iron (II) sulphate** powder decompose on further heating to yields a **fine reddish-brown powder** of iron (III) oxide and a **colourless gasses** are given off.

Equation:



(b) Iron (III) oxide,  $\text{Fe}_2\text{O}_3$ .

Iron (III) oxide is also a basic oxide and it can be prepared as a brown solid by heating iron (II) sulphate.

Equation:



Iron (III) oxide can be prepared by heating iron (II) sulphide (iron pyrite) in dry air.

Equation:



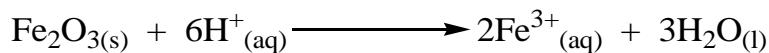
Iron (III) oxide can be prepared also by heating strongly iron (III) hydroxide.

Equation:



Iron (III) oxide dissolves in a dilute mineral acids when it is strongly heated to form iron (III) salt.

Equation:



Notes:

Iron do not dissolves in dilute nitric acid but instead it dissolves in dilute sulphuric & hydrochloric acid.

Iron (III) hydroxide is unaffected by excess alkalis but instead dissolves in dilute mineral acids to form iron (III) salt, but the solution is much hydrolyzed.

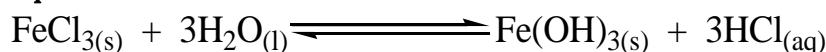
Equation:



Notes:

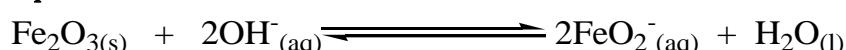
Iron (III) chloride like all other iron (III) salts is hydrolyzed in water to forming acidic solution.

Equation:



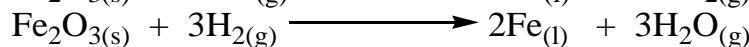
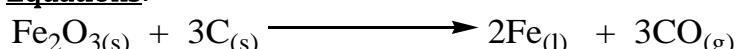
Iron (III) oxide when heated with concentrated or fused alkali since it has very slight acidic tendencies, it reacts to form ferrate or iron (III).

Equation:



In showing amphoteric character in this way, it resembles  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  and iron (III) oxide is reduced to iron when strongly heated with carbon, carbon monoxide and hydrogen gas.

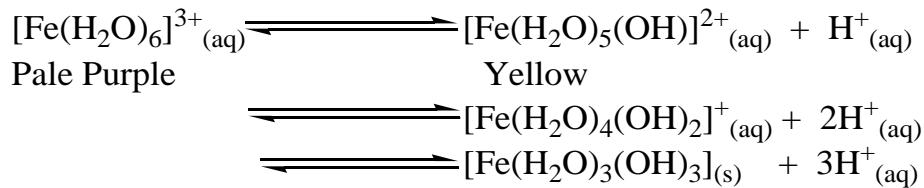
Equations:



Golden tips:

In strongly acidic solution, iron (III) exists as the pale purple ion  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ . As the pH increases yellow aqua/hydroxo complexes are formed, and above pH 3 value hydrated iron (III) oxide is precipitated. The hydrated  $\text{Fe}^{3+}$  ion can be considered as proton donor.

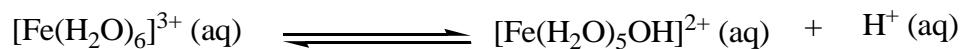
Equations:



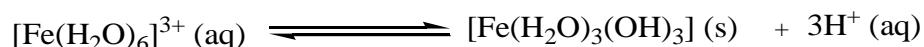
**Notes:**

**Iron (III) compounds**

The iron (III) ions have a high charge density and are heavily hydrated therefore in aqueous solution they exist as  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  hence it undergoes hydrolysis to release protons which cause the solution to be acidic.

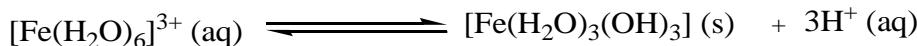


Complete hydrolysis is represented as

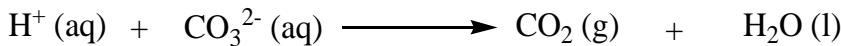


- Sodium carbonate solution was added to aqueous solution of iron (III) sulphate. Bubbles of a colourless gas and a brown precipitate were observed. Explain this observation.

Due to high charge density, the hydrated ion undergoes hydrolysis to form insoluble iron (III) hydroxide and hydrogen ions which cause the solution to be acidic i.e.



The hydrogen ions react with carbonate ions from sodium carbonate to form carbon dioxide gas which is colourless gas

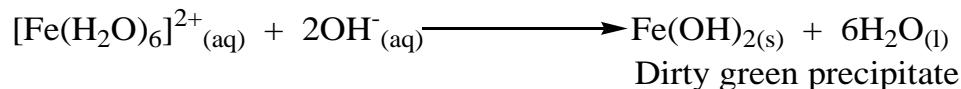


- Describe how you can distinguish iron (II) from iron (III) salt.

## **ADDITION OF AN ALKALI**

- (e) Addition of an alkali such as sodium or potassium hydroxide solution to an aqueous solution of an iron (II) salt produces a dirty green precipitate of iron (II) hydroxide.

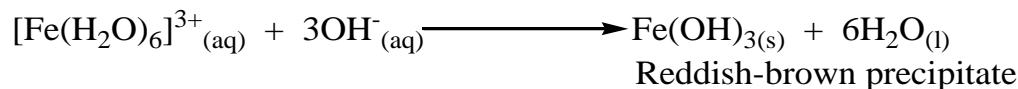
**Equation:**



The precipitate is slowly oxidized by air, forming hydrated iron (III) oxide,  $\text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ .

- (f) Addition of an alkali such as sodium or potassium hydroxide solution to an aqueous solution of an iron (III) salt produces a reddish-brown precipitate of iron (III) hydroxide.

**Equation:**



Or:

The ferric ion has a rather high charge density, which causes solutions of ferric salts to be acidic as a result of the reaction.

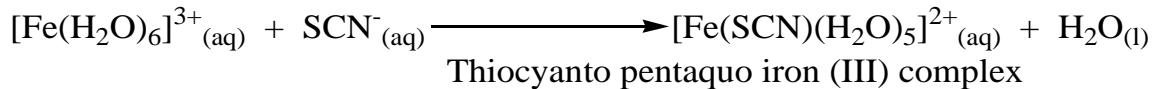
Equation:



- (g) Addition of potassium Thiocyanate solution.

When a solution of potassium thiocyanate solution, is added to a solution containing hydrated iron (III) ion, a blood red or deep red colour is produced. $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$ .

Equation:

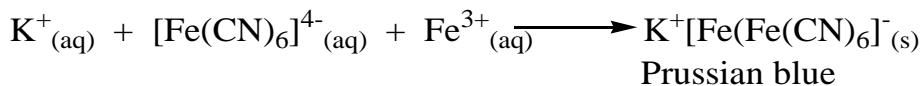


No observable change occurs with iron (II) ions.

- (h) Addition of potassium hexacyanoferrate (II) solution.

The addition of potassium hexacyanoferrate (II) solution containing iron (III) ions produces a **deep blue precipitate** known as Prussian blue.

Equation:

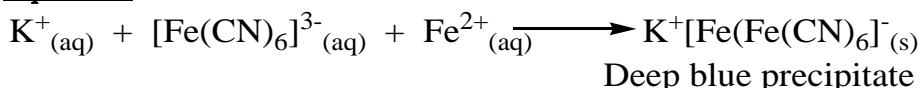


The addition of potassium hexacyanoferrate (II) solution containing iron (II) ions produces a **white precipitate**.

- (i) Addition of potassium hexacyanoferrate (III) solution.

The addition of potassium hexacyanoferrate (III) solution containing iron (II) ions produces a **deep blue precipitate** known as Turnbull's blue.

Equation:



The addition of potassium hexacyanoferrate (III) solution containing iron (III) ions produces a **brown solution**.

- (c) Iron (II) diiron (III) oxide or tri iron tetra oxide,  $\text{Fe}_3\text{O}_4$  (Mixed oxide).

This oxide reacts with warm, moderately concentrated hydrochloric acid to produce iron (II) and iron (III) chlorides in solution.

Equation:

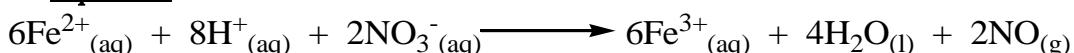


**Some examples of the iron (II) to iron (III) conversion.**



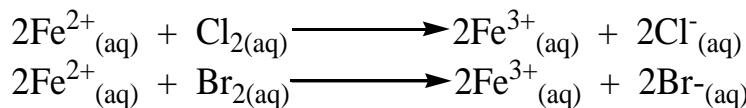
- (a) With concentrated nitric acid and heat. Brown fumes (nitrogen dioxide gas) are evolved.

Equation:



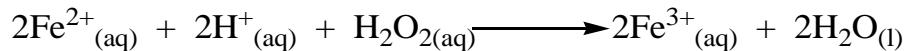
- (b) With chlorine water or bromine water. The halogen colour is discharged.

Equations:



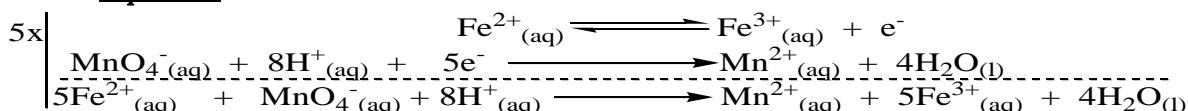
(c) With hydrogen peroxide solution.

Equation:



(d) With acidified potassium managate (VII) solution. The purple colour of manganate (VII) is discharged.

Equation:



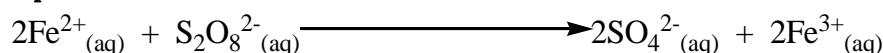
(e) With acidified potassium dichromate (VI) solution. The golden yellow dichromate (VI) solution turns dark green.

Equation:



(e) With sodium thiosulphate solution.

Equation:

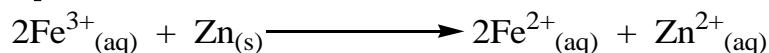


### Some examples of the iron (III) to iron (II) conversion.

— With zinc and dilute sulphuric acid or hydrochloric acid.

On boiling iron  $\text{Fe}^{3+}$  ion with zinc powder, a green iron (II) ion is produced.

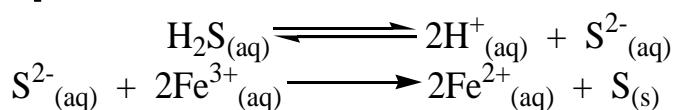
Equation:



— With hydrogen sulphide gas. Sulphur appears as a yellow precipitate.

When hydrogen sulphide gas is passed via a solution of iron (III) ion, a green solution of iron (II) ion and a yellow precipitate is formed.

Equations:

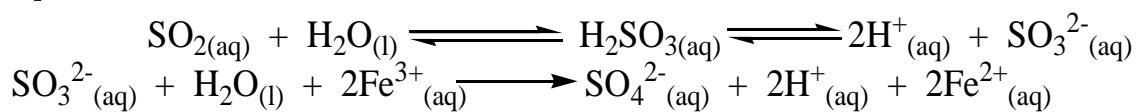


Or:



— With sulphur dioxide gas. Or sulphite ion.

Equations:



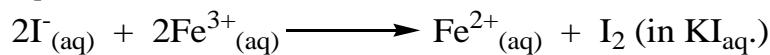
Observation:

Water acts as a chemical in the reaction, not a solvent. A pale green iron (II) solution is formed.

— With acidified potassium iodide solution.

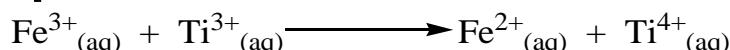
Iodine is produced, usually as a brown solution in excess iodide.

Equation:



— With titanium ion.

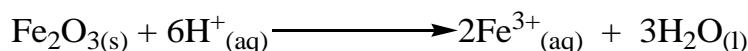
Equation:



## 9. Discuss the determination of percentage purity of an iron ore.

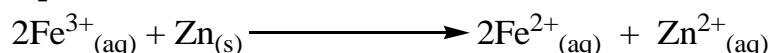
— In the analysis of an iron ore, the ore of known mass containing iron (III) oxide is first crushed and dissolved in a dilute mineral acid [E.g. Dilute sulphuric or hydrochloric acid] forming iron (III) ion.

Equation:



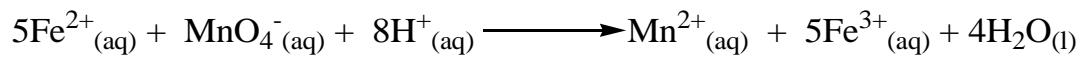
— The iron in the +3 oxidation state is reduced by zinc granule or zinc powder to iron (II) ion.

Equation:



— The solution containing the iron (II) ion is acidified and analyzed by titration with a standard solution of potassium manganate (VII) solution. The endpoint during the titration is when a drop of manganate (VII) solution gives a purple colour to the contents of the flask.

Equation:



The results obtained is used to calculate the mass of the iron ore and the percentage purity is calculated from:

Mathematically:

$$\text{Percentage purity of the ore} = \frac{\text{mass of pure sample}}{\text{mass of original sample}} \times 100\%$$

1. 25.0cm<sup>3</sup> portion of a solution containing iron (II) ion and iron (III) ion was acidified and titrated against potassium manganate (VII) solution. 15.0cm<sup>3</sup> of 0.02moldm<sup>-3</sup> solution of the manganate (VII) were required. A second 25.0cm<sup>3</sup> portion was reduced with zinc metal and titrated against the same manganate (VII) solution. 19.0cm<sup>3</sup> of the oxidant solution were required.

Calculate the concentration of:

- (a) Iron (II) ion [0.06M]
  - (b) Iron (III) ion [0.1M]
2. State the condition (s) and write equation leading to the formation of anhydrous iron (III) chloride.

3. At 400°C and 1.0 atmospheric pressure, 3.00g of anhydrous iron (III) chloride occupies a volume of 510cm<sup>3</sup>.Workout the apparent relative molecular mass of iron (III) chloride at this temperature and hence suggest a formula for the molecular species present.
  4. Hydrogen sulphide gas was bubbled through a solution of iron (III) chloride.
    - i. State what was observed.
    - ii. Write the equation for the reaction that took place.
    - iii. State one application of an iron (III) compound in qualitative analysis (include observations that would be made).
  5. Explain what meant by the following terms:
    - i. d-block elements.
    - ii. Transition metal elements.
  6. With reference to iron, state any three properties of transition element.
  7. A solution of iron (III) chloride in acidic medium is ..... Explain this observation.
  8. Describe the uses of iron compound in:
    - i. Qualitative analysis.
      - ↗ Freshly prepared iron (II) sulphate solution is used to test for the presence of nitrate ion in the brown ring test.
      - ↗ Iron (III) ions is used to test for the presence of iodide ions in solution in which a brown solution is formed.
      - ↗ Use of hexacyanoferrate (II) and hexacyanoferrate (III) in differentiating iron (II), iron (III), zinc (II) and copper (II) ions
    - ii. Quantitative analysis.
      - ↗ Iron (II) ions is also used as a catalyst in the titration of persulphate ion with potassium iodide solution.
- Equation:**
- $$\text{S}_2\text{O}_8^{2-} \text{(aq)} + 2\text{I}^- \text{(aq)} \longrightarrow 2\text{SO}_4^{2-} \text{(aq)} + \text{I}_2 \text{(aq)}$$
- ↗ Iron (II) ion is used as a reducing agent in redox titration especially in titrations with potassium manganate (VII) and potassium dichromate (VI) solution.
9. Steel wire (steel is mostly iron) of mass 3.225g was dissolved in dilute sulphuric acid and the solution made up to 250.0cm<sup>3</sup> .A 25.0cm<sup>3</sup> portion of this solution was further acidified and titrated against potassium dichromate (VI) of concentration 0.031M. The volume required was 31.0cm<sup>3</sup>.Calculate the percentage of iron in the steel wire.

## (d) COBALT

Electronic configuration.  ${}_{27}\text{Co}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$ . Or Co: [Ar]  $4s^2 3d^7$ .

$\text{Co}^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^7$ . Or Co: [Ar]  $4s^0 3d^7$ .

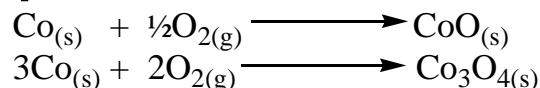
$\text{Co}^{3+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^6$ . Or Co: [Ar]  $4s^0 3d^6$ .

### PROPERTIES OF COBALT.

With air.

Cobalt is not affected by air at room temperature but on heating, reacts slowly to give a mixture of Cobalt (II) oxide and mixed oxide of Cobalt.

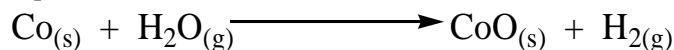
Equations:



With water.

Cobalt does not react with water at ordinary conditions but when strongly heated it reacts with steam to form cobalt (II) oxide and hydrogen gas.

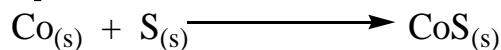
Equation:



With sulphur.

Cobalt combines directly with sulphur, on **heating** to form cobalt (II) sulphide.

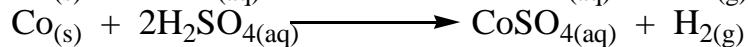
Equation:



With acids.

Cobalt is attacked by both hot dilute sulphuric & hydrochloric acids forming a corresponding cobalt (II) salts.

Equations:



Concentrated nitric acid may render the metal passive by forming a layer of oxide,  $\text{Co}_3\text{O}_4$ .

Cobalt reacts with dilute nitric acid to form cobalt (II) nitrate and oxide of nitrogen.

Hot concentrated sulphuric acid oxidizes cobalt to:

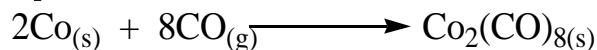
Equation:



With carbon monoxide gas.

Cobalt reacts with carbon monoxide gas on heating to form an orange powder.

Equation:

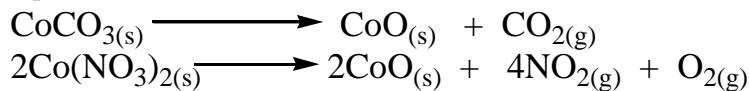


## Compounds in the +2 oxidation state:

(a) Cobalt (II) oxide, CoO.

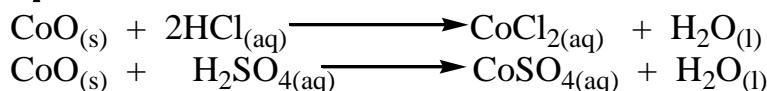
Cobalt (II) oxide is formed if cobalt (II) carbonate or nitrate is heated in the absence of air. Cobalt (II) oxide is a greenish powder and is a basic oxide.

Equations:



Cobalt (II) oxide reacts with dilute mineral acids to form cobalt (II) salts.

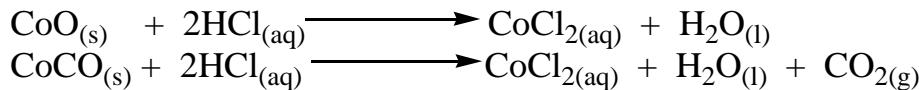
Equations:



(b) Cobalt (II) chloride, CoCl<sub>2</sub>.

Cobalt (II) chloride is formed in solution by the action of dilute hydrochloric acid on cobalt (II) oxide or carbonate.

Equations:

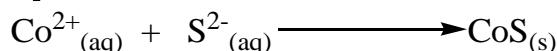


- Cobalt (II) sulphide, CoS.

Cobalt (II) sulphide is a black compound, insoluble in water, and precipitated by action of ammonium sulphide solution on a solution of cobalt (II) salt.

Cobalt (II) sulphide is a black compound prepared by passing hydrogen sulphide gas through a solution of a cobalt (II) salt in presence of ammonia and ammonium chloride.

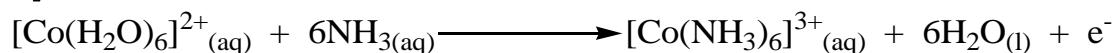
Equation:



The +2 is the most stable oxidation state of cobalt. Aqueous solution of Co<sup>2+</sup> is pink and exist as [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>.

The +2 oxidation state is oxidized even by atmospheric oxygen gas or hydrogen peroxide to Co<sup>3+</sup> which is a pale yellow or yellowish-orange.

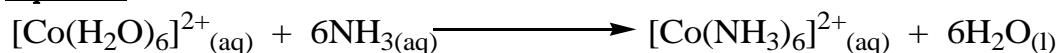
Equation:



Notes:

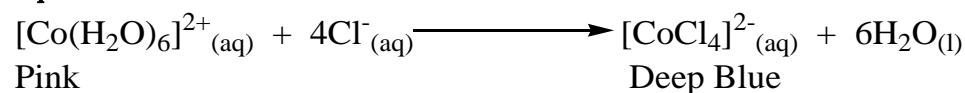
[Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> dissolves in excess ammonia, forming a pale yellow or yellowish-orange or red-brown.

Equation:



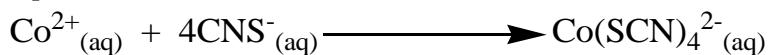
[Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> dissolves in concentrated hydrochloric acid, forming a deep blue solution.

Equation:



- Cobalt (II) ion dissolves in a concentrated potassium or ammonium thiocyanate solution.

Equation:

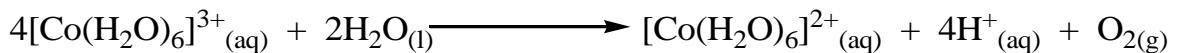


Observation:

A blue solution of potassium or ammonium tetrathiocyanatocobalt (II) ion is formed.

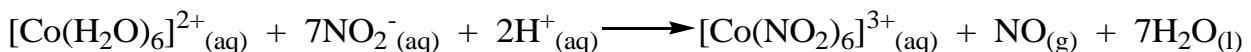
- $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  dissolves in water, owing to the products below.

Equation:



$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is oxidized to the +3 oxidation state by excess sodium nitrite in the presence of ethanoic acid to form a yellow precipitate.

Equation:



## (e) COPPER

Electronic configuration,  ${}_{29}\text{Cu}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$  or Cu: [Ar]  $4s^1 3d^{10}$ .

$\text{Cu}^+$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^{10}$  or  $\text{Cu}^+$ : [Ar]  $4s^0 3d^{10}$ .

$\text{Cu}^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^9$  or  $\text{Cu}^{2+}$ : [Ar]  $4s^0 3d^9$ .

### Ores of copper:

(viii) Copper Pyrites ( $\text{CuFeS}_2$ )

(ix) Copper glance ( $\text{Cu}_2\text{S}$ )

(x) Cuprite ( $\text{CuO}$ )

(xi) Malachite ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ )

### Extraction of copper:

- Describe briefly how pure copper can be extracted or manufactured from copper pyrites,  $\text{CuFeS}_2$ .

The extraction of copper involves four major stages, namely:

- Concentration of the ore by flotation (selective wetting).

The ore is crushed and then mixed with water, frothing agent inclusive. Air is blown via the mixture to produce froth. Earthly materials are wetted by water and sink to the bottom. The ore is driven to the surface in froth, the froth is skimmed off, an acid is added to break the ore from the froth, and the mixture is filtered.

- Roasting (reduction) of the ore.

The ore is roasted in air. The iron (II) sulphide is converted to iron (II) oxide by roasting in limited supply of air.

Equation:



- Smelting.

Sand and limestone are added. The mixture is heated in a blast furnace, in absence of air, to convert iron (II) oxide in to iron (II) silicate (slag).

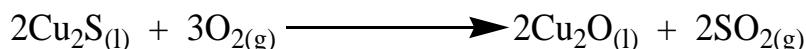
Equation:



- Conversion to 'blister copper'.

As more air is blown, copper (I) sulphide is heated in supply of air to form copper (I) oxide and sulphur dioxide gas.

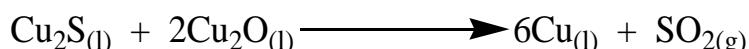
Equation:



Note:

The mixture of copper (I) oxide and the unchanged copper (I) sulphide is heated strongly in the absence of air forming copper.

Equation:



- Purification of blister copper.

The blister copper is purified by electrolysis. Impure blister copper is made the anode while copper is made the cathode. The electrolyte is acidified copper (II) sulphate solution.

During electrolysis, the anode dissolves to form copper (II) ions which are deposited at the cathode as pure copper.

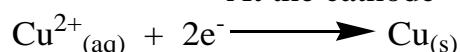
Reactions taking place are:

At the anode



and

At the cathode



## CHEMICAL PROPERTIES OF COPPER:

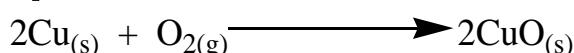
10. Discuss the reaction of copper with:

- Air.

Copper when heated in dry air, copper oxidizes superficially, giving a mixture of:

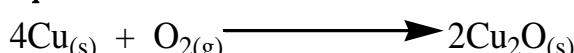
At **300°C**, it reacts with oxygen gas forming a black layer of copper (II) oxide.

Equation:



At **1000°C**, it reacts with oxygen gas forming copper (I) oxide instead of copper (II) oxide.

Equation:



- Water.

Copper **DOES NOT** reacts with water **at any condition**.

Reason:

Copper is less electropositive than hydrogen gas, so will no displace hydrogen from water under any conditions, nor from pure dilute sulphuric and hydrochloric acid

- Acids.

Copper DOES NOT reacts with dilute hydrochloric and sulphuric acids.

Reason:

Copper is less electropositive than hydrogen gas, so will no displace hydrogen from water under any conditions, nor from pure dilute sulphuric and hydrochloric acid

Copper however, it does react with hot concentrated sulphuric acid where it is oxidized to copper (II) sulphate and some other products.

Equation:



Copper however, it reacts with cold concentrated nitric acid where it is oxidized to copper (II) nitrate and is itself reduced to nitrogen dioxide gas and water.

Equation:



Copper however, it reacts with cold moderately nitric acid or dilute nitric acid to copper (II) nitrate and is itself reduced to nitrogen monoxide gas and water.

Equation:



Golden tips:

Copper has one electron on its outermost  $4s^1$ -orbital like group (I) elements but differs from group (I) elements.

Reasons:

- Because of having 10 electrons on 3d sub-shell.
- Poor shielding by the 3d electrons makes the atoms of copper bigger in size and having a higher 1st ionization energy than potassium atom hence copper forms compounds less readily than potassium.

COMPOUNDS OF COPPER:

Copper shows oxidation states of +1 and +2 only.

**Electronic configuration,**  ${}_{29}\text{Cu}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$  or Cu: [Ar]  $4s^1 3d^{10}$ .

$\text{Cu}^+$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^{10}$  or  $\text{Cu}^+$ : [Ar]  $4s^0 3d^{10}$ .

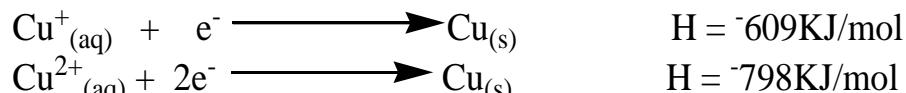
$\text{Cu}^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^9$  or  $\text{Cu}^{2+}$ : [Ar]  $4s^0 3d^9$ .

11.Explain why  $\text{Cu}^{2+}$  ion is more stable than  $\text{Cu}^+$  ion.

$\text{Cu}^{2+}$  ion is more stable than  $\text{Cu}^{1+}$  ion because of two factors. Namely:

☛ Energy factor.

Equation:



Since copper,  $\text{Cu}^{2+}$  ion gives copper, Cu atom more heat than copper,  $\text{Cu}^+$  ion then it is more stable.

☛ Poor shielding effect.

$3d^{10}$  electrons are poorly shielded making  $4s^1$  electron to be more firmly held and hence 1<sup>st</sup> ionization energy is greater than 2<sup>nd</sup> ionization energy.

Copper,  $\text{Cu}^{2+}$  ion shows a typical transition metal properties E.g it forms complexes, i.e  $\text{CuCl}_4^{2-}$ ,  $\text{Cu}(\text{NH}_3)_4^{2+}$  etc, its compounds are coloured (Blue or Green), has incomplete  $3d^9$  sub-energy level, etc.

## 12. Explain why copper (I) compounds are white or colourless.

This is because the five 3d-orbitals are completely filled with electrons. However, the oxide  $\text{Cu}_2\text{O}$  is reddish-brown.

Copper (I) ions in water are unstable in aqueous solution because they readily disproportionate. Copper,  $\text{Cu}^+$  ion is oxidized to Copper,  $\text{Cu}^{2+}$  ion and reduced to copper.

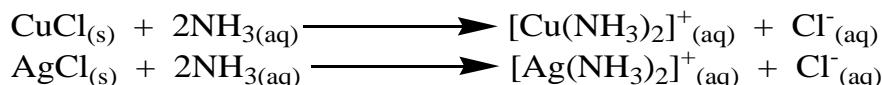
Equation:



Golden tips:

Copper (I) chloride like silver chloride is insoluble in water but instead dissolves in aqueous ammonia solution.

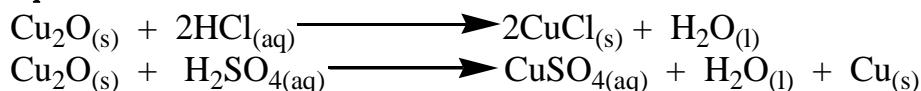
Equations:



## COMPOUNDS OF COPPER IN +1 OXIDATION STATE.

Copper (I) oxide is a basic and covalent. It reacts with acids to form the products below.

Equations:

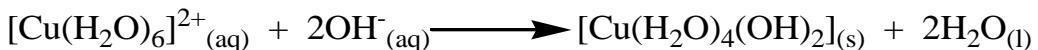


## COMPOUNDS OF COPPER IN +2 OXIDATION STATE.

Copper (II) ions exist in aqueous as the hexaaquacopper (II) complex ion,  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ . These have a characteristic blue or green colour.

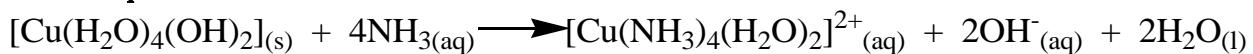
When sodium hydroxide solution is added to a solution containing these ions, a pale blue precipitate of hydrated copper (II) hydroxide is produced.

Equation:



Hydrated copper (II) hydroxide is also produced if ammonia solution is used as an alkali. The hydroxide then dissolves in excess ammonia forming the royal blue diaquatetraamine complex.

Equation:



If an excess concentrated hydrochloric acid is added to an aqueous solution containing copper (II) ions, the yellow anionic complex tetrachlorocuprate (II) is formed.

Equation:

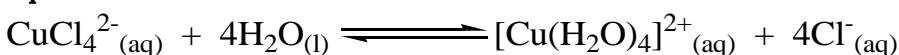


13. State what is observed when water is added to tetrachlorocupper(II) ion and write the equation for the reaction.

Observations:

When the **yellowish-brown solution** is diluted with water, the complex breaks up forming a **pale blue solution** due to the formation of hydrated copper (II) ion.

Equation:

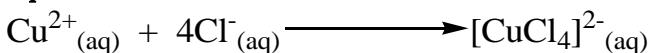


14. State what is observed when concentrated hydrochloric acid or solution of either potassium chloride or sodium chloride is added to copper (II) ion and write the equation for the reaction.

Observations:

The **blue solution** turns to **yellowish-brown solution** which is due to the formation of a complex ion.

Equation:

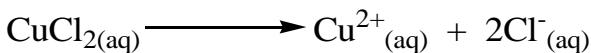


15. State what is observed when copper (II) chloride is dissolved in water and write an equation for the reaction.

Observations:

A **blue solution** is formed.

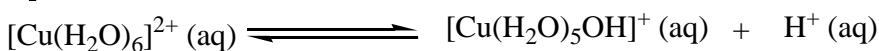
Equation:



Golden tips:

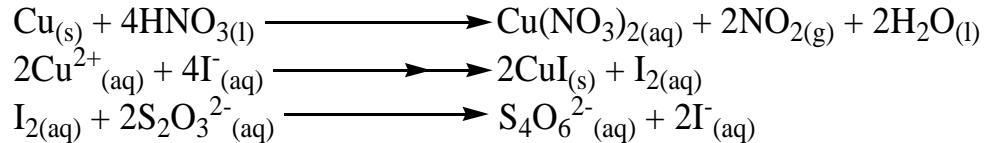
An aqueous solution of copper (II) salts are slightly acidic because the  $\text{Cu}^{2+}$  ions have a high charge density therefore they are heavily hydrated as  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  and this undergoes hydrolysis to release hydrogen ions in solution which causes the solution to be acidic.

Equation:



- Discuss the determination of percentage of copper in a copper ore by titrimetry (Iodine titration).
  - The impure copper of a known mass,  $m_1$  g is dissolved in concentrated nitric acid. The solution containing the copper (II) ions is diluted with distilled water up to a known volume,  $V$  say  $250.0\text{cm}^3$  in a volumetric flask.
  - A known volume,  $V_1 \text{ cm}^3$  of the solution is pipetted and transferred in to a clean conical flask, neutralized with sodium carbonated solution and ethanoic acid and treated with an excess of potassium iodide solution.
  - The iodine liberated is titrated with a standard solution of sodium thiosulphate using starch indicator. The reaction equations are:

**Equations:**



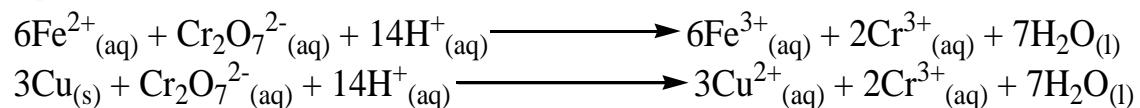
- Using the volume of sodium thiosulphate solution required to reach the end-point, the concentration of copper (II) ions is calculated and hence the percentage.

**Mathematically:**

$$\text{Percentage of copper} = \frac{\text{mass of copper}}{\text{mass of sample used}} \times 100\%$$

- A known mass of impure copper is dissolved in a known volume of excess acidified potassium dichromate (VI) solution.
- The mixture is warmed and the cooled. It's then titrated with a standard solution of ammonium iron (II) sulphate using redox indicator i.e. Diphenylamine.

**Equations:**



The results are used to calculate the mass of copper:

**Mathematically:**

$$\text{Percentage purity} = \frac{\text{mass of copper}}{\text{mass of sample}} \times 100\%$$

## (f) ZINC

Electronic configuration,  ${}_{30}\text{Zn}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$  or  $\text{Zn}$ :  $[\text{Ar}] 4s^2 3d^{10}$ .

$\text{Zn}^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^{10}$  or  $\text{Zn}^{2+}$ :  $[\text{Ar}] 4s^0 3d^{10}$ .

16. Explain the reasons why zinc is not a transition element.

Zinc is not a transition element because all five of its 3d-orbitals are completely filled with electrons. Besides zinc exhibits only a single oxidation state in its compounds which is due to  $+2$  and due to the loss of the  $4s^2$ -electrons.

17. State the reasons why zinc is not a transition element.

- ✓ It forms colourless compounds in aqueous state
- ✓ It exhibits only one oxidation state
- ✓ It is not paramagnetic
- ✓ It does not act as catalyst or has limited catalytic activity

However, like other transition elements, Zinc forms complexes.

### Extraction of zinc.

#### Ores of zinc.

2. **Calamine, ZnCO<sub>3</sub>.**
3. **Zinc blende, ZnS.**
4. **Galena (Lead sulphide), PbS.**

18. Describe briefly how pure zinc can be extracted or manufacture from zinc blende, ZnS.

During extraction of zinc, there are three stages involved namely:

- ☛ Concentration of the ore.

Concentration is a process of removing or eliminating unwanted earthly materials (impurities from an ore so as to increase its amount).

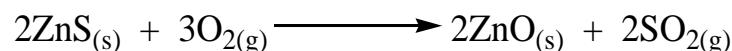
The ore is concentrated by froth flotation. The ore is crushed and then mixed with water and frothing agent.

Air is blown through the mixture to form froth. Earthly materials are wetted by water and sink to the bottom. The ore is driven to the surface in froth, the ore is skimmed off.

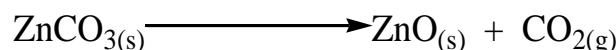
- ☛ Roasting of the ore in air.

The concentrated blende, or calamine, are roasted in air to convert it to zinc oxide.

**Equation:** Zinc blende is oxidized by oxygen gas of the air.



**Equation:** Calamine decomposes as shown below.



In both cases, zinc oxide is produced as a solid, sulphur dioxide and carbon dioxide gases are also an important products produced.

- ☛ Reduction of zinc oxide.

The coke burns to give carbon dioxide gas which then reduced to carbon monoxide gas by the unburnt coke.

**Equations:**



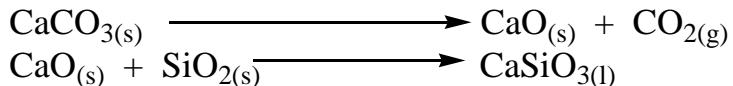
The produced carbon monoxide gas reduces zinc oxide, zinc oxide is also reduced by coke.

**Equations:**



The limestone decomposes to quicklime which combines with silicon (IV) oxide present as an impurity to form calcium silicate (slag).

**Equations:**



### **PROPERTIES OF ZINC:**

19. Discuss the reaction of zinc with:

(d) Air or oxygen gas.

Zinc burns in oxygen gas with a bluish flame to form a yellow-hot and white-cold solid, but in a moist air, it forms a basic carbonate which protects it from further attack.

**Equation:**



(e) Water.

Zinc does not react with water but instead decomposes steam at red heat to form a yellow-hot and white-cold solid.

**Equation:**



(f) Acids.

Zinc is oxidized by dilute nitric acid forming nitrogen monoxide gas.

**Equations:**



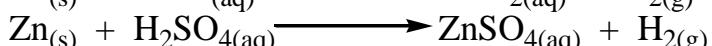
When the dilute nitric acid is very dilute, dilute nitric acid is reduced to dinitrogen oxide gas.

**Equation:**



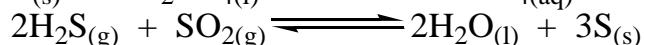
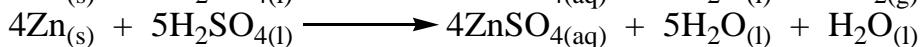
Zinc reacts with warm hydrochloric acid (both concentrated & dilute) and warm dilute sulphuric acid forming a colourless gas that burns with a pop sound when tested.

**Equations:**



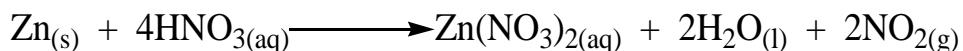
Zinc is oxidized with hot concentrated sulphuric acid to form a colourless gas that turns orange potassium dichromate solution to green colour when tested.

**Equations:**



Zinc is oxidized with hot concentrated nitric acid to the following products below in the equation.

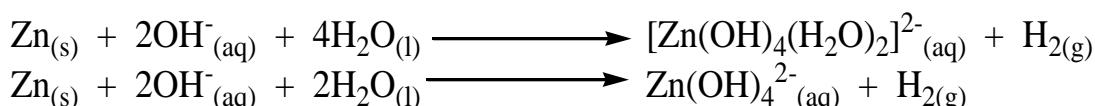
**Equation:**



(g) Aqueous alkali.

Powdered zinc reacts with hot, aqueous alkali to liberate hydrogen gas.

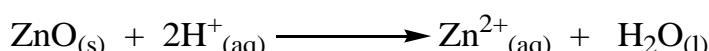
**Equation:**



**Golden tips:**

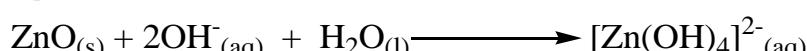
Zinc oxide is amphoteric. It reacts with acids forming zinc ions.

**Equation:**



With aqueous alkalis, zinc oxide forms tetrahydroxozincate(II) anionic complex.

**Equation:**



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1. State any seven properties of periodic table.
2. Explain the following terms:
 

a) Melting point.	b) Boiling point.
c) Atomic radius.	e) Electropositivity.
d) Electronegativity.	g) First electron affinity.
f) Ionization energy.	
3. Describe and explain the variation in electron affinity, electronegativity, ionization energy, electropositivity & atomic radius:
  - i. Down the group.
  - ii. Across the period.
  - iii. Along a period including the first transition series.
4. Explain the variation of melting & boiling points among period 2 & 3 elements of the Periodic Table.
5. State and explain the factors affecting the above properties of periodic table.
6. The table below shows the ionization energies (in Kj/mol) of five elements lettered A, B, C, D & E.

Element	1 <sup>st</sup> Ionization Energy	2 <sup>nd</sup> I.E.	3 <sup>rd</sup> I.E.	4 <sup>th</sup> I.E.
A	500	4600	6900	9500

B	740	1500	7700	10500
C	630	1600	3000	4800
D	900	1800	14800	2100
E	580	1800	2700	11600

- a) Which of the elements is most likely to form an ion with a charge of +1? Give reasons for your answers.
- b) Which two of the elements are in the same group of the periodic table? Which group do they belong?
- c) In which group of the periodic table is element E likely to occur? Give reasons for your answer?
- d) Which element would require the least energy to convert one mole of gaseous atoms into ions carrying two positive charges?
- e) List three factors which influence the size of the first ionization energy of an element.
7. Explain the following observations.
- a) The first ionization energy of Boron is lower than that of beryllium whereas the second ionization energy of Boron is higher than that of beryllium.
- b) The 1<sup>st</sup> I.E of nitrogen is higher than that of oxygen whereas the 2<sup>nd</sup> I.E of oxygen is higher than that of nitrogen.
- c) The 1<sup>st</sup> ionization energy of aluminium is less than that of magnesium.
- d) The electronegativity increases from lithium to fluorine in period 2.
- e) Diamond have a higher melting point than boron and nitrogen?
- f) The first ionization energy for oxygen lower than for nitrogen.
- g) Magnesium carbonate is insoluble in water while sodium carbonate is soluble.
- h) Magnesium carbonate is insoluble in water while magnesium chloride is soluble.
- i) Sodium carbonate is used as a base in acid-base titration.
- j) The atomic radius of Group (II) elements increases down the group?
- k) Melting points of Group (II) elements decreases down the group?
- l) Lithium carbonate decomposes while other carbonates of group I do not.
- h) Melting point of group (II) is higher than those of group (I) metals.
- i) Ice floats on water.
- j) Water boils at 100°C while hydrogen fluoride boils at 19°C.
- k) Magnesium oxide dissolves in dilute sulphuric acid whereas barium oxide doesn't.
- l) Sodium Nitrite is more stable than Sodium Nitrate.
- m) Across the transition elements series, the atomic radius remains almost constant.
- n) The boiling point of beryllium chloride is 487°C and that of magnesium chloride is 1418°C.
- o) The solubility of sulphates of group (II) elements of the periodic table decrease down the group.
- p) Graphite conducts electricity in solid state but solid sodium chloride doesn't.
- q) Lithium carbonate is insoluble in water.
- r) Aluminium trifluoride is ionic while aluminium trichloride is covalent.
- s) Boron trichloride is a non-polar molecule whereas Nitrogen trichloride is polar.

- t) Beryllium doesn't behave like other S block elements.  
 u) A solution of Sodium chloride has a higher boiling point than pure water.
8. Explain why Lithium doesn't form peroxide or superoxide when burn in oxygen.  
 9. Discuss the action of water on oxides of element of Group (I) metals of the periodic table.  
 10. Discuss the action of water on the hydrides of element of Group (I) metals of the periodic table.  
 11. State and explain the factors affecting Hydration energy.  
 12. State and explain the factors affecting Lattice energy.  
 13. Li, Na, K, Rb and Cs belong to group (I) metal elements of the periodic table.  
 Describe the reactions of the elements with: (i) Air ii. Water iii. Hydrogen gas
14. Discuss the action of water on oxides of element of Group (I) metals of the periodic table.  
 15. Discuss the action of water on the hydrides of element of Group (I) metals of the periodic table.  
 16. Explain the following observations:  
 a) Successive ionization energy are arranged as  $1^{\text{st}}\text{I.E} < 2^{\text{nd}} \text{I.E} < 3^{\text{rd}} \text{I.E} \dots < n^{\text{th}} \text{I.E}$ .  
 b) Ionization energy of orbitals are arranged as s>p>d>f.  
 c) Boron has got a low first ionization potential compare to beryllium.
- | Chlorides      | NaCl | MgCl <sub>2</sub> | AlCl <sub>3</sub> |
|----------------|------|-------------------|-------------------|
| Melting points | 801  | 746               | sublimes          |
| Charge         | +1   | +2                | +3                |
- e) The variation in melting point +1, +2, +3.  
 d) The melting and boiling point of halide of aluminium are in the order of  $\text{AlI}_3 < \text{AlBr}_3 < \text{AlCl}_3 < \text{AlF}_3$ .
17. Explains why potassium is a stronger reducing agents than Sodium.  
 (b). State three factors that makes group (I) elements a stronger reducing agents than group (I) elements.  
 (c). Give one reason in each case to explain why the elements of group (I) of the periodic table:  
 (i) Are monovalent. (ii) Do not form complexes.  
 (iii) Are strong reducing agents. (iv) Form mainly ionic compounds.
18. Explain why:  
 (i) The solubility of sulphates of group (IIA) decreases down the group.  
 (ii) Beryllium forms predominantly covalent compounds  
 (iii) The elements of group (IIA) form the divalent ion  $\text{m}^{2+}$  although the second ionization energies are high.  
 (b). Calcium reacts with water and dilute hydrochloric acid. By using equations show how the reactions occur.  
 (c). Do you think Calcium can react with Sodium hydroxide. Give a reason for your answer.
19. Name the reagents that can be used to distinguish between each of the following and in each case state what would be observed & write an equations where possible.

1.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$
2.  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$
3.  $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$
4.  $\text{Sn}^{4+}$  and  $\text{Sn}^{2+}$
5.  $\text{Pb}^{2+}$  and  $\text{Ag}^+$
6.  $\text{C}_2\text{O}_4^-$  and  $\text{HCO}_3^-$
7.  $\text{Cl}^-$  and  $\text{Br}^-$
8.  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$
9.  $\text{NO}_2^-$  and  $\text{NO}_3^-$
10.  $\text{HCOO}^-$  and  $\text{CH}_3\text{COO}^-$
11.  $\text{F}^-$  and  $\text{Cl}^-$
12.  $\text{SO}_4^{2-}$  and  $\text{SO}_3^{2-}$
13.  $\text{SO}_3^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$

20. Define the following terms: Charge density, Polarization, Principal quantum No.  
(b). Explain why the value for the second electron affinity of oxygen is positive whereas the value for the first electron affinity is negative.

21. Briefly explain the following observations:

- (i) The ions of both potassium,  $\text{K}^+$  and chloride,  $\text{Cl}^-$  have the same electronic configuration, but potassium ion is smaller than chloride ion.
- (ii) In moving from sodium to chloride along third period, there is a steady decrease in atomic size.
- (iii) The first electron affinity of oxygen is negative but the second electron affinity is positive.

22. Write equation(s) for the following reactions:

- a) Calcium oxide reacting with water.
- b) Sodium Carbonate with water and Carbon dioxide
- c) Sodium Hydrogen Carbonate heated.
- d) Carbon dioxide is passed in Calcium hydroxide solution. State observation.
- (b) What would happen to (d) above if more carbon dioxide is passed. Write equation and state observation.
- (c) Group (II) metals form few complexes. However, the tendency to form complexes decreases down the group. Explain this observation.

23. Both Boron and Silicon exhibit diagonal relationship.

- a) State:
  - (i). what is meant by the term diagonal relationship?
  - (ii). three properties in which Boron and Silicon show similarities.
- b) Name two other pairs of elements that show diagonal relationship.
- c) Write equation(s) for the reaction of Boron and Silicon with water.
- d) State five properties in which Beryllium and Aluminium but differs from the rest of the group (II).
- e) Give one reason for the anomalous behavior of Beryllium.

24. Explain the following observations.

- a) The salts of group II elements in the periodic Table are generally less soluble than those of the corresponding group I metal salts.
- b) Calcium carbonate is less soluble in water than calcium chloride.
- c) Solubility of group (II) A chlorides decreases as the group is descended.
- d) Solubility of group (II) A hydroxides increases as the group is descended.
- (b). Although beryllium is in group II of the periodic table, its properties resemble those of aluminium which is in group III.
  - a) Discuss the similarities in the properties of the two elements.
  - b) Explain why the two metals show similar properties.

25. A certain oxide of the elements in group (II) was mixed with carbon and heated to a very high temperature and a compound B was formed. B reacted with cold water to give gas K which decolourised bromine water.

- (i) Identify the element in Group II and the substances B and K.  
(ii) Write equations for the reactions leading to the formation of K.
26. Lithium is in group I and magnesium is in group (II) of the periodic table but the two elements show some common chemical properties.
- State the name given to this type of relationship.
  - Give **FOUR** examples of the properties in which the two elements show similarities.
  - Name **TWO** other pairs of elements that show similar type of relation as Lithium and magnesium.

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- Write equations to show how hydrides of period 3 elements reaction with water.
  - Both lead (II) and (IV) chlorides react with water.
    - Write equations show how they react with water.
    - Explain the differences in the reactions above.
- When red lead  $Pb_3O_4$  was reacted with nitric acid a solid was formed.
  - Write the equation for the reaction.
  - The mixture from (a) was filtered and the residue warmed with concentrated hydrochloric acid, state.
    - what was observed? Explain your answer.
    - Write equation for the reaction.
  - The filtrate from (a) was divided into two parts;
    - to the 1<sup>st</sup> part was added aqueous potassium iodine. State what was observed and write equation for the reaction
    - the 2<sup>nd</sup> part was evaporated to dryness and heated strongly: Explain what was observed and write equation for the reaction that took place.
- Briefly describe the laboratory synthesis of chlorides of group (IV) elements.
  - Write equations to show how the chlorides of group (IV) elements react with water.
  - Oxides of group (IV) elements can be in oxidation states +2 or +4.
    - Name the oxides of group IV elements.
    - Explain why oxides in oxidation state +2 become more stable as the group is descended.
- Discuss the reactivity of group (IV) element (carbon, silicon, germanium, tin and lead) of the periodic table with.
  - Soaps. (c) Water (d) Dilute mineral acids. (e)Concentrated mineral acid.
  - Dilute sodium hydroxide solution.
- Write an ionic equation for the reaction between Sodium hydroxide and:
  - Silicon (IV) oxide. (ii). Lead (IV) oxide.
- Write equations and state characters for reaction of group (IV) oxides with Sodium hydroxide.



was titrated with **0.02M** potassium permanganate until the colour turned pink. The volume of Potassium permanganate solution used was **20cm<sup>3</sup>**.

- Calculate the percentage impurity of tin (II) oxide ( $Sn= 119, O=16$ )
- Write an ionic equations when tin (II) ions are added to:

- Acidified potassium dichromate solution
- Sodium oxalate solution
- Iron (III) chloride solution

13. When a yellow solid **A** is heated with air at  $450^{\circ}\text{C}$ , a red solid **B** is formed. **B** reacts with hot dilute nitric acid to form a dark brown solid **C** on precipitation and after filtration and crystallization of the filtrate; a white solid **D** is obtained. When **C** is heated with concentrated hydrochloric acid, a pale green gas was evolved and when hydrochloric acid is added to aqueous solution of **D** at room temperature, a white precipitate **E** was formed.

- Identify the substances **A-E** inclusive
- Account for your answers in (a) above with aid of equations of reactions.

14. The standard enthalpy of formation of tin tetrachloride is  $-508\text{KJmol}^{-1}$ . The standard enthalpy of atomization of tin and chlorine are  $+301$  and  $+121\text{KJmol}^{-1}$  respectively. The average bond energy of Si-Cl bond is  $+383\text{KJmol}^{-1}$ .

- Determine the average bond energy of Sn-Cl bond
- Comment on the difference between the average bond energies.
- State a reagent that can be used to differentiate between the following ions and in each case state what would be observed when each is treated with the reagent. (i)  $\text{Pb}^{2+}$  &  $\text{Sn}^{2+}$  (ii)  $\text{Pb}^{2+}$  &  $\text{Al}^{3+}$  (iii)  $\text{Sn}^{2+}$  &  $\text{Zn}^{2+}$ .

15. A compound **Q** contains **90.65%** by mass of lead and the rest Oxygen.

- Deduce the molecular formula of **Q** if its molar mass is **685g**.
- State what is observed when **Q** is reacted with the following and in each case write the equation of reaction.
  - Dilute Nitric acid
  - Hot concentrated sulphuric acid.
  - Hot concentrated hydrochloric acid

16. Gaseous hydride of silicon diffuses through a narrow hole for **27.8s**. The same volume of carbon dioxide under the same temperature and pressure through the same in **32.6s**.

- Determine the molecular formula of the hydride.
- Write the equation of reaction between the hydride of silicon and sodium hydroxide solution.

17. Tin and to a greater extend, Lead are said to show the inert pair effect.

- What is inert pair effect?
- Give a reason for the existence of the inert pair effect.

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