STRAIGHTFORWARD REVIEW CHEMISTRY

FAMILIAR FLAT CHEMISTRY

REVIEWED NOTES

Still have glitches or weedy in the subject?

Respite term assistance / Holiday Program.

Contact and Book Senior Tutor

Duty station : Pajule Home

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Objective : helping you understand Fundamental Principles of the subject.

IN THE NAME OF GOD MOST GRACIOUS & MERCIFUL,

PERSEVERANCE:

I pledge this book to my parents Mr.P'Ochure Michael Ocaya & Mrs.Ocaya Christian Akumu the late (RIP) 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*.**

ACKNOWLEGEMENTS:

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** & **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.

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.*

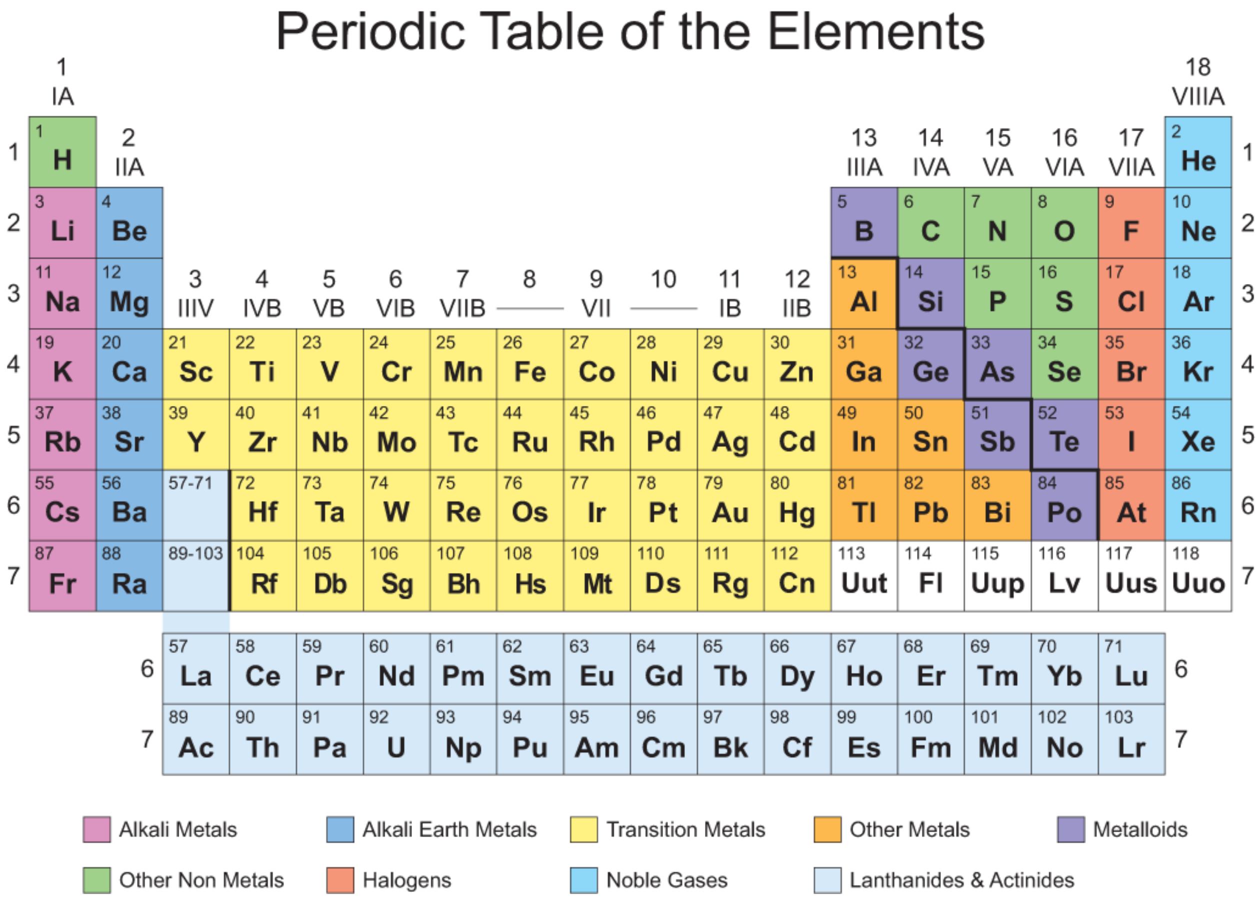
Periodic table: is a list of all the elements, in order of increasing atomic number, giving their names and symbols.

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 IA	2 IIA	3 IIIV	4 IVB	5 VB	6 VIB	7 VIIB	8 —	9 VII	10 —	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA	
1	1 H																	2 He	1
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	2
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	3
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	4
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	5
6	55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	6
7	87 Fr	88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo	7

6	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	6
7	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	7

1. Define what is meant by the following terms?

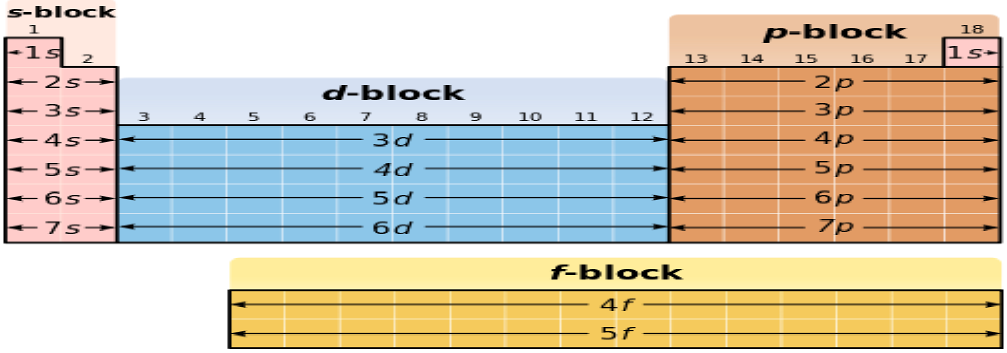
✓ **s-Block elements:** these are elements which have got their outer most electrons in s-sub energy level; they are mostly elements in Group 1, Group 2 & **only** Helium in Group 0.I.e elements with atomic no 1 to 88.

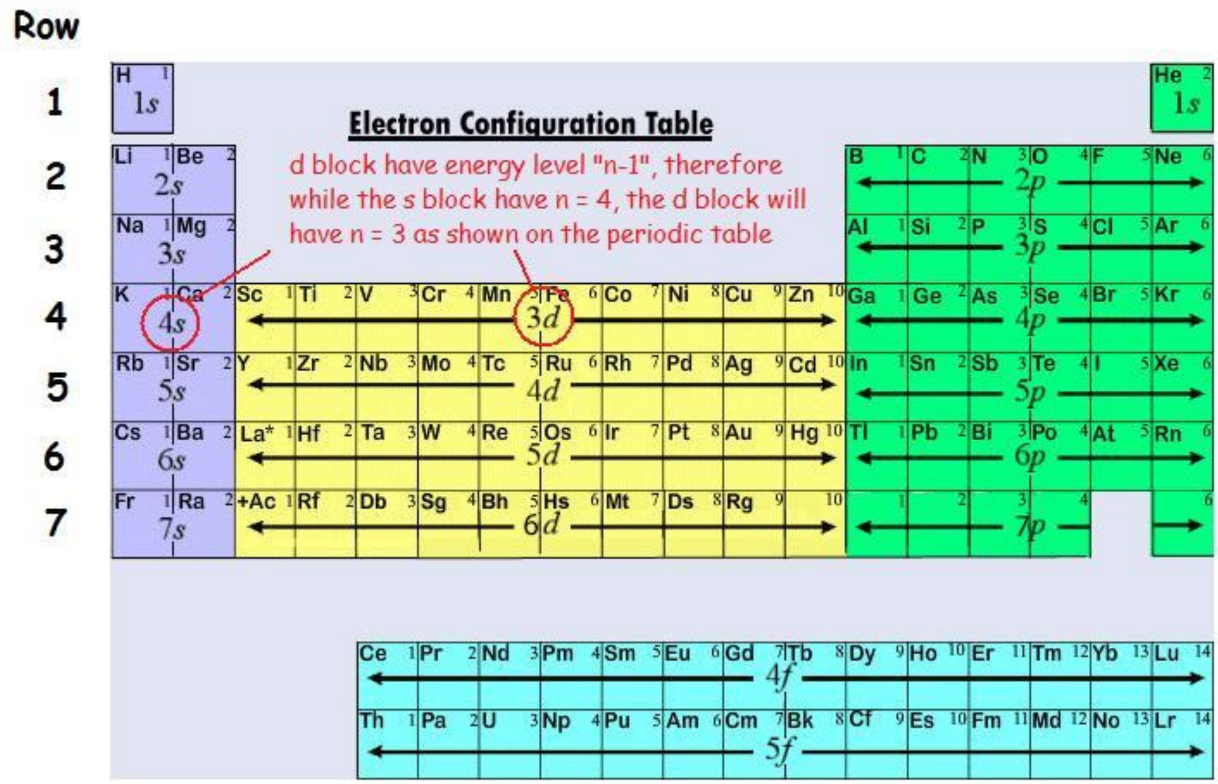
✓ **p-Block elements:** these are elements which have got their outer most electrons in p-sub energy level; they are mostly elements starting from Group 3 to the rest of the remaining elements in Group 0.I.e elements with atomic no 5 to 118.

✓ **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.

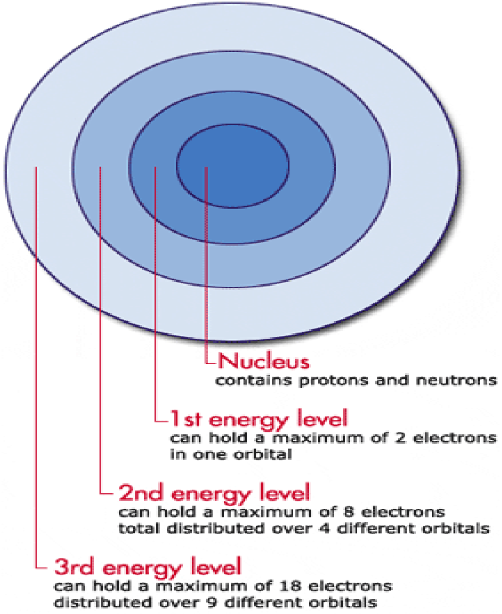
✓ Some of the groups have special names:
Group 1 - **the alkali metals** Group 7 **– the halogens** Group 0 **– the noble gases.**





d block have energy level "n-1", therefore while the s block have n = 4, the d block will have n = 3 as shown on the periodic table

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.



Nucleus
contains protons and neutrons

1st energy level
can hold a maximum of 2 electrons in one orbital

2nd energy level
can hold a maximum of 8 electrons total distributed over 4 different orbitals

3rd energy level
can hold a maximum of 18 electrons distributed over 9 different orbitals

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 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 1st energy level n = 1 has 1 sub shell given as **1s**

✓ The 2nd energy level n = 2 has 2 sub shells given as **2s,2p**

✓ The 3rd energy level n = 3 have 3 sub shells given as **3s,3p,3d**

✓ The 4th energy level n = 4 have 4 sub shells given as **4s,4p,4d,4f**

✓ The 5th energy level n = 5 and beyond have 4-subshells.

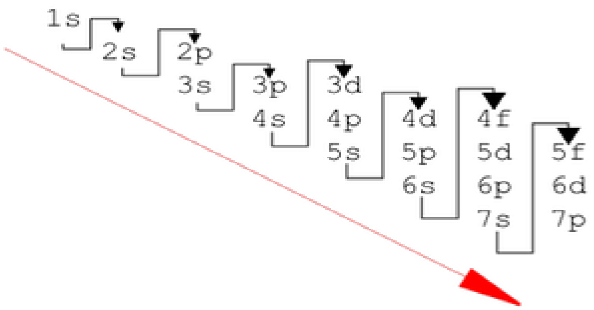
Golden tips:

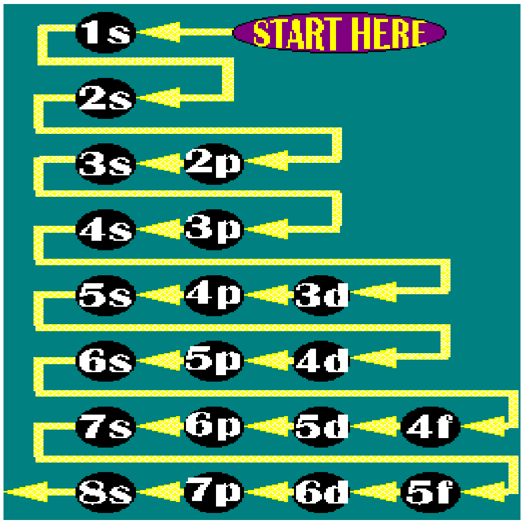
✗ An orbital can accommodate a maximum of two electrons with opposite spins ie.

✗ Electron 1st occupies each orbital singly 1st with parallel spins before pairing starts.

✗ Half-filled orbital's are thermodynamically **VERY** stable.i.e p^3, d^5 & f^7.

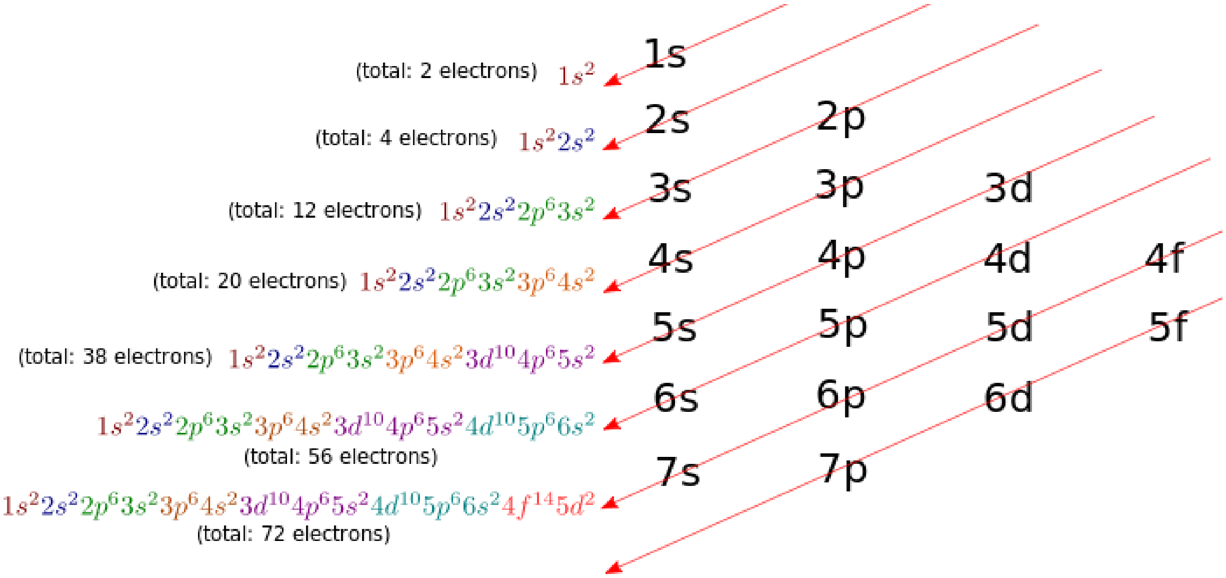
ELECTRONIC CONFIGURATION:





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.

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



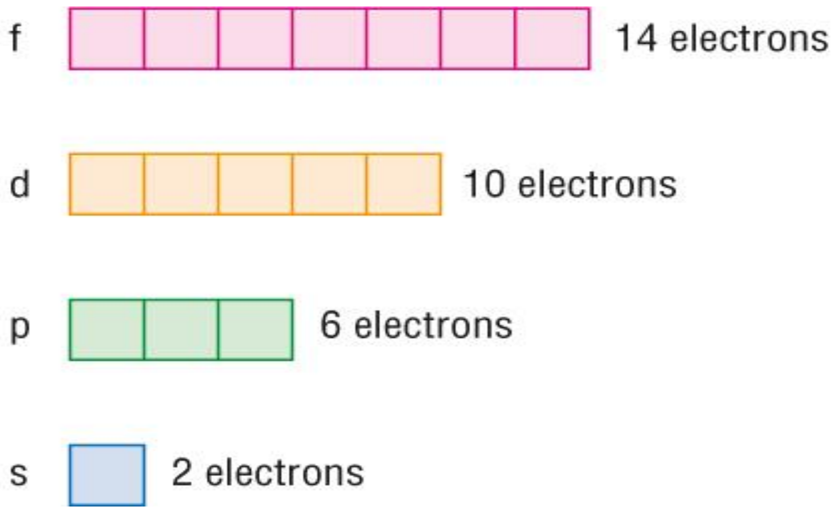
The 4ft principal quantum number m_s (electron spin quantum number) has the valence of +½,-½ which are the two possible values of m_s.meaning that there are two electrons spinning in opposite directions in an orbital.i.e an orbital is occupied by two electrons. Therefore:

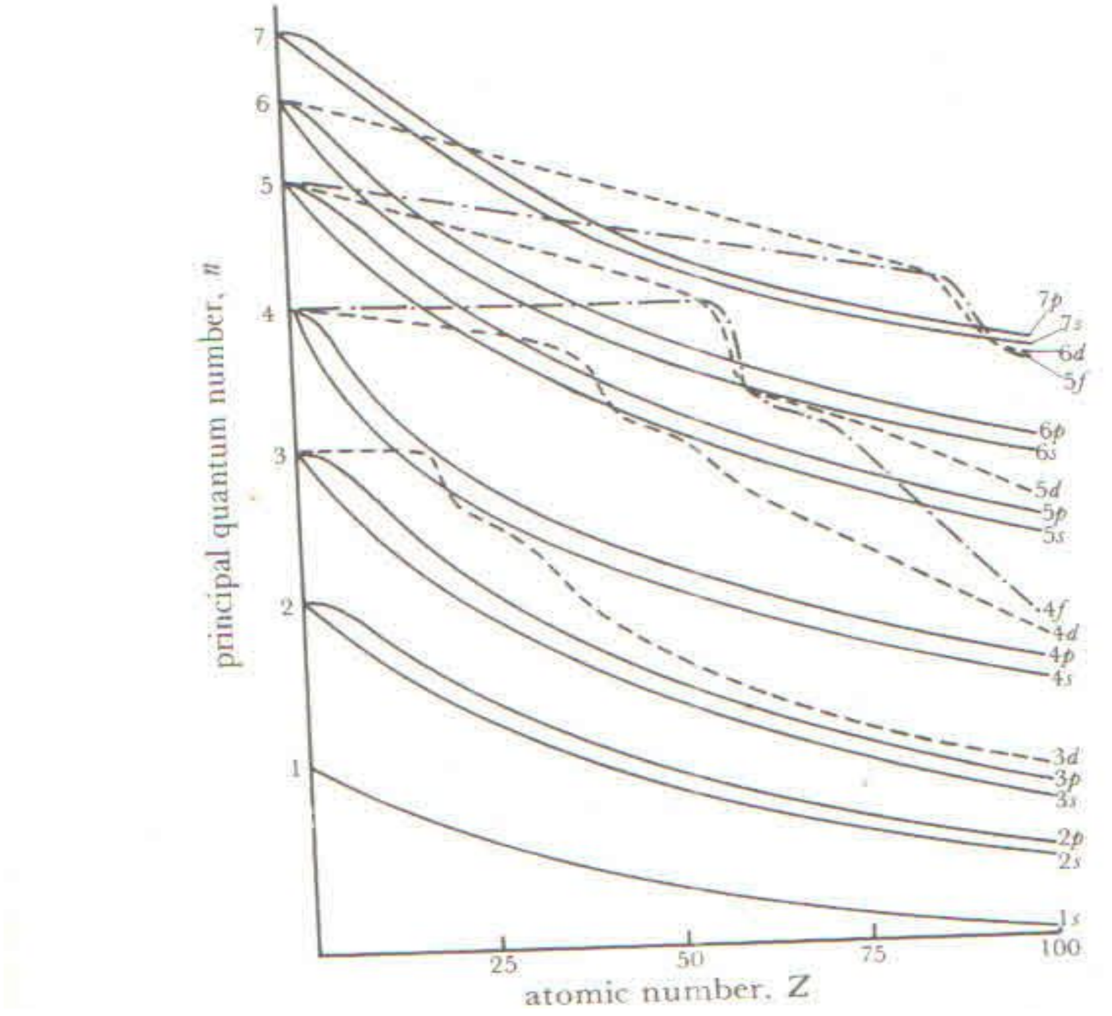
s-sub energy level is filled by 2 electrons.

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





Attentions please Boys & Women:

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

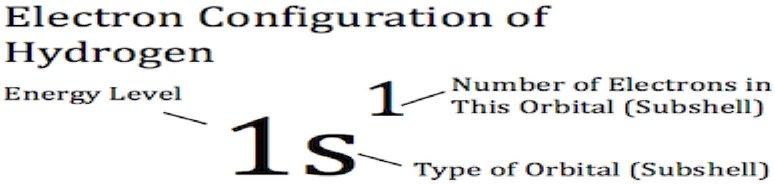
$\underbrace{1s^2}_{1}\quad \underbrace{2s^2 2p^6}_{2}\quad \underbrace{3s^2 3p^6 3d^{10}}_{3}\quad \underbrace{4s^2 4p^6 4d^{10} 4f^{14}}_{4}\quad \underbrace{5s^2 5p^6 5d^{10} 6s^2 6p^6}_{5}\quad \underbrace{5f^{14} 6d^{10} 7s^2 7p^6}_{6}$

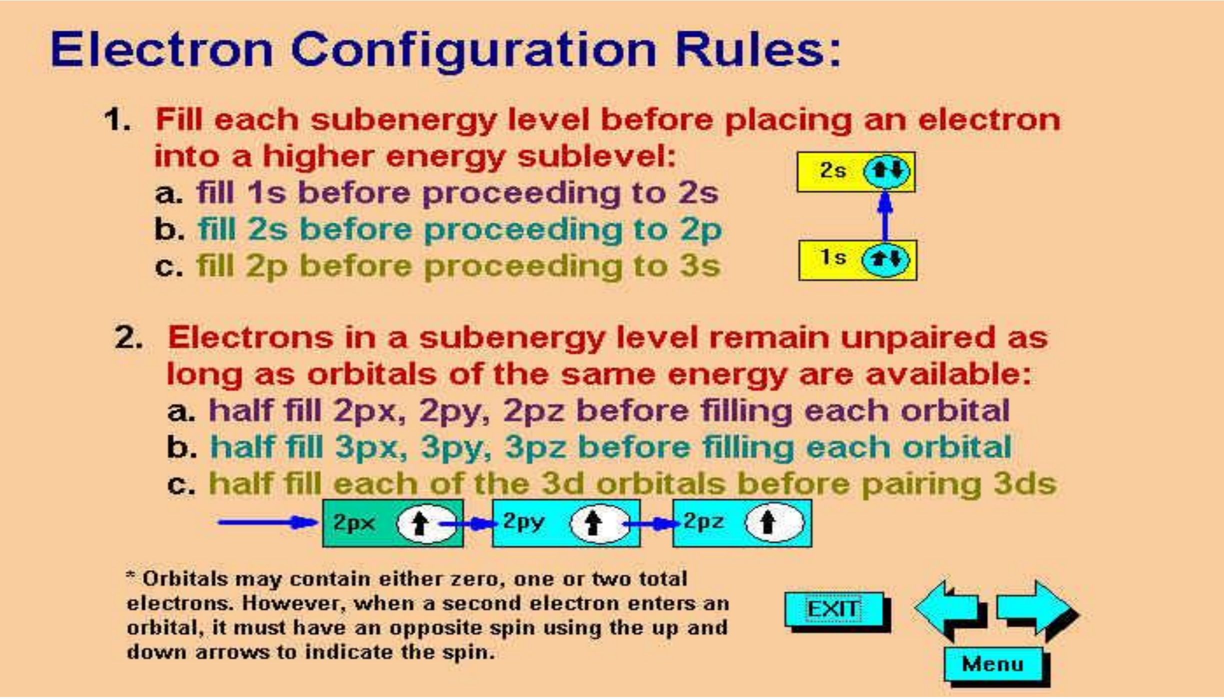
The right order is below:


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 Rules:

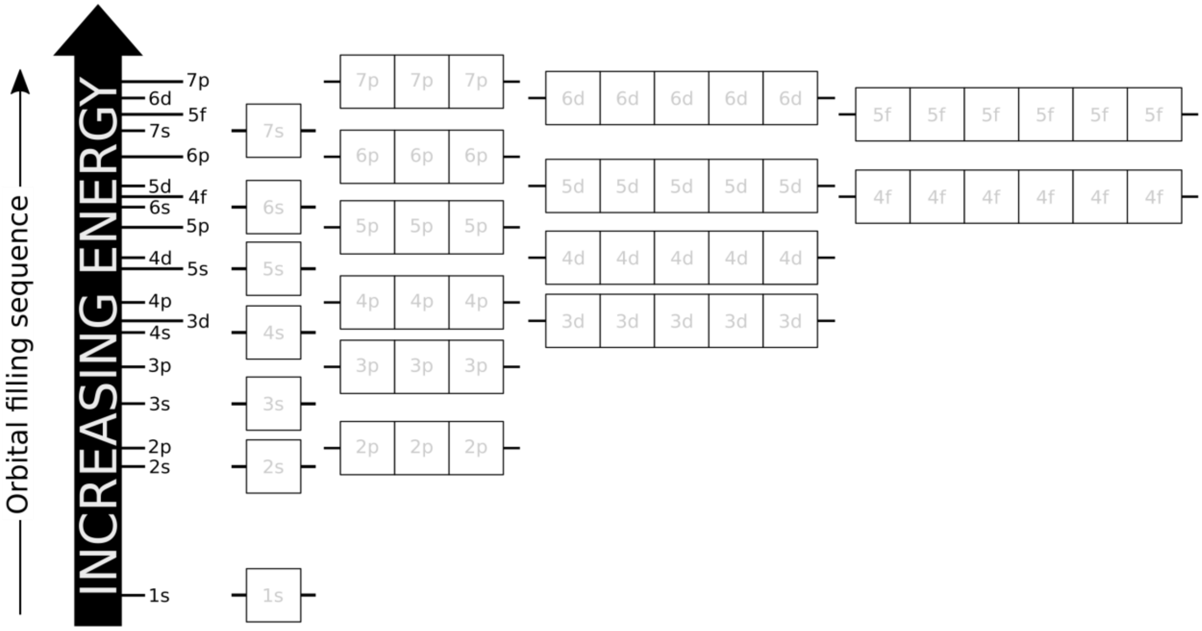
1. Fill each subenergy level before placing an electron into a higher energy sublevel:
   a. fill 1s before proceeding to 2s
   b. fill 2s before proceeding to 2p
   c. fill 2p before proceeding to 3s

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.

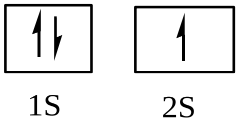
Rules for filling electrons

Rule 1: Aufbau Principle:

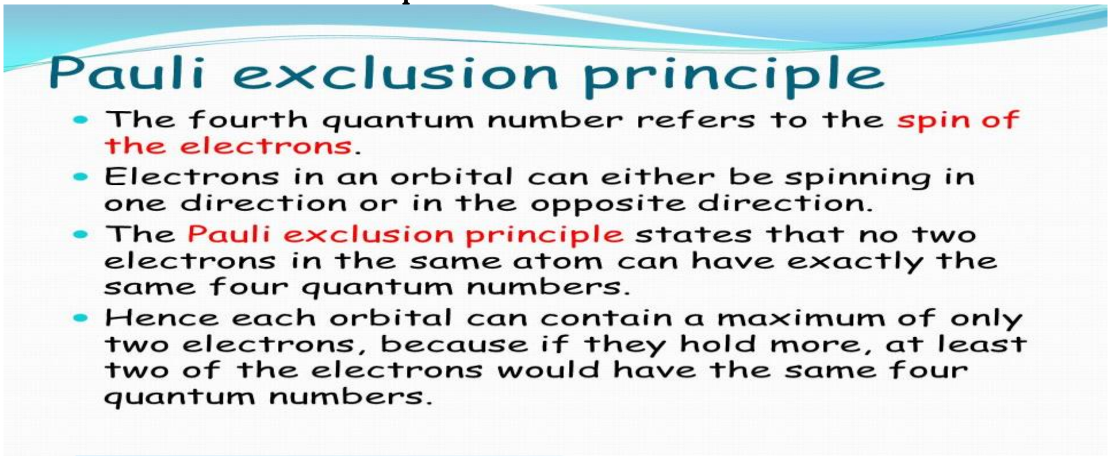


The electrons in the ground state occupy orbital's in order of the orbital energy levels. The lowest energy orbital's are always filled first.

e.g. for $_3Li$

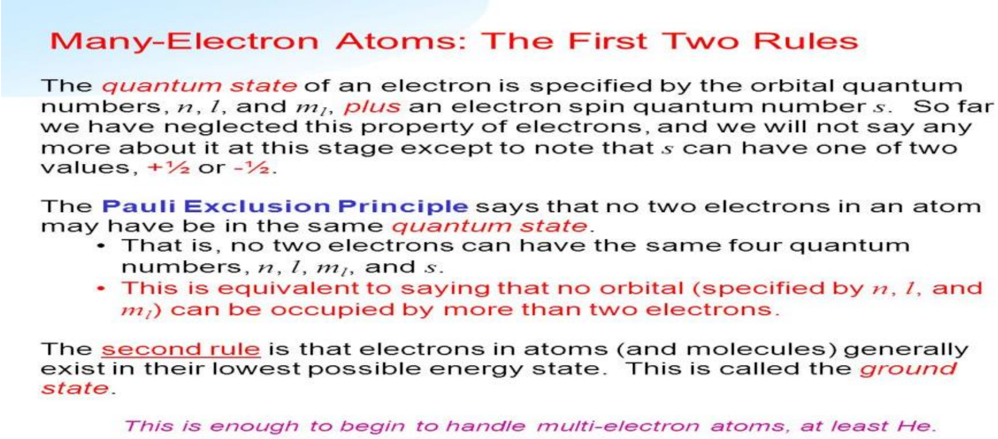


Rule 2: Pauli Exclusion Principle.



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, +½ or -½.

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

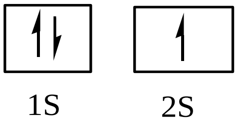
- That is, no two electrons can have the same four quantum numbers, n, l, m_l, and s.
- This is equivalent to saying that no orbital (specified by n, l, and m_l) can be occupied by more than two electrons.

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.

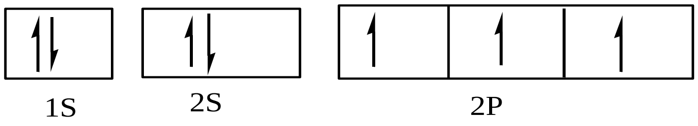
e.g. $_3Li$



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. $_7N$



$1S^2 2S^2 2P^3$

Rule 4:

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

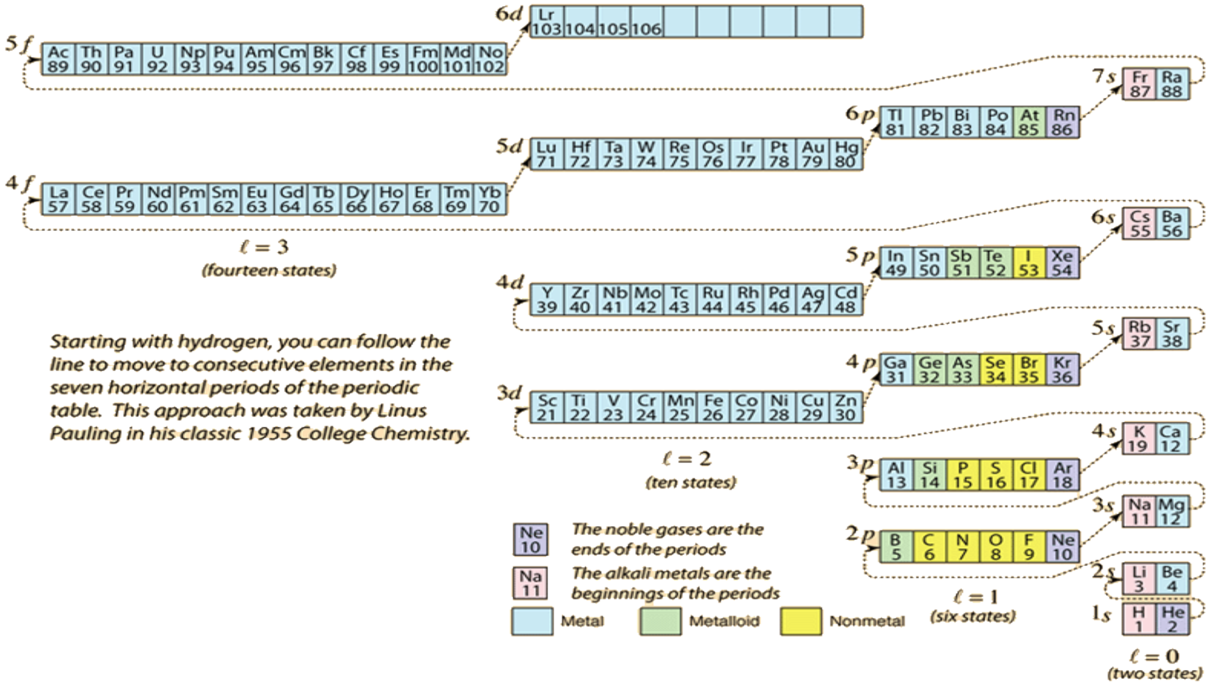
The order of filling in the electrons in atoms is:

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

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.

H ($Z = 1$): $1s^1$

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. He ($Z = 2$): $1s^2$

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

Li ($Z = 3$): $1s^2\ 2s^1$

The fourth electron fills this orbital. 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.

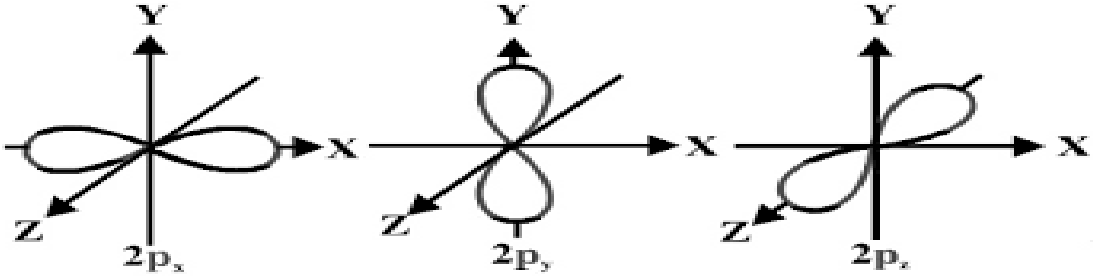
B ($Z = 5$): $1s^2\ 2s^2\ 2p^1$

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

C ($Z = 6$): $1s^2\ 2s^2\ 2p^2$

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 (↑) stands for an electron spinning in one direction, and an arrow pointing downward (↓) 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
- ✓ Para magnetism

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

Para magnetism: 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	↑						
He	↑↓						
Li	↑↓	↑					
Na	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑			
O	↑↓	↑↓	↑↓ ↑ ↑				
Cr	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	↑ ↑ ↑ ↑ ↑

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 ml which has different spatial distributions minimizing the overlap and thus the Coulomb energy.
- Ferromagnetism of the 3d metals iron ($_{26}$Fe), cobalt ($_{27}$Co) and nickel ($_{28}$Ni) is a consequence of Hund's rule. $_{26}$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 a rises 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.) C ($Z = 6$): $1s^2\ 2s^2\ \mathbf{2p_x^1\ 2p_y^1}$

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 $s = +½$ with an arrow pointing up and an electron for which $s = -½$ with an arrow pointing down.

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

$\underline{\ \uparrow\ }\ \underline{\ \uparrow\ }\ \underline{\ \ \ \ }$

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

N ($Z = 7$): **$1s^2\ 2s^2\ 2p^3$** $\underline{\ \uparrow\ }\ \underline{\ \uparrow\ }\ \underline{\ \uparrow\ }$

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.

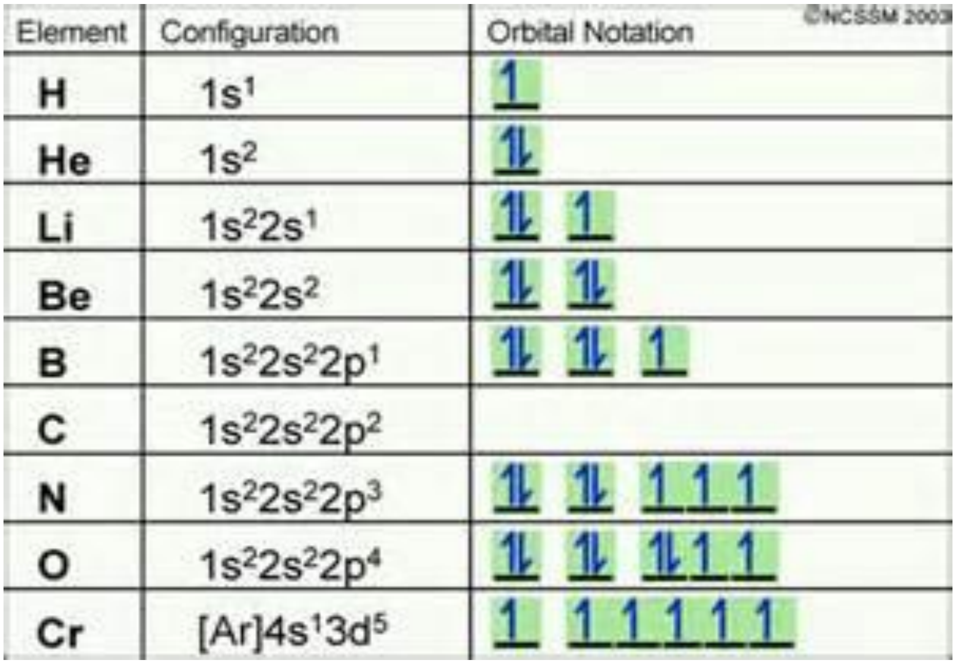
O ($Z = 8$): **$1s^2\ 2s^2\ 2p^4$** $\underline{\ \uparrow\downarrow\ }\ \underline{\ \uparrow\ }\ \underline{\ \uparrow\ }$

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

F ($Z = 9$): $1s^2\ 2s^2\ 2p^5$ $\underline{\ \uparrow\downarrow\ }\ \underline{\ \uparrow\downarrow\ }\ \underline{\ \uparrow\ }$

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

Ne ($Z = 10$): $1s^2\ 2s^2\ 2p^6$ $\underline{\ \uparrow\downarrow\ }\ \underline{\ \uparrow\downarrow\ }\ \underline{\ \uparrow\downarrow\ }$



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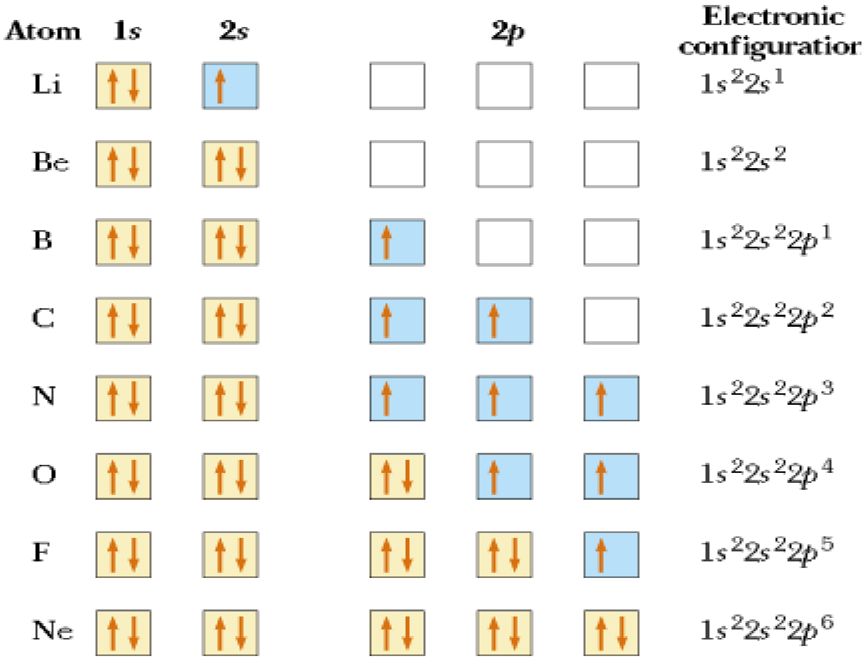
Element	Configuration	Orbital Notation
H	$1s^1$	↑
He	$1s^2$	↑↓
Li	$1s^2 2s^1$	↑↓ ↑
Be	$1s^2 2s^2$	↑↓ ↑↓
B	$1s^2 2s^2 2p^1$	↑↓ ↑↓ ↑
C	$1s^2 2s^2 2p^2$	
N	$1s^2 2s^2 2p^3$	↑↓ ↑↓ ↑ ↑ ↑
O	$1s^2 2s^2 2p^4$	↑↓ ↑↓ ↑↓ ↑ ↑
Cr	$[Ar]4s^1 3d^5$	↑ ↑ ↑ ↑ ↑ ↑



Atom	1s	2s	2p			Electronic configuratior
Li	↑↓	↑	☐	☐	☐	$1s^2 2s^1$
Be	↑↓	↑↓	☐	☐	☐	$1s^2 2s^2$
B	↑↓	↑↓	↑	☐	☐	$1s^2 2s^2 2p^1$
C	↑↓	↑↓	↑	↑	☐	$1s^2 2s^2 2p^2$
N	↑↓	↑↓	↑	↑	↑	$1s^2 2s^2 2p^3$
O	↑↓	↑↓	↑↓	↑	↑	$1s^2 2s^2 2p^4$
F	↑↓	↑↓	↑↓	↑↓	↑	$1s^2 2s^2 2p^5$
Ne	↑↓	↑↓	↑↓	↑↓	↑↓	$1s^2 2s^2 2p^6$

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.

Na ($Z = 11$): [Ne] $3s^1$ Mg ($Z = 12$): [Ne] $3s^2$

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 ⌊ 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)

Atomic Number	*Symbol*	*Electron Configuration*
1	H	$1s^1$
2	He	$1s^2$ = [He]
3	Li	[He] $2s^1$
4	Be	[He] $2s^2$
5	B	[He] $2s^2\ 2p^1$
6	C	[He] $2s^2\ 2p^2$
7	N	[He] $2s^2\ 2p^3$
8	O	[He] $2s^2\ 2p^4$
9	F	[He] $2s^2\ 2p^5$
10	Ne	[He] $2s^2\ 2p^6$ = [Ne]
11	Na	[Ne] $3s^1$
12	Mg	[Ne] $3s^2$
13	Al	[Ne] $3s^2\ 3p^1$
14	Si	[Ne] $3s^2\ 3p^2$
15	P	[Ne] $3s^2\ 3p^3$
16	S	[Ne] $3s^2\ 3p^4$
17	Cl	[Ne] $3s^2\ 3p^5$
18	Ar	[Ne] $3s^2\ 3p^6$ = [Ar]
19	K	[Ar] $4s^1$
20	Ca	[Ar] $4s^2$
*21	Sc	[Ar] $4s^2\ 3d^1$
22	Ti	[Ar] $4s^2\ 3d^2$
23	V	[Ar] $4s^2\ 3d^3$
*24	Cr	[Ar] $4s^1\ 3d^5$
25	Mn	[Ar] $4s^2\ 3d^5$
26	Fe	[Ar] $4s^2\ 3d^6$
27	Co	[Ar] $4s^2\ 3d^7$
28	Ni	[Ar] $4s^2\ 3d^8$
*29	Cu	[Ar] $4s^1\ 3d^{10}$
30	Zn	[Ar] $4s^2\ 3d^{10}$
31	Ga	[Ar] $4s^2\ 3d^{10}\ 4p^1$
32	Ge	[Ar] $4s^2\ 3d^{10}\ 4p^2$
33	As	[Ar] $4s^2\ 3d^{10}\ 4p^3$
34	Se	[Ar] $4s^2\ 3d^{10}\ 4p^4$
35	Br	[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 4*s* orbital to a 3*d* orbital, even though the 3*d* orbitals are supposed to be at a higher level than the 4*s* 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] $2s^1$	N ($Z = 7$):	[He] $2s^2\ 2p^3$
Be ($Z = 4$):	[He] $2s^2$	O ($Z = 8$):	[He] $2s^2\ 2p^4$
B ($Z = 5$):	[He] $2s^2\ 2p^1$	F ($Z = 9$):	[He] $2s^2\ 2p^5$
C ($Z = 6$):	[He] $2s^2\ 2p^2$	Ne ($Z = 10$):	[He] $2s^2\ 2p^6$

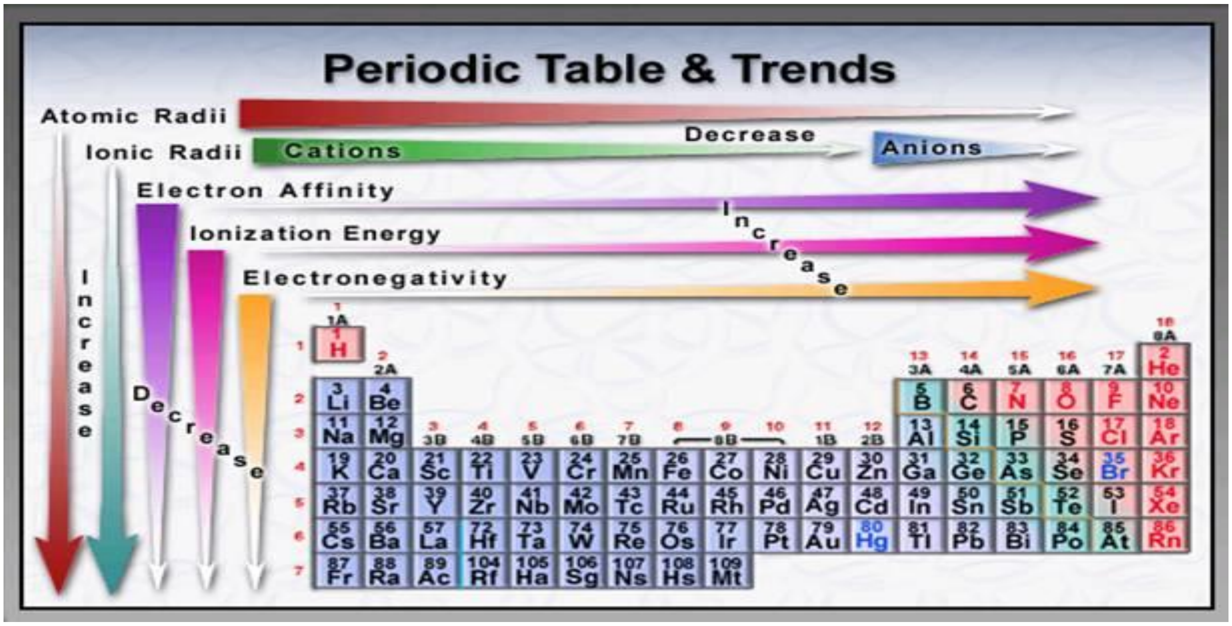
There is an obvious pattern within the vertical columns, or groups, of the periodic table as well. The elements in a group have similar configurations for their outermost electrons. This relationship can be seen by looking at the electron configurations of elements in columns on either side of the periodic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

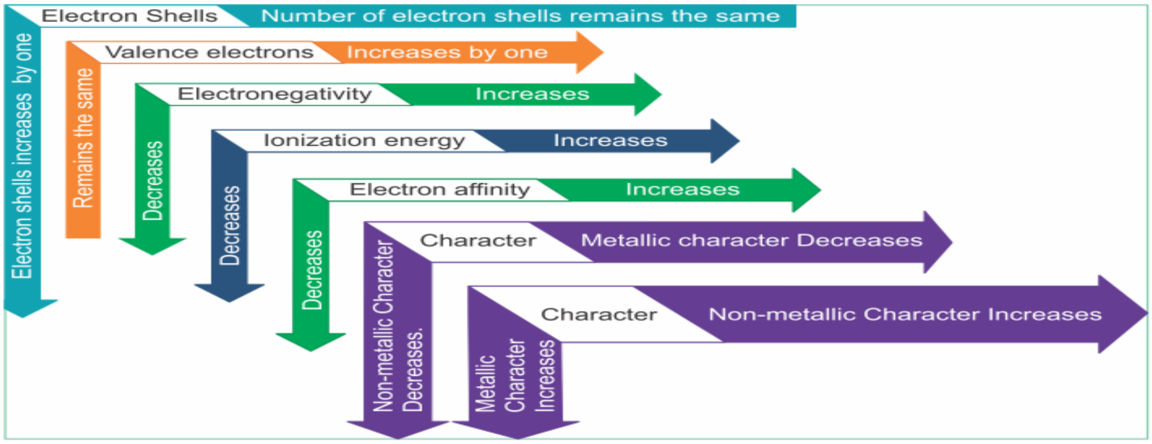
Group IA		*Group VIIA*	
H	$1s^1$		
Li	[He] $2s^1$	F	[He] $2s^2\ 2p^5$
Na	[Ne] $3s^1$	Cl	[Ne] $3s^2\ 3p^5$
K	[Ar] $4s^1$	Br	[Ar] $4s^2\ 3d^{10}\ 4p^5$
Rb	[Kr] $5s^1$	I	[Kr] $5s^2\ 4d^{10}\ 5p^5$

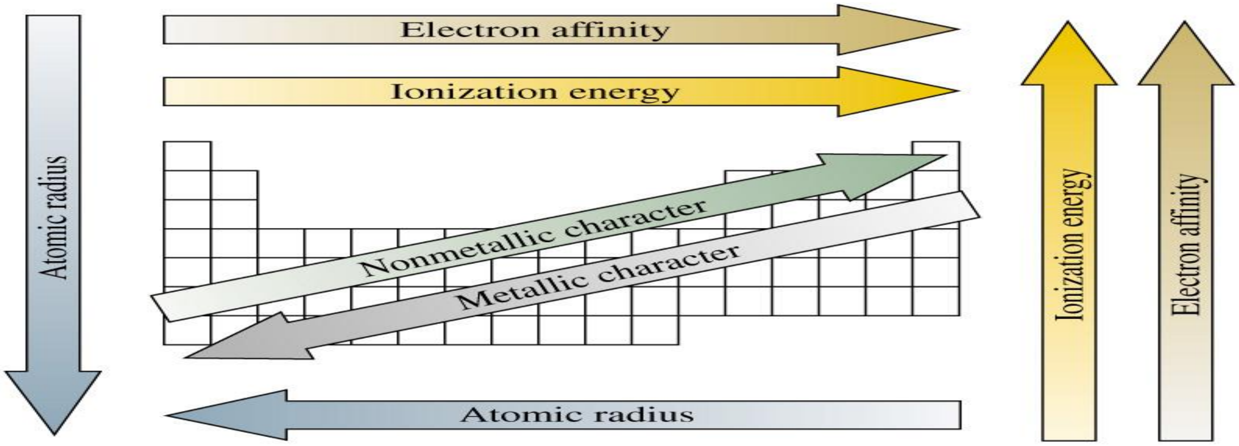
The figure below shows the relationship between the periodic table and the orbitals being filled during the Aufbau process. The two columns on the left side of the periodic table correspond to the filling of an *s* orbital. The next 10 columns include elements in which the five orbitals in a *d* sub 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
Period 1		
Hydrogen	1	$1s^1$
Helium	2	$1s^2$
Period 2		
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	$1s^2\ 2s^2 2p^6$
Period 3		
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	$1s^2\ 2s^2 2p^6 3s^2 3p^6$
Period 4		
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.

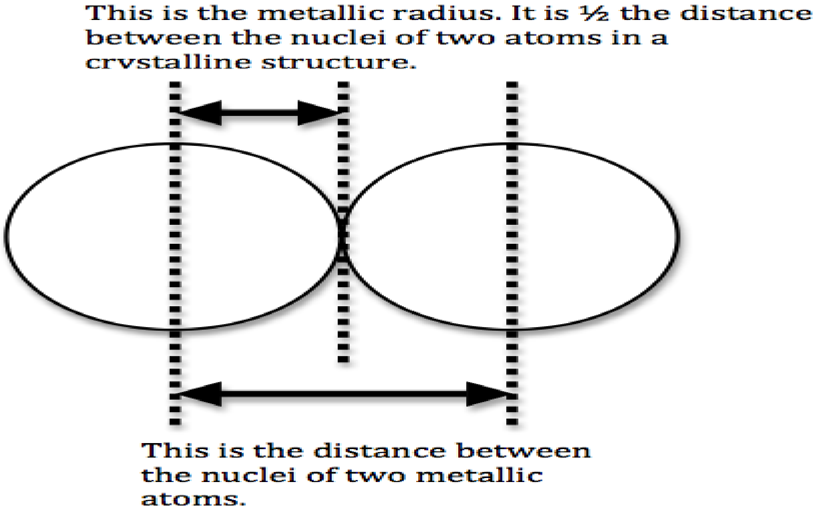
Atomic radii: is the half the inter-nuclear distance between two covalently bonded atoms.

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

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

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

Illustration:



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_2 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.

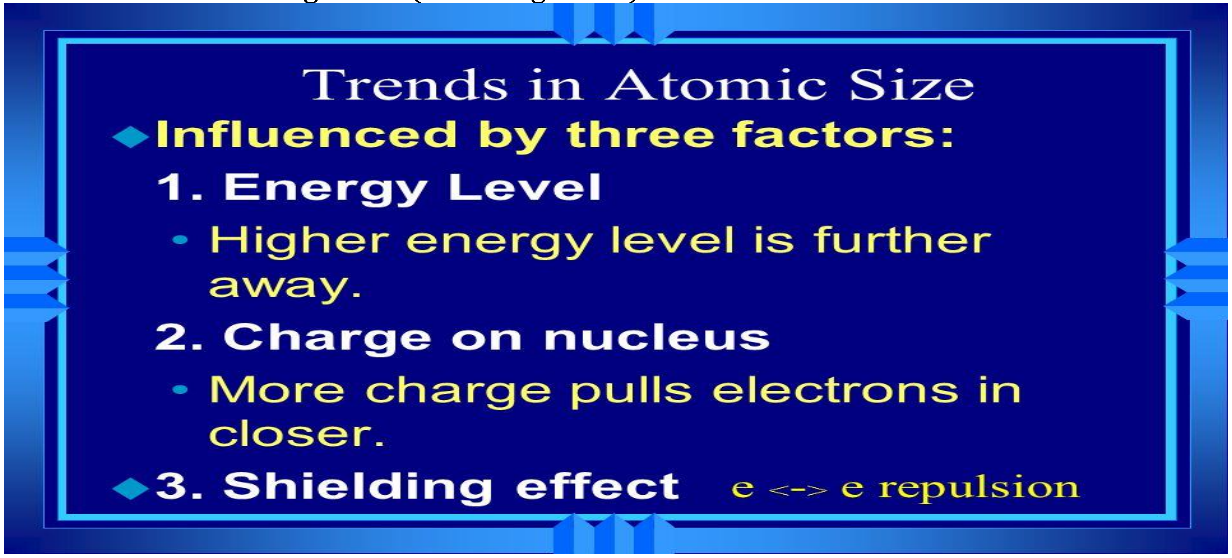
Van der Waal's radius: is half the distance between two atoms which are not chemically bonded.

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 <–> 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.

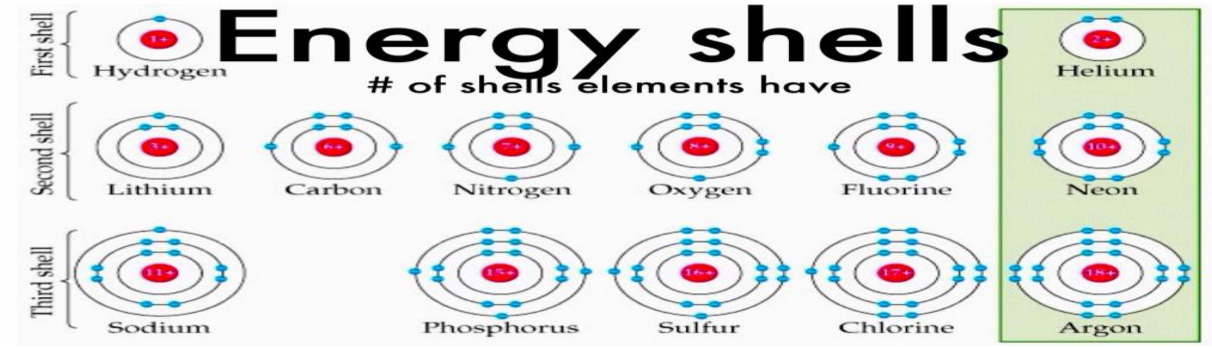
   Notes:

   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:

9. Explain the variation of atomic radius.



As we go from lithium to neon we are adding electrons to the outer shell, the second shell. The charge on the nucleus is increasing from 3+ to 10+ (or 1+ to 8+ allowing for the shielding of the inner shell).This tends to pull the electrons in closer to the nucleus. So the size of the atom decreases as we go 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 change of just 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+.

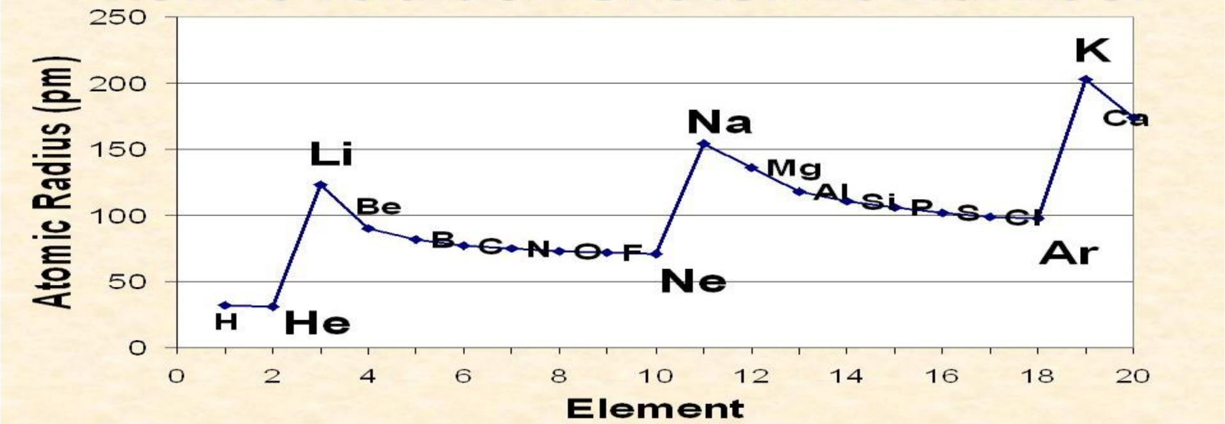
(i).**Across the period.**

a) **Period (II) elements.**

Elements	Li	Be	B	C	O	F
Radius(nm)	0.123	0.089	0.082	0.070	0.066	0.064

a) Period (III) elements.

Elements	Na	Mg	Al	Si	P	S
Radius(nm)	0.15	0.136	0.125	0.117	0.110	0.090



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	Symbols	Atomic radius(	Electronic configurations			
			K	L	M	N
Scandium	$_{21}$Sc	1.62	$1s^2$	$2s^22p^2$	$3s^23p^63d^1$	$4s^2$
Titanium	$_{22}$Ti	1.50	$1s^2$	$2s^22p^6$	$3s^23p^63d^2$	$4s^2$
Vanadium	$_{23}$V	1.35	$1s^2$	$2s^22p^6$	$3s^23p^63d^3$	$4s^2$
Chromium	$_{24}$Cr	1.30	$1s^2$	$2s^22p^6$	$3s^23p^63d^5$	$4s^1$*
Manganese	$_{25}$Mn	1.29	$1s^2$	$2s^22p^6$	$3s^23p^63d^5$	$4s^2$
Iron	$_{26}$Fe	1.29	$1s^2$	2s22p6	$3s^23p^63d^6$	$4s^2$
Cobalt	$_{27}$Co	1.29	$1s^2$	$2s^22p^6$	$3s^23p^63d^7$	$4s^2$
Nickel	$_{28}$Ni	1.29	$1s^2$	$2s^22p^6$	$3s^23p^63d^8$	$4s^2$
Copper	$_{29}$Cu	1.31	$1s^2$	$2s^22p^6$	$3s^23p^63d^{10}$	$4s^1$*
Zinc	$_{30}$Zn	1.41	$1s^2$	$2s^22p^6$	$3s^23p^63d^{10}$	$4s^2$*
					↑ '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.

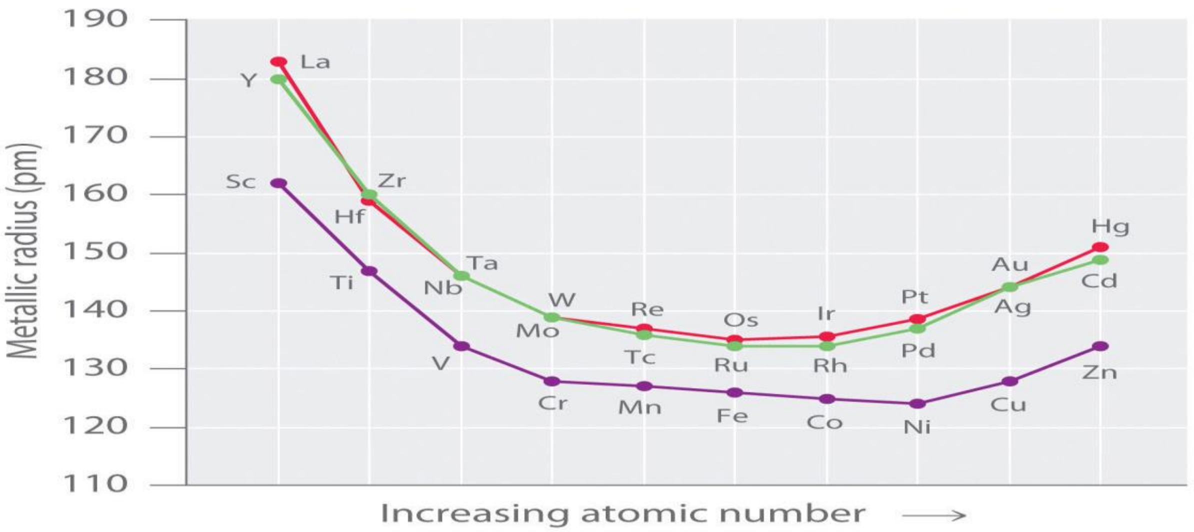
From chromium to nickel, the atomic radius is almost constant because the 3d is being paired and this adds to the screening effect to balance the increase in nuclear charge.

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] $3s^1$ $1s^2,2s^22p^6,3s^1$
$_{19}\text{K}$	2.03	[Ar] $4s^1$ $1s^2,2s^22p^6,3s^23p^6,4s^1$
$_{37}\text{Rb}$	2.16	[Kr] $5s^1$ $1s^2,2s^22p^6,3s^23p^63d^{10},4s^24p6,5s^1$
$_{55}\text{Cs}$	2.37	[Xe] $6s^1$ $1s^2,2s^22p^6,3s^23p^63d^{10},4s^24p^6,5s^25p^66s^1$
$_{87}\text{Fr}$	2.49	[Rn]$7s^1$ $1s^2,2s^22p^6,3s^23p^63d^{10},4s^24p^64d^{10}4f^{14},5s^25p^65d^{10},6s^26p^67s^1$

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:

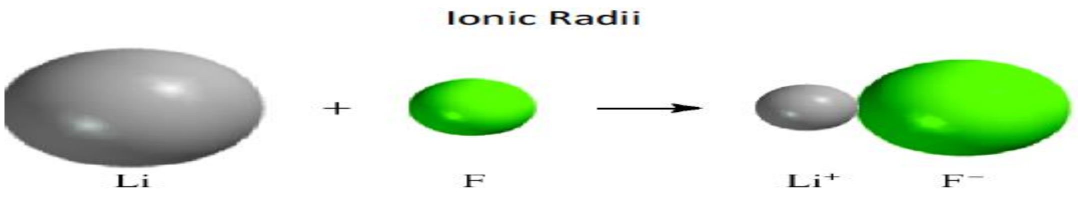
Down the group, both nuclear charge and number of electrons are increasing.

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. It's 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+ and Mg^{2+} have the same electronic configuration, yet the ionic radius of Mg^{2+} is smaller than Na^{+}.
Both Na+ and Mg^{2+} have 10 electrons but different number of protons.
Mg^{2+} ion with 12 protons attracts the 10 electrons more strongly than Na^{+} ion with only 11 protons making Mg^{2+} 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 to increased screening effect, making the ion formed bigger than the corresponding atom.

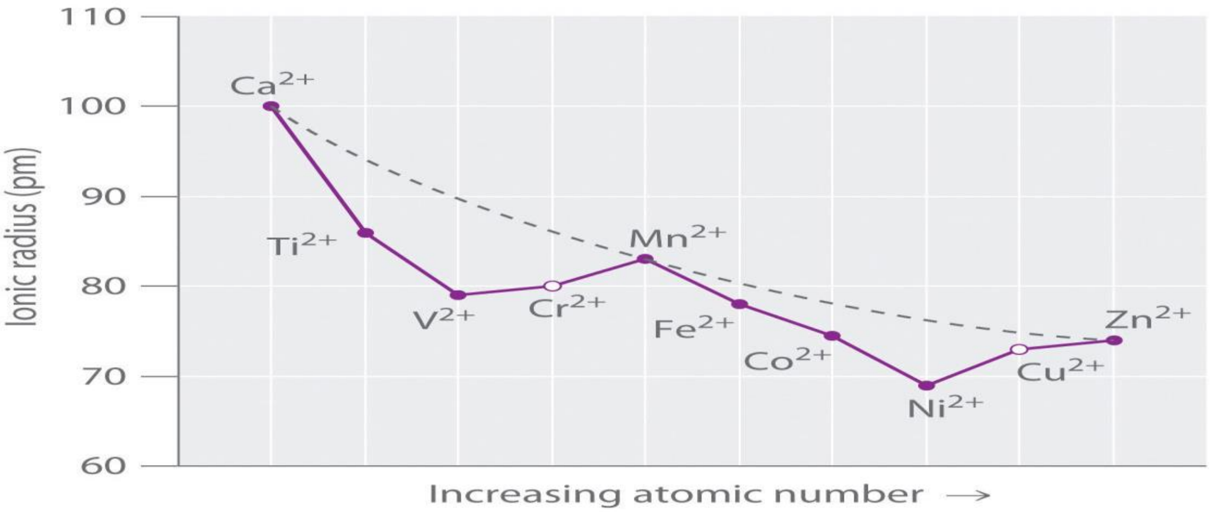
Golden tips:

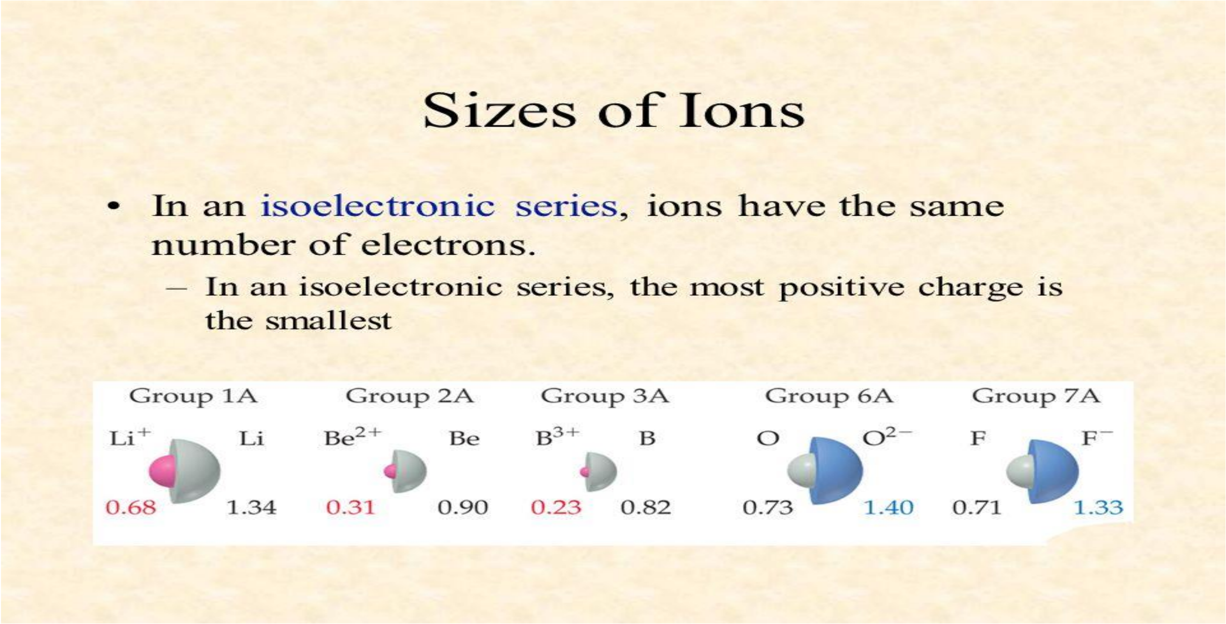
The negative ions (anions) are longer than the parent atoms as they have gained electrons, resulting in more electron-electron repulsion.

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 for 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:

1st 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.

1st 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.

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

1st ionization energy: is the energy required to remove one mole of electrons from one mole of atoms of an element.

Equation:

$$Al(g) \rightarrow Al^+(g) + e^- \qquad I_1 = 580\ kJ/mol$$

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

Equation:

$$Al^+(g) \rightarrow Al^{2+}(g) + e^- \qquad I_2 = 1815\ kJ/mol$$

Golden tips:

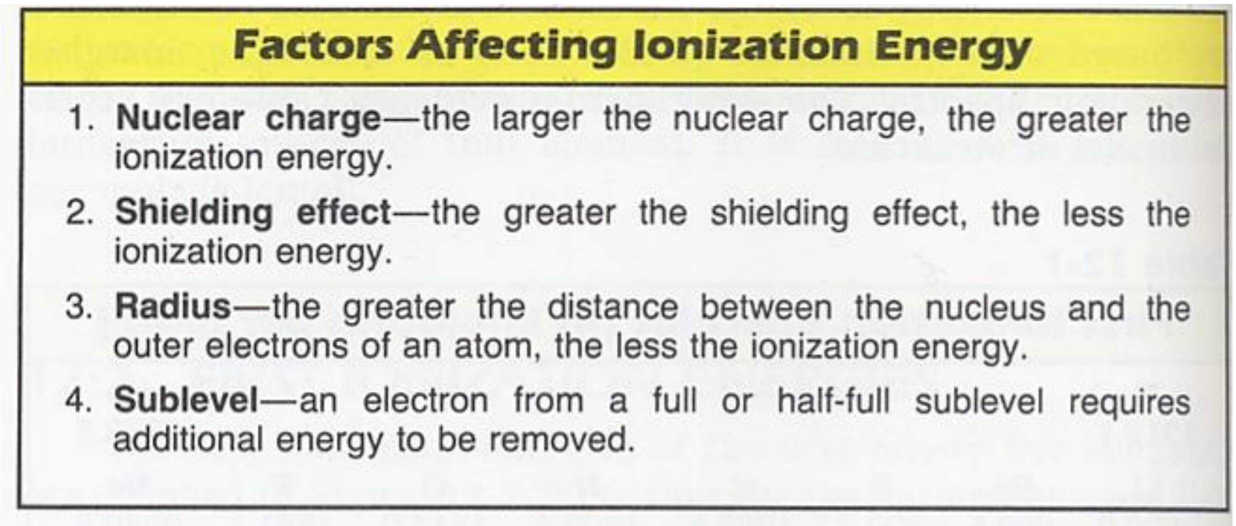
If the electron removed is 1st to be removed from that atom, then the energy is referred to as ionization energy. If it is second electron, then it is second ionization energy and so on.
Figure below shows a plot of ionization energy against number of electrons removed from a gaseous atom of magnesium.
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/attraction 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 2nd ionization energy is always higher than the 1st ionization energy and the 3rd ionization energy is higher than the 2nd 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.

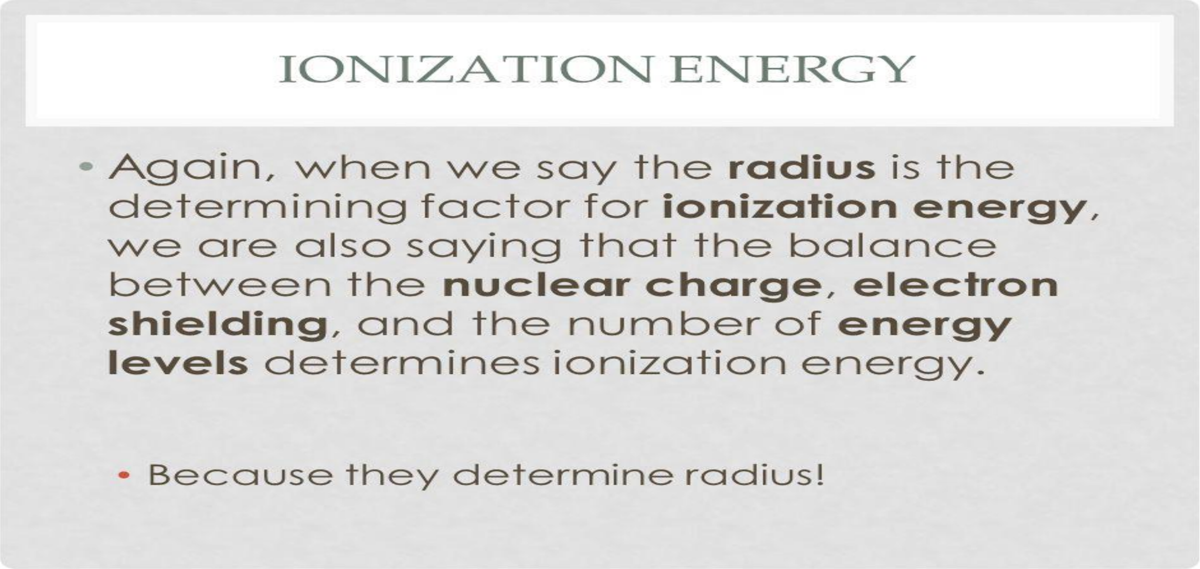
- The screening effect of inner electrons.
- Electron configuration of the atom or ion.
- The penetrating power of the valence electrons.

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



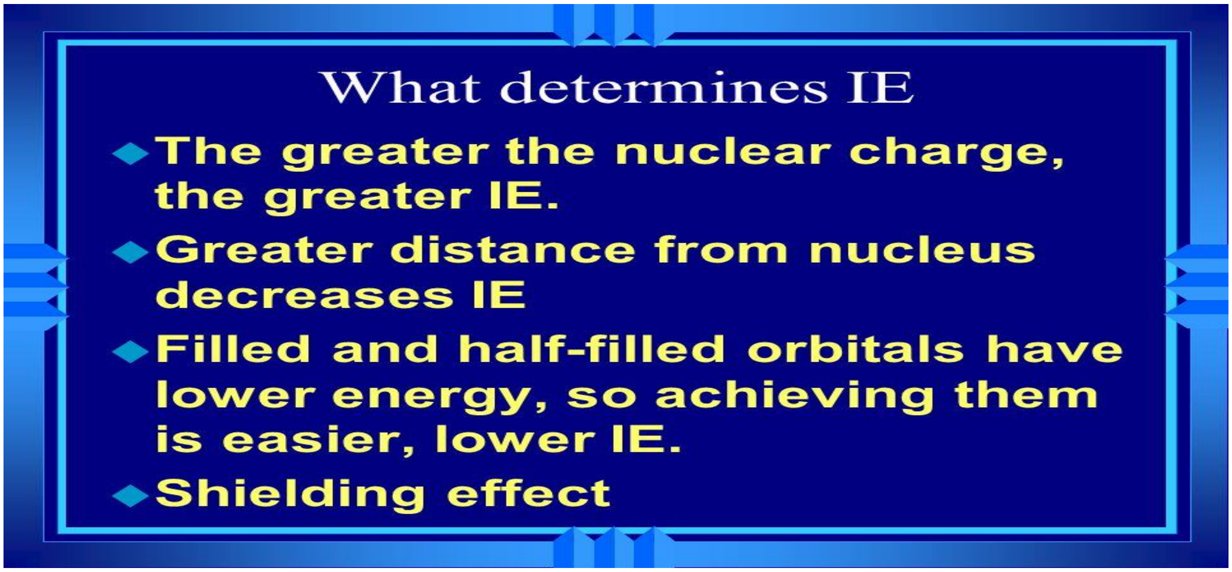
Factors Affecting Ionization Energy

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 1st<2nd< 3rd <4th 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 1st, 2nd and 3rd ionization energies (in KJ/Mol^{1}) of aluminium are 577, 1816 and 2745 respectively. Explain this trend:

The ionization energies increases from the 1st to the 3rd via 2nd.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 Na^+,Mg^{2+} and Al^{3+} are in the order of $Na^+<Mg^{2+}<Al^{3+}$. Explain this observation:

From Na^+ via Mg^{2+} to 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 Na^+ via Mg^{2+} to 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 1st<2nd< 3rd <4th 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.

Successive ionization energy increases in the order of 1st I.E <2nd I.E<3rd I.E<4th I.E etc.

Consider successive ionization energy of element T.

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

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

- ✍ 1st 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.
- ✍ ***<u>The screening (shielding) effect of inner electrons</u>***.

  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:

  1st ionization energy of Nitrogen,$_7$N:1s^2,2s^{2}2p^3 is higher than that if Oxygen,$_8$O:1s^2,2s^{2}2p^4 although Oxygen has a higher nuclear charge than Nitrogen. This is because Nitrogen has a half-filled 2p^3 sub energy level which is more stable than partially filled 2p^4 sub energy level in Oxygen.

  Similarly, 1st ionization energy of helium (with 2s^2 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***].

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

Elements	Ionization energies (KJ/Mol)		
	1st I.E	2nd I.E	3rd 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 1st ionization energies are below 800KJ/Mol.

- Element A show some little metallic character.
- Element D is a typical nonmetallic element why? Because it's 1st ionization energy is above 800KJ/Mol.
- Element A belongs to group 2 because there is a big rise in energy to remove the 3rd electron implying that the 3rd 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 2nd electron, implying that the 2nd 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 3rd 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

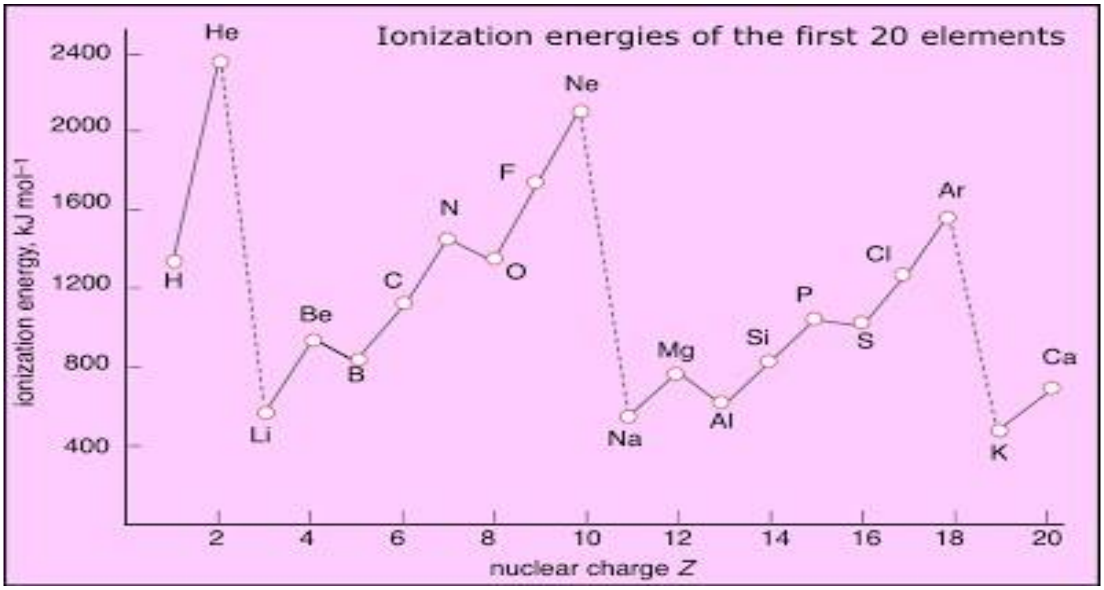
However, beryllium, neon and nitrogen have abnormally high ionization energy because the electrons are removed from $2s^2$, 2p6 and $2p^3$ which are fully filled and half-filled respectively and are regarded as thermodynamically stable.

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

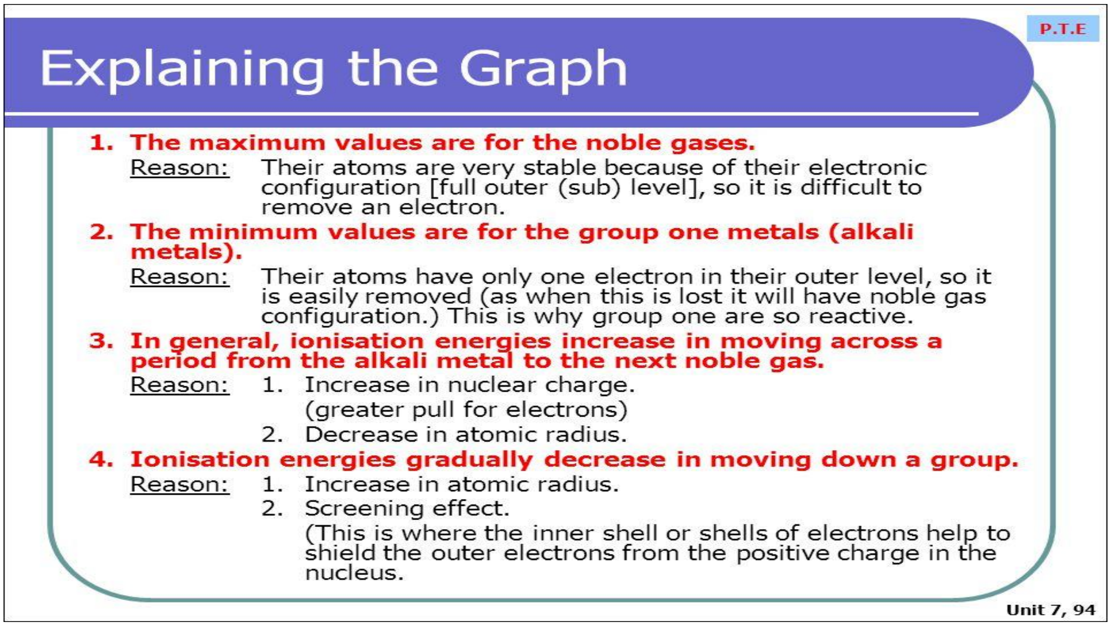
Element,Z	$_{11}$Na	$_{12}$Mg	$_{13}$Al	$_{14}$Si	$_{15}$P	$_{16}$S	$_{17}$Cl	$_{18}$Ar
1st I.E	502	745	587	791	1020	1000	1260	1530

Element,Z	$_3$**Li**	$_3$**Be**	$_5$**B**	$_6$**C**	$_7$**N**	$_8$**O**	$_9$**F**	$_{10}$**Ne**
I.E(KJmol^{-1})	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 1st 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 1st 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 1st ionization energy than expected why?
- Alumimium ($1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^1$), the fully filled $3s^2$ has a stable electronic configuration and shields the 3p1 electron hence lower 1st ionization energy.
- Also sulphur ($1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^4$), the half-filled $3p^4$ sub energy level has stable configuration and relatively good shield hence lower 1st ionization energy.

16. Explain why beryllium atom has higher 1st 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: $1s^2$, $2s^2 2p^2$.
    - ☞ Which of the two elements, ie beryllium and boron has more stable electron structure?

<u>Explanation</u>:

- ✍ 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 1st ionization energy is greater than that of boron.

17. Explain why the 1st ionization energy of aluminium is less than that of magnesium?
    - This is due to their electronic configurations: $_{13}Al:1s^2, 2s^22p^6, 3s^23p^1$ & $_{12}Mg: 1s^2, 2s^22p^6, 3s^2$.
    - The 1st 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 1st 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 1st ionization energy of nitrogen is higher than that of oxygen?
    - Special explanation for abnormality between nitrogen and oxygen atoms.

      Electron configuration:

      $_7N:1s^2, 2s^22p^3$ & $_8O:1s^2, 2s^22p^4$.
    - 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 1st ionization energy for nitrogen atom than oxygen atom.

❖ ***Down the group***:

Elements	**Be**	**Mg**	**Ca**	**Sr**	**Ba**
1st 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.

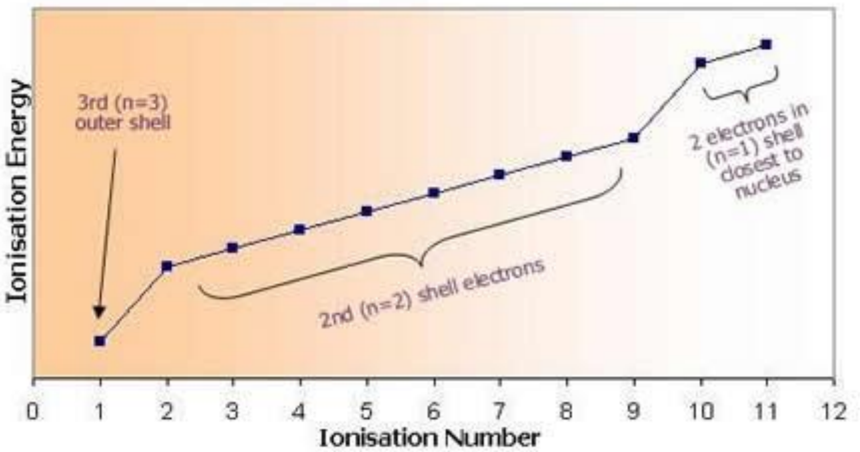
IMPORTANCE OF IONIZATION ENERGY IN THE DETERMINATION OF THE CHEMISTRY OF AN ELEMENT:

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 1st ionization energy is usually below 800KJmol^{-1}.*

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 (3rd)] is the outermost shell.
- The third ionization energy is much greater than the 1st 2 electrons because the 3rd 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 3rd to 10th 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) ***Electro negativity***.

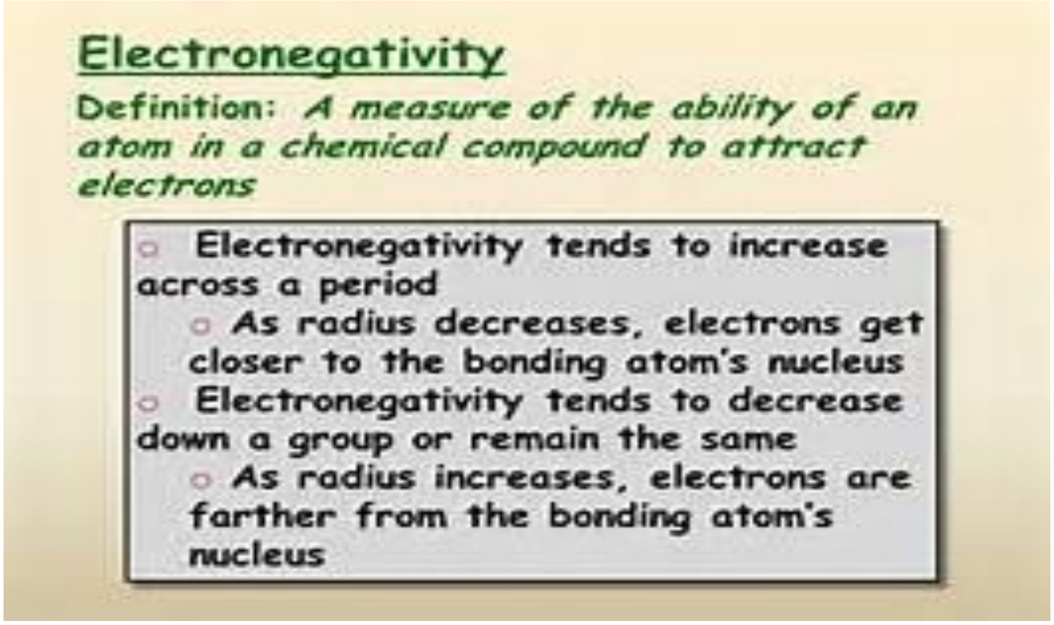
Electronegativity: is the tendency of an atom to become negatively charged in its covalent compounds.

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 neared 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:

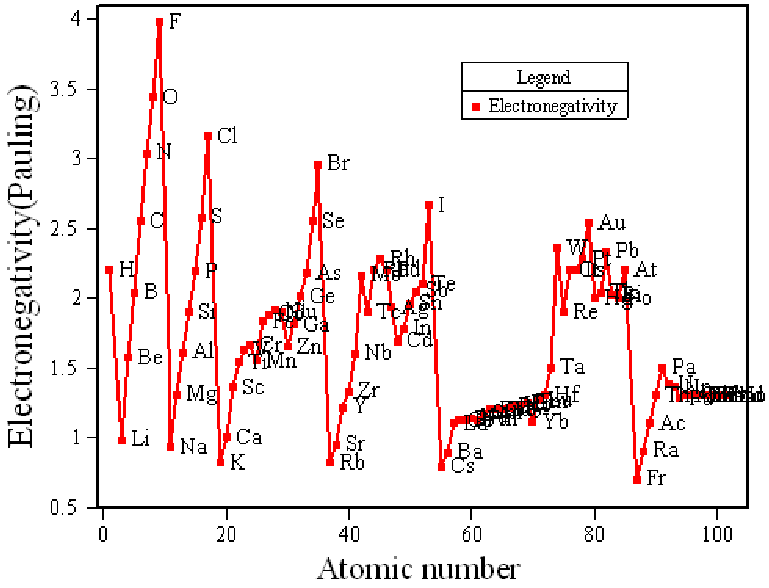
In moving from left to right across a period, from one element to the next, the nuclear charge increases by almost one unit and an electron is added to the outer shell. As the nuclear charge increases across, the atoms have an increasing electron attracting power and therefore an increase in electronegativity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

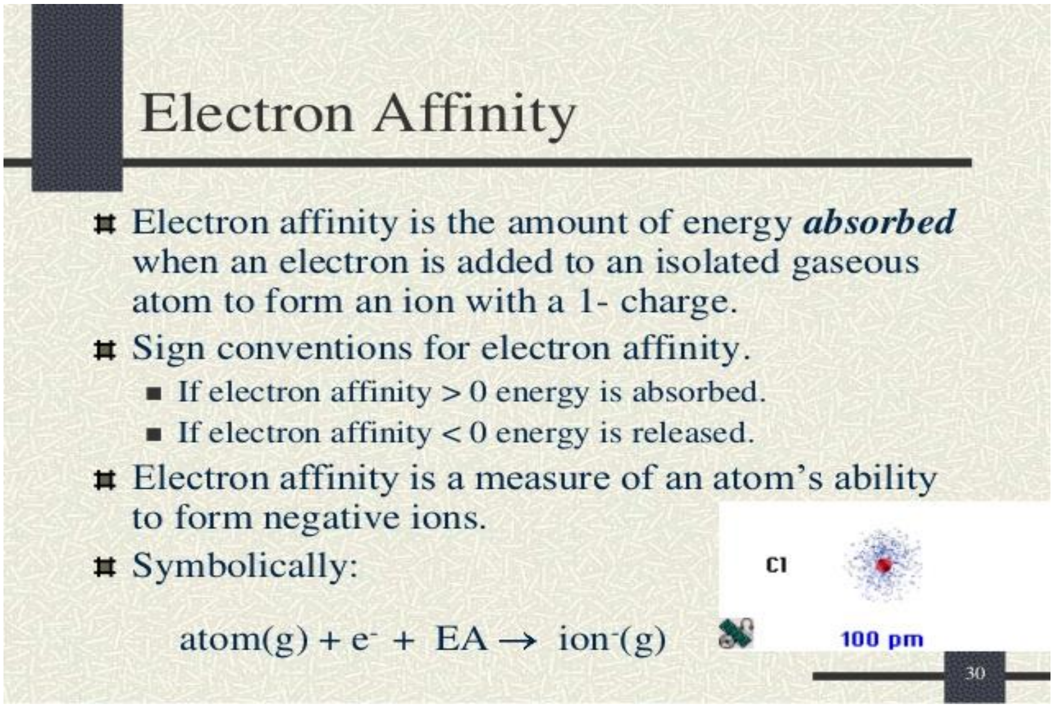
Explanation:

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.

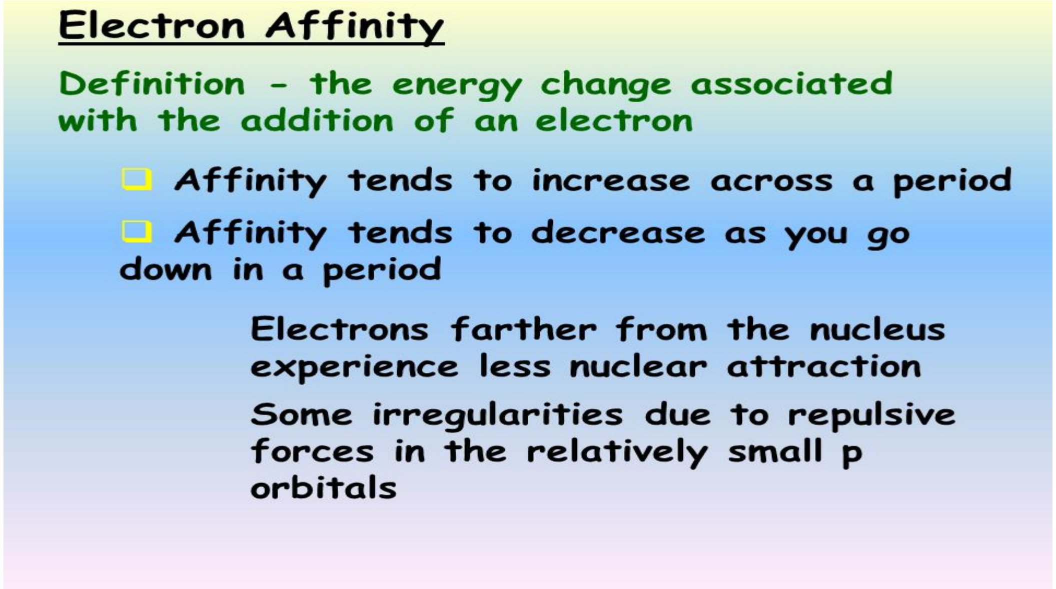
4). ELECTRON AFFINITY (E.A.)



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:

$$\text{atom(g)} + e^- + \text{EA} \rightarrow \text{ion}^-\text{(g)}$$



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 of 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 1st 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 2nd 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 2nd 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 $2^{nd} < 3^{rd} < 4^{th}$ 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 inners 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.

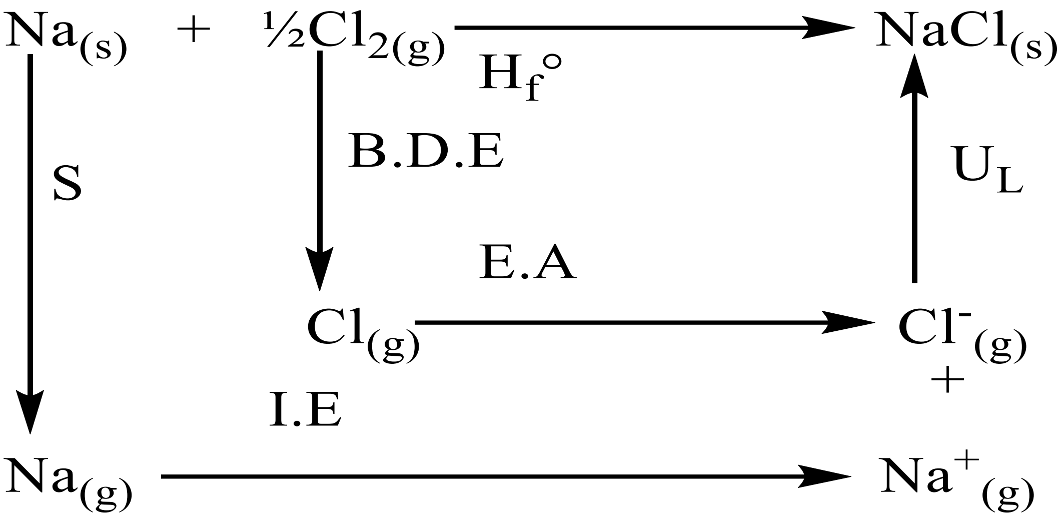
Electronic structure of an atom affects the value of electrons affinity in that, atoms with filled or half-filled outer with outer electronic configuration are stable and resist addition of the electron leading

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_L = Lattice energy.

E.A = Electron affinity.

I.E = Ionization energy.

S = Sublimation energy.

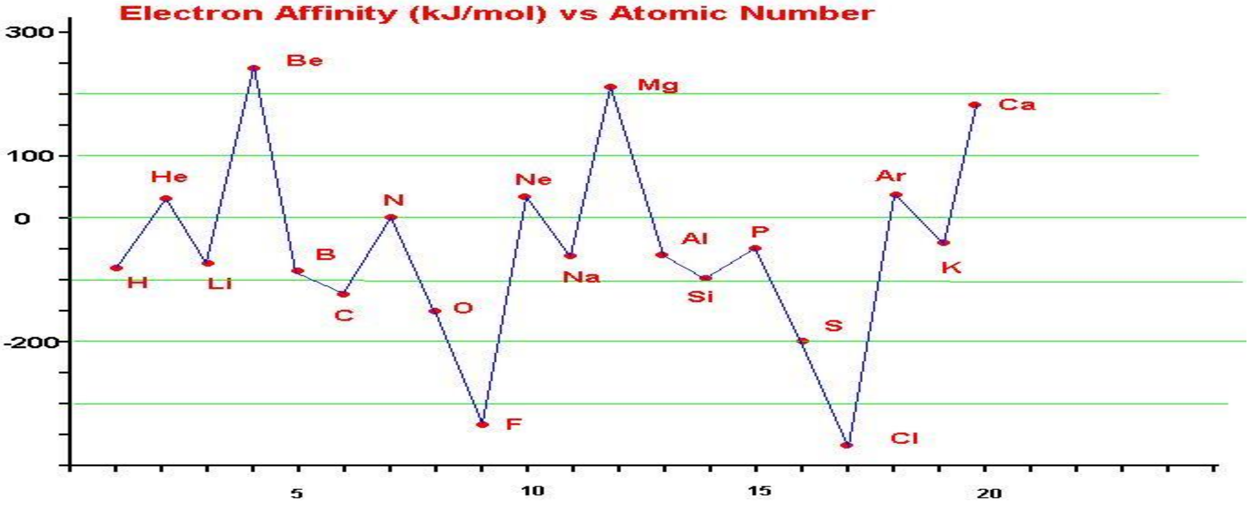
ΔHf° = Enthalpy of formation of Sodium Chloride. B.D.E = Bond dissociation energy.From Hess's law. ΔHf° = S + B.D.E + E.A + I.E + UL, E.A = ΔHf°- S + B.D.E + I.E + UL

VARIATION OF ELECTRON AFFINITY ACROSS A PERIOD:

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

Elements	$_{11}$Na	$_{12}$Mg	$_{13}$Al	$_{14}$Si	$_{15}$P	$_{16}$S	$_{17}$Cl
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:

$_{12}$Mg: $1s^2\ 2s^2 2p^6\ 3s^2$, 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.

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

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?
    - ${}_{12}$Mg: $1s^2\ 2s^2 2p^6\ 3s^2$ ${}_{15}$P:$1s^2\ 2s^2 2p^6\ 3s^2 3p^3$
    - 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 income 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 on 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: Electroposivity 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.

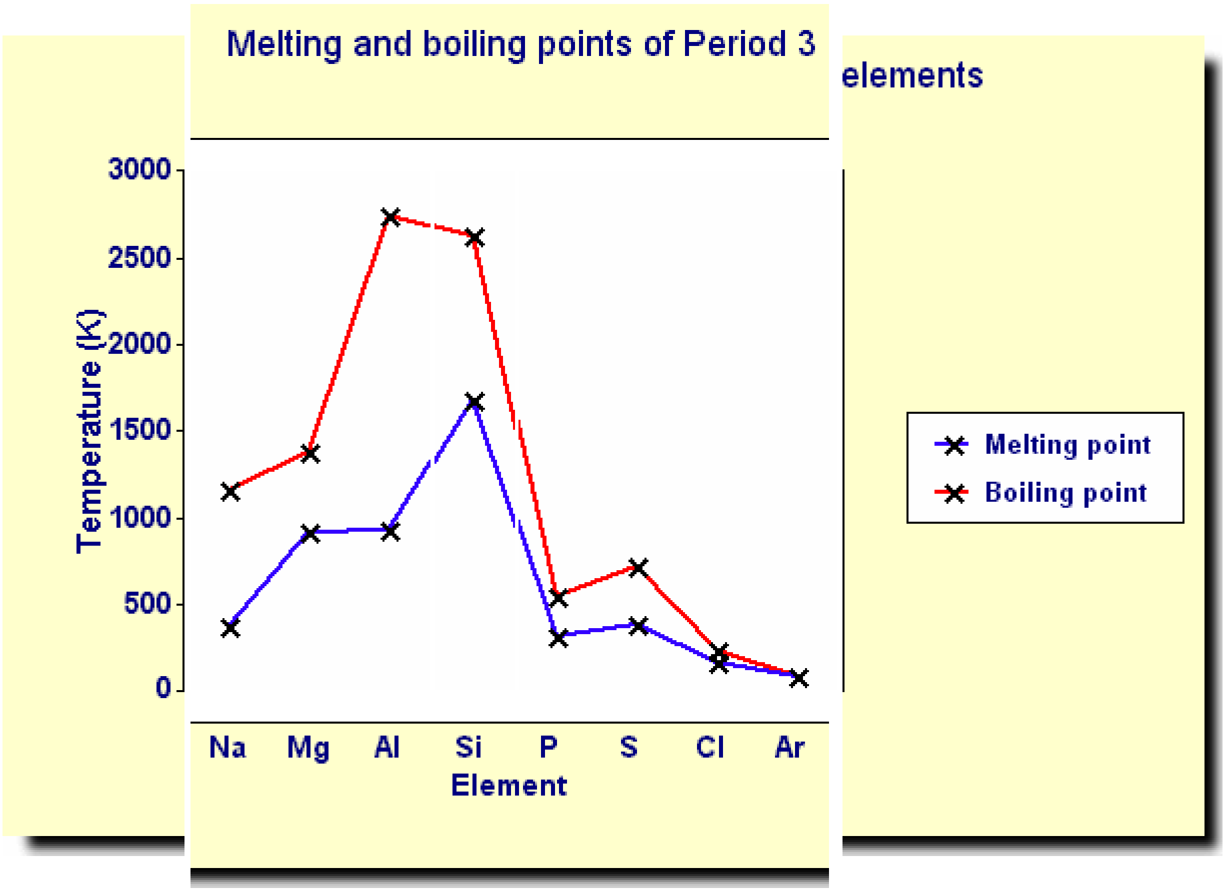
MELTING AND BOILING POINT:

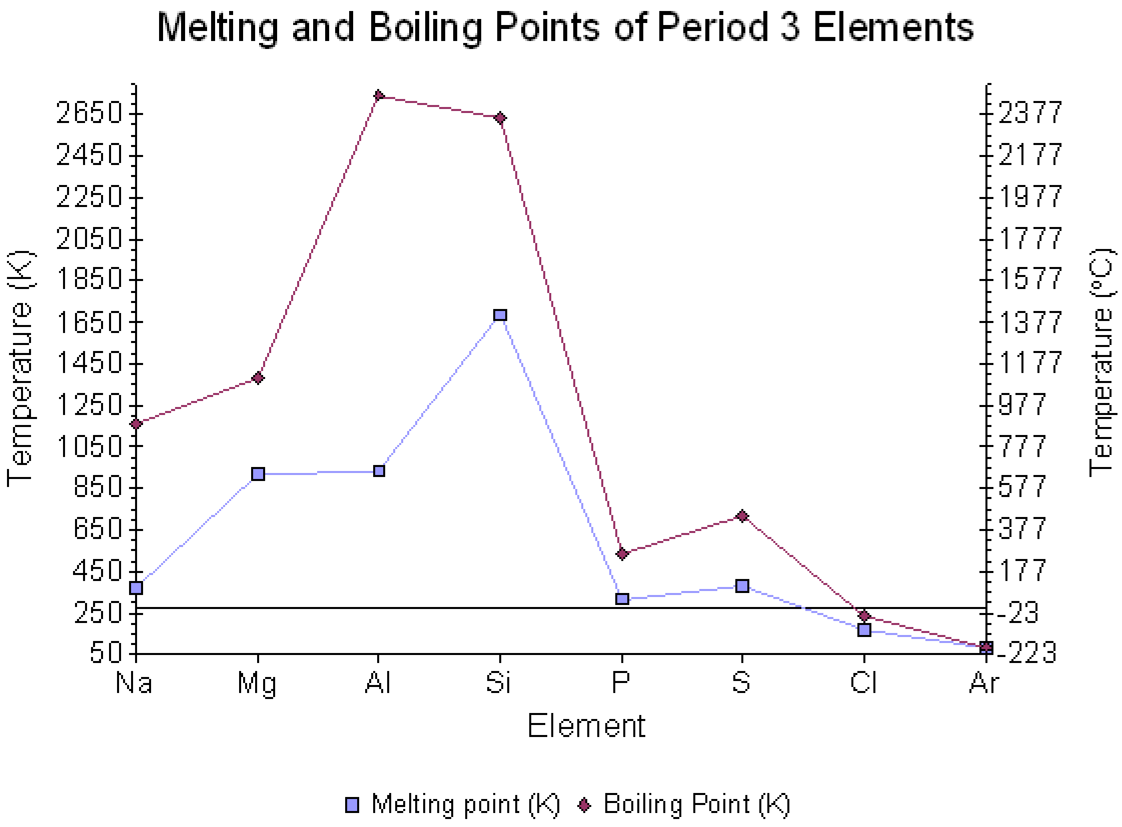
11. What is melting point?
    - ☞ **Melting point**: is a constant temperature at which pure solid is in equilibrium with the pure liquid at atmospheric pressure.
    - ☞ **Melting point**: is the constant temperature at which a pure substance turns from solid to liquid state at a given pressure when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


Melting and boiling points of Period 3 elements
Temperature (K)
3000
2500
2000
1500
1000
500
0
Na
Mg
Al
Si
P
S
Cl
Ar
Element
Melting point
Boiling point


Melting and Boiling Points of Period 3 Elements
Temperature (K)
2650
2450
2250
2050
1850
1650
1450
1250
1050
850
650
450
250
50
2377
2177
1977
1777
1577
1377
1177
977
777
577
377
177
-23
-223
Temperature (°C)
Na
Mg
Al
Si
P
S
Cl
Ar
Element
Melting point (K)
Boiling Point (K)

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.

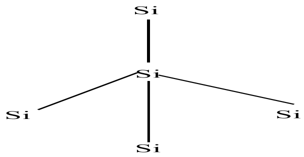
Sulphur has a higher melting point and boiling point than the other three because:

- phosphorus exists as P_4 molecules ...
- sulphur exists as S_8 molecules ...
- chlorine exists as Cl_2 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 $S_8 > P_4 > Cl_2 > Ar$.

Summary:

- Metals form giant metallic structure which requires a lot of energy. Magnesium has higher melting point than sodium because it contribute 2 electrons per atom to the metallic bond while sodium only contribute 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 electron 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 mas.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 in 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 side (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 ratio of the charge of a cation to the ionic radius. It's known as the polarizing power of a cation.

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

Mathematically:

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

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^+	Mg^{2+}	Al^{3+}
Ionic radius (nm)	0.095	0.065	0.050
Charge on the ion	$^+1$	$^+2$	$^+3$
Charge density (Polarizing power)	$\frac{+1}{0.096} = 10.5$	$\frac{+2}{0.065} = 30.8$	$\frac{+3}{0.060} = 60.0$
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_L) (b) Hydration energy,(ΔHh)

Mathematically:

Enthalpy of solution = Lattice energy + Hydration energy

$\Delta H_{sol.} = U_L + \Delta H_h$

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:

$NaCl_{(s)} \longrightarrow Na^+_{(aq)} + Cl^-_{(g)} \qquad U_L = {}^+180KJ/Mol$

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

Equation:

$Na^+_{(aq)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)} \qquad H_h = {}^-180KJ/Mol$

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^{2+} and Cl^- 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:

$Na^+_{(g)} + (aq) \longrightarrow Na^+_{(aq)}$ Change in energy = $^-$ve

$Cl^-_{(g)} + (aq) \longrightarrow Cl^-_{(aq)}$ " " " " "

$Mg^{2+}_{(g)} + (aq) \longrightarrow Mg^{2+}_{(aq)}$ " " " " "

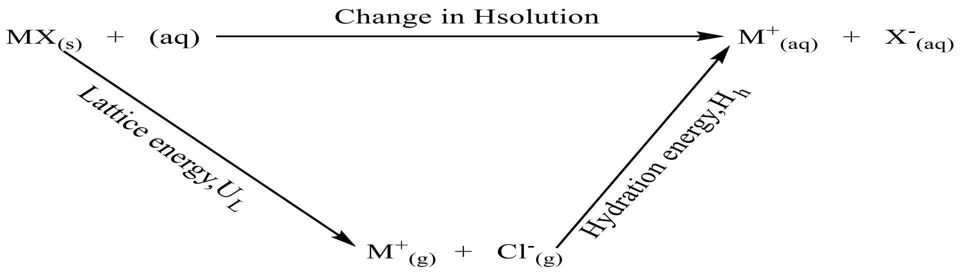
Hydration energy is an exothermic process

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

$$\text{Enthaply of solution,}H_{SOL} = \text{Lattice energy,}U_{L} + \text{Hydration energy,}H_{H}$$

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^{1})	Hydration energy (KJ/Mol^{1})
AX	$^{+}880$	$^{-}860$
BX	$^{+}790$	$^{-}800$

a)
Calculate the enthalpy of solution of each salt.

- Salt AX.

$$\text{Enthaply of solution,}H_{SOL} = \text{Lattice energy,}U_{L} + \text{Hydration energy,}H_{H}$$
$$= {}^{+}880 + {}^{-}860$$
$$= {}^{+}20\ \text{KJ/Mol}^{1}$$

- Salt BX.

$$\text{Enthaply of solution,}H_{SOL} = \text{Lattice energy,}U_{L} + \text{Hydration energy,}H_{H}$$
$$= {}^{+}790 + {}^{-}800$$
$$= {}^{-}10\ \text{KJ/Mol}^{1}$$

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_{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.
  - $CaCO_3$ is insoluble in water while $CaCl_2$ is soluble.
  - This is because the attraction between the double positive ion on Ca^{2+} ion and the double negative charge on CO_3^{2-} ion is much higher than between the Ca^{2+} ion and 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	Al_2O_3	Al_2Cl_3	CaO	$CaCl_2$
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 is 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 (A°)		Electron configurations
$_3$Li	180	1330	0.15	0.06	[He] 2s^1 (2:1) **$1s^2,2s^1$**
$_{11}$Na	98	892	0.19	0.10	[Ne] 3s^1 (2:8:1) **$1s^2,2s^22p^6,3s^1$**
$_{19}$K	63	760	0.23	0.13	[Ar] 4s^1 (2:8:8:1) **$1s^2,2s^22p^6,3s^23p^6,4s^1$**
$_{37}$Rb	39	688	0.24	0.15	[Kr] 5s^1 (2:8:18:8:1) **$1s^2,2s^22p^6,3s^23p^63d^{10},4s^24p6,5s^1$**
$_{55}$Cs	29	690	0.26	0.17	[Xe] 6s^1 (2:8:18:18:8:1) **$1s^2,2s^22p^6,3s^23p^63d^{10},4s^24p^6,5s^25p^66s^1$**
$_{87}$Fr	T_m/°C	T_b/°C	AR/nm	IR/nm	[Rn]7s^1 (2:8:18:32:18:8:1) **$1s^2,2s^22p^6,3s^23p^63d^{10},4s^24p^64d^{10}4f^{14},5s^25p^65d^{10},6s^26p^67s^1$**
	Radioactive elements artificially made				

Elements	Li	Na	Rb	Cs	Fr	**KEY:**
1st IE/KJmol^{-1}	519	494	418	402	376	T_m = melting temperature T_b = boiling temperature AR = Atomic radius 1st I.E = 1st Ionization energy 2nd I.E = 2nd Ionization energy
2nd IE/KJmol^{-1}	7300	4600	3100	2700	2440	
Density/gcm^{-3}	0.53	0.97	0.86	1.53	1.90	
Standard electrode potential, E^θ/V $M^+_{(aq)}/M_{(s)}$/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^1; 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:**

  $$Na \longrightarrow Na^{+}_{(aq)} + e \qquad H_1 = 500KJmol^{-1}$$

  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, Na^+ for example. High 2nd I.E of Group (I) elements prohibits the formation of other ions such as 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
$Li^+_{(aq)} + e \rightleftharpoons Li_{(s)}$	$^{-}3.04$
$Na^+_{(aq)} + e \rightleftharpoons Na_{(s)}$	$^{-}2.71$
$K^+_{(aq)} + e \rightleftharpoons K_{(s)}$	$^{-}2.93$
$Rb^+_{(aq)} + e \rightleftharpoons Rb_{(s)}$	$^{-}2.99$
$Cs^+_{(aq)} + e \rightleftharpoons Cs_{(s)}$	$^{-}3.02$

Li ↓ Cs: Ionisation energy decreases

Li(*1) Has the most negative electrode potential

Na ↓ Cs: Value of electrode potential becomes negative

(*1) The small size of Li^+ gives it a high standard enthalpy of hydration. This is why Li^+ has the most negative value of electrode potential in the group. The small size of 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 1st 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:

     $$4Li_{(s)} + O_{2(g)} \xrightarrow{\text{Heat}} 2Li_2O_{(s)}$$

     Lithium oxide (Normal oxide)

     $$2Li_{(s)} + \tfrac{1}{2}O_{2(g)} \longrightarrow Li_2O_{(s)}$$

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

     $$4Na_{(s)} + O_{2(g)} \xrightarrow{\text{Heat}} 2Na_2O_{(s)}$$

     Sodium oxide (Normal Oxide)

   - 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:

     $$2Na_{(s)} + O_{2(g)} \xrightarrow{\text{Heat}} Na_2O_{2(s)}$$

     Sodium peroxide (peroxide)

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

     $$K_{(s)} + O_{2(g)} \xrightarrow{\text{Heat}} KO_{2(s)}$$

     Potassium superoxide

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

     $$Rb_{(s)} + O_{2(s)} \xrightarrow{\text{Heat}} RbO_{2(s)}$$

     Rubidium superoxide

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

     $$Cs_{(s)} + O_{2(g)} \xrightarrow{\text{Heat}} CsO_{2(s)}$$

     Caesium superoxide

     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-}.Therefore,Li^+ 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:
     $2K_2O_{(s)} + 2H_2O_{(l)} \longrightarrow 2KOH_{(aq)} + H_2O_{2(aq)} + O_{2(g)}$
   - Rubidium superoxide
     Rubidium superoxide dissolves in water to form rubidium hydroxide solution.
     Equation
   - 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:

$$2Li_{(s)} + H_{2(g)} \longrightarrow \underset{\text{White solid}}{2LiH_{(s)}}$$

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

$$2Na_{(s)} + H_{2(g)} \longrightarrow \underset{\text{White solid}}{2NaH_{(s)}}$$

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

$$2K_{(s)} + H_{2(g)} \longrightarrow \underset{\text{White solid}}{2KH_{(s)}}$$

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:

$$LiH_{(s)} + H_2O_{(l)} \longrightarrow LiOH_{(aq)} + H_{2(g)}$$

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

$$\underset{\text{White solid}}{NaH_{(s)}} + H_2O_{(l)} \longrightarrow NaOH_{(aq)} + H_{2(g)}$$

   - Potassium hydride.
     Equation:

$$\underset{\text{White solid}}{KH_{(s)}} + H_2O_{(l)} \longrightarrow KOH_{(aq)} + H_{2(g)}$$

   - Rubidium hydride.
   - Caesium hydride.

(iii) Water.

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

$$2Li_{(s)} + 2H_2O_{(l)} \longrightarrow 2LiOH_{(aq)} + H_{2(g)}$$

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 sate 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:

$$2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$$

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:

$$2K_{(s)} + 2H_2O_{(l)} \longrightarrow 2KOH_{(aq)} + H_{2(g)}$$

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

Equation:

$$2Rb_{(s)} + 2H_2O_{(l)} \longrightarrow 2RbOH_{(aq)} + H_{2(g)}$$

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

Equation:

$$2Cs_{(s)} + 2H_2O_{(l)} \longrightarrow 2CsOH_{(aq)} + H_{2(g)}$$

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:

  $$Li_2CO_{3(s)} \xrightarrow{\text{Heat}} Li_2O_{(s)} + CO_{2(g)}$$

- ☞ 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:

  $$CO^{2-}_{(aq)} + H_2O_{(l)} \rightleftharpoons HCO_3^-{}_{(aq)} + OH^-_{(aq)}$$

  $$HCO_3^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} + OH^-_{(aq)}$$

  - ☞ The carbonate ion is highly negatively charge; 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 exist in solution.
- Hydrogen carbonates are easily decomposed to form carbonates, carbon dioxide gas and water:

  Equation:

$$2NaHCO_{3(s)} \xrightarrow{Heat} Na_2CO_{3(s)} + H_2O_{(l)} + CO_{2(g)}$$
$$2KHCO_{3(s)} \xrightarrow{Heat} K_2CO_{3(s)} + H_2O_{(l)} + CO_{2(g)}$$

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:
   $$2NaHCO_{3(s)} \xrightarrow{Heat} Na_2CO_{3(s)} + H_2O_{(l)} + CO_{2(g)}$$
   Therefore, because HCO^{-}_{3} has charge, it is therefore, decomposes.
   $HCO_3^{-} > CO_3^{2-} > O^{2-}$.
   Also in Magnesium carbonate, $MgCO_3$.
   Equation:
   $$MgCO_{3(s)} \longrightarrow MgO_{(s)} + CO_{2(g)}$$
   $CO_3^{2-} > O^{2-}$.

NITRATES:

- The nitrate decomposes when heated to form the respective metal nitrite and oxygen gas.
  Equation:
  $$2NaNO_{3(s)} \xrightarrow{Heat} 2NaNO_{2(l)} + O_{2(g)}$$
  $$2KNO_{3(s)} \xrightarrow{Heat} 2KNO_{2(l)} + O_{2(g)}$$
- However, Lithium nitrate is unstable; it decomposes completely when heated to form lithium oxide, nitrogen dioxide and oxygen gas.
  Equation:
  $$4LiNO_{3(s)} \xrightarrow{Heat} 2Li_2O_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

HALIDES:

- They form ionic halides which are soluble in water except lithium halide.
  Equation:
  $$2Na_{(s)} + Cl_{2(g)} \longrightarrow 2NaCl_{(s)}$$
  $$2K_{(s)} + Cl_{2(g)} \longrightarrow 2KCl_{(s)}$$
- 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
- ♣ Boron and silicon
- ♣ Beryllium and aluminium

The similarity in chemical properties is due to following reasons:

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

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

Li and Mg	Be and Al	B and Si
Both react with nitrogen on heating to form nitrides.	Oxides and hydroxides are amphoteric. $Be(OH)_2 (s) + 2OH^- (aq) \longrightarrow Be(OH)_4^{2-} (aq)$ $Al(OH)_3 (s) + OH^- (aq) \rightarrow Al(OH)_4^- (aq)$	Both form acidic oxide as B_2O_3 and SiO_2
Their hydrogen carbonates exist in solution	Both react with Conc. Sodium hydroxide solution to form a complex and hydrogen gas. $Be(s) + 2OH^- (aq) + 2H_2O (l) \rightarrow Be(OH)_4^{2-} (aq) + H_2(g)$	Both form series of covalent hydrides.

	$2Al(s) + 2OH^-(aq) + 6H_2O(l) \rightarrow 2Al(OH)_4^-(aq) + 3H_2(g)$	
Both form normal oxides when heated in oxygen (air)	Their chlorides and bromides are covalent and dimerize in vapour phase as Be_2Cl_4 and Al_2Cl_6. $2AlCl_3\ (s) \rightleftharpoons Al_2Cl_6\ (g)$	Both form chlorides which hydrolyze readily.
Their hydroxides and carbonates are sparingly soluble in water	Both form ionic carbides which hydrolyze to form methane. $Be_2C\ (s) + 4H_2O(l) \rightarrow CH_4(g) + 2Be(OH)_2\ (aq)$ $Al_4C_3(s) + 12H_2O(l) \rightarrow 3CH_4(g) + 4Al(OH)_3(aq)$	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. 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:

$$6Li_{(s)} + N_{2(g)} \longrightarrow 2Li_3N_{(s)}$$
$$3Mg_{(s)} + N_{2(g)} \longrightarrow Mg_3N_{2(S)}$$

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

Equations:

$$4Li_{(s)} + O_{2(g)} \longrightarrow 2Li_2O_{(s)}$$
$$2Mg_{(s)} + O_{2(g)} \longrightarrow 2MgO_{(s)}$$

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:

$$LiCO_{3(s)} \longrightarrow Li_2O_{(s)} + CO_{2(g)}$$
$$MgCO_{3(s)} \longrightarrow MgO_{(s)} + CO_{2(g)}$$

Equations:

$$2LiOH_{(s)} \longrightarrow Li_2O_{(s)} + H_2O_{(l)}$$
$$Mg(OH)_{2(s)} \longrightarrow MgO_{(s)} + H_2O_{(l)}$$

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:

$$2LiNO_{3(s)} \longrightarrow Li_2O_{(s)} + 2NO_{2(g)} + ½O_{2(g)}$$
$$Mg(NO_3)_{2(s)} \longrightarrow MgO_{(s)} + 2NO_{2(g)} + ½O_{2(g)}$$

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:

$$Be_{(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \longrightarrow Be(OH)_4{}^{2+}{}_{(aq)} + H_{2(g)}$$
$$2Al_{(s)} + 2OH^-_{(aq)} + 6H_2O_{(l)} \longrightarrow Al(OH)_4{}^-{}_{(aq)} + 3H_{2(g)}$$

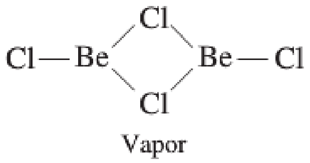
Both oxides are amphoteric and reacts with hot concentrated alkalis.
Equation:

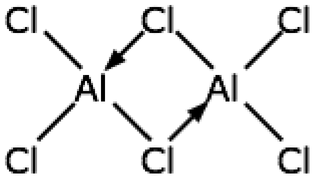
$$BeO_{(s)} + 2OH^-_{(aq)} + H_2O_{(s)} \longrightarrow Be(OH)_4{}^{2-}{}_{(aq)}$$
$$Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \longrightarrow 2Al(OH)_4{}^-{}_{(aq)}$$

Carbides of both metals yields methane on hydrolysis.
Equations:

$$Be_2C_{(s)} + 4H_2O_{(l)} \longrightarrow 2Be(OH)_{2(s)} + CH_{4(g)}$$
$$Al_4C_{3(s)} + 12H_2O_{(l)} \longrightarrow 4Al(OH)_{3(s)} + 3CH_{4(g)}$$

Chlorides 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:

$$BeCl_{2(s)} + 4H_2O_{(l)} \longrightarrow [Be(H_2O)_4]^{2+}{}_{(aq)} + 2Cl^-_{(aq)}$$

Or:

$$Be(H_2O)_{4(aq)} \longrightarrow [Be(H_2O)_2 2OH]_{(s)} + 2H^+_{(aq)}$$
$$AlCl_{3(s)} + 6H_2O_{(l)} \longrightarrow [Al(H_2O)_6]^{3+}{}_{(aq)} + 3Cl^-_{(aq)}$$

Or:

$$[Al(H_2O)_6]^{3+}{}_{(aq)} \longrightarrow [Al(H_2O)_3 3OH]_{(s)} + 3H^+_{(aq)}$$

Boron and Silicon.

Both burns in air to form acidic oxides.

Equations:

$$4B_{(s)} + 3O_{2(g)} \longrightarrow 2B_2O_{3(s)}$$
$$Si_{(s)} + O_{2(g)} \longrightarrow SiO_{2(s)}$$

Both burns in nitrogen gas to form nitrides.

Equations:

$$2B_{(s)} + N_{2(g)} \longrightarrow 2BN_{(s)}$$
$$3Si_{(s)} + 2N_{2(g)} \longrightarrow Si_3N_{4(s)}$$

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:

$$SiCl_{4(l)} + H_2O_{(l)} \longrightarrow Si(OH)_{4(aq)} + 4HCl_{(aq)}$$
$$BCl_{3(l)} + 3H_2O_{(l)} \longrightarrow B(OH)_{3(aq)} + 3HCl_{(aq)}$$

Both form weak acids like H_3BO_3 and H_2SiF_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:

$$2B_{(s)} + 6HNO_{3(l)} \longrightarrow 2H_2BO_{3(s)} + 6NO_{2(g)}$$

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:

$$Si_{(s)} + 6HF_{(l)} \xrightarrow{HNO_3} H_2SiF_{6(l)} + 2H_{2(g)}$$

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

Their carbides are very hard and used as abrasives.

4. 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
    - ✓ Magnesium, Mg
    - ✓ Calcium, Ca
    - ✓ Strontium, Sr
    - ✓ Barium, Ba
    - ✓ 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.

EFFECTS OF IONIC RADIUS OF GROUP (II) IONS AS COMPAIRED 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.
    - ✍ Thermal stability.
    - ✍ Melting & boiling points.

(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.

10. Explain the following.
    a) 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.
    b) 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:

$$2Be_{(s)} + O_{2(g)} \longrightarrow 2BeO_{(s)}$$

$$2Mg_{(s)} + O_{2(g)} \longrightarrow 2MgO_{(s)}$$

$$2Ca_{(s)} + O_{2(g)} \longrightarrow \underset{\text{White solid}}{2CaO_{(s)}}$$

Golden tips:

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

Equation:

$$2Mg_{(s)} + O_{2(g)} \longrightarrow 2MgO_{(s)}$$

$$3Mg_{(s)} + N_{2(g)} \longrightarrow Mg_3N_{2(s)}$$

$$2Sr_{(s)} + O_{2(g)} \longrightarrow 2SrO_{(s)}$$

$$3Sr_{(s)} + N_{2(g)} \longrightarrow Sr_3N_{2(s)}$$

Golden tips:

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

Equation:

$$Mg_3N_{2(s)} + 6H_2O_{(l)} \longrightarrow 3Mg(OH)_{2(aq)} + 2NH_{3(g)}$$
$$Sr_3N_{2(s)} + 6H_2O_{(l)} \longrightarrow 3Sr(OH)_{2(aq)} + 2NH_{3(g)}$$

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

Equation:

$$2BaO_{(s)} + O_{2(g)} \longrightarrow 2BaO_{2(s)}$$
$$2SrO_{(s)} + O_{2(g)} \longrightarrow 2SrO_{2(s)}$$

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:

$$Mg_{(s)} + H_2O_{(g)} \longrightarrow MgO_{(s)} + H_{2(g)}$$

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:

$$Ca_{(s)} + 2H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)} + H_{2(g)}$$
$$Sr_{(s)} + 2H_2O_{(l)} \longrightarrow Sr(OH)_{2(aq)} + H_{2(g)}$$
$$Ba_{(s)} + 2H_2O_{(l)} \longrightarrow Ba(OH)_{2(aq)} + H_{2(g)}$$

COMPARE WITH GROUP (I) ELEMENTS:

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

Equation:

$$2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$$
$$2K_{(s)} + 2H_2O_{(l)} \longrightarrow 2KOH_{(aq)} + H_{2(g)}$$

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:

$$Be_{(s)} + 2HCl_{(aq)} \longrightarrow BeCl_{2(aq)} + H_{2(g)}$$
$$Mg_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_{2(g)}$$
$$Ba_{(s)} + 2HCl_{(aq)} \longrightarrow BaCl_{2(aq)} + H_{2(g)}$$

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:

$$Be_{(s)} + H_2SO_{4(aq)} \longrightarrow BeSO_{4(aq)} + H_{2(g)}$$

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:

$$Ca_{(s)} + H_2SO_{4(aq)} \longrightarrow CaSO_{4(s)} + H_{2(g)}$$
$$Sr_{(s)} + H_2SO_{4(aq)} \longrightarrow SrSO_{4(s)} + H_{2(g)}$$
$$Ba_{(s)} + H_2SO_{4(aq)} \longrightarrow BaSO_{4(s)} + H_{2(g)}$$

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:

$$3Mg_{(s)} + 8HNO_{3(aq)} \longrightarrow 3Mg(NO_3)_{2(aq)} + 4H_2O_{(l)} + 2NO_{(g)}$$

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:

$$Be_{(s)} + 2H_2SO_{4(l)} \longrightarrow BeSO_{4(aq)} + SO_{2(g)} + 2H_2O_{(l)}$$
$$Ba_{(s)} + 2H_2SO_{4(l)} \longrightarrow BaSO_{4(aq)} + SO_{2(g)} + 2H_2O_{(l)}$$
$$Mg_{(s)} + 2H_2SO_{4(l)} \longrightarrow MgSO_{4(aq)} + SO_{2(g)} + 2H_2O_{(l)}$$

- ✘ 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 M^{2+} (metal nitrate) and the acid is reduced to nitrogen dioxide gas.
Equation:

$$Mg_{(s)} + 4HNO_{3(l)} \longrightarrow Mg(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$$
$$Ba_{(s)} + 4HNO_{3(l)} \longrightarrow Ba(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$$

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:

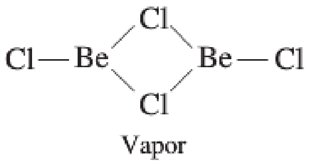
$$Be_{(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \longrightarrow Be(OH)_4{}^{2-}{}_{(aq)} + H_{2(g)}$$
Or
$$Be_{(s)} + 2OH^-_{(aq)} \longrightarrow BeO_2{}^{2-}{}_{(aq)} + H_{2(g)}$$

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:

$$Be_{(s)} + Cl_{2(g)} \longrightarrow BeCl_{2(s)}$$

Beryllium chloride dimerises in vapour state (phase) and exist as beryllium chloride, Be_2Cl_4.



Formula:

Beryllium chloride is covalent because Beryllium forms a cation which is highly charge 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:

$$Mg_{(s)} + Cl_{2(g)} \longrightarrow MgCl_{2(s)}$$
$$Ca_{(s)} + Cl_{2(g)} \longrightarrow CaCl_{2(s)}$$
$$Ba_{(s)} + Cl_{2(g)} \longrightarrow BaCl_{2(s)}$$

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)
Be^{2+}	$\frac{2}{0.031}=64.5$			Li^{+}	$\frac{1}{0.060}=16.7$	
Mg^{2+}	$\frac{2}{0.065}=30.8$	$^{-}1920$		Na^{+}	$\frac{1}{0.095}=10.5$	$^{-}406$
Ca^{2+}	$\frac{2}{0.099}=20.2$	$^{-}1650$		K^{+}	$\frac{1}{0.133}=07.5$	$^{-}322$
Sr^{2+}	$\frac{2}{0.191}=10.5$	$^{-}1440$		Rb^{+}	$\frac{1}{0.152}=06.6$	$^{-}301$

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.

1) Hydroxides.

The hydroxides can be prepared by either:

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

Equation:

$$CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)}$$
$$MgO_{(s)} + H_2O_{(l)} \longrightarrow Mg(OH)_{2(aq)}$$
$$BaO_{(s)} + H_2O_{(l)} \longrightarrow Ba(OH)_{2(aq)}$$

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

Equations

$$Mg^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Mg(OH)_{2(aq)}$$

SOLUBILITY OF THE HYDROXIDES:

Hydroxides	Solubility at 25°C Mol^{-1}/100g of water	
$Be(OH)_2$	INSOLUBLE	Insoluble
$Mg(OH)_2$	2.0×10^{-5}	0.002
$Ca(OH)_2$	1.5×10^{-3}	0.150
$Sr(OH)_2$	3.4×10^{-3}	0.400
$Ba(OH)_2$	1.5×10^{-2}	4.000

11. State and explain the trend of the solublities 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 dissolves 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, SO_4^{2-} to any soluble salt except, Beryllium and Magnesium sulphates which are soluble.

   Equations:

$$Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \longrightarrow CaSO_{4(s)}$$
$$Sr^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \longrightarrow SrSO_{4(s)}$$
$$Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \longrightarrow BaSO_{4(s)}$$

SOLUBILITY OF THE SULPHATES.

Sulphates	Solubility at 25°C in gm/100g of water
$BeSO_4$	4.3000
$MgSO_4$	8.6000
$CaSO_4$	0.2000
$SrSO_4$	0.1100
$BaSO_4$	0.0024

12. State and explain the trend of the solublities 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:

$Ba(OH)_{2(aq)} + 2HCl_{(aq)} \longrightarrow BaCl_{2(aq)} + H_2O_{(l)}$
$CaCO_{3(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$

Chlorides	Conductivity $(\Omega^{-1}cm^2/Mol)$	Bonding	Melting point (°C)
$BeCl_2$	00.09	Covalent	405
$MgCl_2$	32.00	Ionic	714
$CaCl_2$	58.00	″	782
$SrCl_2$	63.00	″	872
$BaCl_2$	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:
  $BeCl_{2(s)} + 2H_2O_{(l)} \rightleftharpoons Be(OH)_{2(s)} + 2HCl_{(g)}$
- Magnesium chloride can only undergo partial hydrolysis by water.
  Equation:
  $MgCl_{2(s)} + H_2O_{(l)} \rightleftharpoons Mg(OH)Cl_{(s)} + HCl_{(g)}$
- 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:
  $MgCl_{2(s)} + H_2O_{(l)} \longrightarrow MgO_{(s)} + 2HCl_{(g)}$
- Calcium chloride is only hydrolysed to a small extent to form calcium oxide or calcium hydroxide. Strontium 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:

$Mg^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \longrightarrow MgCO_{3(s)}$
$Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \longrightarrow CaCO_{3(s)}$
$Ba^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \longrightarrow BaCO_{3(s)}$

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	Temperature (°C)
$BeCO_3$	100
$MgCO_3$	350
$CaCO_3$	900
$SrCO_3$	1290
$BaCO_3$	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:
  $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$
  $Be(NO_3)_2 < Mg(NO_3)_2 < Ca(NO_3)_2 < Sr(NO_3)_2 < Ba(NO_3)_2$

  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 M^{2+} ions have higher charge density than M^+ ions therefore they polarize the large carbonates more than M^+.

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

   Magnesium ion, Mg^{2+} has a high charge, small ionic radius than sodium ion, Na^+.it therefore has high polarizing power which makes it easy to polarize the big carbonate ions,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 Na^+, hence magnesium carbonate easily decomposes.

5) Oxides

The oxides can be prepared by:

- Heating the metals in oxygen.

  Equation:

  $$2Be_{(s)} + O_{2(g)} \longrightarrow 2BeO_{(s)}$$
  $$2Mg_{(s)} + O_{2(g)} \longrightarrow 2MgO_{(s)}$$

- Passing steam over heated metals.

  Equations:

  $$Mg_{(s)} + H_2O_{(g)} \longrightarrow MgO_{(s)} + H_{2(g)}$$

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

  Equations:

  $$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$$
  $$2Be(NO_3)_{2(s)} \longrightarrow 2BeO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$
  $$Ca(OH)_{2(s)} \longrightarrow CaO_{(s)} + H_2O_{(l)}$$

  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 reacts with water because it forms an insoluble beryllium hydroxide while the rest of the metals oxides do reacts readily with water liberating heat and metal hydroxides. The metal oxides become more soluble down the group.

Equations:

$$MgO_{(s)} + H_2O_{(l)} \longrightarrow Mg(OH)_{2(s)}$$
$$CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(s)}$$
$$SrO_{(s)} + H_2O_{(l)} \longrightarrow Sr(OH)_{2(s)}$$
$$BaO_{(s)} + H_2O_{(l)} \longrightarrow Ba(OH)_{2(s)}$$

6. Explain why beryllium oxide do not reacts with water?

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

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

Because Beryllium hydroxide is amphoteric and therefore it forms complex.

Equation:

$$Be(OH)_2\,(s) + 2OH^-\,(aq) \longrightarrow Be(OH)_4^{2-}\,(aq)$$

7) Reactions with alkalis:

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

Equation:

$$BeO_{(s)} + 2OH^-_{(l)} + 2H_2O_{(l)} \longrightarrow Be(OH)_4^{2-}{}_{(aq)} + H_{2(g)}$$

Or

$$BeO_{(s)} + 2OH^-_{(l)} + H_2O_{(l)} \longrightarrow Be(OH)_4^{2-}{}_{(aq)}$$

Reasons why the rest do not reacts 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:

$$BeO_{(s)} + 2H^+_{(aq)} \longrightarrow Be^{2+}_{(aq)} + H_2O_{(l)}$$
$$CaO_{(s)} + 2H^+_{(aq)} \longrightarrow Ca^{2+}_{(aq)} + H_2O_{(l)}$$
$$MgO_{(s)} + 2H^+_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + H_2O_{(l)}$$
$$BaO_{(s)} + 2H^+_{(aq)} \longrightarrow Ba^{2+}_{(aq)} + H_2O_{(l)}$$
$$SrO_{(s)} + 2H^+_{(aq)} \longrightarrow Sr^{2+}_{(aq)} + H_2O_{(l)}$$

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:

$$CaO_{(s)} + H_2SO_{4(aq)} \longrightarrow CaSO_{4(s)} + H_2O_{(l)}$$
$$SrO_{(s)} + H_2SO_{4(aq)} \longrightarrow SrSO_{4(s)} + H_2O_{(l)}$$
$$BaO_{(s)} + H_2SO_{4(aq)} \longrightarrow BaSO_{4(s)} + H_2O_{(l)}$$

White Precipitate (Insoluble salt)

CALCIUM OXIDE, CaO (QUICK LIME):

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

Procedures:

It is obtained by heating calcium carbonate.

Equation:

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$$

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:

$$CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(s)}$$

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

$$CaO_{(s)} + 3C_{(s)} \xrightarrow[\text{Temperature/C}]{1800\text{-}2000} CaC_{2(s)} + CO_{(g)}$$

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

$$CaC_{2(s)} + 2H_2O_{(l)} \longrightarrow HC \equiv CH_{(g)} + Ca(OH)_{2(s)}$$

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

9. 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°C.

Beryllium carbide can also be prepared by reduction of beryllium oxide with carbon at a temperature above **1500°C**.
Equation:

$$2BeO_{(s)} + 3C_{(s)} \longrightarrow Be_2C_{(s)} + 2CO_{(g)}$$

Beryllium carbide obtained is hydrolyzed or decomposes slowly in water.
Equation:

$$Be_2C_{(s)} + 2H_2O_{(l)} \longrightarrow 2BeO_{(s)} + CH_{4(g)}$$

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

$$Be_2C_{(s)} + 4H^+_{(aq)} \longrightarrow 2Be^{2+}_{(aq)} + CH_{4(g)}$$

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

$$Be_2C_{(s)} + 4OH^-_{(l)} \longrightarrow 2BeO_2^{2+}{}_{(aq)} + CH_{4(g)}$$

HYDROLYSIS OF GROUP (II) SALTS:

10. What is Hydrolysis?

Hydrolysis: is a reaction between water molecules and highly charged cations and anions (CO_3^{2-}) which disturbs the water equilibrium hence producing more hydroxide ions (OH^-) or hydrogen ions giving a solution of P^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 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:

$$[Be(H_2O)_4]^{2+}_{(aq)} + 2H_2O_{(l)} \rightleftharpoons [Be(H_2O)_4.2OH]_{(s)} + 2H^+_{(aq)}$$

$$Mg(H_2O)_6{}^{2+}_{(aq)} \rightleftharpoons [Mg(H_2O)_4.2OH]_{(s)} + 2H^+_{(aq)}$$

COMPLEX FORMATION:

11. 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:

12. 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 charges 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.

13. 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:

$Be(H_2O)_4{}^{2+}$, $Be(H_2O)_4{}^{2-}$, $BeF_4{}^{2+}$, $Al(H_2O)_6{}^{3+}$, $BeF_3{}^-$

IDENTIFICATIONS OF Ca^{2+}, Mg^{2+} and Ba^{2+}:

Dilute Sodium hydroxide Solution until in excess:

A white precipitate insoluble in excess is observed by Ca^{2+}, Mg^{2+} and Ba^{2+}
Equations:

$$Mg^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Mg(OH)_{2(s)}$$

$$Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Ca(OH)_{2(s)}$$

$$Ba^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Ba(OH)_{2(s)}$$

Dilute Ammonia solution until in excess

Ba^{2+} and **Mg^{2+} -** White precipitate insoluble in excess.
Equation:

$Mg^{2+}{}_{(aq)} + 2OH^{-}{}_{(aq)} \longrightarrow Mg(OH)_{2(s)}$
$Ba^{2+}{}_{(aq)} + 2OH^{-}{}_{(aq)} \longrightarrow Ba(OH)_{2(s)}$

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, NH_4^+ which suppresses the ionization of aqueous ammonia due to common ion effect. Therefore the concentration of Hydroxyl ion is low.

Equations:

$NH_4Cl_{(aq)} \rightleftharpoons NH_4^{+}{}_{(aq)} + Cl^{-}{}_{(aq)}$
$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^{+}{}_{(aq)} + OH^{-}{}_{(aq)}$

Ca^{2+}- No observable change.

Notes:

Calcium ions, 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

Mg^{2+} - No observable change **Ca^{2+}** and **Ba^{2+}** - White precipitate

Equations:

$Ca^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)} \longrightarrow CaSO_{4(s)}$
$Ba^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)} \longrightarrow BaSO_{4(s)}$

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

Equation:

$CaSO_{4(s)} + SO_4^{2-}{}_{(aq)} \longrightarrow Ca(SO_4)_2^{2-}{}_{(aq)}$

Dilute Sulphuric acid does not precipitate magnesium sulphate hence it's used to differentiate Mg^{2+} ion from Ca^{2+} and 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, Ca^{2+} and Barium, 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

Ba^{2+} - Yellow precipitate insoluble in Ethanoic acid
Ca^{2+} - Yellow precipitate soluble in Ethanoic acid
Mg^{2+}-No observable change.

Equations:

$Ca^{2+}{}_{(aq)} + CrO_4^{2-}{}_{(aq)} \longrightarrow CaCrO_{4(s)}$ But soluble in dilute acid
$Ba^{2+}{}_{(aq)} + CrO_4^{2-}{}_{(aq)} \longrightarrow BaCrO_{4(s)}$ But soluble in dilute acid

Ammonium Oxalate (Ethandiote) and Ethanoic acid

Ba^{2+} and **Ca^{2+}** - white precipitate **Mg^{2+}**- No observable change

Equations:

$Ba^{2+}_{(aq)} + C_2O_4^{2-}_{(aq)} \longrightarrow Ba(COO)_{2(s)}$

Or:

$Ba^{2+}_{(aq)} + C_2O_4^{2-}_{(aq)} \longrightarrow BaC_2O_{4(s)}$

$Ca^{2+}_{(aq)} + C_2O_4^{2-}_{(aq)} \longrightarrow Ca(COO)_{2(s)}$

Or:

$Ca^{2+}_{(aq)} + C_2O_4^{2-}_{(aq)} \longrightarrow BaC_2O_{4(s)}$

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 Ba^{2+} from Ca^{2+} ions.

Disodium Hydrogen Phosphate or sodium phosphate/sodium dihydrogen phosphate

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

Equations:

$Mg^{2+}_{(aq)} + NH_4^+_{(aq)} + PO_4^{3-}_{(aq)} \longrightarrow MgNH_4PO_{4(s)}$

Or:

$Mg^{2+}_{(aq)} + NH_4^+_{(aq)} + PO_4^{3-}_{(aq)} + 6H_2O_{(l)} \longrightarrow MgNH_4PO_4.6H_2O_{(s)}$

$3Ca^{2+}_{(aq)} + 2HPO_4^{2-}_{(aq)} + 2OH^-_{(aq)} \longrightarrow 3Ca(H_2PO_4)_{2(s)} + 2H_2O_{(l)}$

Notes:

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

Equation:

$Ca_3(PO_4)_{2(s)} + 2H_2SO_{4(aq)} \longrightarrow Ca(H_2PO_4)_{2(s)} + 2CaSO_{4(s)}$

Ammonium carbonate solution

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

Equations:

$Ba^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \longrightarrow BaCO_{3(s)}$

$Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \longrightarrow CaCO_{3(s)}$

$Mg^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \longrightarrow MgCO_{3(s)}$

Notes:

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

$NH_4^+_{(aq)} + CO_3^{2-}_{(aq)} \longrightarrow NH_{3(aq)} + HCO_3^-_{(aq)}$

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

14. Name the reagents used to differentiate Magnesium, Mg^{2+} from Calcium, Ca^{2+} and Ba^{2+} ions.
15. Name the reagents used to differentiate Calcium, Ca^{2+} from Barium, Ba^{2+} ions.

GROUP IV ELEMENTS:

Elements	$_{6}$**C**	$_{14}$**Si**	$_{32}$**Ge**	$_{50}$**Sn**	$_{82}$**Pb**
Electronic configuration	$[He]2s^22p^2$ $1s^22s^22p^2$	$[Ne]3s^23p^2$ $1s^22s^22p^63s^23p^2$	$[Ar]4s^24p^2$	$[Kr]5s^25p^2$	$[Xe]6s^26p^2$
Atomic radius (nm)	0.077	0.117	0.122	0.141	0.154
Boiling points/°C	$4830^{d.}$	2680	2830	2270	1730
Melting points/°C	$3730^{d.}$	1410	937	232	327
Electronegativity	2.5	1.8	1.8	1.8	1.8
1st I.E (KJ/Mol)	1086	787	760	707	715
Type of structure	Giant molecular	Giant molecular similar to diamond		Giant metallic	

(a) Existence

Carbon exists as graphite, diamond and amorphous carbon. Silicon occurs as Silica (SiO_2). Tin exist as grey tin and white tin. Lead occurs as an ore in form of galena (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 ns^2np^2 promoted to ns^1np^3 i.e., sp^3 hybridization hence are able to form four covalent bonds with a tetrahedral structure.

(b) 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.

<u>**Graph**</u>:

<u>**Explanation:**</u>

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.

(c) 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 <u>**inert pair effect.**</u> Therefore the stability of $^{+}2$ oxidation state increases while that of $^{+}4$ decreases,

<u>STABILITY OF GROUP (VI) ELEMENTS</u>:

Oxidation state:

Elements	$^{+}2$ O.S ↓	$^{+}4$ O.S ↑
Carbon		
Silicon		
Germanium		
Tin		
Lead		
Lead		

16. 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.

(d) 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

$PbCl_{4\,(l)} \longrightarrow PbCl_{2\,(s)} + Cl_{2\,(g)}$

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

$2PbO_{2\,(s)} \longrightarrow 2PbO_{(s)} + O_{2\,(g)}$

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 in $^{+}2$ oxidation state.

$2CO_{(g)} + O_{2\,(g)} \longrightarrow 2CO_{2\,(g)}$

$2SiO_{(g)} + O_{2\,(g)} \longrightarrow 2SiO_{2\,(g)}$

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:

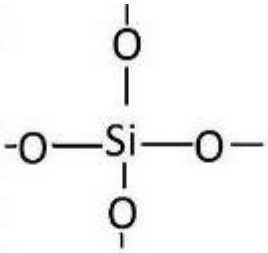
3. State some properties in carbon is different from the rest of the group members.
   - The halides are stable to hydrolysis.
   - It forms gaseous oxides unlike other members.
   - It forms a stable multiple bonds with itself and with other non-metals.

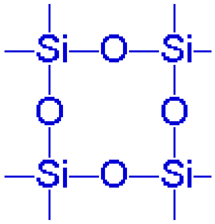
- Carbon can form a number of hydrocarbons because it can catenate. **Catenation** is the ability of the element to form bonds between atoms of the same element.

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 to 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. Discus 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:

   $C_{(s)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)}$

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

   Equation:

   $2C_{(s)} + O_{2\,(g)} \longrightarrow 2CO_{(g)}$

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

Equation:

$Si_{(s)} + O_{2(g)} \longrightarrow SiO_{2(s)}$

Germanium burns strongly in air to form germanium oxide.

Equation:

$Ge_{(s)} + O_{2(g)} \longrightarrow GeO_{2(s)}$

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

Equation:

$Sn_{(s)} + O_{2(g)} \longrightarrow SnO_{2(s)}$

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:

$2Pb_{(s)} + O_{2(g)} \longrightarrow \underset{\text{Yellow solid}}{2PbO_{(s)}}$

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

Equation:

$6PbO_{(s)} + O_{2(g)} \longrightarrow 2Pb_3O_{4(s)}$

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:

$H_2O\ (g) + C\ (s) \rightleftharpoons CO\ (g) + H_2\ (g)$

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:

$Si_{(s)} + 2H_2O_{(g)} \longrightarrow SiO_{2(s)} + 2H_{2(g)}$

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:

$Sn_{(s)} + 2H_2O_{(g)} \longrightarrow SnO_{2(s)} + 2H_{2(g)}$

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

Equation:

$2Pb_{(s)} + 2H_2O_{(l)} + O_{2(g)} \longrightarrow Pb(OH)_{2(s)}$

Notes:

Hard water containing CO_3^{2-} and 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** reacts 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.

  Equation:

  $Sn_{(s)} + 2HCl_{(aq)} \longrightarrow SnCl_{2(aq)} + H_{2(g)}$

  $Sn_{(s)} + 2H^+_{(aq)} \longrightarrow Sn^{2+}_{(aq)} + H_{2(g)}$

  $Pb_{(s)} + 2HCl_{(aq)} \longrightarrow PbCl_{2\,(aq)} + H_{2\,(g)}$

  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:

  $4Sn_{(s)} + 10HNO_{3(aq)} \longrightarrow 4Sn(NO_3)_{2(aq)} + NH_4NO_{3(aq)} + 3H_2O_{(l)}$

  Silicon only reacts with hydrofluoric acid, owing to the stability of hexafluorosilicate (IV) complex, SiF_6^{2-}, formed and NO reactions with any metal of Group (IV) elements.

  Equation:

  $Si_{(s)} + 6HF_{(aq)} \longrightarrow H_2SiF_{6(aq)} + 2H_{2(g)}$

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

  Equation:

  $Pb_{(s)} + 2CH_3COOH_{(l)} + \frac{1}{2}O_{2(g)} \longrightarrow (CH_3COO)_2Pb_{(s)} + H_2O_{(l)}$

- 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:

  $Sn_{(s)} + 2HCl_{(l)} \longrightarrow SnCl_{2(aq)} + H_{2(g)}$

  $Pb_{(s)} + 2HCl_{(l)} \longrightarrow PbCl_{2(aq)} + H_{2(g)}$

  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:

$$C_{(s)} + 2H_2SO_{4(l)} \longrightarrow CO_{2(g)} + 2SO_{2(g)} + 2H_2O_{(l)}$$
$$Ge_{(s)} + 2H_2SO_{4(l)} \longrightarrow GeO_{2(s)} + 2SO_{2(g)} + 2H_2O_{(l)}$$
$$Sn_{(s)} + 4H_2SO_{4(l)} \longrightarrow Sn(SO_4)_{2(s)} + 2SO_{2(g)} + 4H_2O_{(l)}$$
$$Pb_{(s)} + 2H_2SO_{4(l)} \longrightarrow PbSO_{4(s)} + SO_{2(g)} + 2H_2O_{(l)}$$

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:

$$C_{(s)} + 4HNO_{3(l)} \longrightarrow CO_{2(g)} + 4NO_{2(g)} + 2H_2O_{(l)}$$
$$3Ge_{(s)} + 4HNO_{3(l)} \longrightarrow GeO_{2(s)} + 4NO_{2(g)} + 2H_2O_{(l)}$$
$$Sn_{(s)} + 4HNO_{3(l)} \longrightarrow SnO_{2(s)} + 4NO_{2(g)} + 2H_2O_{(l)}$$
$$3Pb_{(s)} + 8HNO_{3(l)} \longrightarrow 3Pb(NO_3)_{2(s)} + 2NO_{2(g)} + 4H_2O_{(l)}$$

Or:

$$Pb_{(s)} + 4HNO_{3(l)} \longrightarrow Pb(NO_3)_{2(s)} + 2NO_{2(g)} + 2H_2O_{(l)}$$

(d) **Alkalis**

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

Equations:

$$Si_{(s)} + 2OH^-_{(aq)} + H_2O_{(l)} \longrightarrow SiO_3^{2-}{}_{(aq)} + 2H_{(g)}$$
$$Ge_{(s)} + 2OH^-_{(aq)} + H_2O_{(l)} \longrightarrow GeO_3^{2-}{}_{(aq)} + 2H_{2\,(g)}$$
$$Sn_{(s)} + 2OH^-_{(aq)} + H_2O_{(l)} \longrightarrow SnO_3^{2-}{}_{(aq)} + 2H_{(g)}$$
$$Pb_{(s)} + 2OH^-_{(aq)} + H_2O_{(l)} \longrightarrow PbO_2^{2-}{}_{(aq)} + 2H_{2(g)}$$

Notes:

SiO_3^{2-}, GeO_3^{2-}, SnO_3^{2-} & PbO_2^{2-} are often written in hydrated form as follows.

Equations:

$$Ge_{(s)} + 2OH^-_{(aq)} + 4H_2O_{(l)} \longrightarrow Ge(OH)_6^{2-}{}_{(aq)} + 2H_{2(g)}$$
$$Sn_{(s)} + 2OH^-_{(aq)} + 4H_2O_{(l)} \longrightarrow Sn(OH)_6^{2-}{}_{(aq)} + 2H_{2(g)}$$
$$Pb_{(s)} + 4OH^-_{(aq)} + 2H_2O_{(l)} \longrightarrow Pb(OH)_6^{4-}{}_{(aq)} + H_{2(g)}$$

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:

$C(s) + 2Cl_{2(g)} \longrightarrow CCl_{4(l)}$
$Sn_{(s)} + 2Cl_{2(g)} \longrightarrow SnCl_{4(l)}$
$Pb_{(s)} + Cl_{2(g)} \longrightarrow PbCl_{2(s)}$
$Si_{(s)} + 2Cl_{2(g)} \longrightarrow SiCl_{4(l)}$
$Ge_{(s)} + 2Cl_{2(g)} \longrightarrow GeCl_{4(g)}$

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

Equations:

$C_{(s)} + 2S_{(s)} \longrightarrow CS_{2(l)}$
$Pb_{(s)} + S_{(s)} \longrightarrow PbS_{(s)}$

COMPOUNDS OF GROUP (IV) ELEMENTS:

Elements	T_m/K	T_b/K	Electronic configuration
Carbon, $_6C$	3930	Sublimes	$1s^2\ 2s^22p^2$ [He]$2p^2$
Silicon, $_{14}Si$	1683	2628	$1s^2\ 2s^22p^6\ 3s^23p^2$ [Ne] $3s^2\ 3p^2$
Germanium, $_{32}Ge$	1210	3103	$1s^2\ 2s^22p^6\ 3s23p^6\ 4s^2\ 3d^{10}\ 4p^2$ [Ar] $4s^2\ 3d^{10}4p^2$
Tin, $_{50}Sn$	505	2533	$1s^2\ 2s^22p^6\ 3s^23p^6\ 4s^2\ 3d^{10}\ 4p^64d^{10}\ 5s^25p^2$ [Kr] $4d^{10}5s^25p^2$
Lead, $_{82}Pb$	601	2013	$1s^2\ 2s^22p^6\ 3s23p^6\ 4s^23d10\ 4p^64d^{10}4f^{14}\ 5s^25p^65d^{10}\ 6s^26p^2$ [Xe] $4f^{14}5d^{10}6s^26p^2$
Keys: T_m/K = Melting points /Kelvin, T_b/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_2	SiO_2	GeO_2	SnO_2	PbO_2
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	← - →		$GeCl_2$	$SnCl_2$	$PbCl_2$
Physical states	″		Pale yellow	← White solid →	
Nature	″		Ionic bond		Ionic bond

Tetrachlorides	CCl_4	$SiCl_4$	$GeCl_4$	$SnCl_4$	$PbCl_4$
Physical states	← Colourless liquid →				Yellow liquid
Nature	Covalent bonds			Ionic bonds	
Structures	Simple molecular	Giant molecular			
Bonding	Covalent	Ionic			
Hydrides	Methane, CH_4	Silane, SiH_4	Germanane GeH_4	Stannane, SnH_4	Plumbane, PbH_4

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:

$$CO_{2(g)} + C_{(s)} \xrightarrow[\text{Heat}]{} 2CO_{(g)}$$

By dehydration of methanoic acid with concentrated sulphuric acid.

Equation:

$$HCOOH_{(l)} \xrightarrow[\text{Conc.}H_2SO_4]{} H_2O_{(l)} + CO_{(g)}$$

By the action of concentrated sulphuric acid on oxalic acid.

Equation:

$$C_2H_2O_{4(s)} \xrightarrow[\text{Conc.}H_2SO_4]{} CO_{2(g)} + CO_{(g)} + H_2O_{(l)}$$

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 reacts 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:

$$CuO_{(s)} + CO_{(g)} \longrightarrow Cu_{(s)} + CO_{2(g)}$$
$$PbO_{(s)} + CO_{(g)} \longrightarrow Pb_{(s)} + CO_{2(g)}$$
$$Fe_2O3_{(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(s)} + 3CO_{2(g)}$$

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

Equation:

$$2CO_{(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)}$$

-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:

$$SiO_{2(s)} + Si_{(s)} \longrightarrow 2SiO_{(s)}$$

-Germanium (II) oxide, GeO

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

Equation:

$$GeO_{2(s)} + Ge_{(s)} \longrightarrow 2GeO_{(s)}$$

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

Equation:

$$GeCl_{2(s)} + H_2O_{(l)} \longrightarrow GeO_{(s)} + 2HCl_{(aq)}$$

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

Equation:

$$GeCl_{2(s)} + H_2O_{(l)} \longrightarrow GeO_{(s)} + 2HCl_{(aq)}$$

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

Equations:

$$Sn(OH)_{2(s)} \longrightarrow SnO_{(s)} + H_2O_{(l)}$$
$$2Sn(NO_3)_{2(s)} \longrightarrow 2SnO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$
$$SnC_2O_{4(s)} \longrightarrow SnO_{(s)} + CO_{2(g)} + CO_{(g)}$$
$$Pb(OH)_{2(s)} \longrightarrow PbO_{(s)} + H_2O_{(l)}$$
$$2Pb(NO_3)_{2(s)} \longrightarrow 2PbO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

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_2 is acidic.

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

Equation:

$$CO_{(g)} + NaOH_{(aq)} \xrightarrow[\text{Heat}]{\longrightarrow} HCOONa_{(s)}$$

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:

$GeO_{(s)} + 2OH^-_{(aq)} + H_2O_{(l)} \longrightarrow Ge(OH)_4^{2-}{}_{(aq)}$

Or:

$GeO_{(s)} + 2OH^-_{(aq)} \longrightarrow GeO_2^{2-}{}_{(aq)} + H_2O_{(l)}$

$SnO_{(s)} + 2OH^-_{(aq)} + H_2O_{(l)} \longrightarrow Sn(OH)_4^{2-}{}_{(aq)}$

Or:

$SnO_{(s)} + 2OH^-_{(aq)} \longrightarrow SnO_2^{2-}{}_{(aq)} + H_2O_{(l)}$

$PbO_{(s)} + 2OH^-_{(aq)} + H_2O_{(l)} \longrightarrow Pb(OH)_4^{2-}{}_{(aq)}$

Or:

$PbO_{(s)} + 2OH^-_{(aq)} \longrightarrow PbO_2^{2-}{}_{(aq)} + H_2O_{(l)}$

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

Equations:

$GeO_{(s)} + 2H^-_{(aq)} \longrightarrow Ge^{2-}{}_{(aq)} + H_2O_{(l)}$

$SnO_{(s)} + 2H^-_{(aq)} \longrightarrow Sn^{2-}{}_{(aq)} + H_2O_{(l)}$

$PbO_{(s)} + 2H^-_{(aq)} \longrightarrow Pb^{2-}{}_{(aq)} + H_2O_{(l)}$

(b) Dioxides, **MO_2** where the oxidation state of the elements s **+4**.

Oxides	CO_2	SiO_2	GeO_2	SnO_2	PbO_2
M.pts(°C)	-56.5	2590	1116	1827	752**(Sublimes)**

<u>Explanations</u>:

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, CO_2.

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

Equation:

$CaCO_{3(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$

On large scale, it is prepared by heating calcium carbonate.

Equation:

$CaCO_{3(s)} \xrightarrow[\text{Heat}]{} CaO_{(s)} + CO_{2(g)}$

<u>PROPERTIES</u>:

Carbon dioxide gas is an acidic oxide.

Carbon dioxide gas is a colourless, it is moderately soluble in water forming weak carbonic acid.

Equation:

$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$

-Silicon (IV) oxide, SiO_2.

It is prepared by hydrolysis of silane.

Equation:

$$SiH_{4(g)} + 2O_{2(g)} \longrightarrow SiO_{2(s)} + 2H_2O_{(l)}$$

-Germanium (IV) oxide, GeO2.

It is prepared by hydrolysis of Germanium (II) or (IV) chloride.

Equation:

$$GeCl_{4(l)} + 2H_2O_{(l)} \longrightarrow GeO_{2(s)} + 4HCl_{(aq)}$$

-Tin (IV) oxide, SnO2.

It is prepared by the action of concentrated nitric acid on tin metal. This amphoteric oxide.

Equation:

$$Sn_{(s)} + 4HNO_{3(l)} \longrightarrow SnO_{2(s)} + 4NO_{2(g)} + 2H_2O_{(l)}$$

-Lead (IV) oxide, PbO2.

Lead (IV) oxide is prepared by the action of concentrated nitric acid on Tri lead tetra oxide.

Equation:

$$Pb_3O_{4(s)} + 4HNO_{3(l)} \longrightarrow 2Pb(NO_3)_{2(aq)} + PbO_{2(s)} + 2H_2O_{(l)}$$

It can be also be prepared by oxidizing lead (II) salt using warm sodium chlorate (I).

Equation:

$$Pb^{2+}{}_{(aq)} + 2ClO^-{}_{(aq)} + H_2O_{(l)} \longrightarrow PbO_{2(s)} + Cl^-{}_{(aq)} + 2H^+{}_{(aq)}$$

<u>Golden tips on BASICITY OF THE DIOXIDES:</u>

(a). Reaction with alkalis.

GeO2, SnO2 & PbO2 are amphoteric oxides though acidic character predominates. They reacts with hot concentrated alkalis to form complex soluble salts.

Equations:

$$GeO_{2(s)} + 2OH^-{}_{(l)} \longrightarrow GeO_3{}^{2-}{}_{(aq)} + H_2O_{(l)}$$

Or:

$$GeO_{2(s)} + 2OH^-{}_{(l)} + 2H_2O_{(l)} \longrightarrow Ge(OH)_6{}^{2-}{}_{(aq)}$$

$$SnO_{2(s)} + 2OH^-{}_{(l)} \longrightarrow SnO_3{}^{2-}{}_{(aq)} + H_2O_{(l)}$$

Or:

$$SnO_{2(s)} + 2OH^-{}_{(l)} + 2H_2O_{(l)} \longrightarrow Sn(OH)_6{}^{2-}{}_{(aq)}$$

$$PbO_{2(s)} + 2OH^-{}_{(l)} \longrightarrow PbO_3{}^{2-}{}_{(aq)} + H_2O_{(l)}$$

Or:

$$PbO_{2(s)} + 2OH^-{}_{(l)} + 2H_2O_{(l)} \longrightarrow Pb(OH)_6{}^{2-}{}_{(aq)}$$

But carbon dioxide gas is more acidic than other dioxides hence it can reacts with cold dilute alkalis to form sodium carbonate.

Equation:

$$CO_{2(g)} + 2NaOH_{(aq)} \xrightarrow[\text{Cold}]{} Na_2CO_{3(aq)} + H_2O_{(l)}$$

Note:
When carbon dioxide gas is in excess, a white precipitate of sodium hydrogen carbonate is formed.
Equation:

$$CO_{2(g)} + Na_2CO_{3(aq)} + H_2O_{(l)} \xrightarrow[\text{Excess } CO_{2(g)}]{} 2NaHCO_{3(s)}$$

(a). Reaction with acids.
Both Carbon dioxide & Silicon (IV) oxide are acidic in nature and therefore, they **<u>DON'T</u>** react with any dilute non-oxidizing acids.
Silicon dioxide (Silicon (IV) oxide) reacts **ONLY** with dilute hydrofluoric acid to form silicon tetraflouride.
Equation:

$$SiO_{2(s)} + 4HF_{(aq)} \longrightarrow SiF_{4(g)} + 2H_2O_{(l)}$$

Lead (IV) oxide reacts with warm concentrated hydrochloric acid. Which it oxidizes the acid to chlorine gas and leaves a white precipitate of lead (II) chloride.
Equation:

$$PbO_{2(s)} + 4HCl_{(l)} \longrightarrow PbCl_{2(s)} + 2H_2O_{(l)} + Cl_{2(g)}$$

Red lead oxide (Tri Lead tetra oxide) also gives a similar reactions.
Equation:

$$Pb_3O_{4(s)} + 8HCl_{(l)} \longrightarrow 3PbCl_{2(s)} + 4H_2O_{(l)} + Cl_{2(g)}$$

Notes:
When excess concentrated hydrochloric acid is reacted with lead (IV) oxide at **0^oC** it forms a complex ion.
Equation:

$$PbO_{2(s)} + 4HCl_{(aq)} + 2Cl^-_{(aq)} \longrightarrow PbCl_6{}^{2-}{}_{(aq)} + 2H_2O_{(l)}$$

Addition of concentrated ammonium chloride to the complex produces a yellow precipitate. i.e.
Equation:

$$PbCl_6{}^{2-}{}_{(aq)} + 2NH_4{}^+{}_{(aq)} \longrightarrow (NH_4)_2PbCl_{6(s)}$$

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:

$$2PbO_{2(s)} + 2H_2SO_{4(l)} \longrightarrow 2PbSO_{4(s)} + 2H_2O_{(l)} + O_{2(g)}$$

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:

$$2Pb_3O_{4(s)} + 6H_2SO_{4(l)} \longrightarrow 6PbSO_{4(s)} + 2H_2O_{(l)} + O_{2(g)}$$

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 respectivelys.
Equation:

$$Pb_3O_{4(s)} + 4HNO_{3(aq)} \longrightarrow PbO_{2(s)} + 2Pb(NO_3)_{2(aq)} + 2H_2O_{(l)}$$

Germanium & Tin (IV) oxides reacts with dilute acids to form salts and water respectively. Equations:

$$GeO_{2(s)} + 4H^+_{(aq)} \longrightarrow Ge^{4+}_{(aq)} + 2H_2O_{(l)}$$
$$SnO_{2(s)} + 4H^+_{(aq)} \longrightarrow Sn^{4+}_{(aq)} + 2H_2O_{(l)}$$

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

$$PbO_{2(s)} + S_{(s)} \longrightarrow Pb_{(s)} + SO_{2(g)}$$
$$PbO_{2(s)} + SO_{2(s)} \longrightarrow PbSO_{4(s)}$$

Red lead (Tri lead tetra oxides, Pb_3O_4).

This is a mixed oxide. It contains both lead (II) and (IV) oxides.

Equation:

$$Pb_3O_{4(s)} \xRightarrow[\text{decomposes on Heating}]{} 2PbO_{(s)} + PbO_{2(s)}$$

It can be prepared by heating lead (II) oxide in oxygen gas at a temperature of about 400°C.

Equation:

$$6PbO_{(s)} + O_{2(g)} \xrightarrow[\text{Heating}]{} 2Pb_3O_{4(s)}$$

7. 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:

$$Sn^{2+}_{(aq)} + S^{2-}_{(aq)} \longrightarrow SnS_{(s)}$$
$$Pb^{2+}_{(aq)} + S^{2-}_{(aq)} \longrightarrow \underset{\text{A Black solid}}{PbS_{(s)}}$$

B. <u>CHLORIDES:</u>

They form two types of chlorides. Namely: Dichlorides, MCl_2 and Tetrachlorides, MCl_4.However, carbon and silicon <u>**DO NOT**</u> form chlorides in the $^+2$ oxidation state.

Elements	Carbon	Silicon	Germanium	Tin	Lead
Dichlorides	-	-	Pale yellow	White solid	
Compounds	-	-	$GeCl_2$	$SnCl_2$	$PbCl_2$
Tetrachlorides	Colourless liquid				Yellow liquid
Compounds	CCl_4	$SiCl_4$	$GeCl_4$	$SnCl_4$	$PbCl_4$
Bonding	Covalent			Ionic	

B.pts(°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 Pb^{2+} to 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.

PREPARATIONS DICHLORIDES, MCL_2:

-Germanium (II) chloride is a pale yellow solid made by passing a vapour of germanium (IV) over hot germanium.

Equation:

$$GeCl_{4(g)} + Ge_{(s)} \rightleftharpoons 2GeCl_{2(s)}$$

-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 $SnCl_2.2H_2O$, Known as tin salt.

Equation:

$$Sn_{(s)} + 2HCl_{(l)} \longrightarrow SnCl_{2(s)} + H_{2(g)}$$

-Tin (II) chloride is also obtained by heating Tin in dry hydrogen chloride gas.

Equation:

$$Sn_{(s)} + 2HCl_{(g)} \longrightarrow SnCl_{2(s)} + H_{2(g)}$$

-Lead (II) chloride is a white precipitate obtained by the action of cold dilute hydrochloric acid on lead salts or a solution containing Pb^{2+} ion.

Equation:

$$Pb^{2+}{}_{(aq)} + 2Cl^{-}{}_{(aq)} \longrightarrow PbCl_{2(s)}$$

-Lead (II) chloride is also prepared by the action of hot concentrated hydrochloric acid on lead metal.

Equation:

$$Pb_{(s)} + 2HCl_{(l)} \longrightarrow PbCl_{2(s)} + H_{2(g)}$$

-Lead (II) chloride is also prepared by passing dry chlorine gas over heated lead metal.

Equation:

$$Pb_{(s)} + Cl_{2(g)} \longrightarrow PbCl_{2(s)}$$

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:

$$PbCl_{2(s)} + H_2O_{(l)} \rightleftharpoons Pb(OH)Cl_{(aq)} + HCl_{(aq)}$$

Lead (II) Chloride is sparingly soluble in water and does not undergo hydrolysis. However it dissolves on heating since solubility increases with temperature.
Equation:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

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:

$$PbCl_2(s) + 2Cl^-(aq) \rightleftharpoons [PbCl_4]^{2-}(aq)$$

REACTION WITH WATER (HYDROLYSIS) OF DICHLORIDES:

General, the dichlorides hydrolyse 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:

$$GeCl_{2(s)} + H_2O_{(l)} \longrightarrow GeO_{(s)} + 2HCl_{(aq)}$$

-Tin (II) chloride in cold water undergoes partial hydrolysis to form a (cloudy solution) or white basic hydroxide and hydrochloric acid.
Equation:

$$SnCl_{2(s)} + H_2O_{(l)} \rightleftharpoons Sn(OH)Cl_{(s)} + HCl_{(aq)}$$

Note:
However, Tin (II) chloride undergoes complete hydrolysis in hot excess water to form Tin (II) hydroxide and hydrochloric acid.
Equation:

$$SnCl_{2(s)} + 2H_2O_{(l)} \longrightarrow Sn(OH)_{2(s)} + 2HCl_{(aq)}$$

The hydrolysis is partial because the charge density of Sn2+ ion is not high enough in order for it to undergo complete hydrolysis.

REDUCING PROPERTIES OF TIN (II) CHLORIDE:

8. 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, Sn^{2+} donates two electrons to form Tin (IV) ion, Sn^{4+}.
   Equation:

$$Sn^{2+}_{(aq)} \longrightarrow Sn^{4+}_{(aq)} + 2e^-$$

9. 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:

$$Sn^{2+}_{(aq)} + 2Fe^{3+}_{(aq)} \longrightarrow Sn^{4+}_{(aq)} + 2Fe^{2+}_{(aq)}$$

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:

$$Sn^{2+}_{(aq)} + I_2 \quad [(In\ KI_{(aq)}] \longrightarrow Sn^{4+}_{(aq)} + 2I^-_{(aq)}$$

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:

$$2MnO_4^-{}_{(aq)} + 5Sn^{2+}_{(aq)} \ 16H^+_{(aq)} \longrightarrow 2Mn^{2+}_{(aq)} + 5Sn^{4+}_{(aq)} + 8H_2O_{(l)}$$

d) Potassium dichromate (VI).

Tin (II) chloride reduces acidified potassium dichloride (VI) from golden yellow solution to a green solution containing the chromium (II) ion.

Equation:

$$Cr_2O_7^{2-}{}_{(aq)} + 3Sn^{2+}_{(aq)} + 14H^+_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 3Sn^{4+}_{(aq)} + 7H_2O_{(l)}$$

PREPARATIONS TETRACHLORIDES, MCL$_4$:

-Carbon tetrachloride, CCl_4.

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:

$$CS_{2(l)} + 3Cl_{2(g)} \xrightarrow[I_2 \text{ or } FeCl_3 \text{ as a Cat}]{} CCl_{4(l)} + S_2Cl_{2(l)}$$

10. 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 a 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, $SiCl_4$, Germanium, $GeCl_4$ & Tin tetrachloride, $SnCl_4$ are prepared by direct synthesis (passing dry chlorine gas).

Equations:

$Si_{(s)} + Cl_{2(g)} \longrightarrow SiCl_{4(l)}$ At a temperature of 720K

$Ge_{(s)} + 2Cl_{2(g)} \longrightarrow GeCl_{4(g)}$ " " " " 340-450K

$Sn_{(s)} + 2Cl_{2(g)} \longrightarrow SnCl_{2(l)}$

-Silicon tetrachloride, $SiCl_4$ can also be prepared by passing dry heated chlorine gas over a mixture of silica and carbon.

Equation:

$$SiO_{2(s)} + 2C_{(s)} + 2Cl_{2(g)} \longrightarrow SiCl_{4(l)} + 2CO_{(g)}$$

-Lead tetrachloride, $PbCl_4$ can be prepared by the action of cold concentrated hydrochloric acid on lead (IV) oxide and it's obtained as a yellow liquid.

Equation:

$$PbO_{2(s)} + 4HCl_{(l)} \longrightarrow PbCl_{4(l)} + 2H_2O_{(l)}$$

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:

$$PbCl_{4(l)} \longrightarrow PbCl_{2(s)} + Cl_{2(g)}$$

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.

11. The thermal stability of the tetrachlorides are in the order of $CCl_4 > SiCl_4 > GeCl_4 > SnCl_4 > PbCl_4$.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.
12. 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.
    $PbO_{2(s)} + 4HCl_{(l)} \longrightarrow PbCl_{2(s)} + Cl_{2(g)} + 2H_2O_{(l)}$

REACTION OF TETRACHLORIDES WITH WATER (HYDROLYSIS):

13. 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 $SiCl_4 > GeCl_4 > SnCl_4 > PbCl_4$.

-$SiCl_4$ is highly hydrolysed even in damp air because Si^{4+} ion has the highest charge density. It strongly attract the lone pair of electron from water while Pb^{4+} ion has the least charge density and $PbCl_4$ is least hydrolyzed.

Equations:

$$SiCl_{4(l)} + 4H_2O_{(l)} \longrightarrow SiO_2.2H_2O_{(s)} + 4HCl_{(aq)}$$
$$GeCl_{4(l)} + 2H_2O_{(l)} \longrightarrow GeO_{2(s)} + 4HCl_{(aq)}$$
$$SnCl_{4(l)} + 4H_2O_{(l)} \longrightarrow SnO.2H_2O_{(s)} + 4HCl_{(aq)}$$
$$PbCl_{4(l)} + 4H_2O_{(l)} \longrightarrow PbO_2.2H_2O_{(s)} + 4HCl_{(aq)}$$

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°C in the presence of dry ether.

Equations:

$$SiCl_{4(l)} \longrightarrow SiH_{4(g)} + AlCl_{3(s)} + LiCl_{(s)}$$
$$GeCl_{4(l)} \longrightarrow GeH_{4(g)} + AlCl_{3(s)} + LiCl_{(s)}$$
$$SnCl_{4(l)} \longrightarrow SnH_{4(g)} + AlCl_{3(s)} + LiCl_{(s)}$$
$$PbCl_{4(l)} \xrightarrow[LiAlH_{4(s)}/Ether/0C]{} PbH_{4(g)} + AlCl_{3(s)} + LiCl_{(s)}$$

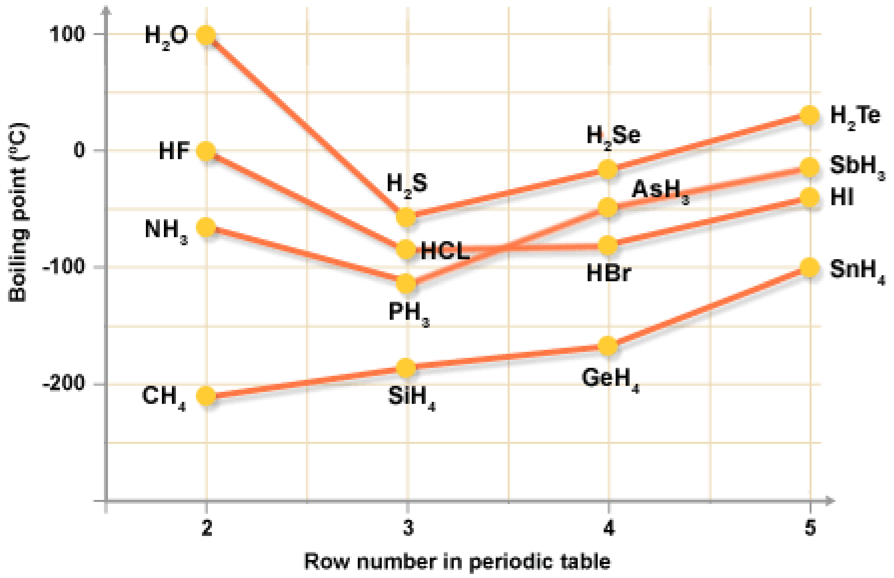
Methane is made by decarboxylation of sodium ethanoate,

Equation:

$$CH_3COONa_{(s)} \xrightarrow[Ca(OH)_2/NaOH_{(s)}]{Heat} CH_{4(g)} + Na_2CO_{3(s)}$$

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 $CH_4 < SiH_4 < GeH_4 < SnH_4 < PbH_4$.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:

  $$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$$
  $$SiH_{4(g)} + 2O_{2(g)} \longrightarrow SiO_{2(g)} + 2H_2O_{(l)}$$
  $$GeH_{4(g)} + 2O_{2(g)} \longrightarrow GeO_{2(g)} + 2H_2O_{(l)}$$
  $$SnH_{4(g)} + 2O_{2(g)} \longrightarrow SnO_{2(g)} + 2H_2O_{(l)}$$
  $$PbH_{4(g)} + 2O_{2(g)} \quad \text{Heating} \quad PbO_{2(g)} + 2H_2O_{(l)}$$
- 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:

  $$SiH_{4(g)} + 2OH^{-}_{(aq)} + H_2O_{(l)} \longrightarrow SiO_3{}^{2-}{}_{(aq)} + 4H_{2(g)}$$
  Or
  $$SiH_{4(g)} + 4H_2O_{(l)} \longrightarrow Si(OH)_{4(s)} + 4H_{2(g)}$$
  $$SnH_{4(g)} + 2OH^{-}_{(aq)} + H_2O_{(l)} \longrightarrow SnO_3{}^{2-}{}_{(aq)} + 4H_{2(g)}$$
  Or
  $$SnH_{4(g)} + 4H_2O_{(l)} \longrightarrow Sn(OH)_{4(s)} + 4H_{2(g)}$$

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:

$SiH_{4(g)} + HCl_{(aq)} \longrightarrow SiCl_{4(l)} + 4H_{2(g)}$

$PbH_{4(l)} + HCl_{(aq)} \longrightarrow PbCl_{4(l)} + 4H_{2(g)}$

<u>IDENTIFICATIONS OF Pb^{2+}, Sn^{2+} and Sn^{4+}:</u>

Dilute sodium hydroxide solution until in excess:
A white precipitate soluble in excess forming colourless solution.
Equations:

$Pb^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Pb(OH)_{2(s)}$

$Pb(OH)_{2(s)} + 2OH^{-}_{(aq)} \longrightarrow Pb(OH)_4{}^{2-}{}_{(aq)}$

$Sn^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Sn(OH)_{2(s)}$

$Sn(OH)_{2(s)} + 2OH^{-}_{(aq)} \longrightarrow Sn(OH)_4{}^{2-}{}_{(aq)}$

$Sn^{4+}_{(aq)} + 4OH^{-}_{(aq)} \longrightarrow Sn(OH)_{4(s)}$

$Sn(OH)_{(s)} + 2OH^{-}_{(aq)} \longrightarrow Sn(OH)_6{}^{2-}{}_{(aq)}$

Dilute ammonium hydroxide solution until in excess:
A white precipitate insoluble in excess.
Equations:

$Pb^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Pb(OH)_{2(s)}$

$Sn^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Sn(OH)_{2(s)}$

$Sn^{4+}_{(aq)} + 4OH^{-}_{(aq)} \longrightarrow Sn(OH)_{4(s)}$

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.

Sodium sulphate/dilute sulphuric acid.
A white precipitate insoluble on warming.
Equation:

$Pb^{2+}_{(aq)} + SO_4{}^{2-}{}_{(aq)} \longrightarrow PbSO_{4(s)}$

No observable change occurs with both Sn^{2+} & Sn^{4+}.

Dilute hydrochloric acid /sodium chloride solution.
A white precipitate, soluble on warming (hot water).
Equation:

$Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \longrightarrow PbCl_{2(s)}$

A white precipitate dissolves on warming and reappears on cooling, the precipitate dissolves in concentrated hydrochloric acid forming a complexes.
Equation:

$PbCl_{2(s)} + 2Cl^{-}_{(aq)} \longrightarrow PbCl_4{}^{2-}{}_{(aq)}$

No observable change occurs with both Sn^{2+} & Sn^{4+}.

Potassium iodide solution.
A yellow precipitate, soluble on heating to form a colourless solution.

Equation:

$$Pb^{2+}_{(aq)} + 2I^{-}_{(aq)} \longrightarrow PbI_{2(s)}$$

Potassium chromate solution.

A yellow precipitate insoluble in ethanoic acid.

Equation:

$$Pb^{2+}_{(aq)} + CrO_4{}^{2-}_{(aq)} \longrightarrow PbCrO_{4(s)}$$

Acidified potassium permanganate (VII) solution.

The purple colour of acidified potassium permanganate (VII) solution turns from purple to colourless.

Equation:

$$2MnO_4{}^{-}_{(aq)} + 5Sn^{2+}_{(aq)} + 16H^{+}_{(aq)} \longrightarrow 2Mn^{2+}_{(aq)} + 5Sn^{4+}_{(aq)} + 8H_2O_{(l)}$$

Purple To Colourless

Mercury (II) chloride solution.

A white precipitate that slowly turns grey.

Equation:

$$Sn^{2+}_{(aq)} + 2HgCl_{2(aq)} \longrightarrow Hg_2Cl_{2(s)} + Sn^{4+}_{(aq)} + 2Cl^{-}_{(aq)}$$

Ammonium sulphide/Hydrogen sulphide solution.

A black precipitate, soluble in dilute nitric acid.

Equation:

$$Pb^{2+}_{(aq)} + S^{2-}_{(aq)} \longrightarrow PbS_{(s)}$$

14. 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:
    $$Sn^{2+}_{(aq)} + 2Fe^{3+}_{(aq)} \longrightarrow Sn^{4+}_{(aq)} + 2Fe^{2+}_{(aq)}$$
    The Iron (II) in solution reacts with the sodium hydroxide to form Iron (II) hydroxide.
    Equation:
    $$Fe^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Fe(OH)_{2(s)}$$
    (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:
    $$Pb_3O_{4(s)} + 4HNO_{3(l)} \longrightarrow 2Pb(NO_3)_{2(aq)} + PbO_{2(s)} + 2H_2O_{(l)}$$
15. The resultant mixture in 14 (b) above is filtered to obtain the residue and the filtrate.
    (a) To the 1st 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:

$$Pb^{2+}_{(aq)} + 2I^{-}_{(aq)} \longrightarrow PbI_{2(s)}$$

(b) To the 2nd 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:

$$Pb^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Pb(OH)_{2(s)}$$
$$Pb(OH)_{2(s)} + 2OH^{-}_{(aq)} \longrightarrow Pb(OH)_4{}^{2-}{}_{(aq)}$$

(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:

$$PbO_{2(s)} + 4HCl_{(l)} \longrightarrow PbCl_{2(s)} + 2H_2O_{(l)} + Cl_{2(g)}$$

16. 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 **250cm³** 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	**RADIOACTIVE ELEMENT**				
Elements	**Fluorine, $_9$F**	**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:

$$X + e \longrightarrow X^-$$

- Melting (and also Boiling) points:
  Melting (and also Boling) 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 mas 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:
  $X_{2(g)} \longrightarrow 2X_{(g)}$ H = Bond energy of X-X bond.
  Bond energy usually decreases with increase in bond length.
  Bond energy generally decreases down the group. This is because down the group, atomic radius increases hence causing an increase in bond length of (X-X).The longer the bond, the weaker it is.Flourine 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.

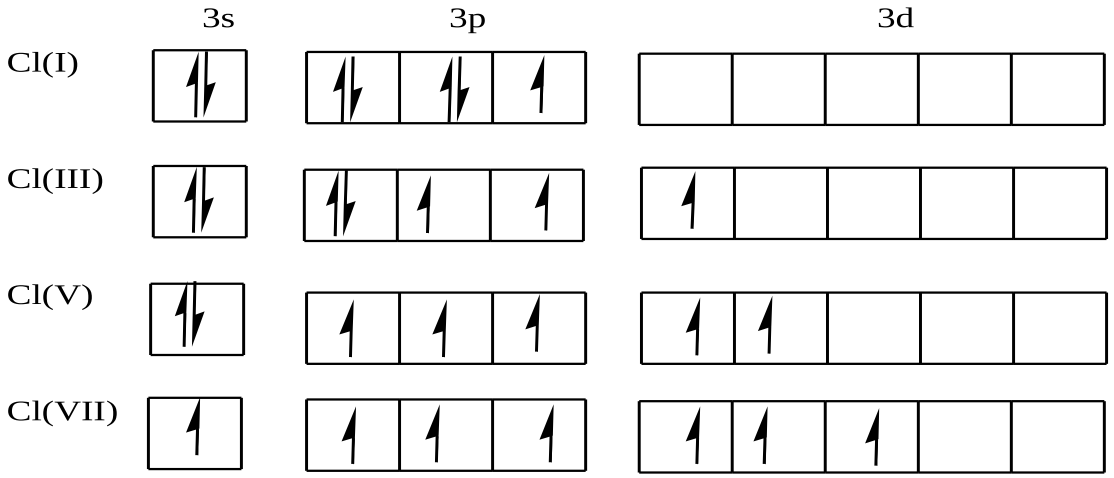
OXIDATION STATES OF THE HALOGENS

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 17Cl $1s^22s^22p^63s^23p^5$



Examples

Compounds	HCl	HOCl	$HClO_2$	$HClO_3$	$HClO_4$
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:

17. 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.

18. 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
19. State reasons why Fluorine behaves differently from the rest of the members due.
    - Low bond energy
    - High electronegativity
    - Small atomic radius
    - High electrode potential
20. 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 tetra 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:

21. Discuss the reaction of halogens with the followings:
    a) Nonmetals:

OXIDATION REACTIONS:

(i) Iron (II) to Iron (III).

Fluorine, Chlorine, Bromine & Iodine are shaken with a solution of iron (II) sulphate, it oxidizes Fe^{2+} to Fe^{3+} ions.

Equation:

$$2Fe^{2+}_{(aq)} + Cl_{2(g)} \longrightarrow 2Fe^{3+}_{(aq)} + 2Cl^{-}_{(aq)}$$

Or:

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

(ii) Tin (II) to Tin (IV).

Fluorine, Chlorine, Bromine & Iodine oxidizes Tin (II) to Tin (IV) ion.

Equations:

$$Sn^{2+}_{(aq)} + Cl_{2(g)} \longrightarrow Sn^{4+}_{(aq)}$$

$$Sn^{2+}_{(aq)} + Br_{2(g)} \longrightarrow Sn^{4+}_{(aq)}$$

$$Sn^{2+}_{(aq)} + I_{2(g)} \longrightarrow Sn^{4+}_{(aq)}$$

(iii) Sulphite ions (saturated solution of sulphur dioxide)

They all oxidizes sulphites ion to sulphates ions.

Equations:

$SO_3^{2-}{}_{(aq)} + Cl_{2(g)} + H_2O_{(l)} \longrightarrow SO_4^{2-}{}_{(aq)} + 2H^+_{(aq)} + 2Cl^-_{(aq)}$
$SO_3^{2-}{}_{(aq)} + I_{2(g)} + H_2O_{(l)} \longrightarrow SO_4^{2-}{}_{(aq)} + 2H^+_{(aq)} + 2I^-_{(aq)}$
$SO_3^{2-}{}_{(aq)} + Br_{2(g)} + H_2O_{(l)} \longrightarrow SO_4^{2-}{}_{(aq)} + 2H^+_{(aq)} + 2Br^-_{(aq)}$

Sodium thiosulphate
Chlorine reacts with sodium thiosulphate to form sulphate ion with a deposit of yellow solid.
Equation:

$$S_2O_3^{2-}{}_{(aq)} + Cl_{2(g)} + H_2O_{(l)} \longrightarrow SO_4^{2-}{}_{(aq)} + 2Cl^-_{(aq)} + S_{(s)}$$

When chlorine and bromine is in excess, being a stronger oxidizing agent than iodine, it oxidizes the thiosulphate ion to sulphate ion.
Equations:

$$S_2O_3^{2-}{}_{(aq)} + 4Cl_{2(g)} + 5H_2O_{(l)} \longrightarrow 2SO_4^{2-}{}_{(aq)} + 10H^+_{(aq)} + 8Cl^-_{(aq)}$$

Iodine oxidizes thiosulphate ion to tetrathionate ion.
Equation:

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

(iv) Hydrogen sulphide
They all oxidizes hydrogen sulphide gas to a yellow solid of sulphur.
Equations:

$F_{2(g)} + H_2S_{(g)} \longrightarrow 2HF_{(g)} + S_{(s)}$
$Cl_{2(g)} + H_2S_{(g)} \longrightarrow 2HCl_{(g)} + S_{(s)}$
$Br_{2(g)} + H_2S_{(g)} \longrightarrow 2HBr_{(g)} + S_{(s)}$
$I_{2(g)} + H_2S_{(g)} \longrightarrow 2HI_{(g)} + S_{(s)}$

(v) Phosphorous.
Heated phosphorous reacts with dry both bromine and chlorine gas to form phosphorous trichloride.
Equations:

$P_{4(s)} + 6Cl_{2(g)} \longrightarrow 4PCl_{3(l)}$
$P_{2(s)} + 3Br_{2(g)} \longrightarrow 2PBr_{3(l)}$

If more chlorine gas is passed over heated phosphorous, both phosphorous tri bromide or chloride and pentabromide or chloride are formed respectively.
Equations:

$PCl_{3(l)} + Cl_{2(g)} \longrightarrow PCl_{5(s)}$
$PBr_{3(l)} + Br_{2(g)} \longrightarrow PBr_{5(s)}$

But Iodine forms only phosphorous triiodine.
Equation:

$$P_{2(s)} + 3I_{2(l)} \longrightarrow 2PI_{3(l)}$$

(vi) Hydrogen gas.
Fluorine gas explodes in hydrogen gas to form hydrogen fluoride.
Equation:

$$F_{2(g)} + H_{2(g)} \longrightarrow 2HF_{(g)}$$

Reaction with Chlorine gas is slow in diffuse light but explosive in sunlight or ultra violet light but very slow in darkness.

Equation:

$$Cl_{2(g)} + H_{2(g)} \longrightarrow 2HCl_{(g)}$$

Both bromine and iodine only reacts with hydrogen gas in the presence of a catalyst at high temperature (Heat).

Equations:

$$Br_{2(g)} + H_{2(g)} \xrightarrow{Pt/200} 2HBr_{(g)}$$

$$I_{2(g)} + H_{2(g)} \xrightarrow[Pt/400]{} 2HI_{(g)}$$

(vii) Sulphur.

Both Bromine & Chlorine gases reacts with molten sulphur to give disulphur dichloride, which is a yellow liquid.

Equations:

$$Cl_{2(g)} + 2S_{(s)} \longrightarrow S_2Cl_{2(l)}$$

$$Br_{2(g)} + 2S_{(s)} \longrightarrow S_2Br_{2(l)}$$

Both Fluorine and iodine gases **<u>DONOT</u>** reacts with molten sulphur.

(viii) Water

Fluorine reacts with cold water, forming hydrogen fluoride and oxygen gas.

Equation:

$$2F_{2(g)} + 2H_2O_{(l)} \rightleftharpoons 4HF_{(g)} + O_{2(g)}$$

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:

$$Cl_{2(g)} + 2H_2O_{(l)} \rightleftharpoons Cl^-_{(aq)} + H_3O^+_{(aq)} + HClO_{(aq)}$$

$$Br_{2(g)} + 2H_2O_{(l)} \rightleftharpoons Br^-_{(aq)} + H_3O^+_{(aq)} + HOBr_{(aq)}$$

Iodine is very sparingly soluble in water and the reaction is reversible in which oxygen gas oxidizes the iodide ion back to iodine.

22. Define the term Disproportionation?

Disproportionation is a reaction in which the same species undergoes simultaneous oxidation and reduction.

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:

$$2Fe_{(s)} + 3Cl_{2(g)} \longrightarrow 2FeCl_{3(s)}$$

c) Alkalis

(i) Cold dilute alkalis

Fluorine reacts with cold dilute alkalis to form the following products in the equation below.

Equation:

$$2F_{2(g)} + 2OH^-_{(aq)} \longrightarrow OF_{2(g)} + 2F^-_{(aq)} + H_2O_{(l)}$$

Both Chlorine and Bromine produces a pale yellow solution of akalis chlorate & bromate (I), alkalis chloride & bromide and water respectively.

Equations:

$$Cl_{2(g)} + 2OH^-_{(aq)} \longrightarrow OCl^-_{(aq)} + Cl^-_{(aq)} + H_2O_{(l)}$$
$$Br_{2(g)} + 2OH^-_{(aq)} \longrightarrow OBr^-_{(aq)} + Br^-_{(aq)} + H_2O_{(l)}$$

Notes:

The sodium chlorate (I) and sodium bromate (I) formed above disproportionate at temperature above 70°C. i.e,

Equations:

$$3OCl^-_{(aq)} \longrightarrow 2Cl^-_{(aq)} + ClO_3^-{}_{(aq)}$$
$$3OBr^-_{(aq)} \longrightarrow 2Br^-_{(aq)} + BrO_3^-{}_{(aq)}$$

(ii) Hot concentrated alkalis

Fluorine reacts with hot concentrated sodium hydroxide solution.

Equation:

$$2F_{2(g)} + 4OH^-_{(aq)} \longrightarrow 4F^-_{(aq)} + 2H_2O_{(l)} + O_{2(g)}$$

Chlorine, Bromine & Iodine reacts with hot concentrated alkalis the products below.

Equations:

$$3Cl_{2(g)} + 6OH^-_{(aq)} \longrightarrow ClO_3^-{}_{(aq)} + 5Cl^-_{(aq)} + 3H_2O_{(l)}$$
$$3Br_{2(g)} + 6OH^-_{(aq)} \longrightarrow BrO_3^-{}_{(aq)} + 5Br^-_{(aq)} + 3H_2O_{(l)}$$
$$3I_{2(g)} + 6OH^-_{(aq)} \longrightarrow IO_3^-{}_{(aq)} + 5I^-_{(aq)} + 3H_2O_{(l)}$$

23. Discus how the followings are prepared in the laboratory.
    a) Potassium chlorate (V) or Potassium bromate (V) & Potassium iodate (V).
    b) 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:

$$Cl_{2(g)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)} + HOCl_{(aq)}$$

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:

$$Cl_{2(g)} + H_2O_{(l)} \rightleftharpoons HOCl_{(aq)} + HCl_{(aq)}$$
$$HOCl_{(aq)} + \underset{\text{Coloured}}{\text{dye}} \longrightarrow HCl_{(aq)} + \underset{\text{Colourless}}{\text{Oxidised Dye}}$$

The 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:

$$CaF_{2(s)} + H_2SO_{4(l)} \longrightarrow CaSO_{4(s)} + 2HF_{(g)}$$

-Hydrogen Chloride, HCl.

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

Equation:

$$2NaCl_{(s)} + H_2SO_{4(l)} \longrightarrow Na_2SO_{4(aq)} + 2HCl_{(g)}$$

-Hydrogen Bromide, HBr.

Both hydrogen bromide and hydrogen iodide are prepared by hydrolysis of phosphorous tribromide and triiodide respectively.

Equations:

$$PBr_{3(l)} + 3H_2O_{(l)} \longrightarrow H_3PO_{3(aq)} + 3HBr_{(g)}$$

$$PI_{3(s)} + 3H_2O_{(l)} \longrightarrow H_3PO_{3(aq)} + 3HI_{(g)}$$

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^{Ka}	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 p^{Ka} 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 the weaker the bond the stronger is the acid. Hydrofluoric acid is a weaker which is slightly ionized in aqueous solution.

  Equation:

  $$HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$$

  Moist hydrogen fluoride and aqueous solution of the acid attack silica and glass, so the solution is stored in polythene containers.

  Equation:

  $$SiO_{2(s)} + 4HF_{(aq)} \longrightarrow SiF_{4(g)} + 2H_2O_{(l)}$$

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), Cl_2O

- 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:

  $$2HgO_{(s)} + 2Cl_{2(g)} \longrightarrow HgO.HgCl_{2(s)} + \underset{\text{Yellow gas}}{Cl_2O_{(g)}}$$

  Note:

  The yellow gas reacts with water forming chloric (I) acid (Hypochlorous acid), so acting as the anhydride of this acid.

  Equation:

  $$Cl_2O_{(g)} + H_2O_{(l)} \longrightarrow 2HOCl_{(aq)}$$

(ii) Chlorine dioxide, ClO_2

- Chlorine dioxide is prepared by the action of concentrated sulphuric acid on potassium chlorate (V) in the present of heat.

  Equation:

  $$3ClO_3^-{}_{(s)} + 2H^+(\text{Conc.l}) \longrightarrow 2ClO_{2(g)} + ClO_4^-{}_{(aq)} + H_2O_{(l)}$$

Or:

- ✍ Chlorine dioxide is prepared also by the action of dry chlorine gas on silver chlorate (V) at a temperature of about 360K.

  Equation:

  $$2ClO_3^-{}_{(s)} + Cl_{2(g)} \longrightarrow 2ClO_{2(g)} + 2Cl^-_{(Conc.aq)} + O_{2(g)}$$

  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:

  $$\underset{\text{Reddish-Yellow gas}}{2ClO_{2(g)}} + H_2O_{(l)} \longrightarrow \underset{\text{Chloric (V) acid}}{HClO_{3(aq)}} + \underset{\text{Chloric (III) acid}}{HClO_{2(aq)}}$$

(iii) Dichlorine heptoxide, Cl_2O_7

- ✍ Dichlorine hetoxide 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:

  $$2HClO_{4(l)} \xrightarrow[\text{Dehydration } H^+ \text{ from Acid}]{-H_2O_{(l)}} Cl_2O_{7(l)}$$

  Note:

  Dichlorine hetoxide reacts with water to form chloric (VII) acid.

  Equation:

  $$Cl_2O_{7(l)} + H_2O_{(l)} \longrightarrow 2HClO_{4(l)}$$

(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:

  $$HgO_{(s)} + 2Cl_{2(g)} + H_2O_{(l)} \longrightarrow HgCl_{2(aq)} + 2HClO(aq)$$

  Note:

  Chloric acid is a weak acid and it liberates oxygen gas under the action of sunlight exposure.

  Equation:

  $$2HClO_{(aq)} \xrightarrow[\text{Sunlight}]{} 2HCl_{(l)} + O_{2(g)}$$

  Hypochlorous acid is also decomposed by heat.

  Equation:

  $$3HClO_{(aq)} \xrightarrow[\text{Heat}]{} 2HCl_{(l)} + HClO_{3(g)}$$

  The acid liberate oxygen gas when warmed with cobalt (II) salt present as a catalyst.

  Equation:

  $$2ClO^-_{(aq)} \xrightarrow[\text{Warm}]{} 2Cl^-_{(aq)} + O_{2(g)}$$

  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:

$$2Fe^{2+}_{(aq)} + 2H^{+}_{(aq)} + ClO^{-}_{(aq)} \longrightarrow 2Fe^{3+}_{(aq)} + H_2O_{(l)} + Cl^{-}_{(aq)}$$

$$\underbrace{2I^{-}_{(aq)} + 2H^{+}_{(aq)}}_{\text{Acidified KI solution}} + ClO^{-}_{(aq)} \longrightarrow H_2O_{(l)} + Cl^{-}_{(aq)} + Cl^{-}_{(aq)} + I_{2(s)}$$

$$SO_3{}^{2-}_{(aq)} + ClO^{-}_{(aq)} \longrightarrow SO_4{}^{2-}_{(aq)} + Cl^{-}_{(aq)}$$

(iii) Chloric (V) acid, $HClO_3$.

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.

Eqution:

$$Ba(ClO_3)_{2(aq)} + H_2SO_{4(aq)} \longrightarrow BaSO_{4(s)}\downarrow + 2HClO_{3(aq)}$$

Note:

If heated, Chloric (V) acid decompose to some useful products.

Equation:

$$3HClO_{3(aq)} \longrightarrow HClO_{4(aq)} + 2ClO_{2(g)} + H_2O_{(l)}$$

Note:

Chloric acid and its salts like sodium chlorate are powerful oxidizing agents in solution.

Equation:

$$ClO_3{}^{-}_{(aq)} + 6H^{+}_{(aq)} + 6e \longrightarrow Cl^{-}_{(aq)} + 3H_2O_{(l)}$$

Similarly, bromates (V) and iodates (V) ions are powerful oxidizing agents.

Equations:

$$BrO_3{}^{-}_{(aq)} + 6H^{+}_{(aq)} + 6e \longrightarrow Br^{-}_{(aq)} + 3H_2O_{(l)}$$

$$IO_3{}^{-}_{(aq)} + 6H^{+}_{(aq)} + 6e \longrightarrow I^{-}_{(aq)} + 3H_2O_{(l)} \longrightarrow 1$$

The iodate (V) ion oxidizes iodide ions then to iodine.

Equation:

$$2I^{-}_{(aq)} \longrightarrow I_{2(aq)} + 2e \longrightarrow 2$$

The overall reaction equation between iodate (V) ions and iodide ion is:

$$IO_3{}^{-}_{(aq)} + 5I^{-}_{(aq)} + 6H^{+}_{(aq)} \longrightarrow 3I_{2(aq)} + 3H_2O_{(l)} \longrightarrow 3$$

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), $HClO_4^-$.

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:

$$Cl_{2(g)} + 2NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + NaOCl_{(aq)} + H_2O_{(l)}$$

However, in water chlorine reacts reversibly to form hydrochloric acid and chloric (I) acid.

Equation:

$$Cl_{2(g)} + H_2O_{(l)} \rightleftharpoons HCl_{(aq)} + HOCl_{(aq)}$$

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
$HClO_2$	Chloric (III) acid
$HClO_3$	Chloric (V) acid
$HClO_4$	Chloric (VII) acid

$$3Cl_{2(g)} + 6KOH_{(aq)} \longrightarrow 5KCl_{(aq)} + KClO_{3(aq)} + 3H_2O_{(l)}$$

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
$HClO_2$	Chloric (III) acid
$HClO_3$	Chloric (V) acid
$HClO_4$	Chloric (VII) acid

↓
Thermal stability increases
Acid strength increases
Oxidizing power increases

Oxidation States	Acid			Anion	
	Formula	Systematic name	Traditional name	Formula	Systematic name
$^+1$	$HOCl$	Chloric (I) acid	Hypochlorous	OCl^-	Chlorate (I)
$^+3$	$HClO_2$	Chloric (III) acid	Chlorous	ClO_2^-	Chlorate (III)
$^+5$	$HClO_3$	Chloric (V) acid	Chloric	ClO_3^-	Chlorate (V)
$^+7$	$HClO_4$	Chloric (VII) acid	Perchloric	ClO_4^-	Chlorate (VII)

$HClO_4 > HClO_3 > HClO_2 > HClO$ [Or] $HClO < HClO_2 < HClO_3 < HClO_4$.

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:

$HClO$ or $HOCl > HClO_2 > HClO_3 > HClO_4$.

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+ 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:

$H_2S < H_2Se < H_2Te$

Increasing acid strength →
Increasing nonmetal radius →
← Increasing electronegativity of X

- 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_2S	H_2Se	H_2Te
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.

$PH_3 < H_2S < HCl$

Increasing acid strength →
← Increasing nonmetal radius
Increasing electronegativity of X →

	PH_3	H_2S	HCl
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,HNO_3 is stronger than the 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 H_2S
     - 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 H_2S.
   - $HClO_3$ or $HBrO_3$
     - Within this group the strengths of the acids increases with increasing electronegativity of the central atom. The electronegativity values of Cl^- ion is greater than that of Br^- ion.
   - H_3PO_3 or H_3PO_4
     - H_3PO_3 & H_3PO_4 are oxoacids of the same element. The acid strength increases as the number of oxygen atoms increase. H_3PO_4 is the stronger acid because of the greater number of oxygen atoms bonded to the phosphorus atom. In H_3PO_4, phosphorus has a higher oxidation number than H_3PO_3.

Oxidizing power and thermal stability: The oxidizing power of these acids decreases as the oxidation number increases in the order of $HClO < HClO_2 < HClO_3 < HClO_4$. Stability of Oxo acids of chlorine in the increasing order is, $HClO < HClO_2 < HClO_3 < HClO_4$ and the increasing stability order of anions of Oxo acids of chlorine is, $CIO^- < CIO_2^- < CIO_3^- < CIO_4^-$. 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 name oxidation number, the thermal stability decreases with increase in atomic number *i.e.*, it is in the order $HClO > HBrO > HIO$ *and* $ClO^- > BrO^- > IO^-$ However, in HXO_3 is most stable. The stability order being $HClO_3 < HBrO_3 < HIO_3$.

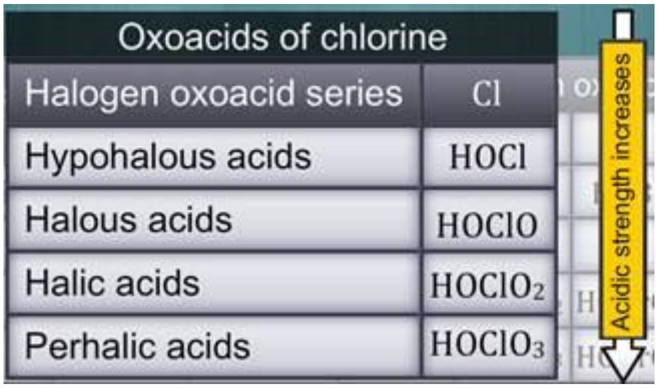
The acidity of Oxo acids of different halogens having the same oxidation number decreases with increase in the atomic size of the halogen i.e. $HCIO_4 > HBrO_4 > HIO_4$.

Reasons why different halogen having the same oxidation states decreases in the order of: $HClO_3 < HBrO_3 < HIO_3$ or $HClO_4 > HBrO_4 > HIO_4$.

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.

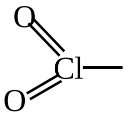
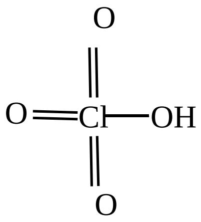
Example:

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	HOCl
Halous acids	HOClO
Halic acids	$HOClO_2$
Perhalic acids	$HOClO_3$

Oxy acid	Formula	structure (Not accurate)
Chloric (I) acid	HClO	Cl—O—H
Chloric (III) acid	$HClO_2$	O═Cl —OH
Chloric (V) acid	$HClO_3$	
Chloric (VII) acid	$HClO_4$	

ACIDIC STRENGTH:

Acidic strength of the acids decreases in the order of: $HClO_4 > HClO_3 > HClO_2 > HClO$ and increases in the order of: HClO or HOCl $>$ $HClO_2 > HClO_3 > HClO_4$.

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 $HClO_4 > HClO_3 > HClO_2 > HClO$.

Or:

The greater the number of oxygen atoms the acid has, the greater the acidity. Therefore Perhalic acid, $HClO_4$ 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: $HClO < HClO_2 < HClO_3 < HClO_4$.

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 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 is able to 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:

$HClO_4 > HClO_3 > HClO_2 > HClO$

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 *(HXO)*, halous acid *(HXO_2)* halic acid *(HXO_3)* and perhalic acid *(HXO_4).*

REACTIONS OF OXIDES OF CHLORINE WITH SODIUM HYDROXIDE SOLUTION:

EQUATIONS:

$Cl_2O_{(g)} + 2NaOH_{(aq)} \longrightarrow 2NaOCl_{(aq)} + H_2O_{(l)}$

Orange

$2ClO_{2(g)} + 2NaOH_{(aq)} \longrightarrow NaClO_{2(aq)} + NaClO_{3(aq)} + H_2O_{(l)}$

Yellow

$Cl_2O_{6(l)} + 2NaOH_{(aq)} \longrightarrow NaClO_{3(aq)} + NaClO_{4(aq)} + H_2O_{(l)}$

Red

$Cl_2O_{7(l)} + 2NaOH_{(aq)} \longrightarrow 2NaClO_{4(aq)} + H_2O_{(l)}$

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, 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, Cl^- ion. The precipitate dissolves in excess ammonia due to formation of complex ion.

Equation:

$$Ag^+_{(aq)} + Cl^-_{(aq)} \longrightarrow \underset{\text{White precipitae}}{AgCl_{(s)}}$$

$$AgCl_{(s)} + 2NH_{3(aq)} \longrightarrow Ag(NH_3)_2{}^+_{(aq)} + Cl^-_{(aq)}$$

Observation:

✍ Formation of a cream precipitate (or pale yellow) indicates the presence of bromide, Br- ion.

Equation:

$$Ag^+_{(aq)} + Br^-_{(aq)} \longrightarrow \underset{\text{Pale yellow or Cream precipitate}}{AgBr_{(s)}}$$

Observation:

✍ Formation of a yellow precipitate indicates the presence of iodide ion, I- ion.

Equation:

$$Ag^+_{(aq)} + I^-_{(aq)} \longrightarrow \underset{\text{Yellow precipitate}}{AgI_{(s)}}$$

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, Cl^- ion.

Equation:

$$MnO_{2(s)} + 4H^+_{(aq)} + 2Cl^-_{(aq)} \longrightarrow Mn^{2+}_{(aq)} + Cl_{2(g)} + 2H_2O_{(l)}$$

✍ Evolution of brown fumes (reddish) shows the presence of bromide, Br^- ion.

Equation:

$$MnO_{2(s)} + 4H^+_{(aq)} + 2Br^-_{(aq)} \longrightarrow Mn^{2+}_{(aq)} + Br_{2(g)} + 2H_2O_{(l)}$$

✍ Evolution of a purple vapour (or dark solution) shows the presence of iodide, I^- ion.

Equation:

$$MnO_{2(s)} + 4H^{+}_{(aq)} + 2I^{-}_{(aq)} \longrightarrow Mn^{2+}_{(aq)} + I_{2(g)} + 2H_2O_{(l)}$$

Notes:

A mixture of manganese (IV) oxide and concentrated sulphuric acid are very powerful oxidizing agent which oxidizes chloride, Cl- ,bromide, Br^- ,& iodide, I^- ions to chlorine, bromide & 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, Cl^- or bromide, Br^- ions.

Equations:

$$\left.\begin{array}{l} Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \longrightarrow PbCl_{2(s)} \\ Pb^{2+}_{(aq)} + 2Br^{-}_{(aq)} \longrightarrow PbBr_{2(s)} \end{array}\right\} \text{White precipitate}$$

✍ Note:
white precipitate of Bromide, Br^- ion soluble in hot water.

✍ Formation of a yellow precipitate soluble on heating shows the presence of iodide, I^- ion.

Equation:

$$Pb^{2+}_{(aq)} + 2I^{-}_{(aq)} \longrightarrow \underset{\text{Yellow precipitate}}{PbI_{2(s)}}$$

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 $3cm^3$ of carbon tetrachloride. Shake well and allow to settle.

Observations:

✍ A brown (or red) carbon tetrachloride layer shows the presence of bromide, Br^- ion.

Reason:

☞ This is because the reagent oxidizes bromide, Br^- ion to bromine which is dissolves in carbon tetrachloride layer turning to brown.

✍ A purple (or violet) carbon tetrachloride layer shows the presence of iodide, I^- ion.

Qn: Describe how the hydrides of group (VII) elements are prepared in the Laboratory.

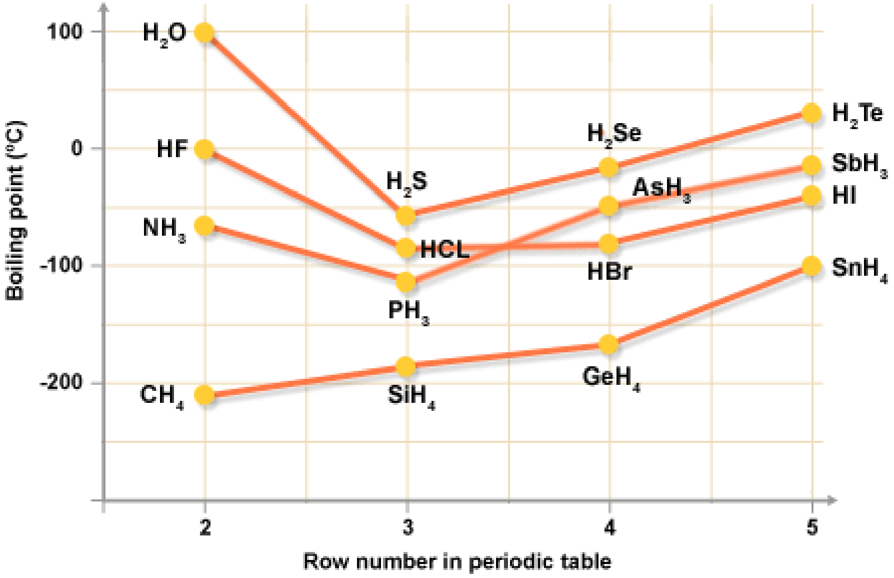
PHYSICAL PROPERTIES OF THE HYDROGEN HALIDES.

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 X 10^{-4}	1.0 X 10^{7}	1.0 X 10^{9}	1.0 X 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:

$$\text{HF (aq)} \rightleftharpoons \text{H}^+\text{ (aq)} + \text{F}^-\text{ (aq)}$$

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.

$$\text{2HF (aq)} \rightleftharpoons \text{H}^+\text{ (aq)} + \text{HF}_2^-\text{ (aq)}$$

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 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.

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^+ 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	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3,PCl_5	S_2Cl_2,SCl_2	Cl_2	
B.pt.(°C)	1465	1418	423	57	74,164	138	-35	
Bonds	Ionic		← Covalent →					
Structure	Giant ionic		← Simple molecular structure →					
Oxides	Na_2O Na_2O_2	MgO	Al_2O_3	SiO_2	P_2O_5	SO_2,SO_3	Cl_2O, Cl_2O_7	

Bonds	← Ionic →			← Covalent →				
Nature	← Basic →		Amphoteric	← Acidic →				
Structure	← Giant ionic →			Giant molecular	← simple molecular →			
Hydrides	NaH	MgH_2	AlH_3	SiH_4	PH_3	H_2S	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.
  - ✍ Acid-base 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).

$$\underbrace{\begin{matrix}\text{Na} & \text{Mg} & \text{Al}\\ {}^{-}2.71 & {}^{-}2.37 & {}^{-}1.66\end{matrix}}_{\text{Powerful reducing agents}} \quad \overbrace{\begin{matrix}\text{Si}\\ -\end{matrix}}^{\text{Very weak reducing agent}} \quad \underbrace{\begin{matrix}\text{P} & \text{S}\\ - & {}^{-}0.48\end{matrix}}_{\text{Weak reducing agents and weak oxidizing agents}} \quad \overbrace{\begin{matrix}\text{Cl}\\ {}^{+}1.36\end{matrix}}^{\text{Powerful oxidzing agent}}$$

Melting & boiling points, Electronegativity, Electronaffinity, Atomic radius, Electropositititivity & 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.

$$\underbrace{\text{Na} \qquad \text{Mg} \qquad \text{Al}}_{\text{React vigorously}} \quad \overbrace{\text{Si}}^{\text{React slowly}} \quad \underbrace{\text{P} \qquad \text{S}}_{\text{React vigorously}} \quad \overbrace{\text{Cl} \qquad \text{Ar}}^{\text{Do not react}}$$

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

  Equation:

  $$4Na_{(s)} + O_{2(g)} \xrightarrow{\text{Heat}} 2Na_2O_{(s)}$$

  Sodium oxide (Normal Oxide)

- ✍ 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:

  $$2Na_{(s)} + O_{2(g)} \xrightarrow{\text{Heat}} Na_2O_{2(s)}$$

  Sodium peroxide (peroxide)

- ✍ Magnesium burns with a brilliant bluish-white flame in air when heated forming oxides which are white in colour.

  Equations:

  $$\left.\begin{array}{l} 2Mg_{(s)} + O_{2(g)} \longrightarrow 2MgO_{(s)} \\ 3Mg_{(s)} + N_{2(g)} \longrightarrow Mg_3N_{2(s)} \end{array}\right\} \text{White solid}$$

- ✍ When heated in air, Powdered Aluminium burns to form a white oxide and a smaller amount of nitride.

  Equations:

  $$4Al_{(s)} + 3O_{2(g)} \longrightarrow 2Al_2O_{3(s)}$$
  $$2Al_{(s)} + N_{2(g)} \longrightarrow 2AlN_{(s)}$$

- Amorphous Silicon burns readily in oxygen at red-heat, but, in air, oxidizes. Silicon dioxide is produced.

  Equation:

  $$Si + O_2 \longrightarrow SiO_2$$

- 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:

  $$P_{4(s)} + 3O_{2(g)} \longrightarrow P_4O_{6(s)} \longrightarrow \text{Phosphorus (III) oxide}$$
  $$P_{4(s)} + 5O_{2(g)} \longrightarrow P_4O_{10(s)} \longrightarrow \text{Phosphorus (V) oxide}$$

  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:

  $$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

- Traces of sulphur trioxide gas is also formed, which gives a misty appearance to the gas.

  Equation:

  $$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{V_2O_5 \text{ Catalyst}} 2SO_{3(g)}$$

  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:

  $$2Na_{(s)} + H_{2(g)} \longrightarrow \underset{\text{White solid}}{2NaH_{(s)}}$$

- Magnesium reacts with heated dry hydrogen gas to form a white solid of magnesium hydride at a temperature of about 350°C.

  Equation:

  $$Mg_{(s)} + H_{2(g)} \longrightarrow MgH_{2(s)}$$

- Aluminium, Silicon and Phosphorous <u>**DO NOT**</u> react with hydrogen gas.
- Sulphur combined directly with hydrogen gas to form hydrogen sulphide.

  Equation:

  $$S_{(s)} + H_{2(g)} \longrightarrow H_2S_{(g)}$$

- Chlorine combined directly with hydrogen gas in the presence of activated charcoal with absorption of hydrogen chloride in water.

  Equation:

$$Cl_{2(g)} + H_{2(g)} \longrightarrow 2HCl_{(g)}$$

(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.

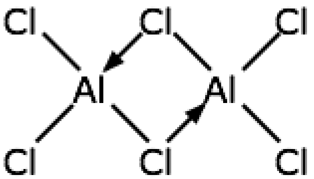
  Equations:

$$\left.\begin{array}{l} 2Na_{(s)} + Cl_{2(g)} \longrightarrow 2NaCl_{(s)} \\ Mg_{(s)} + Cl_{2(g)} \longrightarrow MgCl_{2(s)} \end{array}\right\} \text{White solid}$$

- 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 Al_2Cl_6.and aluminium chloride condenses as a white powder.

  Equation:

$$2Al_{(s)} + 3Cl_{2(g)} \longrightarrow \underset{\text{White powder}}{Al_2Cl_{6(s)}}$$



Note:

The structure of Al_2Cl_6.This anhydrous form of results from $AlCl_3$ 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:

$$Si_{(s)} + 2Cl_{2(g)} \longrightarrow \underset{\text{Colourless liquid}}{SiCl_{4(l)}}$$

$$SiO_{2(s)} + 2C_{(s)} + 2Cl_{2(g)} \longrightarrow SiCl_{4(g)} + 2CO_{(g)}$$

- Heating phosphorus in excess chlorine gas forms phosphorus pentachloride, excess phosphorus forms trichloride.

  Equations:

$$P_{4(s)} + 10Cl_{2(g)} \longrightarrow 4PCl_{5(s)} \longrightarrow \text{Excess } Cl_2$$

$$P_{4(s)} + 6Cl_{2(g)} \longrightarrow 4PCl_{3(l)} \longrightarrow \text{Excess } P_4$$

  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:

$$2S_{(s)} + Cl_{2(g)} \longrightarrow \underset{\text{Red liquid}}{S_2Cl_{2(l)}}$$

(d) Reaction with water (steam).

✍ Sodium reacts with cold water vigorously to form sodium hydroxide solution and hydrogen gas.
Equation:

$$2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$$

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:

$$Mg_{(s)} + H_2O_{(l)} \longrightarrow \underset{\text{White solid}}{MgO_{(s)}} + H_{2(g)}$$

✍ Aluminium **<u>DOES NOT</u>** 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:

$$Si_{(s)} + 2H_2O_{(g)} \longrightarrow SiO_{2(s)} + 2H_{2(g)}$$

✍ 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:

$$4P_{(s)} + 6H_2O_{(l)} \longrightarrow P_4O_{6(s)} + 6H_{2(g)}$$

✍ Sulphur does not reacts with water.

✍ Chlorine gas reacts with cold water to form chloric (I) and hydrochloric acid.
Equation:

$$Cl_{2(g)} + H_2O_{(l)} \rightleftharpoons HOCl_{(aq)} + HCl_{(aq)}$$

(e) Reaction with alkalis (sodium hydroxide solution).

✍ Both sodium and magnesium **<u>DO NOT</u>** reacts 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:

$$2Al_{(s)} + 2OH^-_{(aq)} + 6H_2O_{(l)} \longrightarrow 2Al(OH)_4{}^-_{(aq)} + 3H_{2(g)}$$

✍ Silicon reacts with hot concentrated sodium hydroxide solution to form sodium silicate and hydrogen gas.
Equation:

$$Si_{(s)} + 2OH^-_{(aq)} + H_2O_{(l)} \longrightarrow SiO_3{}^{2-}_{(aq)} + 2H_{2(g)}$$

$$Si_{(s)} + 2OH^-_{(aq)} + 4H_2O_{(l)} \longrightarrow Si(OH)_6{}^{2-}_{(aq)} + 2H_{2(g)}$$

- Phosphorus reacts with hot concentrated sodium hydroxide solution to form sodium hypophosphate and phosphine gas.

  Equation:

  $$P_{4(s)} + 3OH^-_{(aq)} + 3H_2O_{(l)} \longrightarrow 3NaH_2PO_{2(s)} + PH_{3(g)}$$

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

  Equation:

  $$3S_{(s)} + 6OH^-_{(aq)} \longrightarrow SO_3{}^{2-}{}_{(aq)} + 2S^{2-}{}_{(aq)} + 3H_2O_{(l)}$$

  Note:

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

  Equation:

  $$4S_{(s)} + 6OH^-_{(aq)} \longrightarrow S_2O_3{}^{2-}{}_{(aq)} + 2S^{2-}{}_{(aq)} + 3H_2O_{(l)}$$

- Chlorine gas react with cold concentrated sodium hydroxide solution to form sodium chloride, sodium chlorate (I) and water.

  Equation:

  $$Cl_{2(g)} + 2OH^-_{(aq)} \longrightarrow Cl^-_{(aq)} + OCl^-_{(aq)} + H_2O_{(l)}$$

- Chlorine gas also reacts with hot concentrated sodium hydroxide solution to form sodium chloride, sodium chlorate (V) and water.

  Equation:

  $$3Cl_{2(g)} + 6OH^-_{(aq)} \longrightarrow ClO_3{}^-{}_{(aq)} + 5Cl^-_{(aq)} + 3H_2O_{(l)}$$

(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, Cl^- and sulphate, $SO_4{}^{2-}$ ions respectively.

  Equations:

  $$2Na_{(s)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_{2(g)}$$
  $$2Na_{(s)} + H_2SO_{4(aq)} \longrightarrow Na_2SO_{4(aq)} + H_{2(g)}$$

- Magnesium reaction with both dilute hydrochloric and sulphuric acid to form salts and hydrogen gas.

  Equation:

  $$Mg_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_{2(g)}$$
  $$Mg_{(s)} + H_2SO_{4(s)} \longrightarrow MgSO_{4(aq)} + H_{2(g)}$$

- Aluminium reacts rapidly with hot dilute hydrochloric acid **BUT** do not reacts with dilute sulphuric acid perhaps because of the insolubility of the oxide layer in the acid.

  Equation:

  $$2Al_{(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3(aq)} + 3H_{2(g)}$$

- Silicon, phosphorus, sulphur **do not** reacts with any dilute mineral acids **BUT** silicon is attacked **ONLY** by hydrofluoric acid.

  Equation:

  $$Si_{(s)} + 6HF_{(l)} \longrightarrow H_2SiF_{6(l)} + 2H_{2(g)}$$

  <u>Reason:</u>

Silicon, Phosphorus & Chlorine **DONOT** reacts 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** reacts with oxidizing nitric acid.

  Equation:

$$Mg_{(s)} + 2HNO_{3(aq)} \longrightarrow Mg(NO_3)_{2(aq)} + H_{2(g)}$$

(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:

$$3Mg_{(s)} + 8HNO_{3(aq)} \longrightarrow 3Mg(NO_3)_{2(aq)} + 4H_2O_{(l)} + 2NO_{(g)}$$

- Magnesium also reacts with hot concentrated sulphuric acid to yields sulphur dioxide gas and other useful products.

  Equation:

$$Mg_{(s)} + 2H_2SO_{4(l)} \longrightarrow MgSO_{4(aq)} + 2H_2O_{(l)} + SO_{2(g)}$$

- Aluminium reacts with hot concentrated sulphuric acid to form sulphate, SO_4^{2-} ion, water and sulphur dioxide gas.

  Equation:

$$2Al_{(s)} + 6H_2SO_{4(l)} \longrightarrow Al_2(SO_4)_{3(aq)} + 6H_2O_{(l)} + 3SO_{2(g)}$$

- Sulphur is oxidized by both hot concentrated sulphuric and nitric acid to useful products.

  Equations:

$$S_{(s)} + 2H_2SO_{4(l)} \longrightarrow 2H_2O_{(l)} + 3SO_{2(g)}$$

$$S_{(s)} + 6HNO_{3(aq)} \longrightarrow H_2SO_{4(l)} + 6NO_{2(g)} + 2H_2O_{(l)}$$

- Phosphorus is oxidized by hot concentrated nitric acid to useful products and is itself reduced to nitrogen dioxide gas.

$$P_{4(s)} + 20HNO_{3(Conc.aq)} \longrightarrow 4H_3PO4_{(l)} + 4H_2O_{(l)} + 20NO_{2(g)}$$

$$P_{(s)} + 5HNO_{3(Conc.aq)} \longrightarrow H_3PO_{4(aq)} + H_2O_{(l)} + 5NO_{2(g)}$$

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:

$$4Na_{(s)} + O_{2(g)} \longrightarrow \underset{\text{White solid}}{2Na_2O_{(s)}}$$

- Sodium peroxide is manufactured by heating sodium metal in excess supply of air (oxygen gas) at a temperature of about 600K.

  Equation:

$$2Na_{(s)} + O_{2(g)} \longrightarrow \underset{\text{Yellow solid}}{Na_2O_{2(s)}}$$

- Magnesium oxide is prepared by burning either magnesium metal in air (oxygen gas) or by decomposition of either magnesium carbonate or nitrate.
  Equations:
  $2Mg_{(s)} + O_{2(g)} \longrightarrow 2MgO_{(s)}$
  $MgCO_{3(s)} \longrightarrow MgO_{(s)} + CO_{2(g)}$
  $2Mg(NO_3)_{2(s)} \longrightarrow 2MgO_{(s)} + 4NO_{2(g)} + O_{2(g)}$
- 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:
  $4Al_{(s)} + 3O_{2(g)} \longrightarrow 2Al_2O_{3(s)}$
  $4Al(NO_3)_{3(s)} \longrightarrow 2Al_2O_{3(s)} + 12NO_{2(g)} + 3O_{2(g)}$
  $2Al(OH)_{3(s)} \longrightarrow Al_2O_{3(s)} + 3H_2O_{(l)}$
- Silicon (IV) oxide is prepared by burning silicon in oxygen gas (air).
  Equation:
  $Si_{(s)} + O_{2(g)} \longrightarrow SiO_{2(s)}$
- Silicon (IV) oxide is also prepared by burning silicon over steam at red heat.
  Equation:
  $Si_{(s)} + 2H_2O_{(l)} \longrightarrow SiO_{2(g)} + 2H_{2(g)}$
- Silicon (IV) oxide is prepared by burning silane over air (oxygen gas).
  Equation:
  $SiH_{4(g)} + O_{2(g)} \longrightarrow SiO_{2(s)} + 2H_2O_{(g)}$
- Phosphorus (III) oxide is prepared by burning phosphorus in limited supply in air (oxygen gas).
  Equation:
  $4P_{(s)} + 3O_{2(g)} \longrightarrow 2P_2O_{3(s)}$
- Phosphorus (V) oxide is prepared by burning phosphorus in excess supply in air (oxygen gas).
  Equation:
  $4P_{(s)} + 5O_{2(g)} \longrightarrow 2P_2O_{5(s)}$
- Phosphorus (V) oxide is prepared by burning phosphine in air (oxygen gas).
  Equation:
  $4PH_{3(g)} + 8O_{2(g)} \longrightarrow P_4O_{10(s)} + 6H_2O_{(l)}$
- Phosphorus (V) oxide is prepared by burning calcium phosphate (V) and silica at a higher temperature.
  Equation:
  $2Ca_3(PO_4)_{2(s)} + 3SiO_{2(s)} \longrightarrow 6CaSiO_{3(l)} + P_4O_{10(g)}$
- Sulphur dioxide gas is prepared by burning sulphur in limited supply of air (oxygen gas).
  Equation:
  $S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$
  $S_{(s)} + 2H_2SO_{4(Conc.\ l)} \longrightarrow 2H_2O_{(l)} + SO_{2(g)}$

- Sulphur trioxide gas is prepared by burning sulphur in excess supply of air (oxygen gas).
  Equation:
  $2S_{(s)} + 6O_{2(g)} \longrightarrow 2SO_{3(g)}$
  $2SO_{2(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)}$
- Dichlorine oxide is prepared by burning chlorine gas in limited supply oxygen gas.
  Equation;
  $2Cl_{2(g)} + O_{2(g)} \longrightarrow 2Cl_2O_{(g)}$

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:
  $2Na_{(s)} + H_{2(g)} \longrightarrow 2NaH_{(s)}$
- Aluminium hydride is a white solid precipitated when lithium hydride is treated with excess aluminium chloride in a solution of ether.
  Equation:
  $3LiH_{(s)} + AlCl_{3(s)} \longrightarrow AlH_{3(s)} + 3LiCl_{(s)}$
- Silane is obtained by fractional distillation from a mixture of silicon hydrides formed when magnesium silicide is treated with hydrochloric acid.
  Equation:
  $Mg_2Si_{(s)} + 4HCl_{(aq)} \longrightarrow 2MgCl_{2(s)} + SiH_{4(g)}$
- However, a more convenient way of preparing silane is by reduction of silicon tetrachloride with lithium aluminium hydride.
  Equation:
  $SiCl_{4(l)} + LiAlH_{4(s)} \longrightarrow SiH_{4(g)} + LiCl_{(s)} + AlCl_{3(s)}$
- Phosphorus trihydride (phosphine) is prepared by heating concentrated sodium hydroxide solution with white phosphorus.
  Equation:
  $P_{4(s)} + 3OH^-_{(aq)} + 3H_2O_{(l)} \longrightarrow 3H_2PO_2^-{}_{(aq)} + PH_{3(g)}$
- Hydrogen sulphide gas is prepared by action of dilute hydrochloric acid on iron (II) sulphide.
  Equation:
  $FeS_{(s)} + 2HCl_{(aq)} \longrightarrow FeCl_{2(aq)} + H_2S_{(g)}$
- Hydrogen chloride gas is prepared by the action of concentrated sulphuric acid on sodium chloride.
  Equation:
  $NaCl_{(s)} + H_2SO_{4(Conc.l)} \longrightarrow NaHSO_{4(s)} + HCl_{(g)}$

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:

$2Na_{(s)} + Cl_{2(g)} \longrightarrow 2NaCl_{(s)}$

$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$

- Magnesium chloride is prepared by reacting its carbonate, oxide or hydroxide with dilute hydrochloric acid.$MgCl_2$ is also an ionic chloride. Vigorous reaction when the elements are heated.

  Equations:

  $Mg_{(s)} + Cl_{2(g)} \longrightarrow MgCl_{2(s)}$

  $MgO_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_2O_{(l)}$

  $Mg_{(s)} + 2HCl_{(g)} \longrightarrow MgCl_{2(s)} + H_{2(g)}$

- 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_2Cl_6.

  Equation:

  $2Al_{(s)} + 3Cl_{2(g)} \longrightarrow Al_2Cl_{6(s)}$

- Aluminium (III) chloride is prepared by heating aluminium metal in either dry chlorine or hydrogen chloride gas.

  Equation:

  $2Al_{(s)} + 3Cl_{2(g)} \longrightarrow 2AlCl_{3(s)}$

  $2Al_{(s)} + 6HCl_{(g)} \longrightarrow 2AlCl_{3(s)} + 3H_{2(g)}$

  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:

  $Si_{(s)} + 2Cl_{2(g)} \longrightarrow SiCl_{4(l)}$

  $SiO_{2(s)} + 2C_{(s)} + 2Cl_{2(g)} \longrightarrow SiCl_{4(g)} + 2CO_{(g)}$

  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:

  $S_2Cl_{2(l)} + Cl_{2(g)} \rightleftharpoons 2SCl_{2(l)}$

  $2S_{(s)} + Cl_{2(g)} \longrightarrow S_2Cl_{2(l)}$

- Chlorine gas is prepared by heating lead (IV) oxide with concentrated hydrochloric acid.

  Equation:

  $PbO_{2(s)} + 4HCl_{(aq)} \longrightarrow PbCl_{2(aq)} + 2H_2O_{(l)} + Cl_{2(g)}$

- Phosphorus trichloride is a colourless liquid prepared by passing dry chlorine gas over heated white phosphorus.

Equation:

$$P_{4(s)} + 6Cl_{2(g)} \longrightarrow 4PCl_{3(l)}$$

- Phosphorus pentachloride is prepared by passing excess dry chlorine gas over phosphorus.

  Equation:

$$2P_{(s)} + 5Cl_{2(g)} \longrightarrow 2PCl_{5(s)}$$

Physical properties of chlorides:

NaCl and $MgCl_2$ are ionic chlorides. Since a large amount of energy is required to separate the ions, the melting point is high.

$AlCl_3$ and $SiCl_4$ are molecular covalent chlorides, and so only intermolecular forces exist between the molecules. The melting points are thus much lower than the ionic chlorides.

$AlCl_3$ 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_5 is ionic so its melting point is thus high. On heating, however, it reverts to a simple covalent structure and sublimes.

D. **PREPARATION OF PERIOD (III) HYDROXIDES.**
(ATTENTION BOYS 'READ ABOUT PREAPARATION OF HYDROXIDE')

COMPOUNDS OF PERIOD (III):

Period (III) elements forms several compounds including:

A. 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^+ to Al^{3+}.

The oppositely charged ions approach each other closely in Al_2O_3 and strongly attracts themselves because of the high charge on Al^{3+} hence stronger ionic bond in Al_2O_3 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:

$$Na_2O_{(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(aq)}$$

☞ Magnesium oxide is a white powder which is only slightly (sparingly) soluble in water to form weak basic aqueous solution.
Equation:

$$MgO_{(s)} + H_2O_{(l)} \longrightarrow Mg(OH)_{2(s)}$$

☞ 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:

$$SiO_{2(s)} + H_2O_{(l)} \xrightarrow{\text{Heat}} H_2SiO_{3(aq)}$$

☞ Phosphorus (V) and phosphorus (III) oxide reacts with water to form aqueous solution.
Equations:

$$P_4O_{10} \text{ Or } 2P_2O_{5(s)} + 6H_2O_{(l)} \longrightarrow 4H_3PO_{4(aq)}$$
$$P_2O_{3(s)} + 3H_2O_{(l)} \rightleftharpoons 2H_3PO_{4(aq)}$$

☞ Sulphur dioxide and sulphur trioxide gas reacts with water to form an acidic solution because of its moderate solubility in water.
Equations:

$$SO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2SO_{3(aq)}$$
$$SO_{3(g)} + H_2O_{(l)} \longrightarrow H_2SO_{4(aq)}$$

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:

$$Cl_2O_{(g)} + H_2O_{(l)} \longrightarrow 2HOCl_{(aq)}$$

☞ Chlorine dioxide reacts with water to form mixed acidic anhydride of chloric (III) and chloric (V) acid (chloric acid).
Equation:

$$2ClO_{2(g)} + H_2O_{(l)} \longrightarrow HClO_{3(aq)} + HClO_{2(aq)}$$

☞ Dichlorine heptoxide reacts with water to form aqueous perchloric acid.
Equation:

$$Cl_2O_{7(l)} + H_2O_{(l)} \longrightarrow 2HClO_{4(l)}$$

2) Alkalis (i.e. sodium hydroxide solution).

☞ Sodium and magnesium oxides are basic in nature and therefore DONOT reacts with alkalis in any condition.

☞ Aluminium (III) oxide reacts with concentrated alkalis to form a complex salts (aluminate).
Equation:

$$Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \longrightarrow 2Al(OH)_4{}^-{}_{(aq)}$$

☞ Silicon (IV) oxide reacts with concentrated alkalis to form silicate (complex salts).
Equation:

$$SiO_{2(s)} + 2OH^-_{(aq)} \longrightarrow SiO_3{}^{2-}{}_{(aq)} + H_2O_{(l)}$$

☞ The rest of the peroxide (III) oxide's members reacts with alkalis to form salts and water.
Equations:

$$P_2O_{5(s)} + 4NaOH_{(aq)} \longrightarrow 2Na_2HPO_{4(aq)} + H_2O_{(l)}$$
$$P_4O_{6(s)} + 8NaOH_{(aq)} \longrightarrow 4Na_2HPO_{3(aq)} + 2H_2O_{(l)}$$
$$SO_{2(g)} + 2NaOH_{(aq)} \longrightarrow Na_2SO_{3(aq)} + H_2O_{(l)}$$
$$Cl_2O_{7(l)} + 2NaOH_{(aq)} \longrightarrow 2NaClO_{4(aq)} + H_2O_{(l)}$$

3) Acids.

☞ Sodium, magnesium & aluminium oxides reacts with dilute mineral acids to form their respective salts and water.
Equations:

$$Na_2O_{(s)} + 2H^+_{(aq)} \longrightarrow 2Na^{2+}_{(aq)} + H_2O_{(l)}$$
$$MgO_{(s)} + 2H^+_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + H_2O_{(l)}$$
$$Al_2O_{3(s)} + 6H^+_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3H_2O_{(l)}$$

☞ Silicon (IV) oxide doesn't reacts with any mineral acids except hydrofluoric acid.
Equation:

$$SiO_{2(s)} + 4HF_{(l)} \longrightarrow SiF_{4(g)} + 2H_2O_{(l)}$$

☞ And the rest of the remaining period (III) oxides **DONOT** reacts with any mineral acids.

B. Hydrides.

<u>Bonding and structures</u>:

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:

$$NaH_{(s)} + H_2O_{(l)} \longrightarrow NaOH_{(aq)} + H_{2(g)}$$
$$MgH_{2(s)} + 2H_2O_{(l)} \longrightarrow Mg(OH)_{2(aq)} + 2H_{2(g)}$$
$$AlH_{3(s)} + 3H_2O_{(l)} \longrightarrow Al(OH)_{3(s)} + 3H_{2(g)}$$

Notes:

The reaction indicates that the hydroxyl, 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:

$$SiH_{4(g)} + 2H_2O_{(l)} \longrightarrow SiO_{2(s)} + 4H_{2(g)}$$

- Silane is also hydrolysed by cold water in presence of an alkali to form sodium silicate and hydrogen gas.

  Equation:

$$SiH_{4(g)} + 2OH^-_{(aq)} + H_2O_{(l)} \longrightarrow SiO_3^{2-}{}_{(aq)} + 4H_{2(g)}$$

- 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:

$$H_2S_{(g)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + HS^{2-}_{(aq)}$$
$$H_2S_{(g)} + 2H_2O_{(l)} \longrightarrow 2H_3O^+_{(aq)} + S^{2-}_{(aq)}$$
$$HCl_{(g)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

2) Alkalis.
   - Silane is hydrolysed by water in the presence of an alkalis to form silicate and hydrogen gas.

     Equation:

$$SiH_{4(g)} + 2OH^-_{(aq)} + H_2O_{(l)} \longrightarrow SiO_3^{2-}{}_{(aq)} + 4H_{2(g)}$$

- Hydrogen sulphide reacts with sodium hydroxide solution to form sodium hydrogen sulphide and water.

  Equation:

$$H_2S_{(g)} + NaOH_{(aq)} \rightleftharpoons NaHS_{(aq)} + H_2O_{(l)}$$
$$H_2S_{(g)} + 2NaOH_{(aq)} \longrightarrow Na_2S_{(aq)} + 2H_2O_{(l)}$$

✍ Aqueous hydrogen chloride reacts with sodium hydroxide solution to form sodium chloride solution and water.

Equation:

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$

3) Acids

✍ Hydrogen sulphide gas reduces both concentrated sulphuric and nitric acid to very useful products.

Equations:

$$H_2S_{(g)} + 2HNO_{3(Conc.aq)} \longrightarrow S_{(s)} + 2H_2O_{(l)} + 2NO_{2(g)}$$
$$H_2S_{(g)} + 8HNO_{3(Conc.aq)} \longrightarrow H_2SO_{4(aq)} + 4H_2O_{(l)} + 8NO_{2(g)}$$
$$3H_2S_{(g)} + H_2SO_{4(Conc.l)} \longrightarrow 3S_{(s)} + 4H_2O_{(l)}$$
$$H_2S_{(g)} + H_2SO_{4(Conc.l)} \longrightarrow S_{(s)} + 2H_2O_{(l)} + SO_{2(g)}$$

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, Na^+ to aluminium, Al^{3+} ion. The charge on the cations increases for sodium, Na^+ to aluminium, Al^{3+} ions. This results in aluminium, Al^{3+} ion having the greatest polarizing power.

  Table:

Ions	Ionic radius	Charge	Polarizing power
Na^+	0.095	1	$\frac{1}{0.095}=10.5$
Mg^{2+}	0.065	2	$\frac{2}{0.065}=30.7$
Al^{3+}	0.050	3	$\frac{3}{0.050}=60.0$

- Aluminium, Al^{3+} ion greatly polarizes the chloride, Cl^- ion than both magnesium, Mg^{2+} and sodium, 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, 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 PCl_4^- and PCl_6^- ions though in vapour state it consists of PCl_5 molecules.
- It is this ionic character that is responsible for its abnormally high melting 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.

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:

$$NaCl_{(s)} \xrightarrow{H_2O_{(l)}} Na^+_{(aq)} + Cl^-_{(aq)}$$
$$MgCl_{2(s)} \longrightarrow Mg^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

✍ 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^{2+} ion.
Note:
Magnesium chloride undergo partial hydrolysis in cold water to form a basic chloride.
Equations:

$$MgCl_{2(aq)} + H_2O_{(l)} \rightleftharpoons Mg(OH)Cl_{(s)} \text{ or } MgCl(OH)_{(s)} + HCl_{(aq)}$$

However, if heated magnesium chloride undergo hydrolysis to form magnesium oxide which is a white solid.
Equation:

$$MgCl_{2(s)} + H_2O_{(l)} \longrightarrow MgO_{(s)} + 2HCl_{(g)}$$

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:

$$AlCl_{3(s)} + 3H_2O_{(l)} \longrightarrow Al(OH)_{3(s)} + 3HCl_{(g)}$$

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:

$$Al(H_2O)_6{}^{3+}{}_{(aq)} + 6H_2O_{(l)} \rightleftharpoons [Al(H_2O)_6]^{3+}{}_{(aq)} \text{ or } [Al(H_2O)_5(OH)]^{2+}{}_{(aq)} + H_3O^{+}{}_{(aq)}$$

✍ The chlorides of silicon, phosphorus, disulphur dichloride and chlorine gas are predominantly covalent. They all reacts with water (are hydrolysed) rather than simply dissolving in water, hence fume in air to form acidic solutions.

✍ Equations:

$$SiCl_{4(l)} + 2H_2O_{(l)} \longrightarrow SiO_{2(s)} + 4HCl_{(g)}$$
$$PCl_{3(l)} + 3H_2O_{(l)} \longrightarrow H_3PO_{3(s)} + 3HCl_{(g)}$$
$$PCl_{5(s)} + 4H_2O_{(l)} \longrightarrow H_3PO_{3(aq)} + 5HCl_{(g)}$$
$$2S_2Cl_{(l)} + 2H_2O_{(l)} \longrightarrow 3S(s) + 4HCl_{(g)} + SO_{2(g)}$$
$$2S_2Cl_{(l)} + 3H_2O_{(l)} \longrightarrow 3S_{(s)} + H_2SO_{4(aq)} + 4HCl_{(g)}$$
$$Cl_{2(g)} + H_2O_{(l)} \rightleftharpoons HOCl_{(aq)} + HCl_{(aq)}$$

2) Acids.

✍ Sodium chloride reacts with concentrated sulphuric acid to yields hydrogen chloride gas.

Equation:

$$NaCl_{(s)} + H_2SO_{4(l)} \longrightarrow NaHSO_{4(s)} + HCl_{(g)}$$

✍ Chlorides of phosphorus reacts with carboxylic acids to yield corresponding acyl chlorides.

Equations:

$$CH_3COOH_{(l)} + PCl_{5(s)} \longrightarrow CH_3COCl_{(l)} + POCl_{3(l)} + HCl_{(g)}$$
$$3CH_3COOH_{(l)} + PCl_{3(l)} \longrightarrow 3CH_3COCl_{(l)} + H_3PO_{4(s)}$$

D. Hydroxides.

Basing 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	$Mg(OH)_2$	$Al(OH)_3$	$Si(OH)_4$	$P(OH)_5$	$S(OH)_6$	$Cl(OH)_7$
Hydroxide formed	"	"	"	H_2SiO_3	H_3PO_4	H_2SO_4	$HClO_4$
Character	Strong Base	Weak base	amphoteric	Weak acid		Strong acid	
Expected hydroxide		Water molecule (s) lost			Hydroxide formed		

$Si(OH)_4$	$-H_2O$	H_2SiO_3
$P(OH)_5$	$-H_2O$	H_3PO_4
$S(OH)_6$	$-2H_2O$	H_2SO_4
$Cl(OH)_7$	$-3H_2O$	$HClO_4$

Explanation:

However, hydroxides of non-metals splits 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 increase with increase in ease of loss of the hydroxyl group in form of OH^- 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 **Na<Mg<Al** hence basic strength reduces in the order of **$NaOH > Mg(OH)_2 > Al(OH)_3$**.

The non-metallic hydroxides (known as oxy-acids) are acidic. Their acidic strength increases with increase in the ease of loss of a proton.

The acidic strength increases in the order of: **$H_2SiO_3 < H_3PO_4 < H_2SO_4 < HClO_4$**. This trend can be explained by considering the structures of the acids (not drawn to scale) below.

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: **Si<P<S<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), $Al_2O_3.2H_2O$.
- Cryolite (Sodium hexafloroaluminate (III), Na_3AlF_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:
  - ☞ 1st stage is purification of bauxite by Bayer process to produce anhydrous aluminium oxide (Alumina).
  - ☞ 2nd 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:

  $$Al_2O_3.2H_2O_{(s)} \longrightarrow Al_2O_{3(s)} + 2H_2O_{(l)}$$
- The roasted bauxite ore is crushed in to powder is heated with excess concentrated sodium hydroxide solution under high pressure.

  Equations:

  $$Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \longrightarrow 2[Al(OH)_4]^-_{(aq)}$$
  $$SiO_{2(s)} + 2OH^-_{(aq)} \longrightarrow SiO_3^{2-}{}_{(aq)} + H_2O_{(l)}$$

  Note:

  Aluminium oxide since it is an amphoteric oxide, it will dissolves 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:

  $$[Al(OH)_4]^-_{(aq)} + H^+_{(aq)} \longrightarrow Al(OH)_{3(s)} + H_2O_{(l)}$$
  $$[Al(OH)]^-_{(aq)} \longrightarrow Al(OH)_{3(s)} + OH^-_{(aq)}$$
  $$[Al(OH)_6]^{3-}_{(aq)} \longrightarrow Al(OH)_{3(s)} + 3OH^-_{(aq)}$$
  $$2Al(OH)_4{}^-_{(aq)} + CO_{2(g)} \longrightarrow 2Al(OH)_{3(s)}\downarrow + CO_3^{2-}{}_{(aq)} + H_2O_{(l)}$$
- 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:

  $$2Al(OH)_{3(s)} \longrightarrow Al_2O_{3(s)} + 3H_2O_{(g)}$$
- 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 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:

$$2ZnS_{(s)} + 3O_{2(g)} \longrightarrow 2ZnO_{(s)} + 2SO_{2(g)}$$
$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$$

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 hexaflouroaluminate, Na_3AlF_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°C to give aluminium at the cathode and oxygen gas at the anode respectively.
  Equation:

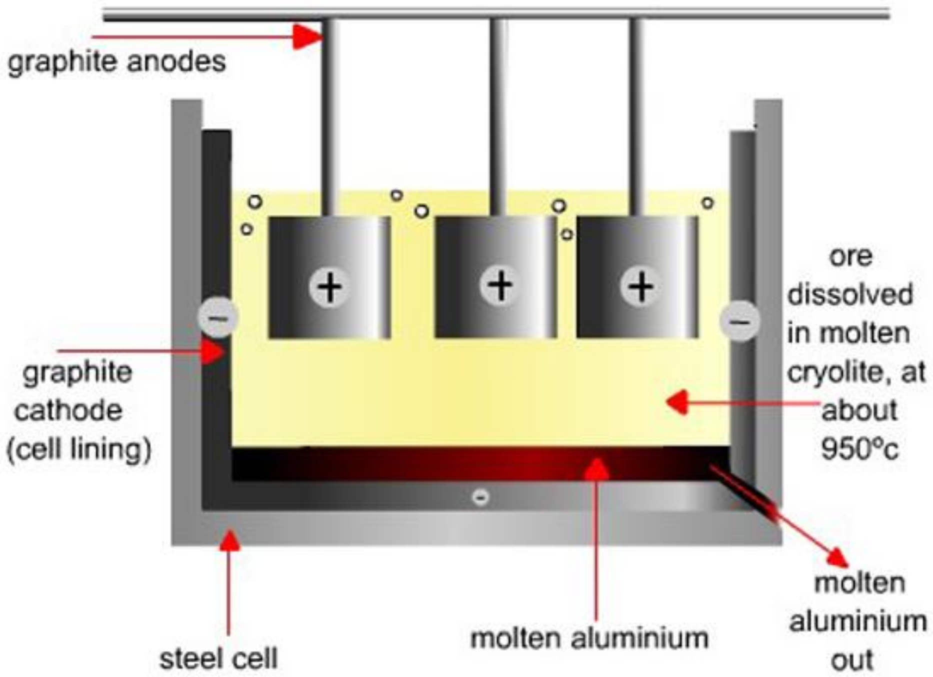
  $Al_2O_{3(s)} \rightleftharpoons Al^{3+}_{(aq)} + AlO_3^{3-}{}_{(aq)}$ Gives rise to the electrode processes
- Aluminium is discharged at the graphite lining of the cell which acts as the cathode.
  Equation at the cathode:

  $$Al^{3+}_{(l)} + 3e^- \longrightarrow Al_{(l)}$$
- 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:

  $$4AlO_3^{3-}{}_{(aq)} \longrightarrow 2Al_2O_{3(l)} + 3O_{2(g)} + 12e^-$$

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 anod 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 AlF_3, $AlCl_3$, $AlBr_3$, and AlI_3.Explains the observations:
- ✓ The above halides are largely covalent because of the high polarizing power of the aluminium, Al^{3+} ion character increases from AlF_3 to AlI_3.Iodide, I^- ion is the most polarized because of the big ionic radius of the iodide, I^- ion.
- ✓ Aluminium fluoride is ionic because of the small ionic radius of the fluoride, 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:

  $$4Al_{(s)} + 3C_{(s)} \longrightarrow Al_4C_{3(s)}$$
  $$Al_4C_{3(s)} + 12H_2O_{(l)} \longrightarrow 4Al(OH)_{3(s)} + 3CH_{4(g)}$$
- ✓ 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:

  $$2Al_{(s)} + 3S_{(s)} \longrightarrow Al_2S_{3(s)}$$
  $$Al_2S_{3(s)} + 6H_2O_{(l)} \longrightarrow 2Al(OH)_{3(s)} + 3H_2S_{(g)}$$

IDENTIFICATION OF ALUMINIUM, AL^{3+}.

1) Using aqueous sodium hydroxide solution.

   Procedure:

- ✓ **T**o a solution, add sodium hydroxide solution.

  Observation:

White precipitate, soluble in excess sodium hydroxide solution forming a colourless solution.

Equations:

$$Al^{3+}_{(aq)} + 3OH^-_{(aq)} \longrightarrow \underset{\text{White precipitate}}{Al(OH)_{3(s)}}$$

$$Al(OH)_{3(s)} + OH^-_{(aq)} \longrightarrow \underset{\text{Colourless solution}}{Al(OH)_4^-{}_{(aq)}}$$

2) Using aqueous ammonia solution.

Procedure:

- ✓ **T**o a solution, add aqueous ammonia hydroxide solution.

Observation:

White precipitate insoluble in excess aqueous ammonia solution.

Equation:

$$Al^{3+}_{(aq)} + 3OH^-_{(aq)} \longrightarrow \underset{\text{White precipitate}}{Al(OH)_{3(s)}}$$

3) Using sodium carbonate solution.

Procedure:

- ✓ **T**o 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:

- ✓ **T**o a solution suspected of 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) **T**o the solution suspected of Al^{3+} ion, add alizarin solution or litmus paper solution followed by ammonia solution.

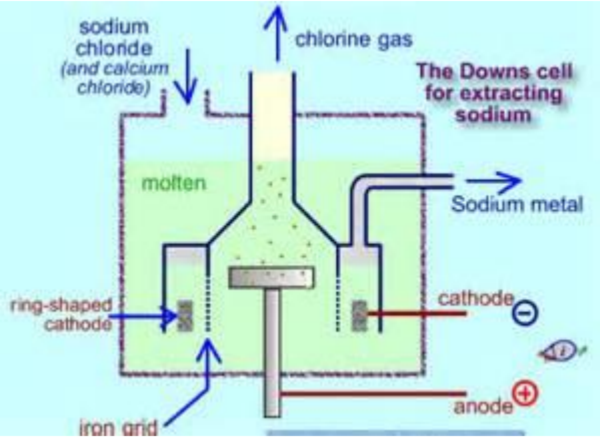
Observation:

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:



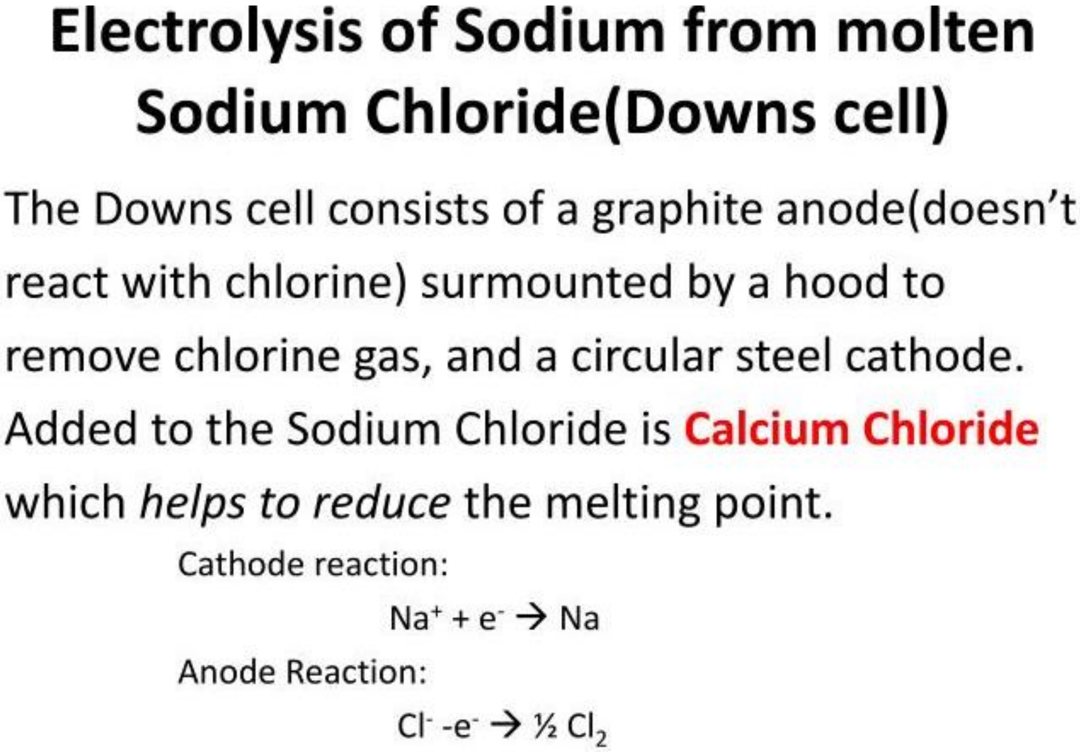
- Sodium chloride melts at a temperature of about 800°C and the steel cell corrodes rapidly while some sodium is produced by electrolysis process.
- Calcium chloride is then added to the molten sodium chloride to lowers the melting points since the melting point of sodium chloride is high. Hence during electrolysis, the sodium, Na^+ ions migrate to the cathode and are discharged while chloride, Cl^- ions migrate to the anode and are oxidized by electron loss to form liquid chlorine gas.

  Equations at the cathode and anode respectively:

  At the cathode: $Na^+_{(l)} + e^- \longrightarrow Na_{(l)}$

  At the anode: $2Cl^-_{(l)} \longrightarrow Cl_{2(g)} + 2e^-$

  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:

$$Na^+ + e^- \rightarrow Na$$

Anode Reaction:

$$Cl^- - e^- \rightarrow \frac{1}{2} Cl_2$$

- **SODIUM HYDROXIDE SOLUTION AND CHLORINE GAS:**

- During manufacture of sodium hydroxide solution by electrolysis of brine (concentrated sodium chloride solution), chlorine and hydrogen gases are vital by-products.
- Manufacture of sodium hydroxide solution, chlorine and hydrogen gases, there are three stages involved.

A. 1st stage is electrolysis of concentrated brine.

During electrolysis process concentrated sodium chloride solution is electrolyzed. Mercury cathode is used to enables sodium ions to be discharged in preference to hydrogen ions while chloride ion is discharged at the anode.

Equations:

$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e$ At the anode

$2Na^+_{(aq)} + 2e \longrightarrow 2Na_{(s)}$ At the cathode

B. 2nd stage is formation of amalgam.

Sodium formed at the cathode dissolves in the mercury, forming sodium amalgam.

Equation:

$Na_{(s)} + Hg_{(l)} \longrightarrow NaHg_{(l)}$

C. 3rd stage is the reaction of amalgam with water.

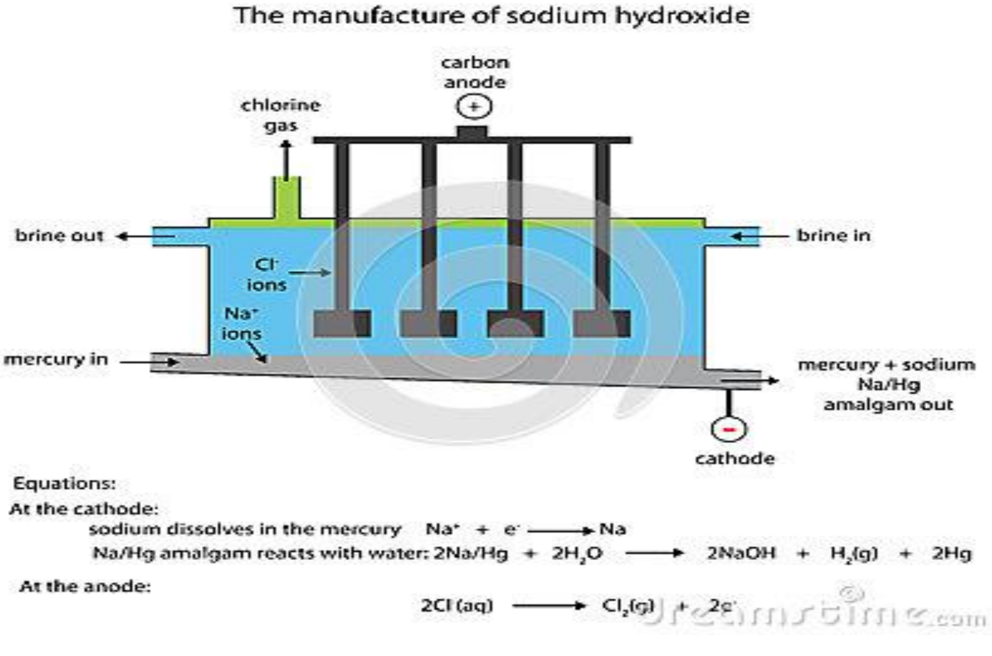
The sodium amalgam formed will flows in to a separate chamber called soda cell (not shown in the diagram).

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:

$2NaHg_{(l)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + 2Hg_{(l)} + H_{2(g)}$

DIAGRAM:



PERIOD 4 (TRANSITIONAL METALS) ELEMENTS:

Self - assessment Test .1.

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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.
   d) Electronegativity.
   e) Electropositivity.
   f) Ionization energy.
   g) First electron affinity.
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	1st Ionization Energy	2nd I.E.	3rd I.E.	4th 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 for 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 period 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 of beryllium whereas the second ionization energy of Boron is higher than that of beryllium.
   b) The 1st I.E of nitrogen is higher than that of oxygen whereas the 2nd I.E of oxygen is higher than that of nitrogen.
   c) The 1st 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 100^0C while hydrogen fluoride boils at 19^0C.
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 487^0C and that of magnesium chloride is 1418^0C.
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 triflouride 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 likes 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 1st I.E <2nd I.E <3rd I.E ……<nth 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	$MgCl_2$	$AlCl_3$
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 $AlI_3 < AlBr_3 < AlCl_3 < AlF_3$.

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 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 distinquish between each of the following and in each case state what would be observed & write an equations where possible.

1. Ca^{2+} and Mg^{2+} 2. Ca^{2+} and Ba^{2+} 3. Ni^{2+} and Cr^{3+} 4. Sn^{4+} and Sn^{2+}
5. Pb^{2+} and Ag^+ 6. $C_2O_4^-$ and HCO_3^- 7. Cl^- and Br^- 8. HCO_3^- and CO_3^{2-}
9. NO_2^- and NO_3^- 10. $HCOO^-$ and CH_3COO^- 11. F^- and Cl^- 12. SO_4^{2-} and SO_3^{2-}
13. SO_3^{2-} and $S_2O_3^{2-}$

20. Define the following terms:
      (i) Charge density. (ii) Polarization.
      (iii) Principal quantum number.
   (b). Explain why the value for the second election 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, K^+ and chloride, 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 is 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.
    a) State the name given to this type of relationship.
    b) Give **FOUR** examples of the properties in which the two elements show similarities.
    c) Name **TWO** other pairs of elements that show similar type of relation as Lithium and magnesium.

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1. Write equations to show how hydrides of period 3 elements reaction with water.
   (b) Both lead (II) and (IV) chlorides react with water.
   a) Write equations show how they react with water.
   b) Explain the differences in the reactions above.
2. When red lead Pb_3O_4 was reacted with nitric acid a solid was formed.
   a) Write the equation for the reaction.
   b) The mixture from (a) was filtered and the residue warmed with concentrated hydrochloric acid, state.
      (i). what was observed? Explain your answer.
      (ii). Write equation for the reaction.
   c) The filtrate from (a) was divided into two parts;
      (i). to the 1st part was added aqueous potassium iodine. State what was observed and write equation for the reaction
      (ii). the 2nd part was evaporated to dryness and heated strongly: Explain what was observed and write equation for the reaction that took place.
3. Briefly describe the laboratory synthesis of chlorides of group (IV) elements.
   a) Write equations to show how the chlorides of group (IV) elements react with water.
   b) Oxides of group (IV) elements can be in oxidation states $^{+}2$ or $^{+}4$.
      (i) Name the oxides of group IV elements.
      (ii) Explain why oxides in oxidation state $^{+}2$ become more stable as the group is descended.
4. Discuss the reactivity of group (IV) element (carbon, silicon, germanium, tin and lead) of the periodic table with.
   (a) Soaps. (c) Water (d) Dilute mineral acids. (e)Concentrated mineral acid.
   (b) Dilute sodium hydroxide solution.
5. Write an ionic equation for the reaction between Sodium hydroxide and:
   (i). Silicon (IV) oxide. (ii). Lead (IV) oxide.
   (b) Write equations and state characters for reaction of group (IV) oxides with Sodium hydroxide.
   (c) State two importance oxidation states exhibited by carbon, silicon and lead.
   (e) Describe how the two oxidation states vary from carbon to lead. Use the oxidation elements to illustrate your answer.
6. Explain why fluorine shows some differences in its properties from the rest of the elements of group (vii) of the periodic table.
   (b) State the differences between the chemistry of fluorine and the rest of group members of the periodic table.
   (c) Write equations to compare the reaction of fluorine and chlorine with:
      (i). Water. (ii). Cold dilute sodium hydroxide.
      (iii). Hot concentrated sodium hydroxide.

(d) Write equations for the reaction between hydrofluoric acid and silicon dioxide.
(e) Explain why hydrogen fluoride is a weaker acid than hydrogen chloride.

7. Chlorine gas can be prepared from sodium chloride in the laboratory. State other reagents and conditions required.
   (b) Write the equation of reaction. (c)State how chlorine gas can be tested.
   (e)Write the equation of reaction when chlorine gas reacts with:
      (i). cold dilute sodium hydroxide. (ii). hot concentrated sodium hydroxide.
8. The boiling of the hydride of group VII elements are given in the table below.

Compounds	**HF**	**HCl**	**HBr**	**HI**
B.P (^oC)	$^+19.9$	$^-85.0$	$^-66.7$	$^-35.4$

   a) Explain the trend in the boiling point of the hydrides.
   b) Giving reasons suggest the trend in acid strength of the hydrides.
   c) Using equations where possible explain what happens when concentrated sulphuric acid is mixed with each of the hydrides.
   d) Arrange the following compounds in order of their increasing acid strength.
      $HClO$, $HClO_2$, $HClO_3$, $HClO_4$
   e) Explain your answer in d above.
9. A solution of halate (V) ion **YO_3^-** contains **2.94g/l. 25cm³** of this solution was added to an equal volume acidified potassium iodide solution. The iodine liberated required **25.2cm³ of 24.8g/l** $Na_2S_2O_3.5H_2O$.
   a) Calculate the relative atomic mass of Y hence identify Y.
   b) Give the I.U.P.A.C name for the following oxide and calculate the oxidation number of the halogen in: (i) ClO_2 (ii) BrO_3 (iii) I_2O_5 (iv) Cl_2O_7.
   c) Explain the following observations:
      (i) The oxidation states of halogen in Oxides are positive.
      (ii) Chlorine dioxide is a mixed acid anhydride.
10. State and explain the variation of reactivity of:
   a) Group (IV) B elements towards dilute sodium hydroxide solution.
   b) Group (VII) B elements towards water.
11. State and explain the trend of acidity among:
   a) HF, HCl, HBr & HI. b) HOCl, HOBr & HOI.
   c) HOBr, HOBrO, $HOBrO_2$ & $HOBrO_3$.
12. **1.5g** of impure tin (II) Oxide was dissolved in excess dilute hydrochloric acid and the resultant solution made to **250cm³** with distilled water. **25cm³** of this solution was titrated with **0.02M** potassium permanganate until the colour turned pink. The volume of Potassium permanganate solution used was **20cm³**.
   a) Calculate the percentage impurity of tin (II) oxide *(Sn= 119, O=16)*
   b) Write an ionic equations when tin (II) ions are added to:
      (i) Acidified potassium dichromate solution
      (ii) Sodium oxalate solution (iii) Iron (III) chloride solution

13. When a yellow solid **A** is heated with air at 450°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.
    a) Identify the substances **A-E** inclusive
    b) Account for your answers in (a) above with aid of equations of reactions.
14. The standard enthalpy of formation of tin tetrachloride is $^-$508KJmol^{-1}. The standard enthalpy of atomization of tin and chlorine are $^+$301 and +121KJmol-1 respectively. The average bond energy of Si-Cl bond is $^+$383KJmol^{-1}.
    a) Determine the average bond energy of Sn-Cl bond
    b) Comment on the difference between the average bond energies.
    c) 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) Pb^{2+} & Sn^{2+} (ii) Pb^{2+} & Al^{3+} (iii) Sn^{2+} & Zn^{2+}.
15. A compound **Q** contains **90.65%** by mass of lead and the rest Oxygen.
    a) Deduce the molecular formula of **Q** if its molar mass is **685g**.
    b) State what is observed when **Q** is reacted with the following and in each case write the equation of reaction.
       (i) Dilute Nitric acid (iii) Hot concentrated sulphuric acid.
       (ii) 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.**
    (i) Determine the molecular formula of the hydride.
    (ii) 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.
    (i) What is inert pair effect?
    (ii) Give a reason for the existence of the inert pair effect.

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1. (a) Bauxite is the principal ore used for the extraction of aluminium.
   (i) Write the formula of Bauxite.
   (ii) Name two impurities present in Bauxite
   (iii) Briefly describe how pure aluminium can be obtained from bauxite. (Include appropriate equations where necessary)

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

(i) State what was observed.

(ii) Write equation of reaction that took place.