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INORGANIC CHEMISTRY

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PREFACE

Lack of books which meet requirements of 2009 new syllabus for advance level of Tanzania secondary education especially for science subjects is a big problem in the country. Lack of enough books of advanced chemistry as one of science subjects is the long time problem to both teachers and students.

This chemistry book is a result of being aware and so much concerned to the problem. It is the result of having strong desire to find appropriate solution to the problem. My hope is that, this book will be part of the solution for the problem especially for the chemistry subject. This is sweet news to hear because the book discuss intensively all matters related to inorganic chemistry as required by the new syllabus.

Organisation

The book is organised into five parts; **part 1** up to **5**. Each part discuss intensively particular topic in the syllabus: **part 1** discusses **introduction to inorganic chemistry**, **part 2** discusses **periodic trend in physical and chemical properties** and **part 3** discusses **extraction of metals**. Also **part 4** discusses **chemistry of selected compounds of metals**, **part** and finally **part 5** discusses **transition elements and complexes**.

Each part is divided into number of chapters which discuss several matters in accordance to the new syllabus.

At the end of each chapter there is a **practice exercise** for reviewing some important concepts covered in the particular chapter. Both students and teachers will find these exercises very useful.

At the end of each part there is **examination questions** which are very useful to students who wish to examine themselves on their understanding capacity of matters discussed in respective part. The questions cover knowledge of all sub-topics discussed in the respective part; therefore students are advised to attempt answering them after completing the study of all sub-topics in the chapters of the respective part. Also teachers will find questions useful in examining students' ability on the particular topic.

Near the end of the book, there are **solutions for examination questions** for providing a guide to students on answering questions relating to different topics of physical chemistry. Students are recommended to check these solutions after an attempt of answering questions through writing down and not just through mind imagination of answers. Solutions for part three are deliberately not given because according to the nature of the topic, their solutions are very direct to the text.

I hope both teachers and students will find this book helpful and interesting.

Acknowledgements

I am indebted to all students and teachers who were used to insist me about the need of preparing this book. Their belief on me provided good motivation in accomplishing difficult work of preparing this book.

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Ngaiza Lusima.

BRIEF CONTENTS

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PART ONE

INTRODUCTION
TO
INORGANIC CHEMISTRY

Chapter 1

CLASSIFICATION OF ELEMENTS

Inorganic chemistry *is the branch of chemistry which deals with the study of properties and behaviour of elements and their compounds (with exceptional of organic compounds*). It is concerned with the properties and behaviour of inorganic compounds.

Many inorganic compounds are ionic compounds, consisting of cations and anions joined by ionic bonding. These kinds of compounds (ionic compounds) are known as **salts**.

Some important features of inorganic compounds are:

- They have high melting and boiling point.
- They have high thermal stability.
- They are capable of doing electrolytic conduction. However are poor conductors in solid state because in that form ions are not free to move.
- (Compared to organic compounds) Many ionic compounds are soluble in water and they can undergo crystallisation easily.
- Their rate of reactions is generally high.

Sources of inorganic compounds

Inorganic compounds can be found:

- In nature as **minerals**, e.g. iron sulphide as pyrites or calcium phosphate as gypsum.
- As **biomolecules**, e.g. polyphosphate backbone in DNA.
- From **artificial synthesis**, e.g. ammonium nitrate which is used for soil fertilization.

Descriptive inorganic chemistry *is concerned with classification of compounds based on their properties*. One part of the classification is concerned with the position in the periodic table and another part is concerned with grouping compounds by their structural similarities.

DEVELOPMENT OF PERIODIC TABLE

The discovery of the chemical elements has been an ongoing process since ancient times. Certain elements such as gold appear in nature in elemental (uncombined) form and were thus discovered thousands of years ago.

- In contrast, some elements such as radium are radioactive and unstable. We know about them only because of technology developed in recent times (in twentieth century).

The majority of elements, although stable readily form compounds. Consequently, they are not found in nature in their elemental form. For centuries, therefore, scientists were unaware of their existence.

- During the early nineteenth century, advances in chemistry made it easier to isolate elements from their compounds. As a result, the number of known elements was increased rapidly in that period of time.
- As the number of known elements increased, scientists began to investigate the possibilities of classifying them in useful ways. In this chapter we are going to discuss those possibilities.

Reasons for classification of elements

(i) To study elements in a systematic manner (Classification may further reveal relationship between one element and another).

(ii) To correlate the properties of elements.

(iii) To know the type of different compounds that different element can form.

Classification of elements into metals and non-metals

Lavoisier, French scientist divided elements into two main types, known as metals and non-metals. Metals and non-metals can be distinguished from each other on the basis of set of physical and chemical properties. However, there are large number of metals and non-metals whose properties are quite different from one another. Below is the summary of properties of metals and non-metals.

	METAL		NON-METAL
1.	It is lustrous, i.e. it has shining surface	1.	It is not lustrous
2.	It is good conductor of heat and electricity	2.	It is bad conductor of heat and electricity
3.	It is ductile, i.e. it can be drawn into wire (Zinc metal is exceptional for this)	3.	It is not ductile
4.	It is malleable, i.e. it can be beaten into thin sheets (again Zinc metal is exceptional for this)	4.	It is not malleable
5.	It is solid at room temperature (mercury and gallium are exceptional, they are liquid)	5.	It is a gas, volatile or brittle solid at room temperature

Drawbacks of classifying elements into metals and non-metals

Classification of elements into metals and non-metals is quite inadequate due to the following reasons:

(i) Such classification hardly serves any purpose as the elements are just divided into two major groups only.

(ii) There is no justification for more active metals and active non-metals.

(iii) Certain elements exhibit both metallic and non-metallic properties. These elements are known as **metalloids** or **semi-metals**.

Dobereiner's triads

A German chemist, Dobereiner observed that certain elements which had similar chemical properties could be grouped together.

- When these elements were arranged in increasing order of their atomic weights (masses), they generally occurred in groups of three. These groups were called **triads**.
- He noticed that the atomic mass of the middle element of the triad was arithmetic mean of the other two elements of the triad. This was known as the **Dobereiner's law of triad** which can be stated as follows:

When elements are placed in increasing order of their atomic masses, groups of three elements having similar properties called triads are obtained. The atomic mass of the middle element of the triad is equal to arithmetic mean of the atomic masses of the other two elements of the triad.

Examples of triads

Example 1: In Alkali metal;

Element	**Atomic mass**
Lithium (Li)	7
Sodium (Na)	23
Potassium (K)	39

Justification: From the Dobereiner's law of triads, the atomic mass of the middle element (sodium) should be arithmetic mean of Li and K.

And $\frac{\text{Atomic mass of Li}+\text{Atomic mass of K}}{2} = \frac{7+39}{2} = 23 = \text{Atomic mas of Na}$

Hence the Dobereiner's law is valid for alkali metal triad.

Example 2: In Alkali earth metal;

Element	**Atomic mass**
Beryllium (Be)	8
Magnesium (Mg)	24
Calcium (Ca)	40

Justification: For Dobereiner's law to be valid, the atomic mass of Mg should be arithmetic mean of Be and Ca.

And $\frac{\text{Atomic mass of Be}+\text{Atomic mass of Ca}}{2} = \frac{8+40}{2} = 24 = \text{Atomic mas of Mg}$

Hence the Dobereiner's law is valid for alkali earth metal triad.

Example 3: In halogens;

Element	**Atomic mass**
Chlorine (Cl)	35.5
Bromine (Br)	80
Iodine (I)	127

Justification: For Dobereiner's law to be valid, the atomic mass of Br should be arithmetic mean of Cl and I.

And $\frac{\text{Atomic mass of Cl}+\text{Atomic mass of I}}{2} = \frac{35.5+127}{2} = 81.25 = \text{Atomic mas of Br}$

But the actual atomic mass of Br is 80 which is nearly equal to 81.25 (arithmetic mean of Cl and I).

Hence the Dobereiner's law is valid for halogen triad.

Advantages of Dobereiner's law of triads

(i) Atomic mass (which is fundamental property of an atom) was considered as basis of classification.

(ii) It made chemists to look at elements in terms of groups of elements with similar physical and chemical properties which eventually led to discovery of modern periodic table.

Drawbacks of Dobereiner's law of triads

(i) Not all known elements can be arranged in the form of triads.

- For example, $\mathrm{F, Cl,}$ and Br cannot be arranged in triads because atomic mass of Cl is not an arithmetic mean of atomic masses of F and Br.

(ii) As the technique for determining atomic masses accurately improved, the law was unable to remain strictly correct.

(iii) Some elements with dissimilar properties were grouped as triads. For example carbon ($^{12}\mathrm{C}$), nitrogen ($^{14}\mathrm{N}$) and oxygen ($^{16}\mathrm{O}$) form a triads;

$\left(\text{Atomic mass of N} = \frac{\text{Atomic mass of C+Atomic mass of O}}{2}\right)$,however the three elements have different properties.

Newland's law of octaves

After Dobereiner, an English Newlands observed that every eighth element showed similar physical and chemical properties when elements were placed in the increasing order of their atomic masses. It was similar to musical note where after seven different notes the eighth note is repetition (harmonic) of the first one and hence the law was called the **law of octaves.** Newlands law of octaves may be stated as follows:

When elements are arranged in the increasing order of their atomic masses, the eighth element resembles the first in physical and chemical properties.

Newlands arranged the elements in the following manner:

Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl

In this arrangement, a row of elements had seven elements and the eighth element fell under the first element

- In those days, the number of discovered elements was very small and noble gases were not known.

Advantages of Newlands law of octaves

(i) Atomic mass (which is fundamental property of an atom) was considered as basis of classification.

(ii) It introduced the idea of periodicity (the core idea in which the modern periodic table is based).

(iii) Dobereiner's triads occurred in the octaves of Newlands.

Drawbacks of Newland law of octaves

(i) It was not valid for elements beyond calcium.

- For example, Co and Ni which were placed below chlorine had different properties.

(ii) When new elements like noble gases were discovered, his table had no place for them.

- Their inclusion (after their discovery) in the table disturbed the entire arrangement.

(iii) Newland thought that only about 50 elements existed in nature and no more elements were likely to be discovered. But he was proved wrong. (Nowadays 115 elements have been discovered).

(iv) Iron element which resembles cobalt and nickel elements in properties, was placed far away from these elements.

Lothar Meyer

Lothar Meyer tried to classify elements by plotting a graph of atomic volume (which is directly related to atomic radius) versus atomic weights (masses) of different elements. He was studying physical properties of elements along with their valence numbers (Meyer was the first scientist to introduce the valence as a periodic property).

- His table showed how the integral valence changed as the atomic mass of elements increased such that elements with the same valence number were kept at the same column.

Like Mendeleeff, Meyer arranged elements in order of increasing their atomic weight. He was also able to leave gaps of some undiscovered elements (also like Mendeleeff).

Advantages of Lothar Meyer's classification

(i) It introduced the idea of periodicity of physical properties like melting points, boiling points and valances.

(ii) It led to the confirmation of periodicity in chemical properties.

Mendeleeff's periodic law

Mendeleeff believed that atomic mass of elements was the most fundamental property of an atom. He successfully arranged the atoms of elements according to increase their atomic weight (mass) in the form of a table in almost the same way as Lothar Meyer did. However Mendeleeff is the one who is considered as the father of periodic table and not Lothar Meyer. Now the question is ***Why is Mendeleeff called "father of periodic table" and not Meyer or both of them?***

This is because, Mendeleeff:

- Stated that if the atomic weight of an element caused it to be placed in the wrong group, then the weight must be wrong. (He corrected the atomic masses of some elements like Beryllium, Indium and Uranium).
- He was so confident in his table that he was used it to predict correctly the physical properties of undiscovered element (like scandium, gallium and germanium).

Mendeleeff's law of periodicity states that:

Properties of elements are ***periodic function*** *of their atomic weight.*

Thus according to Mendeleeff:

- Properties of elements depends on (function of) their atomic weight.
- When elements are arranged in order of increasing of their atomic weight, their properties tend to repeat after certain specified intervals(s) i.e. they tend to show periodic variation on their properties.

Advantages of Mendeleeff's periodic table

Despite of various weaknesses (as we will see later), Mendeleeff's periodic table resulted from the Mendeleeff's law of periodicity have the following strengths:

(i) It is based on atomic mass of element which is considered as fundamental property of an atom.

(ii) Periodic table resulted from Mendeleeff's law, provided the basis of modern periodic table.

- Mendeleeff was able to arrange atoms of elements into periods and groups like in modern periodic table.

(iii) Mendeleeff's periodic table encouraged discovering of new elements.

This is because:

- He was able to leave gaps (boxes) for elements which were not yet discovered in his periodic table.
- He was able to predict properties of elements which were not yet discovered.

(iv) Mendeleeff's periodic table was used to predict the error in the atomic weights of some elements on the basis of their position in the periodic table.

Shortcomings of Mendeleeff's periodic table

Mendeleeff's was successful in arranging the elements according to his law in the form of a table, but the table produced some defects which, he could not explain. These defects are:

(i) **Anomalous pairs:** Some elements with lower atomic weight were kept after those of higher atomic weight and Mendeleeff was unable to give convincing reasons for doing such reverse.

- For example, Tellurium which has greater atomic weight (its relative atomic mass is 127.5) than iodine (which has relative atomic mass of 126.9) was kept before the iodine. Another example of anomalous pair is cobalt (relative atomic mass, 58.9) and nickel (relative atomic mass, 58.6) where cobalt was kept before nickel**.**

(ii) **Position of isotope:** Presence of isotopes makes difficult to arrange some atoms of elements in the periodic table according to Mendeleeff's law.

- For example, carbon exists in three isotopes forms, i.e. $\mathrm{C}-12, \mathrm{C}-13$ and $\mathrm{C}-14$ and one contradiction which is very simple to recognize is: what is the exact position of carbon in the periodic table? Are the three isotopes taking different positions? Is $\mathrm{C}-14$ takes the same position as that of nitrogen which has also atomic weight of 14? What about properties of $\mathrm{C}-14$ and nitrogen; are they the same?

(iii) **Position of isobars:** Presence of isobar makes difficult to arrange some atoms of elements in the periodic table according to the Mendeleeff's law.

- For example both Argon (after its discovery) and calcium have atomic weight of 40! So are they taking the same position in the periodic table? What about their properties………? Are they the same?

(iv) **Wrong grouping of elements (superfluous relationship):** Some elements like copper (Cu) and gold (Au) were placed in the same group in spite of their dissimilar properties and some other elements like palladium and nickel were arranged in different groups without concerning their similar properties.

(v) **Unrecognition of noble gases:** Mendeleeff was unable to recognise the presence of noble gases (he did not leave gaps for noble gases in his periodic table).

(vi) **Position of hydrogen:** The position of hydrogen atom was not clear because it behaves both as a member of first and seventh group of his periodic table.

(vii) **Position of lanthanides and actinides:** Arrangement of these elements as per the basic law of the table produced an undue side-wards projection, which was not explainable to Mendeleeff because their position cannot be justified on the basis of atomic masses.

Moseley periodic law

After Mendeleeff, an English physicist, Moseley (also spelled Mosley) discovered that atomic number is more fundamental property than not atomic mass.

- As result of this; new then modified periodic law called the **modern periodic law** (or **Moseley periodic law** in honour to the discoverer) was discovered.

The law states that:

Properties of elements are periodic function of their atomic numbers.

Thus according to the modern periodic law:

- Properties of elements depend on their atomic number
- When elements are arranged in order of increasing of their atomic numbers, their properties tend to repeat after certain specified interval(s).

Advantages of Modern periodic law

(i) Modern periodic law explains why some elements with greater atomic weight must be kept before those elements with lower atomic weight.

- This is simply because, despite the fact that those elements have greater atomic weight, they have also lower atomic numbers. For example in the case of tellurium and iodine, the first element has atomic number of 52 and the later has atomic number of 53, the fact which leads to the following conclusion. *Although Tellurium has greater atomic weight than iodine, it must be kept before the iodine because the atomic number of the tellurium is lower than that of iodine.*

(ii) Modern periodic law overcomes the difficulty of arranging isotopes in the periodic table.

- This simply because, although isotopes have different atomic weights, the element with isotopes take single position since they have the same atomic number. (The reader should recall that all atoms of the same elements regardless to the existence of isotopes have the same atomic number).

(iii) Modern periodic law overcomes the difficulty of arranging isobar in the periodic table.

- This is simply because no two atoms of different elements have same atomic number even if they have the same atomic weight. For example, in the case of argon and calcium; although the two elements have the same atomic weight of 40, argon which has smaller atomic number of 18 must be written before calcium which has atomic number of 20.

The reader should understand that:

Periodicity of properties of elements *is the result of periodicity of outermost electronic configuration of atoms of the elements.* When elements are arranged according to an increase of their atomic number, their outermost electronic configurations tends to repeat after certain intervals and is the outermost electronic configuration which determines physical and chemical properties of the elements and hence properties of elements appear to repeat after certain interval when they are arranged according to increase of their atomic numbers. For example all group IA elements have outermost electronic configuration of ns^1, group IIA elements have ns^2, group IIIA elements have ns^2np^1 etc, where n is the outermost energy level.

So what was wrong with Mendeleeff?

Mendeleeff thought that properties of elements depend on (function of) of their atomic weights. That was wrong because atomic weight has nothing to do with electronic configurations of elements.

- Electronic configuration (which is the result of **quantum mechanical theory**) and hence outermost electronic configuration is deduced from atomic number and eventually properties of elements will depend on the atomic number as Moseley suggested in the modern periodic law.

Also, Mendeleeff's periodic law allows us to predict **what** the properties of an element will be based on its position on the table. It **does not explain why** the pattern exists.

- **Quantum mechanics** (which led into modern electronic configuration) is a theory that **explains why** the periodic trends in the properties exist. (Knowing why allows us to predict what).

MODERN PERIODIC TABLE

The number of elements known so far is 115. These elements combine together to form very large number of compounds. It is therefore, very difficult to study each element separately. So, in order to make the study of elements and their compounds easier, it has become necessary to arrange and classify the elements in a systematic manner in the periodic table.

- The periodic table we use today is known as **modern periodic table**. It is also known as **long form of periodic**. *It is a tabular representation of all known elements*.
- Modern periodic table is the result of Moseley periodic law and hence it is also known as **Moseley's periodic table**.

Possibility of arranging elements in the periodic table is a result of **periodicity of properties of elements** that is *when elements are arranged in the order of increasing their atomic numbers their properties seems of repeat after certain interval.*

There are two factors which enable classification of elements in the periodic table, which are:

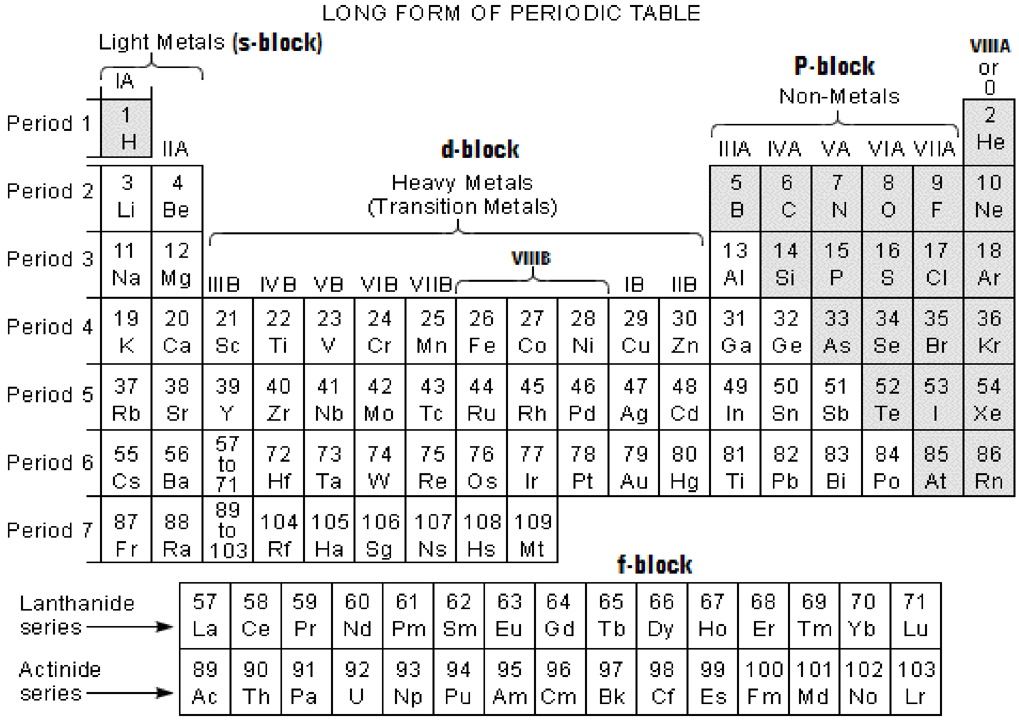
- Periodicity in outermost electronic configuration of elements
- Periodicity in physical and chemical properties of elements

Definition of terms

Periodic table *is the arrangement of atoms of elements into **periods** and **groups** according to an increase in their atomic numbers.* Whereas:

Period *is the horizontal row of the atoms in the periodic table*.

Group (or **family**) *is the vertical column of the atoms in the periodic table*.



LONG FORM OF PERIODIC TABLE

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB	VIIIB	VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA or 0
Period 1	1 H																	2 He
Period 2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
Period 3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
Period 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
Period 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
Period 6	55 Cs	56 Ba	57 to 71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Ti	82 Pb	83 Bi	84 Po	85 At	86 Rn
Period 7	87 Fr	88 Ra	89 to 103	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt									

Lanthanide series →	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
Actinide series →	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

Understanding the modern periodic table

- In the modern periodic table, groups are indicated by using Roman numerals while periods are indicated by using Arabic numerals. This is according to American system (formulated by **Chemistry Abstract Service**, **CAS**). The latest IUPAC system use Arabic numerals for both periods and groups.

- Groups with five or six elements are known as **representative, major, typical,** or **normal groups** and shorter groups are known as **sub- groups.**
  - Similarly elements in long groups are known as **major, typical, representative** or **normal elements**. And elements in short groups are known as **sub-elements**.

- Number of elements in each period is as follows:
  - Period 1 has two elements.
  - Period 2 and 3 has 8 elements in each.
  - Period 4 and 5 has 18 elements in each.
  - Period 6 has 32 elements and similarly period 7 have potentially 32 elements. (Notice the use of the word 'potentially' because some elements in period 7 have not yet discovered).
  - Thus when elements are arranged in the order of increasing of their atomic numbers, their outermost electronic configurations, physical and chemical properties repeats in the following periods of elements: 2, 8, 8, 18, 18, 32, 32 in seven periods. 2, 8, 18 and 32 are known as **magic numbers.**

- **Major groups are A's groups** (IA up to VIIIA and IB up to VIIIB) while **sub-groups are B's groups**. Again this is according to CAS system (which is often used in America). The old IUPAC system (is often used in Europe, that is why is known as European system) assigns A's for groups in the left and B's for groups in the right of the periodic table while the latest IUPAC system assign 1 up to 18 from the left to the right instead of IA, IIA, IIA, IB, IIB etc.
  - As an example, carbon belongs to group IVA according to American system, group IVB according to European system and group 14 according to the latest IUPAC system.

However because still American system is more common than other system; groups in this book will be assigned according to the American (CAS) system.

- Lanthanides are in period 6 and group IIIB.
- Actinides are in period 7 and group IIIB.
- **Group IA and IIA** are found at **s-block** of the modern periodic table.
- **Group IIIA to VIIIA** are found at **p-block** of the periodic table.
- **Transition metals** are found at **d-block** of the periodic table.
- **Lanthanides** (They are known as lanthanides because their properties resemble to those lanthanum which is the first element in the series) and **actinides** (They are known as actinides because they resemble to actinium which is the first element in the series) are found at **f-block.**
    - Lanthanides and actinides are also known as **inner transition elements** because their last electron inter to $(n-2)$f orbital which is inner to penultimate shell ($(n-1)$th shell where n is the outermost shell), the shell to which last electron of transition element enters.
    - Lanthanides elements are also known as **rare earths** because they were originally extracted from oxides, which were called **earths** earlier (by ancient scientists) and which were considered rare.
- **Metallic characters**

Metallic character *is how closely an element's properties match the ideal properties of metal.*

- When an element is more malleable and ductile, better conductors and easier to ionise as positive charge, the element is then said to be more metallic in characters.

Metallic character decreases left to right across a period.

- Metals are found at the left of the periodic table and non metals to the right.
- Actually elements on the left of metalloids are metals and those on the right of metalloids are non-metals. Metalloids which form this boundary are boron, ${}_{5}$B, silicon, ${}_{14}$Si, germanium, ${}_{32}$Ge, arsenic, ${}_{33}$As, and tellurium, ${}_{52}$Te.

Metallic character increases down the group.

- Non-metals are found at the top of the middle main group elements and metals are found at bottom.

Representative elements consist of metals, non-metals and metalloids while elements in sub-groups are all metals.

Electronic configuration and modern periodic table

Quantum-mechanical theory describes the behaviour of electrons in atoms. It explains that electrons in atoms exist in orbitals. A description of the orbitals occupied by electrons is called an electronic configuration. Quantum-mechanical theory and thus electronic configuration is the basis of modern periodic table. There is a large relationship between electronic configuration and modern periodic table as outlined below.

- The **group number** corresponds to the number of valence electrons.

That is $\textbf{Group number} = \textbf{Number of valence electrons}$ (This is only valid for representative elements which are s and p-block elements).

- The **period number** corresponds to the principal energy level of the valence electrons.

That is $\textbf{Period number} = \textbf{Greatest principal quantum number}$

- **Block** type is the of last subenergy level to fill electron. Thus, it is the letter of filled subenergy level with greatest value of $\mathbf{n + l}$ (If there is more than one possibility of giving the same greatest value of $n + l$, the it the letter of subenergy level with greatest n).
- The length of ach "**block**" is the maximum number of electrons the sublevel can hold. For example;
  - In each period, s-block has two elements
  - In each period, p-block has six elements
  - In each period, d-block has ten electrons
- The number of elements in each period can easily be deduced from electronic configuration as shown in the table below:

Electronic configuration of each period

Period	**Orbitals filled**	**Number of elements = Maximum number of electrons filled**
1(short)	1s	2
2(short)	2s,2p	$2 + 6 = 8$
3(short)	3s,3p	$2 + 6 = 8$
4(long)	3d,4s,4p	$2 + 6 + 10 = 18$
5(long)	4d,5s,5p	$2 + 6 + 10 = 18$
6(very long)	4f,5d,6s,6p	$2 + 6 + 10 + 14 = 32$
7(very long)	5f,6d,7s,7p	$2 + 6 + 10 + 14 = 32$

Thus from above table, it can be deduced that total number of potential elements to be $2 + 8 + 8 + 18 + 18 + 32 + 32 = 118\text{elements}$.

Example

Without consulting the periodic table, write down the electronic configuration and hence state the position in the periodic table for the elements with atomic number shown below:

(a) 12 (b) 14 (c) 32 (d) 37

Solution

(a) Electronic configuration: $[\mathrm{Ne}]3s^2$

From which:

- Last subenergy level to fill electron is s-subenergy level.

Thus the element is found at **s-block.**

- Greatest principal quantum number is 3

Thus the element is found at **period 3.**

- Outermost electronic configuration is $3s^2$ with 2 valence electrons.

Thus the element is found at **group IIA.**

(b) Electronic configuration: $[\mathrm{Ne}]3s^2 3p^2$

From which:

- Last subenergy level to fill electron is p-subenergy level.
- Greatest principal quantum number is 3
- Outermost electronic configuration is $3s^2 3p^2$ with total of $2 + 2$ or 4 valence electrons.

Hence the element is found at p-block, group IVA and period 3.

(c) Electronic configuration: $[\mathrm{Ar}]4s^2 3d^{10} 4p^2$

From which:

- Last subenergy level to fill electron is p-subenergy level.
- Greatest principal quantum number is 4
- Outermost electronic configuration is $4s^2 4p^2$ with total of $2 + 2$ or 4 valence electrons.

Hence the element is found at p-block, group IVA and period 4.

(d) Electronic configuration: $[\mathrm{Kr}]5s^1$

From which:

- Last subenergy level to fill electron is s-subenergy level.
- Greatest principal quantum number is 5
- Outermost electronic configuration is $5s^1$ with total 1 valence electron.

Hence the element is found at s-block, group IA and period 5.

You should be aware with this fact!

Group number (according to American system) of only representative elements (s and p-block elements) can easily be deduced from their electronic configuration. To deduce the group number of sub-elements (with given atomic number) you might need to memorise and therefore consulting the skeleton of the periodic table.

- However (from electronic configuration) you can easily assign group number of sub-elements in accordance to latest IUPAC system whereby for transition elements; group number is equal to the total number of electrons in s-subenergy level of outermost shell (nth shell) and electrons in d-subenergy level in penultimate shell ($(n - 1)$th shell).

That is;

$$\textbf{Group number} = \textbf{number of electrons in ns orbital} + \textbf{number of electrons in } (\mathbf{n-1})\textbf{d orbitals}$$

Two 'dots' for concluding…..!

- Electronic configuration can easily be used to deduce **American group number** of elements in representative groups (s and b blocks) and **IUPAC group number** of elements in sub-groups.
- Electronic configuration is not used to deduce American group number of elements in sub-groups and IUPAC group number of elements in representative groups.

Example

Without consulting the periodic table, write down the electronic configuration and hence state the position in the periodic table for the elements with atomic number of 27.

Solution

Electronic configuration: $[\mathrm{Ar}]4s^2 3d^7$

From which:

- Last subenergy level to fill electron is d-subenergy level (This implies that the given element is sub-element; so if we have not to consult the periodic table, we must assign IUPAC group number).

Thus the element is found at **d-block.**

- Greatest principal quantum number is 4.

Thus the element is found at **period 4.**

- Total number of electrons in 4s and 3d orbitals is $2 + 7$ or 9 electrons.

Thus the element is found at **group 9.**

Advantages of long form of periodic table

(i) The modern periodic table is based on atomic number which is more fundamental property of an atom than atomic mass (weight).

- The long form of modern periodic table is therefore free from main defects of Mendeleeff's periodic table.

(ii) The table shows why elements in the same group display similar properties.

(iii) The table shows how and why properties of elements differ in the same period.

(iv) The periodicity is related to electronic configuration.

- As chemical and physical properties depend on the electronic configuration of elements, the modern periodic table is very systematic and follows the fundamental electronic structure of the elements to classify them.

Defects in the long form of the periodic table

(i) **Position of hydrogen:** No clear position for hydrogen (since it shows properties of both alkali metals as well as halogens, position of hydrogen is said to be anomalous).

(ii) **Accommodation of lanthanides and actinides:** Lanthanides and actinides are not accommodated in the main body of the periodic table.

(iii) **Position of helium:** Helium is kept in group VIIIA with noble gases although:

- It has two valence electrons while other noble gases have eight valence electrons.
- Its outermost electronic configuration ends with $1s^2$ suggesting that it should be kept in s-block with alkali earth metals which also end with ns^2 where n is the outermost energy level. This is different to other noble gases whose outermost electronic configuration end with np^6 confirming that they are p-block elements.

Position of hydrogen in the modern periodic table

The word **'hydrogen'** comes from two Greek words **hydros** and **gennen**. **Hydros** means **water** and **gennen** means **maker or creator**. Thus hydrogen is water maker reflecting its feature of being important component of water. It occurs in three isotopic forms which are:

(i) **Normal hydrogen** which is also known as **protium**, H, also denoted as ^{1}H

Deuterium, $^{2}_{1}H$ which is denoted as ^{2}H or D, e.g. oxide of deuterium is donated as D_2O and is known as heavy water while Deuterium itself is known as heavy hydrogen.

(ii) **Tritium,** $^{3}_{1}H$ which is denoted as ^{3}H or T. It is rare and unstable.

Hydrogen has dual characters. It has many properties which make it similar to the alkali metals of group IA and many other properties which make it similar to halogens in group VIIA.

Reasons for placing hydrogen in group VIIA (hydrogen as halogen)

(i) Electronic configuration

It lacks one electron only to attain stable electronic configuration of noble gas (He) like halogens.

(ii) Oxidation state

When it combines with strong electropositive metal, hydrogen has an oxidation state of -1 like halogen e.g. $\overset{-1}{\mathrm{NaH}}$ and $\overset{-1}{\mathrm{NaX}}$ or $\overset{-1}{\mathrm{MgH_2}}$ and $\overset{-1}{\mathrm{MgX_2}}$ where X is halogen

(iii) Atomicity

At room temperature, hydrogen gas exists as diatomic molecule like halogens. It exists as H_2 (hydrogen molecule) while other halogens exist as X_2 like F_2, Cl_2, Br_2 etc.

(iv) Nature of compounds

It forms compounds of the same stoichiometric ratio with group IVA elements like halogens, e.g. CH_4 and CCl_4, or SiH_4 and $SiCl_4$.

(v) Ionisation energy

It has high first ionisation energy whose magnitude resembles to those of halogens

(vi) Non-metallic character

It is non – metal like halogens

(vii) Replacement by halogens

Hydrogen may be replaced by halogens in hydrocarbon indicating that both hydrogen and halogens have similar nature.

$$CH_4 + Cl_2 \overset{\Delta}{\rightarrow} CH_3Cl + HCl$$

(viii) Physical state

Hydrogen molecule is gas at room temperature like F_2 and Cl_2 of group VIIA.

(ix) Oxidising property

It can gain an electron to give hydride (H^-) like halogens which give halide (X^-).

Reasons for placing hydrogen in group IA (hydrogen as alkali metal)

(i) Electronic configuration

The outermost electronic configuration of hydrogen has only one electron in s^- orbital like alkali metals. The outermost electronic configuration of alkali metals is ns^1 where n is outermost energy level while the electronic configuration of hydrogen is $1s^1$.

(ii) Oxidation state

When it combines with strong electronegative element, it shows oxidation number of $+1$ like alkali metals. Example, with halogen it forms HX while alkali metal form MX where X is halogen and M is alkali metal.

(iii) Metallic character

It can ionise by losing electron to give H^+ like alkali metals which give M^+ (Na^+, K^+, Li^+ etc). In electrolysis, both $H^+$and M^+ are discharged at cathode.

(iv) Reducing agent

Like alkali metals, hydrogen is also very good reducing agent.

(v) Combination with non-metals

Hydrogen, like the alkali metals, combines readily with non-metal like halogens, oxygen, sulphur, etc

Conclusion:

The best **group position** hydrogen in periodic table is group IA due t o the following reasons:

- According to modern periodic law, atoms of elements are arranged in the periodic table according to an increase in their atomic numbers. So since hydrogen has lowest atomic number of 1, it must be given first position driving it on the top of group IA
- Valence electron of hydrogen is in s – orbital, so hydrogen must be placed at s - block like alkali metals (halogens are at p – block).

Also the best **period position** of hydrogen in the periodic table is period 1 due to the following reasons:

- Having smallest atomic number, hydrogen must be kept at top of group IA (according to modern periodic law). Being on the top of the group, implies that it is in period 1.
- Having valence shell of 1 (hydrogen has only single electronic shell) justifies that hydrogen must be kept at period 1 of periodic table.

Therefore for reasons explained in the above discussion, the best position of hydrogen in the periodic table is:

- group IA
- period 1
- s - block

Don't forget: when we are talking about 'general' position of element in the periodic table, there are three important information which are required which are information about **group, period** and **block.**

PRACTICE EXERCISE 1

Question 1

Give two ways in which the Newlands' table is inferior to that of Mendeleeff.

Question 2

What is the meaning of the representative elements? Name the groups of the periodic table, which contain representative elements.

Question 3

Mendeleeff listed elements in order of increasing atomic weight (Now called relative atomic mass)

(a) What property is used for the order of the elements?
(b) Which particle within the atom is responsible for this property?

Question 4

To which block does the element with configuration $3d^7 4s^2$ belongs?

Question 5

(a) In terms of their blocks in periodic table, what are normal, transition and inner-transition elements?
(b) What is the difference between normal and transition elements?

Question 6

State two merits and two demerits of long form of the periodic table

Question 7

a) State the periodic law according to Mendeleeff.
b) What was usefulness of the Mendeleeff's periodic table?

Question 8

a) Discuss the statement "Hydrogen is notorious element in the periodic table"

b) What argument can you offer to place hydrogen in

  i. Group IA of the periodic table

  ii. Group VIIA of the periodic table

c) In which group do you think hydrogen should strictly belongs to? Give reasons for your choice.

Chapter 2

ATOMIC SIZE

Atomic size is the one of general periodic properties. Other general periodic properties include ionisation energy, electronegativity and electron affinity. These general periodic properties of elements determine physical and chemical properties of elements in the periodic table.

ATOMIC RADIUS

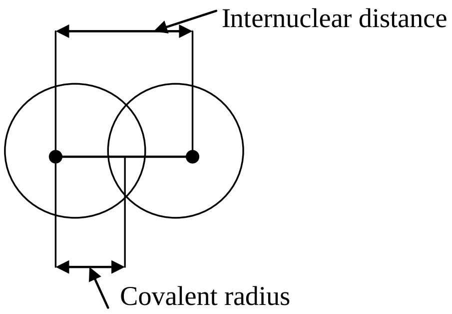
Atomic size is always expressed in terms of **atomic radius**. People of mathematics define radius of a circle as the distance from the centre of the circle to any point on the circumference of the circle. If we refer to this concept of mathematics, the atomic radius would be defined as the distance from the nucleus (centre of a circle) to a valence shell or to an electron which is farthest from the nucleus (a point on circumference of a circle).

However ***we cannot define atomic radius as mathematicians do, why***? Here are reasons:

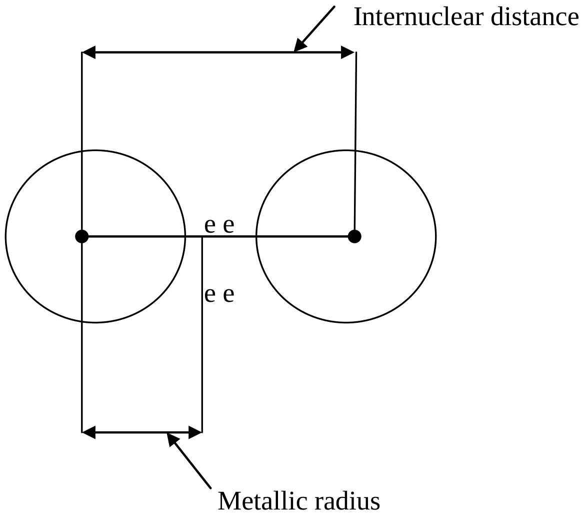
- In order to measure atomic radius defined in that way we need to split an element to get its single isolated atom (remember atoms always exist combined form) which is impossible as there is no any invented instrument of doing such thing.
- Atomic size (radius) is affected by the nature of neighbour atom. So atomic size of given element many vary depending on the nature of another atom it combine with.
- It is impossible to determine the exact position of an electron which is farthest from the nucleus thus making impossible to get its correct distance from the nucleus of the atom.

After that short discussion, now we can define atomic radius as: *A half of internuclear distance between two bonded atoms of an element.* It can be **covalent radius** (for **covalent bonded** atoms), **metallic radius** (for **metallic bonded** atoms) or **Van – der – Waals radius** (for atom which do not form bond with another atom like in noble gases which however in actual sense there is very weak interatomic forces called Van-der-Waals forces). Thus:

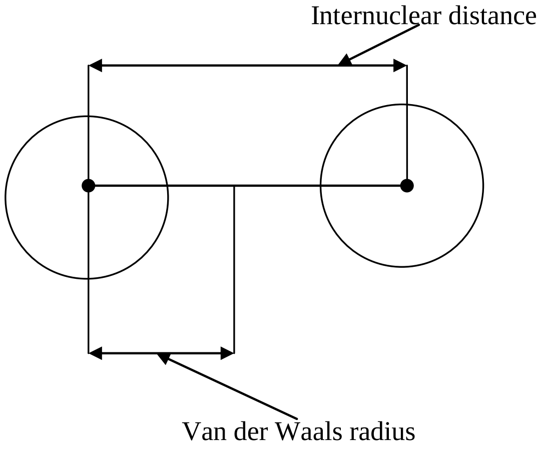
- For two atoms of the same element (non – metals) bonded by covalent bond (like in Cl_2 or O_2), atomic radius (covalent radius) can be illustrated as follows:



- For metal atoms which are bonded by metallic bond, atomic radius (metallic radius) can be illustrated as follows:



- And for unbounded atoms (in noble gases) whereby the atoms are thought to be held together by very weak Van – der - Waals intermolecular forces of attraction, atomic radius (Van – der – Waals radius) can be illustrated as follows:



Therefore:

- **Covalent radius** can be defined as *a half of internuclear distance between two covalent bonded atoms of the same element.*
- **Metallic radius** can be defined as *a half of internuclear distance between two metal atoms bonded by metallic bond*.
- **Van der Waals radius** can be defined as *a half of the internuclear distance between two unbonded atoms when the electrostatic forces between them are balanced.*

The student should understand that (from above discussion):

- In most cases, metallic radius is greater than covalent radius. This is simply because in covalent bonded atoms, due to overlapping of atoms the valence electrons of each atom are experiencing stronger nuclear attractive forces from two nuclei (of two bonded atoms) and hence their atomic sizes become smaller.
- In most cases, Van – der – waals radius is greater than covalent radius and this explains why **noble gases have greater atomic radii than halogens (and most of non – metals) of the same period** although generally atomic radii decrease as you go across the period from the

left to the right hand side (as we will see later). This is simply because **halogens (and other non – metals) have covalent radii as they are covalent bonded while noble gases are bonded by neither covalent bond nor metallic bond and hence they have Van – der – Waals radii.**

Variation of atomic size in the periodic table

Generally atomic size is determined by two factors:

(i) Nuclear attractive force and

(ii) Screening effect

(i) Nuclear attractive force

This is the electrostatic force of attraction exerted by protons present in nucleus of an atom to negatively charged electrons present in shell(s) of the atom. It makes shells including valence shell to contract and hence decreasing size of the atom. So we are expecting:

- More contraction of shells and hence more decrease of atomic size as number of protons (the one responsible for exerting nuclear attractive pull) increases.
- The atomic size to decrease as you go across the period (from left to right) and also to decrease as you descend (go down) the group because number of protons and hence nuclear attractive force increases in both directions.

(ii) Screening effect

This is the effect which arises in an atom or an ion when nuclear attractive force fails to reach electrons in valence shell properly. It may result from:

- **Repulsion** between electrons in outermost shell and electrons in inner shells. This makes valence shell to expand. The repulsion increases with an increase in number of electrons.

\- However it causes very weak screening effect. So it is minor factor for screening effect.

- **Shielding effect** which is caused by electrons in inner shells to shield nuclear attractive force to reach to electrons in outermost shell.

\- **Shielding** occurs when an electron in a multi-electron atom is partially hindered (shielded) from the positive charge of the nucleus by other (inner) electrons in the atom.

\- The strength of shielding effect increases with an increase in number of inner electrons (electrons in inner shells). So **for major groups;** *across the period the shielding effect tends to remain constant while it tends to increase as you descend the groups due to increase in number of shells which implies that number of inner electrons must also increase on descending the group.*

\- The extent of shielding exerted by inner electrons depends on their distance from the nucleus. *If the electron(s) is closer to nucleus then the shielding effect exerted will be stronger and vice – versa.*

\- Thus the strength of shielding effect exerted by inner electrons follows the following trend:

$$\underset{\text{Decrease in shielding effect exerted by electrons}}{\xrightarrow{\text{Electrons in: s – orbital > p – orbital > d – orbital > f – orbital}}}$$

You should understand this:

Unlike the repulsion, shielding effect causes very strong screening effect. Therefore wherever there is shielding effect, screening effect become significant and hence the two terms: shielding effect and screening effect are commonly used interchangeably.

To conclude…..!

From screening effect, we are expecting:

- Very small expansion of valence shell and hence negligible increase of atomic size as you go across the period (from left to right) because in that direction, screening effect is caused by one factor only of repulsion (repulsion of electrons increases with increase in number of electrons) which exerts very weak screening effect.
- Large expansion of outermost shell and hence large increase in atomic size as you descend the group because in that direction screening effect is increased by both strong factor of shielding effect and weak factor of repulsion between inner and outer electrons.

So what conclusion can be made from nuclear attractive force and screening effect with respect to variation of atomic size in the periodic table?

After above discussion on effective nuclear attractive force and screening effect, now we can understand trend of atomic radii across the period and down the group.

Trend across the period

Across the period, there are two contradicting factors; the increase in screening effect which makes the atomic radius to increase and increase in nuclear attractive force which makes the atomic radius to decrease, so……………………..?

However the increase in screening effect in negligible as it is caused by weak factor only of increase of repulsion between inner and outer electrons as result of increase in number of electrons as you go across the period from left to right. This makes the increase in nuclear attractive force to outweigh the increase in screening effect and hence **across the period (from left to right) the increase in nuclear attractive force becomes more dominant.** So……….! What is the conclusion?

Here, it is…!

Atomic radii of ***major groups,*** *decreases as you go across the period (from left to right) due to increase in nuclear attractive force as result of increase of number of protons (nuclear charge) while number of shells and hence screening effect remain constant.*

However the reader should understand that: Transition metals do not show significant change on their atomic radii due to the fact that: in transition metals the increase in nuclear attractive force in enough to counterbalance with increase in nuclear attractive force as electrons are added to inner (penultimate) d-sub-shell.

- Adding electrons in **penultimate shell** (a shell just inner to outermost shell) makes shielding effect to increase as result of increase in number of inner electrons (unlike in major groups whereby electrons are added to the outermost shell); as result transition elements have approximately the same effective nuclear charge and hence atomic radii of transition elements become fairly constant.

Trend down the group

In this case, there are also two contradicting factors: the increase in screening effect which makes the atomic radius to increase and the increase in nuclear attractive force which makes the atomic radius to decrease.

However the increase in screening effect is very large as it is caused by both factors of shielding effect which increase as you descend the group due to increase in number of shells (which is always accompanied with an increase in number of inner electrons) and repulsion between inner and outer electron whose increase is caused by increase in number of electrons. This makes the increase in screening effect to outweigh the increase in nuclear attractive force. Thus as you descend the group, the increase in screening effect is more dominant. So our conclusion….?

Atomic radius increases as you descend the group due to increase in screening effect as result of an increase in number of shells in the same trend.

Understand the term: effective nuclear attractive force!

Effective nuclear attractive force *is the term used to express the net effect of nuclear attractive force and screening effect.*

- It is directly related to **effective nuclear charge**, whereas;

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

Where; Z_{effect} is the effective nuclear charge.

Z is the total number of protons (which determines amount of nuclear charge)

S is the screening constant which roughly is the total number of inner electrons (which determines amount of screening effect).

Thus, **effective nuclear charge** *is the net positive charges that attracting a particular electron.*

From earlier discussion we may conclude that:

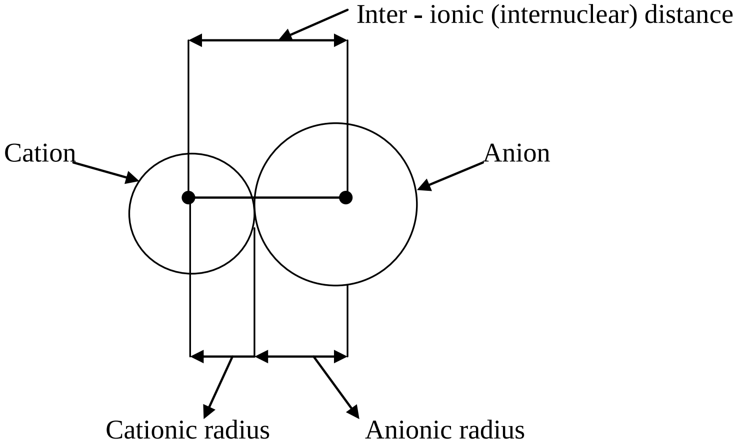
Effective nuclear attractive force *increases across the period and decreases down the group.*

And hence we may use it to explain the trend of atomic radius in the periodic as follows:

- *Atomic radii decreases as you go across the period due to increase in effective nuclear attractive force in the same direction.*
- *Atomic radius increases as you descend the group due to decrease in nuclear attractive force in the same direction.*

IONIC RADIUS

Ionic radius is the way of expressing size of charged atom. It is actually atomic size for ionic bonded atoms. Ionic radius can be defined as *the minimum distance from nucleus of an ion to the boundary region where the ion has an effect on another ion.* It may be anionic or cationic radius as illustrated in the figure below:



Whereas:

Cationic radius *is the minimum distance from a nucleus of a cation to the boundary region where the cation has an effect on an anion.*

Anionic radius *is the minimum distance from a nucleus of an anion to the boundary region where the anion has an effect on a cation.*

It should be noted that:

In most cases, anionic radius is greater than cationic radius, as illustrated in the above figure, **why?** Don't worry; this is what we are going to discuss in the next section.

Comparison of ionic radius to atomic radius of neutral atom

The comparison depends on whether the ion is cation or anion.

Cationic radius

Always cationic radius is smaller than that of its corresponding neutral atom due to the following reasons:

(i) Increase of nuclear attractive force per electron

Explanation:

When an atom loses electron(s) to acquire positive charge, number of protons present in its nucleus remains unaltered. So on re-distribution of number of protons to number of electrons after ionisation, it can be seen that there is an increased nuclear attractive force per electron leading to more contraction of valence shell and hence the ionic size becomes smaller compared to that of neutral atom. For example in neutral calcium (Ca) atom, 20 protons attracts 20 electrons while in Ca^+ (after first ionisation of Ca), 20 protons attracts 19 electrons thus making effective nuclear attractive force per electron in Ca^+ (which is 20 proton per 19 electrons) to become higher than that present in Ca which in turn make more contraction of shells in Ca^+ than in Ca.

(ii) Decrease in number of shells

Explanation:

When an atom loses all of its electrons in valence (outermost) shell, there is a decrease in number of shell as the outermost shell is completely removed thus decreasing screening effect; and hence the ionic radius become smaller compared to that of neutral atom. For example Ca whose electronic configuration can be written as $1s^22s^22p^63s^23p^64s^2$ has 4 shells whereby 2 electrons in the fourth shell (fourth shell is the valence shell in the neutral Ca atom) are screened (shielded) by 18 inner electrons while Ca^{2+} whose electronic configuration is $1s^22s^22p^63s^23p^6$ has only 3 shells whereby 8 electrons in third shell (valence shell in the cation, Ca^{2+}) are screened by only 10 inner electrons and hence less screening effect and more contraction of shells in Ca^{2+} than in Ca.

(iii) Decrease in repulsion force between inner and outer electrons

Explanation:

When an atom loses electron(s) to acquire positive charge, there is decrease in number of valence electrons in the cation thus decreasing repulsion force between outer and inner electrons and hence less expansion of valence shell in the cation; and eventually the cation become smaller in size compared to its neutral atom. For example in Ca (electronic configuration: $1s^22s^22p^63s^23p^64s^2$) there is repulsion between 2 valence (outer) electrons and 18 inner electrons while in Ca^+ (electronic configuration: $1s^22s^22p^63s^23p^64s^1$), there is repulsion between only one valence electron and 18 inner electrons and hence less expansion of valence shell in Ca^+ than in Ca.

Anionic radius

Always anionic is larger than that of its corresponding neutral atom due to the following reasons:

(i) Decrease in nuclear attractive force per electron

Explanation:

When an atom gains electron(s) to acquire negative charge, number of protons present in its nucleus remains unaltered. So on re-distribution of number of protons to number of electrons present in the anion; it will be seen that there is decrease in nuclear attractive force per electron and hence less contraction of valence shell of the anion. Example, in neutral oxygen (O) atom, 8 protons attracts 8 electrons while in O^{2-} , 8 protons attracts 10 electrons.

(ii) Increase in repulsion between inner and outer electrons

Explanation:

When electrons are added to neutral atom to form an anion there is an increase in number of valence electrons leading to more repulsion between inner and valence electrons thus causing more expansion of valence shell. As the result, the radius of the anion becomes larger than that of neutral atom. For example, in neutral oxygen atom there is repulsion between 6 valence electrons and 2 inner electrons while in O^{2-} there is repulsion between 8 valence electrons and 2 inner electrons.

Variation of ionic radii in isoelectronic series

Isoelectronic series (or isoelectronic ions) *is the group of ions with the same number of electrons as well as the same electronic configuration but they differ in their ionic charges.* A good example of isoelectronic ions are $S^{2-}, Cl^{-}, K^{+}, Ca^{2+}$ and Sc^{3+} whereby all ions have 18 electrons with the same electronic configuration as that of argon which is $1s^2 2s^2 2p^6 3s^2 3p^6$.

In the isoelectronic series, ionic radii decrease with an increase in ionic charge, why?

Reason:

This is simply because, as the ionic charge increases, the nuclear attractive force per electron also increases leading to more contraction of shells. For example, from the above example of isoelectronic ions the nuclear attractive force per electron is as shown in the table below:

Ion	**Number of electrons**	**Number of protons**	**Nuclear attractive force per electron**
S^{2-}	18	16	16 protons per 18 electrons
Cl^{-}	18	17	17 protons per 18 electrons
K^{+}	18	19	19 protons per 18 electrons
Ca^{2+}	18	20	20 protons per 18 electrons
Sc^{3+}	18	21	21 protons per 18 electrons

And hence their ionic radii will follow the following trend:

$$\xrightarrow[\text{Increase in ionic radius}]{Sc^{3+} < Ca^{2+} < K^{+} < Cl^{-} < S^{2-}}$$

Trend of ionic radius in the periodic table

Trend across the period

Comparison of ionic radii across the period depends on whether the ion is cation or anion. **Group of cations in the same period form isoelectronic series** whose charges increases as you go across the period (from left to night) and hence *for cations; ionic radii are found to decrease as you go across the period from left to right.*

Once you cross from cation (metallic ion) to anion (non – metallic ion), there is very large sudden increase in ionic radii due to addition of new shell which in turn cause very large increase in screening effect (apart from decrease of nuclear attractive force per electron). Group of anion themselves form **isoelectronic series** whose ionic charge increase (in manner that, become less negative) as you go across the period (from left to right) and hence anionic radius is found to decrease in the same direction.

For example, in period 2; Li^+, Be^{2+} and B^{3+} with electronic configuration of $1s^2$ form one isoelectronic series while N^{3-}, O^{2-}, and F^- with electronic configuration of $1s^2 2s^2 2p^6$ form another isoelectronic series whereby the first electronic series of cations has only one shell in each ion while the second isoelectronic series of anions has two shells in each ion.

Trend down the group

Like in the atomic radii (for neutral atoms), ionic radii tend to increase as you descend down the group due to increase in number of shells and hence the increase of screening effect in the same trend.

EFFECTS OF ATOMIC RADIUS ON PROPERTIES OF ELEMENTS

EFFECT OF ATOMIC RADIUS

Atomic size (radius) has large effects in properties of elements including effects on:

(i) Strength of metallic bond

(ii) Colour formation

Strength of metallic bond

Metallic bond *is the bond formed by delocalised valence electrons of metal atoms which acts as a 'glue' to hold metal ions together.* It is high if there is small metallic (atomic) radius which ensures enough nuclear attractive force to reach easily to the delocalised valence electrons.

It should be remembered that: Apart from small metallic radius, **strength of metallic bond is also fovoured by greater number of valence electrons present in metal atom** which ensures greater number of electrons the metallic atom can contribute into electron sea of their metallic bonding, i.e. the greater the number of valence electrons, the larger the number of metallic bonds formed by metal atoms.

Now the question is, if metallic bond is favoured by small atomic radius and presence of greater number of valence electrons; ***why non – metals do not form metallic bond although they have larger number of valence electrons accompanied with smaller atomic radii compared to metals?***

The reason is; atomic radii of non – metals are so small that their valence electrons are strongly held by nuclear attractive force leading to very high ionisation energy and hence there are no delocalised valence electrons in non–metals - the component which we cannot avoid in the metallic bond formation!

What are the effects of strength of metallic bond on properties of elements?

Metals with strong metallic bond have:

- High melting point which makes them to be hard while metals with weak metallic bond have low melting point which makes them to be soft.
- High boiling point
- High density
- Low solubility in water
- High atomisation (sublimation) energy

Group IA elements having large atomic radii accompanied with only one valence electron have very weak metallic bond which accounts for the following properties:

- They are soft metals with low melting point.
- They have low density
- They dissolve readily in water giving strong alkaline solution and hence the name strong alkali metals.
- They have low atomisation energy

Those are few examples whereby properties of elements are explained by strength of metallic bond which in turn is affected by atomic radius.

Colour formation

With respect to above heading, ***what happen when element has so large atomic radius that its valence electrons are weakly held by nuclear attractive force?***

Elements, whose valence electrons are weakly held by nuclear attractive force, have low ionisation energy such that:

- Normal radiant energy from the sun is enough to excite electrons to higher energy levels and on returning to ground state those electrons tend to emit energy with wavelength which lies within visible spectrum of atomic spectrum and this is observed as definite colour by eyes. For example group IA elements, having large atomic radii are silvery coloured due to the same kind of explanation.
- When flame is brought to elements (metals) or compounds containing their corresponding ions in the salts they tend to impart colour to the flame because heat energy from the flame is enough to excite electrons to higher energy levels and on returning to ground state, the electrons tend to emit energy with wavelength which lies within visible spectrum which can be detected by eyes as definite colour. So metals with large metallic radii or salts whose cations have large cationic radii give positive flame test due to the same kind of explanation

EFFECTS OF IONIC RADIUS ON PROPERTIES OF COMPAOUNDS

Ionic radius has greater effect on properties of ionic compounds including effects on:

- Hydration
- Polarisation
- Packing of ion in space
- Lattice energy

Hydration

Extent of hydration of an ion depend on the ability of the ion to hold molecules of water, that is the ability to hold lone pair electrons in oxygen of water molecules by nuclear attractive force of the ion. Thus the ability of the ion to hold molecules of water and hence the extent of hydration of the ion must depend on:

- **Ionic radius**

- The smaller the size of the ion the easier the nuclear attractive force of the ion reaches to its outermost shell and eventually to lone pair of oxygen atom in water molecule.

- **Ionic charge.**

- The higher (more positive) the charge the stronger nuclear attractive force is experienced by lone pair electrons of oxygen atom in water.

Therefore the hydration of the ion is favoured by:

- Small ionic radius and
- High (more positive) charge of the ion

The hydration of the ion has effects on:

- **Mobility of ions**

- When the ion is highly hydrated, its mobility is lowered because it becomes heavy after being hydrated. This explain why lithium ion (Li^+) which is smallest among alkali metals has lowest mobility in water although being smallest it was expected to have highest mobility. This is simply because; being smallest in the group, Li^+ has greatest ability of undergoing hydration in the group thus making it to be heaviest in water (solution) and hence its mobility become lowest. *The low mobility in water as result of its very high ability of undergoing hydration which is brought about by its small cationic radius explains why* Li^+*has very weak electrolytic conduction in solution while ions of other alkaline metals show strong electrolytic conduction.*

- **Ability of salts to absorb water when exposed in air**

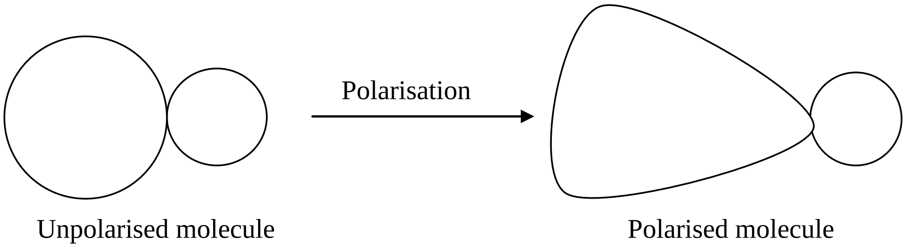
Hygroscopic substances are materials that are able to take up moisture readily from the surrounding air or other moist particles while;

Deliquescent substances become soluble after absorbing water from the surroundings i.e. a solution is produced.

So both hygroscopic substances and deliquescent are similar in the manner that are able to absorb water from surroundings. This requires the substance (compound) to have a cation which has large ability of undergoing hydration. So we can conclude that, *most of salts containing cations of high ability of undergoing hydration (small sized and/or high charged cation) are either hygroscopic or deliquescent substances.*

Polarisation

Polarisation *is the distortion of valence shell of larger ion (anion) by smaller ion (cation).*



Whereby:

- *The ability of smaller ion (cation) to distort valence shell of larger ion (anion)* is known as **polarising power.**
- *The readiness of larger ion (anion) to be distorted by smaller ion (cation*) is known as **polarisability.**

Polarising power is fovoured by:

- Small cationic radius
- High cationic charge

Polarisability is fovoured by:

- Large anionic size (radius)
- High (more negative) anionic charge

The ionic compound with cation of large polarising power and anion of large polarisability is said to have high degree of polarisation. Hence the degree of polarisation of the compound is high if:

- The cationic radius is small
- The anionic radius is large
- The charge on the ions are high (more negative anion and more positive cation in the compound)

Across the period, polarising power is found to increase as you go from left to right while polarisability decreases to the same direction. (However non – metallic and metallic ions should be compared separately, like in the case of ionic radius).

Down the group, polarising power is found to decrease on descending the group while polarisability increases.

Degree of polarisation gives an account on:

(i) Degree of covalent characters in ionic compounds

(ii) Ability of compounds to hydrolyse in water

(iii) Ability of compounds to undergo electrolytic conduction

(iv) Melting and boiling point of compounds

(v) Thermal stability of compounds

(vi) Ability of elements to form normal oxide, peroxide and superoxide

(vii) Solubility of compounds

(i) Degree of covalent characters in ionic compounds

What happen when a cation is brought close to an anion in ionic bonding?

The cation (small ion) starts to attracts (polarise) valence shell, that is valence electrons of the anion towards itself and as result, the negatively charged ion (anion) may partially (or even totally!) lose its excess electrons (which make it to be negative charged) to become neutral again and the cation regain the electrons (which originally were lost to the anion) to become neutral also. Eventually the bond between the two atoms become no longer ionic, it become covalent and the compound which was thought to be ionic starts to attain covalent characters. The extent of this distortion of ionic character will be high if the cation is small in size and high charged so that it can attracts (polarises) easily valence electrons of the anion and hence high polarising power of the cation. Also it is high if the anion is large in size and highly negative so that its valence electrons can be attracted (polarised) easily by smaller ion (cation) and hence high polarisability of the anion.

The above short discussion can be summarised by **Fajan's rule.**

According to Fajan's rule;

There is no compound which is purely ionic every compound possesses some degree of covalence which increases with an increase in degree of polarisation.

Thus according to Fajan, highly polarised compound has more covalent characters and less polarised compound (compound with low degree of polarisation) has more ionic characters (less covalent in characters). For example:

- **AlF_3 is more ionic in characters than $AlCl_3$** because Cl^- being larger in size, has greater polarisability than F^- thus making $AlCl_3$ to have greater degree of polarisation and hence more covalent in characters in $AlCl_3$ than in AlF_3. Being more covalent in characters, in large part $AlCl_3$ exists as molecule rather than as ions while AlF_3 being ionic (less covalent in characters) exists as ions (oppositely charged ions of cations, Al^{3+} and anions, F^-) and only very small part of it exists as molecule.

- **NaCl is more ionic in characters than $AlCl_3$** because Al^{3+} being smaller in size and higher charged has greater polarising power than Na^+, thus making $AlCl_3$ to have greater degree of polarisation and hence more covalent in characters in $AlCl_3$ than in NaCl.

- **$BeCl_2$ is more covalent in characters than $BaCl_2$** because Be^{2+} (which is at the top of group IIA) being smaller in size has greater polarising power than Ba^{2+} (which is at the bottom side of group IIA) resulting to greater degree of polarisation of $BeCl_2$ and hence the compound become more covalent in characters than $BaCl_2$.

(ii) Ability to hydrolyse in water

Ability to undergo hydrolysis when a compound is mixed with water is covalent character. So…………!

- Compounds with high degree of polarisation, hydrolyse in (reacts chemically with) water as they have significant degree of covalent character. For example, both $AlCl_3$ and $BeCl_2$ having significant degree of covalent characters hydrolyse in water to give acidic solution.

- Being reactive to water, these compounds are always kept in their anhydrous form (not in aqueous solution).

- Compounds with low degree of polarisation like NaCl are less covalent in characters and hence they do not hydrolyse in water.

(iii) Ability to undergo electrolytic conduction

Electrolytic conduction of compounds can be done either in:

(i) Molten (fused) state or (ii) aqueous solution

In molten state, is done by melting solid compounds which is physical change and the change is not accompanied by change on number (concentration) of ions, i.e. number of ions in the solid compound is equal to the number of ions in the melted compound.

So **for compound to conduct electricity in the molten state, the compound must have enough concentration of ions even in its solid form.** *The aim of melting the compound in molten state is just to make those ions to be free to move (and not to increase concentration or number of ions).* Hence:

- A compound will be capable of doing electrolytic conduction in molten state, if the compound has high degree of ionic characters as result of its low degree of polarisation which will make it to have high concentration of ions which are responsible of doing electrolytic conduction. That is why molten aluminum fluoride (AlF_3) can conduct electricity.

- Compounds with high degree of polarisation are highly covalent in characters which make them to have low concentration of ions and hence the compounds have very weak electrolytic conduction in their molten state. That is why molten aluminium chloride ($AlCl_3$) does not conduct electricity.

- However these compounds (with high degree of polarisation) being covalent in characters, they are capable of undergoing hydrolysis in water which is the chemical change and the reaction may give greater concentration of free ions which are responsible for doing electrolytic conduction and hence the compounds become good conductor of electricity in the aqueous solution. For example in the case of $AlCl_3$, the chloride is capable of undergoing hydrolysis according to the following equation:

$$AlCl_3(s)) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3H^+(aq) + 3Cl^-(aq)$$

Whereby presence of $H^+(aq)$ and $Cl^-(aq)$ accounts for electrolytic conduction of the resulting solution

(iv) Melting and boiling point of compounds

Before studying how degree of polarisation of compounds, affect their melting and boiling point we must first understand ***why most ionic compounds have greater melting and boiling point than most of covalent compounds?***

Ionic compounds exist as ions of opposite charge which are cations and anions. Thus there is very strong electrostatic force of attraction between these oppositely charged ions, the kind of intermolecular forces of attraction which accounts for very high melting and boiling point of ionic compounds. ***What about covalent compounds?***

Covalent compounds exist as molecules; thus the main intermolecular forces of attraction (with few exceptional where there is giant forces like in SiO_2) is Van – der – Waals dispersion forces of attraction which is are very weak intermolecular forces of attraction. So……………….!

- Compound with lower degree of polarisation is more ionic in characters which make larger part of it to exist as ions and hence its melting and boiling point become higher as result of very strong intermolecular forces of attraction which is electrostatic force of attraction between cations and anions.
- Compound with higher degree of polarisation is less ionic in characters (more covalent in characters) which make larger part of it to exist as molecule an hence its melting and boiling point become smaller as result of presence less electrostatic force of attraction between cations and anions (or presence of Van – der – Waals force of attraction which is very weak intermolecular forces of attraction).

For example we are expecting melting point of K_2CO_3 to be greater than that of Na_2CO_3 because K^+ being larger in size has weaker polarising power than Na^+, the fact which makes K_2CO_3 to have lower degree of polarisation and hence K_2CO_3 becomes more ionic in characters resulting to its greater melting point.

The reader should note that:

Sometimes it occurs in compounds with high degree of polarisation, whereby their low melting and boiling points become very close. When this happens, the compound **sublimes** on heating like in $AlCl_3$.

(v) Thermal stability of compounds

Here when we are talking thermal stability, we refer to *ability of a compound to maintain its chemical form without decomposing to simpler form at certain temperature and even after application of heat.*

One of characters of covalent compounds is that they have low thermal stability while ionic compounds have high thermal stability. Therefore:

- Compounds with higher degree of polarisation are less thermally stable as they are more covalent in characters.
- Compounds with lower degree of polarisation are more thermally stable as they are more ionic characters.

In order to have better understanding of the concept, the following few cases will be considered:

(a) Carbonates
(b) Bicarbonates (hydrogencarbonate)
(c) Hydroxides
(d) Nitrates

(a) Carbonates

Carbonates are ionic compounds which contain carbonate radical (CO_3^{2-}) as an anion. The carbonate ion has large size and enough negative charge to cause it to have very large polarisability. So……………!

- If the anion (CO_3^{2-}) is bonded to the cation with large polarising power, the resulting compound must have very large degree of polarisation and hence the carbonate must decompose easily on heating to give its corresponding oxide which is more thermally stable (compared to the carbonate) because O^{2-} being smaller in size has smaller polarisability than carbonate (CO_3^{2-}) ion and hence the oxide has lower degree of polarisation than the carbonate.
- If the anion (CO_3^{2-}) is bonded to the cation with very small polarising power, the resulting compound may have low degree of polarisation and hence the carbonate cannot undergo **thermal decomposition** (or **thermolysis**) easily on heating as result of their high thermal stability.

For example:

- Lithium being on the top of group IA, has smallest ionic radius leading to its greatest polarising power among alkali metals and therefore its carbonate having greater degree of polarisation decompose on heating to give lithium oxide (which is more thermally stable as it has lower degree of polarisation than Li_2CO_3 because O^{2-} in Li_2O being smaller than CO_3^{2-} has lower polarisability) while carbonate of other alkaline metals do not decompose on heating

i.e. $Li_2CO_3(s) \rightarrow Li_2O(s) + O_2(g)$

While $M_2CO_3(s) \rightarrow$ No reaction

Where M is any group IA element except Li (can be substituted by any symbol of group IA element you want except Li).

- Ion of group IIA elements have greater polarising power leading to greater degree of polarisation of their carbonate than those of group IA elements and hence carbonates of group IIA elements decompose on heating while those of group IA do not.

i.e. $MCO_3(s) \rightarrow MO(s) + CO_2(g)$

Where M is any group IIA elements (can be substituted by any symbol of group IIA element you want).

While $M_2CO_3(s) \rightarrow$ No reaction

Where M is any group IA element except Li

- **Aluminum carbonate does not exists (can never be prepared in the laboratory)** because having very small size and very high cationic charge, Al^{3+} exerts very large polarising power leading to very high degree of polarisation of its carbonate and hence:

- **In solid form** the compound is highly thermally unstable so that only room temperature is enough to decompose the carbonate.

i.e. $Al_2(CO_3)_3(s) \xrightarrow[\text{room (laboratory) temperature}]{} Al_2O_3(s) + 3CO_2(g)$

- **In aqueous solution** (if we try to stabilise the compound through hydration which is exothermic process), the carbonate react with water through hydrolysis (the compound hydrolyse in water by the same reason of its high degree of polarisation which makes it to be covalent) according to the following equation:

$$Al_2(CO_3)_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2CO_3$$

(b) Bicarbonate (hydrogencarbonate)

Compared to carbonate ion(CO_3^{2-}), bicarbonate ion (HCO_3^-) being larger in size, has greater polarisability (the larger ionic size of HCO_3^- outweighs the favour of more negative CO_3^{2-} has on its polarisability). So in this case we have the following facts:

- If the anion (HCO_3^-) is bonded to a cation of large polarising power, the compound will possess very large degree of polarisation and as result the compound will be highly thermally unstable and in most cases these compounds do not exist in solid form. However when the compounds are dissolved in water, the hydration process which is exothermic stabilizes the compound and the compound become thermally stable in aqueous solution unless they are heated.

- If the anion (HCO_3^-) is bonded to cation of small polarising power, the compound will possess low degree of polarisation thus making the compound thermally stable even in solid form unless heat is applied.

For example:

- **Bicarbonate of Lithium and group IIA elements do not exist in the solid form** as result of their high degree of polarisation which makes even room temperature to be enough to decompose to their respective carbonates (their carbonates exist at room temperature because CO_3^{2-} being smaller in size has lower polarisability than HCO_3^-).

i.e. $2LiHCO_3(s) \xrightarrow[\text{room temperature}]{} Li_2CO_3(s) + CO_2(g) + H_2O(l)$

And $M(HCO_3)_2(s) \xrightarrow[\text{room temperature}]{} MCO_3(s) + CO_2(g) + H_2O(l)$

Where M is any group IIA element

However when bicarbonates are dissolved (prepared) in aqueous solution, they become thermally stable unless they are heated.

i.e. $LiHCO_3(aq) \xrightarrow[\text{room temperature}]{}$ No reaction

And $MHCO_3(aq) \xrightarrow[\text{room tempeature}]{}$ No reaction

But:

$$2LiHCO_3(aq) \underset{\Delta}{\rightarrow} Li_2CO_3(s) + CO_2(g) + H_2O(g)$$

$$M(HCO_3)_2(aq) \underset{\Delta}{\rightarrow} MCO_3(s) + CO_2(g) + H_2O(g)$$

Where M is any group IIA element.

This is different to bicarbonates of other group IA elements which have lower degree of polarisation, thus becoming more thermally stable and is possible for them to exist even in solid form unless heat is applied

i.e. $MHCO_3(s) \xrightarrow[\text{room temperature}]{}$ No reaction

But $2MHCO_3(s) \xrightarrow[\text{high temperature}]{} M_2CO_3(s) + CO_2(g) + H_2O(g)$

Where M is any group IA element except Li.

- When sodium hydrogen carbonate is added to copper (II) sulphate solution, we are expecting the double decomposition to occur according to the following equation:

$CuSO_4 + 2NaHCO_3 \rightarrow Na_2SO_4 + Cu(HCO_3)_2$ .... (i)

However carbon dioxide which appears as effervescence of colourless gas is obtained, why?

This is simply because copper (II) hydrogencarbonate ($Cu(HCO_3)_2$) which would be formed is highly thermally unstable as result of its high degree of polarisation which is brought about by large polarising power of small sized Cu^{2+} accompanied with its significant positive charge. This makes the hydrogen carbonate to undergo decomposition according to the following equation:

$Cu(HCO_3)_2 \rightarrow CuCO_3 + CO_2 + H_2O$ ………………. (ii)

And hence the correct overall reaction equation becomes (by taking (i) + (ii)):

$CuSO_4 + 2NaHCO_3 \rightarrow Na_2SO_4 + CuCO_3 + CO_2 + H_2O$ and not simple decomposition reaction equation as was expected.

(c) Hydroxides

When hydroxide ion (OH^-) is bonded to a cation of large polarising power, the compound which is formed has large degree of polarisation and become thermally unstable on heating. For example:

- Hydroxides of lithium and group IIA elements, on heating undergo thermal decomposition to form their respective oxides while hydroxides of other group IA elements (leaving LiOH) have lower degree of polarisation and hence they do not decompose on heating.

i.e. $2LiOH \underset{\Delta}{\rightarrow} Li_2O + H_2O$

And $2M(OH)_2 \underset{\Delta}{\rightarrow} MO + 2H_2O$

Where M is any group IIA element

While $MOH \underset{\Delta}{\rightarrow}$ No reaction

Where M is any group IA element except Li.

- Ag^+ being very small in size (**accompanied with non-noble gas electronic structure**), has very large polarising power thus leading to very large degree of polarisation of silver hydroxide and hence the compound does not exist as it is highly thermally unstable such that only room temperature is enough to decompose it.

$2AgOH \xrightarrow[\text{room temperature}]{} Ag_2O + H_2O$

The above explanation explains why **silver hydroxide is commonly not stored in the laboratory. It is always prepared whenever it is used in reaction mixture as moist silver oxide which is the mixture of silver oxide and water.** So whenever you wish to use silver hydroxide in the chemical equation, use moist silver oxide instead.

Note: Apart from cationic size and charge, another factor which determines polarising power of cation is stability of electronic configuration of the cation. Cations with stable octet electronic structure have small polarising power while those with no stable electronic structure of noble gases like $Ag^+, Cu^+, C^{2+}, Fe^{2+}$ etc, have very large polarising power.

(d) Nitrates

Nitrate ion (NO_3^-) has very large polarisability as result of its very large size. Thus:

- Most of nitrates (if not all) undergo thermal decomposition yielding their respective nitrite or oxides depending on the polarising power of the cation which was combined with the nitrate ion.

- If the cation has large polarising power, the nitrite (NO_2^- still has large polarisability but its amount is smaller compared to NO_3^-) undergo further decomposition to its respective oxide and the **brown fumes of nitrogen dioxide** is evolved. For example, nitrates of Lithium and group IIA elements undergo thermal decomposition in this way.

E.g. for $LiNO_3$:

$2LiNO_3 \underset{\Delta}{\rightarrow} 2LiNO_2 + O_2$ …………………………………….. (i)

Then $4LiNO_2 \underset{\Delta}{\rightarrow} 2Li_2O + 4NO + O_2$……………………………….. (ii)

Finally $2NO + O_2 \rightarrow 2NO_2$…………………………………………… (iii)

Taking $2(\text{i}) + (\text{ii}) + 2(\text{iii})$, then combining and cancelling like terms, gives the following overall reaction equation:

$$4LiNO_3 \underset{\Delta}{\rightarrow} 2Li_2O + 4NO_2 + O_2$$

Similarly for nitrates of group IIA elements:

$$2M(NO_3)_2 \underset{\Delta}{\rightarrow} 2MO + 4NO_2 + O_2$$

Where M is any group IIA element.

- If the cation has small polarising power, the nitrite become thermally stable (despite of the significant polarisability of the nitrite ion , NO_2^-) and therefore it resists further decomposition to its respective oxide.

For example, nitrates of other group IA elements (leaving $LiNO_3$) undergo thermal decomposition to give their respective nitrites according to the following equation:

$$2MNO_3 \underset{\Delta}{\rightarrow} 2MNO_2 + O_2$$

Where M is any group IA element except Li

It should be noted that: ammonium radical (NH_4^+) has very large polarising power such that **ammonium nitrite can undergo further decomposition to give nitrogen gas which appears as effervescence of colourless gas**. This explains why *the nitrogen gas is evolved when ammonium chloride solution is added to warm aqueous solution of sodium nitrite. This is simply because under presence of heat (warm condition of the sodium nitrite), ammonium nitrite which would be formed as result of double decomposition reaction undergo thermal decomposition to give nitrogen gas.*

i.e. $NaNO_2(aq) + NH_4Cl(aq) \rightarrow NaCl(aq) + NH_4NO_2(aq)$ ……………….(i)

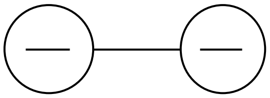
Then $NH_4NO_2(aq) \xrightarrow[warm]{} 2H_2O(l) + N_2(g)$ …………………….…………(ii)

And hence the overall reaction equation become (by taking (i) + (ii))

$$NaNO_2(aq) + NH_4Cl\ (aq) \xrightarrow[warm]{} NaCl(aq) + 2H_2O(l) + N_2(g)$$

(vi) Formation normal oxide, peroxide and peroxide

Peroxide ion (O_2^{2-}) has the following structure:



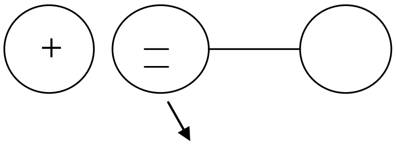
Whereby each oxygen atom has single negative charge. ***So what happen when the cation is brought near the peroxide ion?***

Here there are two possibilities:

First possibility:

If the cation has large polarising power as result of its small cationic radius and/or high cationic charge, the negative charges on peroxide will be attracted (polarised) towards the cation and as result the negative charges will concentrate to the single oxygen atom yielding normal oxide ion and hence normal oxide is formed as shown below:

Polarisation of the peroxide


(The single negative charge on one oxygen atom is attracted towards another oxygen atom which is close to the cation)

Normal oxide ion is formed after breaking the bond between the two oxygen atoms

Second possibility:

If the cation has small polarising power as result of large ionic radius and low cationic charge, the peroxide ion remains undistorted and the peroxide is formed.

Similarly for more complex oxide, **superoxide ion** ($\mathbf{O_2^-}$): Cations with very large polarising power like $\mathrm{Li^+}$, distort the ion to normal oxide, cations with weak polarising power like $\mathrm{Na^+}$, distort the ion to peroxide and cations with very weak polarising power like $\mathrm{K^+}$, cannot distort the ion and hence they can form superoxide. For example:

- **Lithium ion** having small cationic radius is able to polarise the peroxide ion and hence can form normal (simple) oxide ($\mathrm{Li_2O}$) only.
- **Sodium ion,** can form normal oxide and peroxide.
- **Ions of other group IA elements** being larger in size cannot polarize either peroxide or superoxide ions easily and hence they can form normal oxide, $\mathrm{M_2O}$, peroxide, $\mathrm{M_2O_2}$ and superoxide, $\mathrm{MO_2}$.
- **Ions of group IIA elements** having large polarising power as result of their small cationic radii and high cationic charge can polarise peroxide ion and hence forming normal oxide only. However members at the bottom side of the group (strontium and barium) can form peroxides.

(vii) Solubility of compounds

Usually ionic compounds dissolve in polar solvents like water and are insoluble in non-polar solvents like most of organic solvents.

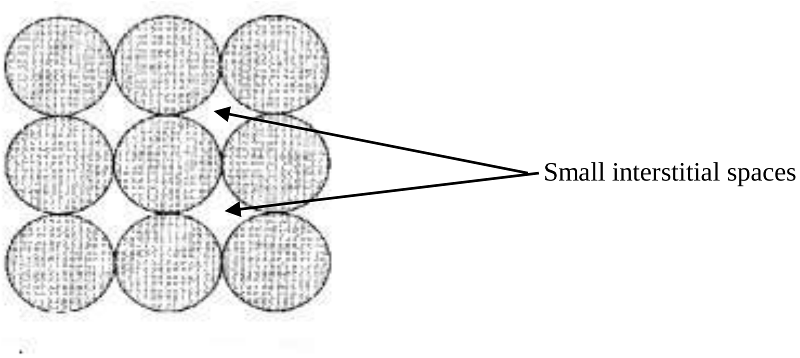
- When the ionic compound has large degree of polarisation, the compound become more covalent in characters and hence the compound becomes:

- less soluble in water (polar solvent)
- more soluble in non – polar solvents

High degree of polarisation explains why AgCl and CuI are very slightly soluble in water. This is because $\mathrm{Ag^+}$ and $\mathrm{Cu^+}$ having electronic configurations which are different to those of noble gases accompanied with their small cationic radii have very large polarising power leading to high degree of polarisation of their respective ions and eventually the compounds become more covalent in characters, the fact which decrease very much their solubility in the polar solvent, water.

Packing of ions in space

When ions (cations and anions) have almost equal sizes, there is good packing of ions in space because there are small interstitial spaces (interstices) as shown below:



Ionic compounds with good packing of ions in space have:

- High melting point
- High density
- High boiling point
- Low solubility

In another hand if the combined ions differ much in their sizes, packing of ions in space will be poor as result of presence of large interstitial spaces. Ionic compound with poor packing of ions in space have:

- Low melting point
- Low boiling point
- Low density
- High solubility

Lattice energy

Lattice energy *is the energy evolved when one mole of solid ionic compound is formed from its constituent gaseous ions*. It is the measure of how easily a cation and an anion combine to form ionic compound. If the cation is of small size and (or) high charged it will be very easy for the cation to combine with the anion and hence the lattice energy (energy evolved) will be large. Generally the lattice energy is high if:

- The cation is small in size
- The cation has high charge
- The anion is highly negative charged
- The anion is small in size

It should be understood that: *thermally any process which involves attraction is exothermic while the process which involves repulsion is endothermic.* **Lattice energy is the measure of attraction between cation and anion and hence must be negative (exothermic). If there is greater force of attraction between cations and anions, greater amount of heat is evolved and hence the lattice energy (heat evolved) must be large also.** *If the lattice energy is large then the compound will be more stable and vice – versa.*

Lattice energy and nitride formation

It is difficult for some metals to combine with nitrogen to form nitride due to the following reasons:

- Very large amount of energy (**dissociation energy**) is needed to break the triple bond ($\mathrm{N} \equiv \mathrm{N}$) joining the two atoms in the nitrogen molecule, $\mathrm{N_2}$. This makes the nitrogen to be fairly unreactive.
- Very large amount of energy is needed to form $\mathrm{N^{3-}}$ as both second and third electron affinities are positive (endothermic). The only negative electron affinity is first electron affinity and hence net electron affinity is positive, i.e. the formation of $\mathrm{N^{3-}}$ from gaseous nitrogen atom absorbs energy.

So for a metal to combine with nitrogen so as to form nitride, this energy must be compensated by another exothermic process which will make overall reaction exothermic otherwise the reaction (formation of nitride) will not occur. ***So how this is done?***

Energy is evolved when the ions (cation and anion, $\mathrm{N^{3-}}$) come together to give crystal lattice and the energy is what we call lattice energy (or lattice enthalpy) as explained earlier. So………………!

- **If the lattice energy is large enough to compensate the dissociation energy of nitrogen and the net electron affinity of nitrogen, the nitride will be formed.**
- **If the lattice energy is too small to compensate the dissociation energy of nitrogen and its net electron affinity, the metal cannot combine with nitrogen to form nitride.**

For example:

- $\mathrm{Li^+}$ (on the top of group IA) being very small in size its nitride has very large lattice energy which is enough to compensate the dissociation energy and the electron affinity of nitrogen and hence the metal can form nitride with nitrogen gas while other group IA elements cannot because the elements having larger cationic radii, their nitrides have small lattice energy which is not enough to compensate the dissociation energy and the net electron affinity of nitrogen.

i.e.
$6Li + N_2 \rightarrow 2Li_3N$

While $M + N_2 \rightarrow$ No reaction

Where M is any group IA element except Li

- All group IIA elements having smaller cationic radii accompanied with greater ionic charges, their nitride have large lattice energy which is enough to compensate the dissociation energy and the net electron affinity of nitrogen and hence all group IIA elements can combine with nitrogen gas to form nitride.

$3M + N_2 \rightarrow M_3N_2$

Where M is any group IIA element

Relationship between lattice energy and hydration energy with respect to solubility

What happen when the solid ionic compound is dissolved in water?

When the solid compound is dissolved in water, its crystalline structure is broken. This requires some energy to accomplish the job of breaking it, i.e. there must certain exothermic process which is responsible for supplying energy for breaking the crystalline lattice. Hydration being exothermic process is the one which supply that energy.

- For compound to dissolve in water, the hydration energy must be large enough to overcome the lattice energy (energy evolved in dissolving the compound must be greater than the energy evolved in forming the crystalline lattice) otherwise the compound will not dissolve.
- So if: Hydration energy $>$Lattice energy, the compound dissolves readily.

  Hydration energy $<$ Lattice energy, the compound does not dissolve readily.

PRACTICE EXERCISE 2

Question 1

Explain why chemists do not define atomic radius like mathematicians.

Question 2

Define radius of:

(i) Cl atom
(ii) Na atom
(iii) Ne atom
(iv) F^- ion
(v) Mg^{2+} ion

Question 3

Explain briefly factors affecting atomic radius and hence deduce the trend of atomic radius in periodic table for representative elements.

Question 4

Explain the following:

(i) Size of Mg^+ ion is smaller than Mg atom.
(ii) Size of O^{2-} is larger than O atom.
(iii) Size of Mg^{2+} is smaller than F^- although both have the same number of electrons.
(iv) The trend of variation of ionic radius across the period is not regular.
(v) Trend of atomic radius in transition elements is quite difference to that of typical elements.

Question 5

Explain how atomic radius affects strength of metallic bond.

Question 6

Account for the following:

(i) Hydration energy is the function of ionic radius.
(ii) It is easier to atomise sodium than magnesium.
(iii) Compounds of magnesium give negative flame test while those of calcium give positive. test although both elements are found in the same group.
(iv) Molten NaCl is more mobile than molten KCl.
(v) Compounds which consist of small sized ions do not dissolve in water.

Question 7

Why sodium atom is bigger than the atoms of both lithium and magnesium?

Chapter 3

IONISATION ENERGY

Ionisation energy *is the minimum energy required to remove completely electrons which are most loosely bound from one mole of neutral isolated gaseous atom or ion.* When ionisation energy is expressed in eV per atom, is called **ionisation potential**.

If an electron is removed from neutral gaseous atom, the energy is then termed as **first ionisation energy.**

Thus, the **first ionisation energy** *is the minimum energy required to remove completely electrons which are most loosely bound from one mole of neutral gaseous atom to form one mole of unipositive (monopositive) ion*.

$$\mathrm{M(g)} \rightarrow \mathrm{M^{+}(g)} + \mathrm{e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \Delta\mathrm{H} = \text{first ionisation energy}$$

If an electron is removed from unipositive charged ion, then the energy is termed as **second ionisation energy.**

Thus the **second ionisation energy** *is the minimum energy required to remove completely electrons which are most loosely bound from one mole of gaseous unipositive ion to form one mole of dipositive ion.*

$$\mathrm{M^{+}(g)} \rightarrow \mathrm{M^{2+}(g)} + \mathrm{e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . \Delta\mathrm{H} = \text{second ionisation energy}$$

If an electron is removed from dipositive ion, then the energy is known as **third ionisation energy** and so on.

Ionisation energy enables us to classify elements into metals and non – metals:

- Metals have low ionisation energy (below $800\mathrm{kJ/mol}$). The energy is so small that can be attained in practice and hence metals always ionises as positively charged by loosing electrons.
- Non metals have very high ionisation energy (above $800\mathrm{kJ/mol}$) which cannot be obtained in practice, so they usually ionise by gaining electrons instead.

FACTORS AFFECTING IONISATION ENERGY

Ionisation energy is the measure of energy required to re move a particular electron away from the attraction of the nucleus. A high value of ionisation energy shows a high attraction between the electron and the nucleus. The size of that attraction will be governed by:

- **The charge on the nucleus**

- The more protons there are in the nucleus, the more positively charged the nucleus is, and the more strongly electrons are attracted.

- **The distance of the electron from the nucleus**

- The nucleus attraction to valence electron decrease very rapidly as the distance of the electron from the nucleus increases. An electron close to the nucleus will be much more strongly attracted than one farther away.

- **The number of electrons between the outer electrons and the nucleus (screening effect)**

- As the number of electrons in inner shells and sub – shells increases, screening (or shielding) effect exerted by those electrons to outer electrons also increase and hence the amount of ionisation energy also decreases.

- **Stability of electronic configuration**

- Two electrons in the same orbital experience some repulsion from each other. This off sets the attraction of the nucleus, so that paired electrons are removed rather easily than it would be expected.

- However the above factor is true if and only if the paired electron is not in the completely full paired electronic structure. **Complete paired (exactly full filled) electronic structure is very stable electronic configuration and hence atom which has such kind electronic configuration has unexpectedly high ionisation energy.**
- Also, **completely unpaired (exactly half filled) electronic configuration** is stable electronic configuration so that the atom which such kind of electronic configuration has unexpectedly high ionisation energy.

In order to have better understanding on factors affecting ionisation energy considers the following few cases of fist ionisation energies:

Case 1: Hydrogen has high ionisation energy

With electronic configuration of $1s^1$, hydrogen has high ionisation energy (1310kJ/mol) like most of non-metals due to the following reasons:

- Being very small in size, its single electron is very close to the nucleus and therefore strongly attracted by the nucleus.
- There are no inner electron(s) screening the single (outer) electron of the hydrogen atom

Case 2: Helium has much higher ionisation energy than hydrogen

With electronic configuration of $1s^2$, helium is similar to hydrogen in the following ways:

- An electron to be ionised in He is removed from first energy level ($n = 1$) and in s-sub energy level like in hydrogen and hence in both cases the electrons are strongly attracted by their nuclei.
- Like in hydrogen, there is no screening effect in helium as there are no inner electrons.

So what is the cause of large difference in their ionisation energy (ionisation energy of hydrogen is 1310kJ/mol while that of helium is 2370$kJmol^{-1}$)?

Helium has one extra proton compared to hydrogen (He has 1 proton while He has 2 protons) thus making nucleus of He to be more positively charged and hence its electrons are more strongly attracted leading to its higher ionisation energy.

Case 3: Ionisation energy of lithium is lower than that of hydrogen.

Lithium has electronic configuration of $1s^2 2s^1$. An electron to be ionised (the most loosely held electron) in Li is to be removed from second energy level ($n = 2$) which is of greater distance from nucleus than that of hydrogen's electron which is to removed from first energy level ($n = 1$). However one may expect this decrease in energy as result of the distance factor may be offset by the fact that Li has 2 more protons compared to H which make it to have greater nuclear charge, ***so what make Li to have lower ionisation energy (kJ/mol)?***

Apart from distance factor which make Lithium to have lower ionisation energy. The most loosely held electron which is to be removed in ionisation process of Lithium is screened by two inner electrons in $1s^2$, the fact which cause further decrease in its ionisation energy.

So in summary we may conclude that; lithium has lower ionisation energy than hydrogen due to the following reasons:

- The electron to be removed from Li is removed from 2s orbital which is of greater distance from the nucleus than hydrogen whose electron is removed from 1S orbital.
- In Li, the electron to be removed is screened by two inner electrons while there is no screening effect in H.

TREND OF IONISATION ENERGY ACROSS THE PERIOD

Across the period, all elements have the same outermost main energy level (but differ in number of electrons in the energy level, i.e. number of valence electrons) and hence:

- The distance of valence electron from the nucleus is almost the same (with small difference in some cases whereby the most loosely electrons are kept into different sub – energy levels) i.e. the electrons have different azimuthal quantum numbers.
- The screening effect is almost constant because the number of electrons between outer electrons and the nucleus is the same. (This also has few exceptional which occur when the most loosely electrons are kept into different sub – energy levels, i.e. the electrons have different azimuthal quantum numbers).
- In few cases, the stability of electronic configuration may differ thus affecting the size of ionisation energy.

So what is the main determinant factor of ionisation energy across the period?

The only factor which we have sure about its pattern of change as you go across the period is the charge on the nucleus, how?

As you go across the period from the left to the right, number of protons in the nucleus of atoms increase regularly thus increasing charges on nucleus and hence electrons in atoms become more strongly attracted to their respective ion leading to more contraction of shells and hence much increase in the ionisation energy as you go across the period.

So what is the conclusion can be made?

Generally ionisation energy increases as you go across the period from left to right (although there are some irregularities) due to the fact that, across the period:

- There is an increase in nuclear charge due to increase in number of protons and hence the outer electron(s) become more strongly attracted to the same direction
- There is contraction of shells (including valence shell as result of an increase in nuclear charge) thus decreasing the distance of the loosely electron from the nucleus such that the electron become much more strongly attracted and hence the ionisation energy is increased much more.

TREND OF IONISATION ENERGY DOWN THE GROUP

As you down the group, the outermost electronic configuration remains the same while number of shells increases and hence:

- The distance of the most loosely electron from the nucleus increases.
- The number of electrons between the outer electrons and the nucleus increases thus increasing screening effect to the same direction.
- Stability of electronic configuration remains constant.

The first two factors suggests that ionisation energy decreases as you descend the group despite the fact that to that direction the charge of nucleus increases also due to increases in number of protons (the first two factors outweighs this single factor of an increase in nuclear attractive force as result of the increase in number of protons).

So it can be concluded that generally ionisation energy decreases as you descend the group due to:

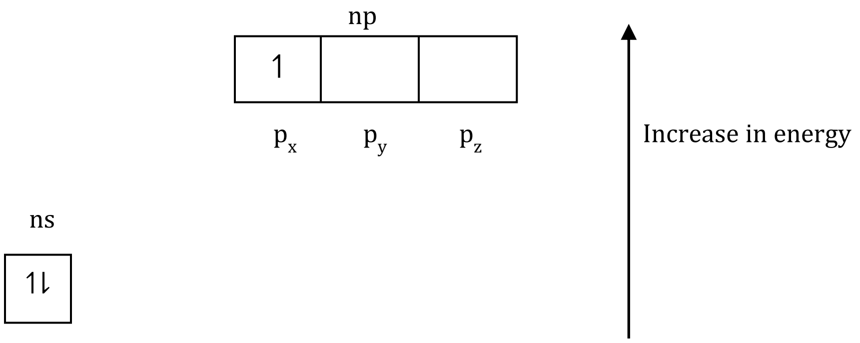
- Increase in distance of the most loosely electron from the nucleus to the same direction
- Increase in screening effect as result of an increase in number of electrons between the outer electrons and nucleus to the same direction.

Irregularity of first ionisation energy down the group

As we have seen, first ionisation energy increases as you go down the group. One of the main factors contributing to this is an increase in screening effect on descending the group. This effect is significant when inner electrons are closer to nucleus; that is if most of inner electrons are s and p-electrons.

- If most of the inner electrons are far from nucleus (d and f-electrons); they will fail to screen outer electrons resulting to unexpectedly high ionisation energy. This effect whereby inner electrons fail to screen outer electrons is known as **inert pair effect** and it increases on descending the group.
- Inert pair effect is significant to elements found in the bottom of the group causing them to have unexpectedly high ionisation energy.
- To have better understanding of this considers ionisation energy of group IIIA elements.

By using boxes and arrows, outermost electronic configuration of group IIIA elements (where 'n' is the outermost energy level) can be shown as follows:



Having three valence electrons, group IIIA elements can lose three electrons to attain a charge of $3+$. ***How this is done?***

- Firstly one s–electron is promoted to higher sub–energy level in p_y orbital through sp^2 hybridisation so as to form three unpaired orbitals. ***Why this is possible?***

- The promotion of s – electron to the p – orbital is possible because the valence s-electrons are highly screened by inner electrons. This makes them to be weakly held by nuclear attractive force such that only small amount of energy is required for doing that promotion.

- Thereafter hybridisation, the three electrons may be ionised one after another. The net ionisation energy of an atom, M to its corresponding tripositive ion, M^{3+} is the summation of first, second and third ionisation energy.

- So in absence of inert pair effect, we would expect ionisation to decrease regularly on descending the group. However the practical values of ionisation energy of group IIIA elements are as follows:

Element	Atomic number	Ionisation energy in kJ/mol
Boron	5	801
Aluminium	13	578
Gallium	31	558
Indium	49	558
Thallium	81	589

If you look at values of net ionisation energies (shown in the table) you will find that, firstly the energy decreases from boron to gallium. Thereafter gallium and indium have the same ionisation energy and finally from indium to thallium ionisation energy increases. Why this?

- As result of inert pair effect, outer s - electrons become tightly held by nuclear attractive force making more difficult for the electrons to be promoted to higher energy, p_y orbital. Thus greater amount of energy is required for doing that promotion and eventually the net ionisation energy in forming tripositive ion, M^{3+} become unexpectedly large. This effect is observed in elements which are at the bottom side of the group which are indium and thallium because in those elements there is greater number of d and f electrons.

So ***what is the effect of unexpectedly high ionisation energy in the formation of tripositive ion****?*

- The unexpectedly high ionisation energy of the elements at the bottom of group, make the tripositive ions unstable. So the atoms prefer forming unipositive ion by losing only one p_y electron to tripositive ion whose formation is more energy consuming. So **for thallium monovalent state is more stable oxidation state than trivalent state**. For example, while thallium (III) chloride, $TiCl_3$ volatile liquid at room temperature, thallium (I) chloride, TiCl is solid.

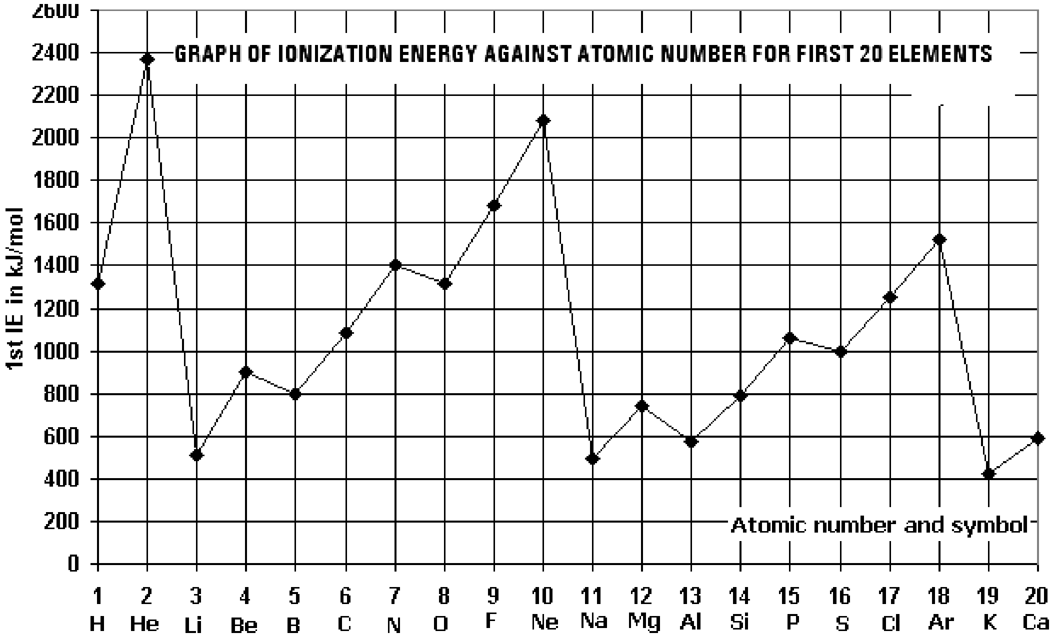
Inert pair effect also explains why tin and lead which are found at the bottom of group IVA (with outermost electronic configuration of $ns^2np_x^1np_y^1$) may show oxidation state of $+2$ apart from more common $+4$. With lead, $+2$ is more stable oxidation state because it experience strongest inert pair effect (lead is below tin) while $+4$ is more stable for tin.

Definition of inert pair effect

Inert pair effect *is the effects which arise in an atom where by inner electrons fail to screen outer s – electrons thus making the s- electrons unreactive.*

FIRST IONISATION ENERGY FOR FIRST TWENTY ELEMENTS

Graph of first ionisation energy for first twenty elements is shown in the figure below:



Important things to note from the graph

First thing: In each group ionisation energy decreases on descending the group.

Second thing: In each period, ionisation energy is generally increases across the period from left to right.

Third thing:

In each period, noble gases have highest ionisation energy due to the following reasons:

- They have stable electronic configuration as they have all of their orbitals paired with electrons (stability of exactly full paired electronic configuration).
- They have highest charge of nucleus (of all elements in each period) and therefore they exert very strong nuclear attractive force to their valence electrons.

Fourth thing:

There are some irregularities in the trend of variation of ionisation energy across the period.

First irregularity:

Unexpectedly, ionisation energy of boron (group IIIA element) seems to be lower than that beryllium (group IIA element) although boron is at the right hand side of the beryllium.

Reasons for irregularity:

To understand thus, consider electronic configurations boron, B, and that of beryllium, Be;

Electronic configuration of Be is $1s^2 2s^2$

Electronic configuration of B is $1s^2 2s^2 2p_x^1$

So the ionisation energy of B is lower than that of Be due to the following factors:

Distance of the most loosely electron in B from the nucleus is greater than that of Be

- In ionisation; the electron of Be is removed from 2s orbital while in B, the electron is removed from $2p_x$ orbital. 2s orbital being closer to nucleus than $2p_x$, the s-electron experience stronger nucleus attractive force than p-electron and hence ionisation in Be become more difficult.

Be has more stable electronic configuration

- Be has stability of exactly full paired electronic configuration thus extra energy is required (absorbed) to overcome magnetic field (that enabled those pair of electrons to settle together in the orbitals) before doing ionisation. This is different to B where an electron to be removed is unpaired.

The most loosely electron in B experience stronger screening effect than in Be

- In B there are extra inner 2s electrons which make it $2p_x$ electron more screened than in the case of Be where there are fewer electrons and the only inner electrons are 1s electrons. Therefore, it become easier to remove the electron from B than in Be.

It should be noted that: The same factors are used to explain why ionisation energy of Mg (another group IIA element like Be) is greater than that of Al (another group IIIA element like B) although Mg is on the left hand side of Al.

Second irregularity

Oxygen (group VIA element) has lower ionisation than nitrogen (group VA element) although the oxygen is on the right hand side of nitrogen.

Reason for irregularity:

To understand this considers electronic configurations of nitrogen and oxygen as shown below:

Electronic configuration of nitrogen is $1s^22s^22p_x^12p_y^12p_z^1$

Electronic configuration of oxygen is $1s^22s^22p_x^22p_y^12p_z^1$

From the above electronic configurations, it is clearly understood that nitrogen has more stable electronic configuration as all of its p-orbitals contain unpaired electrons (stability of totally half filled electronic structure). So it is more difficult to remove an electron from nitrogen than in oxygen and hence the ionisation energy of nitrogen becomes greater.

The same reason is used to explain why ionisation energy of sulphur (is it at group VIA like oxygen) is lower than that of phosphorous (in group VA like nitrogen).

EFFECTS OF IONISATION ENERGY ON PROPERTIES OF ELEMENTS AND THEIR COMPOUNDS

Ionisation energy has effect on:

- Reactivity of metals
- Stability of ions and compounds

Reactivity of metals

Rate of chemical reaction is determined by **activation energy,** the lower the activation energy the faster the chemical reaction will be and vice – versa. And it should be remembered that activation energy is the minimum energy must be absorbed for the reaction to proceed. So **any endothermic process in the reaction contributes to activation energy of the reaction.**

Metals react by losing electrons which is endothermic places because the energy must be absorbed to remove the valence electron(s) of the metal from its ground state to convergent limit (where nuclear attractive force cannot reach) in atomic spectrum and hence the ionisation energy must be positive. So……………..!

- Being positive, ionisation energy has large contribution to activation energy of reactions for metals.
- The lower the ionisation energy the lower the activation energy leading to faster rate of chemical reaction of a metal and hence the metal become more reactive and vice – versa.

Decrease in ionisation energy as you descend the group explains why reactivity of alkali metals (group IA elements) e.g. reactivity towards water increases as you go down the group IA.

It should be remembered that:

When we are talking about ionisation energy, the original state of metal must be in the form of gaseous atom. So before doing ionisation, energy must be absorbed (another endothermic process) to atomise the metal and the energy is known as **atomisation energy**. So apart from ionisation energy, also atomisation energy is another contributing factor to the activation energy and hence to the reactivity of the metal.

Stability of ions (cations) and compounds

If the ionisation energy of an atom is very high, the resulting ion or compound containing the ion becomes unstable. To stabilize the ion or the compound, another way which is exothermic process must be found to compensate (recover) the amount of heat absorbed in the ionisation.

The amount of energy evolved in that exothermic must be large enough to compensate the amount of heat absorbed otherwise the ion or the compound may not exist.

Therefore:

- For an ion, the process may be done by hydrating it through enthalpy of hydration which is negative. For example **boron, B being very small in size has very large net ionisation energy in forming its tripositive ion, B^{3+}. This makes the ion unstable even in aqueous solution because its hydration energy is not large enough to compensate very large of its ionisation energy.**
- For compounds, the stabilisation may be done in different ways like bond formation which is exothermic process. The amount of energy evolved increases with an increase in number of bonds formed. For example in the case of boron; its normal salts have three bonds while its complex salts have four bonds surrounding it. Thus less energy is evolved in forming the normal salts and hence the salts become less stable than complex salts whereby energy evolved in forming four bonds is large enough to compensate the large ionisation energy of boron to Be^{3+}.

- For example; BCl_3 is not common while $[BCl_4]^-$ is common because in forming complex ion, boron coordinate with ligands by four bonds in $[BCl_4]^-$. Forming four bonds in the complex release relatively greater amount of energy (than three bonds in BCl_3) which is enough to compensate the net ionisation energy of B to B^{3+}.

However normal salts can be formed if lattice energy in forming the complex is large enough to compansate the net ionisation energy.

- For example; BF_3 exists because F^- being very small in size is strongly attracted to B^{3+} making lattice energy of BF_3 high enough to compansate the net ionisation energy of B to B^{3+}.

Example

The second ionisation energies are defined as the energy required to remove the second electron from the atom. The third and fourth ionisation energy is defined in a similar manner. Select from among elements X,Y and Z the one that will most clearly exhibit the properties (a), (b) and (c) given below;

(a) To form a monovalent ionic compound with chlorine

(b) To form a covalent bond with chlorine

(c) To have the oxidation number of +2 in most cases

Ionisation energy	1st (kJ/mol)	2nd (kJ/mol)	3rd (kJ/mol)	4th (kJ/mol)
X	738	1450	7730	10550
Y	800	2427	3658	25024
Z	495	4563	6912	9540

Answer

(a) Z (Has very low 1st I.E compared to 2nd I.E suggesting that it ionise to give monopositive ion)

(b) Y (has highest first I.E)

(c) Z (Both 1st and 2nd I.E are small)

PRACTICE EXERCISE 3

Question 1

Variation of ionisation energy across the period is irregular while down the group is regular. Give reason(s) for this.

Question 2

Between beryllium and boron, which one do you expect to be more reactive? Give reason (s) for our choice.

Question 3

Phosphorous and bismuth are found at the same group (group VA), bismuth being in the bottom of the group. However pentavalent compounds of phosphorous are known while those of bismuth do not exist. Give an explanation for this observation.

Chapter 4

ELECTRONEGATIVITY

Electronegativity *is the measure of the tendency of an atom to attract a shared pair of electrons in covalent bond towards itself.* Its opposite term is **electropositivity.**

An element with an atom of large tendency of attracting a bonding pair of electrons is said to be **strong electronegative element** or **weak electropositive element** while an element with an atom of small tendency of attracting a bonding pair of electrons is said to be **weak electronegative element** or **strong electropositive element.**

FACTORS AFFECTING THE SIZE OF ELECTRONEGATIVITY

The attraction that a bonding pair of electrons feels for a particular nucleus of one of bonded atom and hence electronegativity of the atom depends on:

The size of charge in the nucleus

- The greater number of protons present in the nucleus, the higher nuclear charge is and hence high electronegativity of the atom

The distance from the nucleus

- The shorter distance of bonding pair electrons from nucleus of the atom the more attraction to the electrons and hence high electronegativity of the atom.

The amount of screening by inner electrons

- The greater screening effect exerted by inner electrons of the atom to the bonding pair of electrons, the less attraction to the bonding electrons and hence low electronegativity

Trend across the period

As you go across the period from left to right, the electronegativity increases due to increase in the size of nuclear charge as result of an increase in number of protons in the same direction. This makes the effective nuclear attractive force exerted by nucleus of an atom to a bonding pair of electrons to increase and hence the electronegativity of the atom increases also.

Trends down a group

As you go down a group, electronegativity decreases due to:

- An increase in distance from the nucleus of an atom to the bonding pair of electrons due to an increase in number shells of the atom on descending the group.

- An increase in screening effect due to an increase in number of inner electrons on descending the group

The reader should note that:

In explaining trend in electronegativity, noble gases are not included in the pattern, why?

Reason:

Usually noble gases do not form bonds (although in very rarely, some do) and if they cannot form bond, they cannot have an electronegative value (keeping in the mind that the electronegativity is the measure of tendency of an atom to **attract bonding pair of electrons** towards itself).

Understand this fact too!

Electronegativity is a good measure of metallic or non – metallic characters of elements. Metals (are found on a far left hand side of periodic table) have low electronegativities (high electropositivity) while non – metals (are found on a right hand side of periodic table) have high electronegativities (low electropositivity). So we can conclude that:

- Metallic characters decrease across the period and increase down the group
- Non–metallic characters increase as you go across the period (from left to right) and decrease as you descend the group.

EFFECTS OF ELECTRONEGATIVITY ON PROPERTIES OF COMPOUNDS

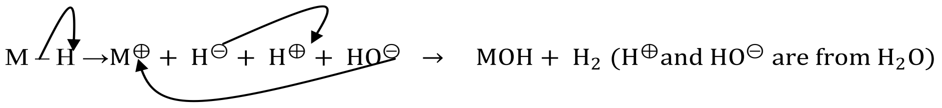
Electronegativity difference between bonded atoms affects:

- Reaction of hydrides with water
- Acidic and basic strength of hydroxides
- Percentage degree of ionic characters of compounds

Reaction of hydrides with water

The reaction of hydride with water depend on whether after breaking the bond between a hydrogen and another atom (which form hydride with hydrogen), the hydrogen is released as positively charge or negatively charged.

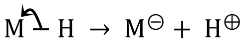
- If the hydrogen leaves as the negative charge, a hydroxide (in most cases and hydrogen gas) is formed and this occurs when the hydrogen atom is more electronegative than another atom, mainly when hydrogen is bonded to metal atom to form an ionic hydride.



$$M - H \rightarrow M^{\oplus} + H^{\ominus} + H^{\oplus} + HO^{\ominus} \rightarrow MOH + H_2 \ (H^{\oplus} \text{and } HO^{\ominus} \text{ are from } H_2O)$$

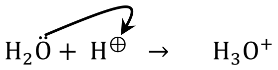
Where hydrogen is stronger electronegative than another atom, M so that it can take all bonding electron pair during the bond cleavage.

- If hydrogen leaves as positive charge, the hydride will act as an acid by donating proton to water to give hydronium ion (H_3O^+) and this happen when the hydrogen atom is less electronegative than the atom it combines with in forming hydride, mainly when hydrogen is bonded to non – metal to form covalent hydride.



$$M - H \rightarrow M^{\ominus} + H^{\oplus}$$

Then



$$H_2\ddot{O} + H^{\oplus} \rightarrow H_3O^+$$

And the overall reaction equation becomes $MH + H_2O \longrightarrow M^- + H_3O^+$

Where hydrogen is les electronegative than another atom, M, so that it become deprived in electrons after the bond cleavage.

- If hydrogen atom and another atom it combines with in forming the hydride do not differ much in their electronegativities, then the hydride will give amphoteric solution when reacted with water; that is the solution which has reaction with both acid and base will be formed.

- If both hydrogen atom and another atom it combine with have similar electronegativities, no breaking of bond will occur and hence no reaction will occur between the hydride and water.

In order to have better understanding of above concept, let us have a look at hydrides of period 3.

Hydride of period 3

Period 3 elements which form hydrides are Na, Mg, Al, Si, P, S, Cl and their respective hydrides are $NaH, MgH_2, AlH_3, SiH_4, PH_5, (or\ PH_3), H_2S$ and HCl.

The first two hydrides and react with water to give basic solution (hydroxide) according to the following equations:

$$NaH + H_2O \rightarrow NaOH + H_2$$

$$MgH_2 + 2H_2O \rightarrow Mg(OH)_2 + 2H_2$$

AlH_3 reacts with water to give amphoteric hydroxide according to the following equation:

$$AlH_3 + 3H_2O \rightarrow Al(OH)_3 + 2H_2$$

SiH_4 (name: **silane**) and **phosphane**, PH_5 (or **phosphine**, PH_3) do not react with water:

$SiH_4 + H_2O \rightarrow$ No reaction

PH_5 (or PH_3) $+ H_2O \rightarrow$ No reaction

H_2S and HCl dissolve in water to give acidic solution according to the following equation:

$$H_2S + H_2O \rightarrow H_3O^+ + HS^-$$

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

Reasons for the trend shown

- The hydrides of first two elements (Na and Mg) gives basic solution suggesting that the period 3 elements are stronger electropositive (less electronegative) than hydrogen.
- Hydride of Al gives amphoteric solution suggesting that electronegativities of Al and H do not differ much.
- Hydrides of Si and P have no reaction with water suggesting that their electronegativities are almost equal to that of hydrogen.
- The last two hydrides of S and Cl give acidic solution suggesting that the elements are more electronegative than hydrogen.

The above facts justify that electronegativity increases as you go across the period from left to right and hence metallic characters of elements decrease at the same direction

The reader should understand that hydrides of period 2 do not show clear trend in their reactions with water. So they are not preferred in the justification of the increase of electronegativity across the period. Let us have a little look at them!

Period 2 element	Li	Be	B	C	N	O	F
Hydride	LiH	Not present	B_2H_6 or BH_3	CH_4	NH_3	H_2O	HF
Property of solution formed after reaction between hydride and water	Basic	–	Acidic	No reaction	Basic	Amphoteric	Acidic

So only last three hydrides which are NH_3, H_2O and HF show regular trend in their properties.

NH_3 dissolve in water to form ammonium hydroxide which is basic. Being basic ammonium hydroxide reacts with acidic solution like HCl to give salt and water but it has no reaction with another alkaline solution like NaOH

$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$; while $NH_4OH + NaOH \rightarrow$ No reaction

H_2O is amphoteric; it can react with both acid and base depending on the strength of the acid or base it react with

As acid; it reacts with stronger base (than itself) like SO_4^{2-}.

$$H_2O + NH_3 \rightarrow NH_4^+ + OH^-$$

As base; it reacts with stronger acid like HCl

$$H_2O + HCl \rightarrow H_3O^+ + Cl^-$$

HF dissolves in water to give acidic solution which reacts with basic solution like NaOH and it has no reaction with another acidic solution like HNO_3

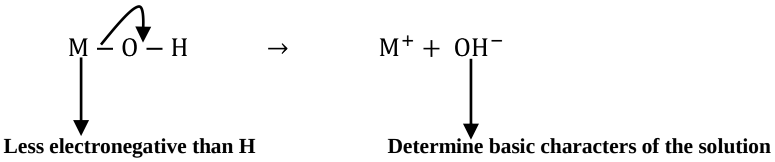
$$HF + NaOH \rightarrow NaF + H_2O$$

$$HF + HNO_3 \rightarrow \text{No reaction}$$

Acidic and basic strengths of hydroxides

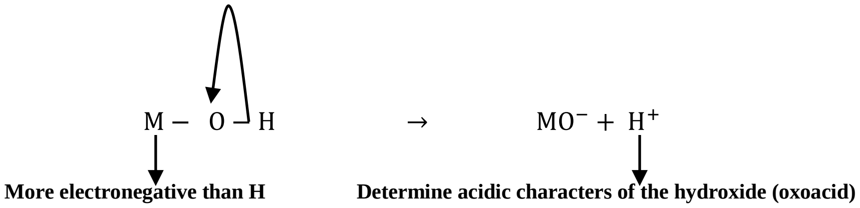
Hydroxide of an element will be acidic, basic or amphoteric depending on electronegativity difference between the elements and hydrogen. In hydroxides, oxygen is more electronegative than both the element which forms hydroxide and hydrogen so the oxygen may take pair of bonding electrons from either the element or hydrogen.

- If the element is less electronegative than hydrogen it will be easier for oxygen to take electrons from the element than from hydrogen and hydroxide ions (OH^-) will be released making the hydroxide basic.



  - *Strong electropositive metals form this kind of hydroxide.*

- If the element is more electronegative than hydrogen it will be easier for oxygen atom to take electrons from hydrogen than from the element and hydrogen protons (H^+) will be released making the hydroxide acidic. Acids formed in this way are known as **oxoacids** or **oxyacids.**



- *Non-metals and metalloids form acidic hydroxide.*

- If electronegativities of the element and hydrogen do not differ much, oxygen can take bonding pair of electrons from either the element or hydrogen releasing hydroxide ions (OH^-) or hydrogen protons (H^+) respectively depending on the strength of acid or base of a compound it react with and hence the hydroxide will be **amphoteric.**

- *Weak electropositive metals like aluminium form amphoteric hydroxide.*

In order to have better understanding of the concept, consider hydroxides of period 3 elements

Hydroxides of period 3 elements and their structures

HYDROXIDE	CONDENSED STRUCTURAL FORMULA
$NaOH$	$NaOH$
$Mg(OH)_2$	$Mg(OH)_2$
$Al(OH)_3$	$Al(OH)_3$
H_2SiO_3	$SiO(OH)_2$
H_3PO_4	$PO(OH)_3$
H_2SO_4	$SO_2(OH)_2$
$HClO_4$	$ClO_3(OH)$

The first two hydroxides are basic. They have no chemical reaction with other alkaline solution but they react with acids like HCl to give salt and water only.

$$NaOH + HCl \rightarrow NaCl + H_2O$$

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$$

$Al(OH)_3$ is amphoteric.

- With strong acid like HCl (aq), $Al(OH)_3$ acts as a base yielding salt and water only.

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$$

- With strong base like $NaOH(aq)$, $Al(OH)_3$ act as acid

$$Al(OH)_3 + 3NaOH \rightarrow Na_3[Al(OH)_6] \xrightarrow[\text{dehydration}]{} Na_3AlO_3 + 3H_2O$$

And the overall reaction equation becomes:

$H_3AlO_3 + 3NaOH \rightarrow Na_3AlO_3 + 3H_2O$ (As the acid, the more understandable form of chemical formula of aluminium hydroxide is H_3AlO_3 and not $Al(OH)_3$).

It should be noted that:

The different form of aluminates, $Na[Al(OH)_4]$ and $Na_3[Al(OH)_6]$ which are formed depending on the concentration of the alkaline solution; with greater concentration of NaOH, $Na_3[Al(OH)_4]$ and hence Na_3AlO_3 (after dehydration) is formed while with lower concentration of NaOH, $Na[Al(OH)_4]$ and hence $NaAlO_2$ (after dehydration) is formed.

$$Al(OH)_3 + \underset{\downarrow}{NaOH} \rightarrow Na[Al(OH)_4] \xrightarrow[-2H_2O]{\text{Dehydration}} NaAlO_2 + 2H_2O$$

1 mole of NaOH instead of 3 mole like in the first case

Hydroxides of phosphorous and silicon were expected to have amphoteric characters because their electronegativities are similar to that of hydrogen, but they are found to show acidic characters, why?

- This is because presence of double bond between Si or P with oxygen atom(s) allows delocalisation of electrons through mesomerism and hence acidic strength is increased.

Hydroxides of S and Cl which are H_2SO_4 and $HClO_4$ are respectively acidic; they react with alkali solution like NaOH give salt and water only.

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

$$HClO_4 + NaOH \rightarrow NaClO_4 + H_2O$$

So hydroxides of period 3 element very regularly from basic, amphoteric to acidic verifying that electronegativity of elements increases as you go across the period from the left to the right and hence metallic characters of elements decrease towards the same direction

It should be noted that:

A part from the electronegativity difference, acidic strength is also determined by number of oxygen atom which makes double bond with the element which forms the hydroxide.

- The greater number of oxygen atoms with double bond the greater acidic strength of the hydroxide because :

- The greater number of double bonds increases the possibility of the molecule to undergo mesomerism in different ways and hence more delocalization of electrons.

- The greater number of oxygen atoms with double bond the greater negative inductive effect.

The mesomerism and negative inductive effect increase the acidic strength of the acid by:

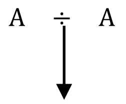
- Making easier for $O - H$ bond to break.

- Stabilising the negative charged ion which is formed after releasing hydrogen protons (H^+) thus making possible for the ion to exist on its own without recombining with the hydrogen proton.

Percentage of ionic characters of compounds

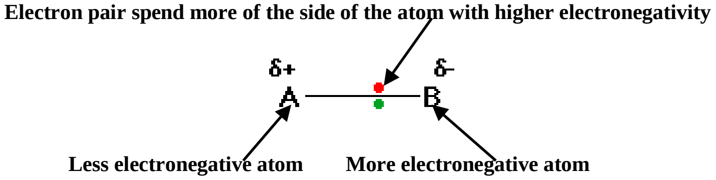
If we are assuming the starting bond is covalent, there are following three possibilities:

First possibility: The bonding of electrons to exist in exactly half way between two bonded atoms and the bond become purely covalent. This occurs if the two atoms come from the same element so that they have exactly equal electronegativity; when this occurs, the molecule become purely **non-polar.**



Electrons spend at mid way between the two atoms

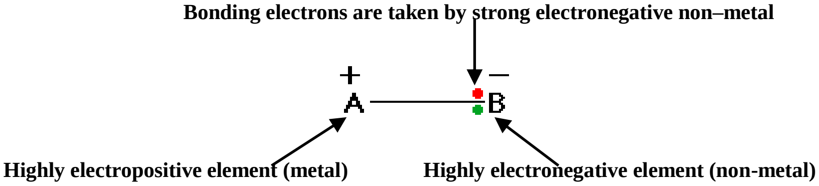
Second possibility: The bonding pair of electrons spends more on one of the bonded atoms resulting to formation of partial charges. This occur if one atom is slightly more electronegative than another bonded atom so that electrons are more attracted towards the side of the atom of higher electronegativity resulting to formation of partial negative charge on the atom while the atom of lower electronegativity attain partial positive charge. When this happen the covalent bond become **polar** (the intermediate of covalent and ionic bond).



Electron pair spend more of the side of the atom with higher electronegativity

Less electronegative atom **More electronegative atom**

Third possibility: The bonding pair of electrons totally shifts to one of bonded atom. This occur when one of bonded atom has much higher electronegativity compared to another bonded atom such that the atom is able to take bonding pair of electrons and become negative charged (anion) while another atom which is deprived with electrons become positive charged (cation) and the bond become ionic. The bond is common when strong electropositive metals are bonded with strong electronegative non – metal.



Bonding electrons are taken by strong electronegative non–metal

Highly electropositive element (metal) **Highly electronegative element (non-metal)**

It should be noted that:

We can use above discussion in the three cases to **justify** that **metallic character decreases (electronegativity increases) as you go across period from the left to the right hand side.**

This can be done by considering:

(i) Oxides of period 3 elements

(ii) Chlorides of period 3 elements

(i) Oxides of period 3

Arguments:

- Ionic oxides (oxides formed by strong electropositive metals) are basic.
- Covalent oxides (**oxides formed by non – metals or metalloids)** are acidic
- Amphoteric oxides (oxides which have both ionic and covalent characters) are formed by less electropositive metals.

Justification

Oxides of period 3 elements are $Na_2O, MgO, Al_2O_3, SiO_2, P_4O_{10}, SO_3, Cl_2O_7$ (some elements like P and S form more than one kind of oxide. Oxides of which the period 3 element has highest oxidation state are chosen although you can use the oxides with lower oxidation states of period 3 elements like. P_3O_6 and SO_2 to reach the same conclusion, don't worry!)

The first two oxides Na_2O and MgO are basic. Being basic:

- They dissolve in water to give alkaline solution

$$Na_2O + H_2O \rightarrow 2NaOH$$

$$MgO + H_2O \rightarrow Mg(OH)_2$$ (However solubility of MgO in water is very low).

- They react with acid to give salt and water only and they have no reaction with other alkaline solution.

$$Na_2O + 2HCl \rightarrow 2NaCl + H_2O$$

$$MgO + 2HCl \rightarrow MgCl_2 + H_2O$$

Al_2O_3 is amphoteric as it can react with both acidic and basic solution.

- Al_2O_3 as a base:

As a base, Al_2O_3 reacts with strong acid to give salt and water only.

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

- Al_2O_3 as an acid:

As an acid, Al_2O_3 reacts with strong base to give the final stable product which is salt and water

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4] \xrightarrow{\text{dehydration}} 2NaAlO_2 + 4H_2O$$

Overall reaction equation (after dehydration) becomes:

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$

It should be noted that:

Al_2O_3 is insoluble in water (Because its lattice energy is very high) . It has no reaction with water.

$$Al_2O_3 + H_2O \rightarrow \text{No reaction}$$

Warning! Don't be confused here because some authors mislead by writing that Al_2O_3 reacts with water to form aluminium hydroxide – that is misconception! If Al_2O_3could be attacked by water, then the aluminium containers would not be used in transportation of various substances because the metal has tendency of reacting with oxygen from the air to form the oxide layer of Al_2O_3. This oxide would be attacked by moist (water from the atmosphere) and hence the aluminium would be useless!

The remaining oxides SiO_2, P_4O_{10}, SO_3 and Cl_2O_7 are acidic. Being acidic:

- They react with alkaline solution like NaOH to give salt and water only and they have no reaction with another acidic solution.

$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$

$P_4O_{10} + 12NaOH \rightarrow 4Na_3PO_4 + 6H_2O$

Or $P_4O_6 + 12NaOH \rightarrow 4Na_3PO_3 + 6H_2O$

$SO_3 + 2NaOH \rightarrow Na_2SO_4 + H_2O$

Or $SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$

$Cl_2O_7\ 2NaOH \rightarrow 2NaClO_4 + H_2O$

- They dissolve in water to give acidic solution. However SiO_2 *being held by giant covalent bond in three dimensional structure which is very strong intermolecular forces of attraction is highly insoluble in water and hence it has no reaction with the water* **–** here there is another **WARNING! Don't be misled by others who mention that SiO_2 dissolves in water to give silicic acid, H_2SiO_3! That is totally misconception! In reality SiO_2 is sand which everyone knows, so ask yourself "Can really sand dissolve in water?!"**

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

Phosphoric acid

Or $P_2O_6 + 6H_2O \rightarrow 4H_3PO_3$

Phosphorous acid

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Sulphuric acid

Or $SO_2 + H_2O \rightarrow H_2SO_3$

Sulphorous acid

$$Cl_2O_7 + H_2O \rightarrow 2HClO_4$$

Chloric (VII) acid (or perchloric acid)

But $SiO_2 + H_2O \rightarrow$ No reaction

So in summary:

Na_2O: Ionic, strong basic	P_40_{10}: Covalent, acidic
MgO: Ionic, mildly basic	SO_3: Covalent, strongly acidic
Al_2O_3: Ionic, amphoteric	Cl_2O_7: Covalent, very strongly acidic
SiO_2: Covalent network, weakly acidic	

Conclusion

Oxides of period 3 vary regularly form basic, amphoteric and finally to acidic as you go across the period. This suggests that their bond vary regularly (in the same direction) from ionic, intermediate of ionic and covalent and finally to covalent bond and therefore their electronegativities increase and hence metallic characters decreases as you go across the period from left to right.

(ii) Chlorides of period 3

Arguments:

- Ionic chloride (chloride which is formed by strong electropositive metal) does not hydrolyse in water.
- Covalent chloride (chloride which is formed by weak electropositive metal or non- metal) hydrolyses in water to give acidic solution.

Justification

Chloride of period 3 are $\mathrm{NaCl}, \mathrm{MgCl_2}, \mathrm{AlCl_3}, \mathrm{SiCl_4}, \mathrm{PCl_5}$ (or $\mathrm{PCl_3}$), $\mathrm{S_2Cl_2}$ and $\mathrm{Cl_2}$

NaCl does not react with water; i.e. does not hydrolyse either in cold water steam. It is only dissolve in water to give neutral solution of its aqueous ions.

$$\mathrm{NaCl(s)} + \mathrm{H_2O} \rightarrow \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)}$$

Action of $\mathrm{MgCl_2}$ with water depend on whether the water is cold or hot

- **With cold water,** the chloride does not undergo hydrolysis. It is only dissolve to give neutral solution of its aqueous ions without any chemical reaction.

$$\mathrm{MgCl_2(s)} + \mathrm{H_2O(l)} \rightarrow \mathrm{Mg^{2+}\,(aq)} + \mathrm{2Cl^-(aq)}$$

- **With hot water or steam,** the chloride undergoes partial hydrolysis to give basic chloride and hydrogen chloride gas.

$$\mathrm{MgCl_2} + \mathrm{H_2O} \underset{\Delta}{\rightarrow} \mathrm{Mg(OH)Cl} + \mathrm{HCl}$$

The reader should understand that:

The ability of $\mathrm{MgCl_2}$ to undergo partial hydrolysis when heat is applied, explains why anhydrous magnesium chloride cannot be prepared by just heating its hydrated salt ($\mathrm{MgCl_2.6H_2O}$) to remove water of crystallisation.

This is simply because by heating $\mathrm{MgCl_2.6H_2O}$, the chloride undergo partial hydrolysis with some water which is to be removed yielding basic chloride ($\mathrm{Mg(OH)Cl}$) and hydrogen chloride gas (HCl) instead of forming anhydrous $\mathrm{MgCl_2}$. Even on further heating of the chloride, MgO is formed and not anhydrous $\mathrm{MgCl_2}$.

$$\mathrm{MgCl_2.6H_2O} \underset{\Delta}{\rightarrow} \mathrm{Mg(OH)Cl} + \mathrm{HCl} + \mathrm{5H_2O}$$

And $$\mathrm{Mg(OH)Cl} \underset{\Delta}{\rightarrow} \mathrm{MgO} + \mathrm{HCl}$$

The remaining chloride undergo hydrolysis to give acidic solution

$$\mathrm{AlCl_3} + \mathrm{3H_2O} \rightarrow \mathrm{Al(OH)_3} + \underbrace{\mathrm{3H^+} + \quad \mathrm{3Cl^-}}_{\textbf{From HCl(aq) which is strong electrolyte}}$$

$$\mathrm{SiCl_4} + \mathrm{2H_2O} \rightarrow \mathrm{SiO_2} + \mathrm{4HCl} \quad (\mathrm{Si(OH)_4} \text{ is unstable, it decompose to give more stable compound, } \mathrm{SiO_2})$$

$$\mathrm{PCl_5} + \mathrm{4H_2O} \underset{\Delta}{\rightarrow} \mathrm{H_3PO_4} + \mathrm{5HCl}$$

S_2Cl_2 (disulphur dichloride) reacts with water in complex way. It undergoes hydrolysis and redox reaction in water, yielding mixture of products ($HCl, H_2S, S, H_2SO_3, H_2SO_4, SO_2$) which is very acidic.

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

In summary:

NaCl: Strictly ionic

MgCl: Ionic

$AlCl_3$: Ionic with covalent character

$SiCl_4$: Polar covalent molecule

PCl_3: Polar covalent molecule

S_2Cl_2 : Polar covalent molecule

Cl_2: Non-polar covalent molecule

Conclusion

Ability of chloride of period 3 element to hydrolyse in water increases as you go across the period from NaCl which does not hydrolyse at all via $MgCl_2$ which undergo partial hydrolysis in hot water to other chlorides which undergo complete hydrolysis to give acidic solution. This confirms that covalent characters of chlorides increases as you go across the period and hence metallic characters of the elements decrease to the same direction.

Be careful:

- In explaining the partial ionic characters of covalent compounds, concentrate on electronegativity difference in forming polar bond (Don't talk about degree of polarisation!). Degree of polarisation has nothing to do with covalent compounds keeping in the mind that in covalent compounds there are no ions; there only partial charges resulted from electronegativity difference.
- In explaining partial covalent characters of ionic compounds, concentrate on degree of polarisation. Here there are some ions which are cations and anions unlike in covalent compounds where if there is no such similar thing.

PRACTICE EXERCISE 4

Question 1

(a) What is the electronegativity?
(b) Why values of electronegativity of noble gases are not known?

Question 2

(a) Between non-metal and metals, which one has higher electronegativity? Explain
(b) Use your answer in (a) above to explain why metals do not form covalent bond between themselves while non-metals do

Question 3

Explain the following:

(i) NaH is basic while HCl is acidic although both Na and Cl are found at the same period
(ii) HF is more ionic than HCl
(iii) KOH is stronger base than LiOH

Question 4

Describe the trend in pH of the solutions formed when the oxides of the period 3 elements, sodium to sulphur, are added separately to water. Explain this trend by reference to the structure and bonding in the oxides and by writing equations for the reactions with water.

Chapter 5

ELECTRON AFFINITY

Electron affinity or **electron gain enthalpy** *is the energy change obtained when electrons are added to one mole of gaseous atom or ion.*

First electron affinity *is the energy released when one mole of isolated gaseous atoms each acquires an electron to form one mole of uninegative ions.*

$$\mathrm{M(g)} + \mathrm{e} \rightarrow \mathrm{M^-(g)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots \Delta\mathrm{H} = -\mathcal{X}\mathrm{kJ/mol} = \text{first electron affinity}$$

Second electron affinity *is the energy absorbed when one mole of uninegative (mononegative) gaseous ions each acquires an electron to form one mole of binegative (dinegative) ions.*

$$\mathrm{M^-(g)} + \mathrm{e} \rightarrow \mathrm{M^{2-}(g)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots \Delta\mathrm{H} = +\mathcal{X}\mathrm{kJ/mol} = \text{second electron affinity}$$

Electron affinity is the measure of ability of an isolated atom to gain (attract) electron and therefore undergoing reduction. In other words; the electron affinity of an element is a measure of that element's tendency to act as an oxidising agent. Greater electron affinity suggests that, the element is stronger oxidising agent. If non-metal is stronger oxidising agent, means that the element is very reactive and has greater ability to form salts. To make it more memorable to you; very high electron affinities means:

- Good oxidising agents: easy to reduce.
- Very reactive; not found uncombined in nature.
- Reacts with metals to form salts.

Why first electron affinity is negative while the second electron affinity is positive?

This is simply because the first electron is attracted to a gaseous atom. Presence of the attraction means the process in thermally fovoured and hence heat is evolved in the process. That is about first electron affinity ***what about second electron affinity?***

Addition of second electron experience the repulsion from first added electron; presence of the repulsion means the process is not thermally fovoured and hence extra energy must be absorbed to overcome the repulsion before adding the second electron.

DIFFERENCES BETWEEN ELECTRONEGATIVITY AND ELECTRON AFFINITY

Electron affinity is closely related to electronegativity. However there is a significant difference between the two terms too. Electron affinity is the measured property of **isolated atom** while electronegativity is the property of **combined atom** in a molecule. And because atoms always exist in combined form (and not isolated form), electronegativity is more useful property than electron affinity. Below are some differences between electronegativity and electron affinity.

	ELECTRONEGATIVITY		ELECTRON AFFINITY
1	It is numerical value (with no unit) associated with an atom ability to attract shared pair of electrons.	1	It is the amount of energy change associated with an atom or ion ability to attract an electron.
2	It cannot be measured and needs to be computed from other atomic properties.	2	It is fixed and measurable value.
3	It is the property of bonded atom.	3	It is the property of isolated atom.
4	An atom has a relative value of electronegativity depending upon its bonding state. For example, sp hybridised carbon is more electronegative than sp^2-hybridised carbon.	4	An atom has an absolute value of electron affinity.
5	It changes regularly in a period or a group.	5	It does not change regularly in a period or group.

It should be noted that:

In most cases atoms of elements with high electronegativity have also high electron affinity. However ***despite the fact that fluorine has highest electronegativity among all elements in the periodic table, its electron affinity is lower than some elements like chlorine, why?***

Reason:

The atomic size of fluorine is so small that there is very large repulsion force existing between outer and inner electrons. So some extra energy must be absorbed to overcome the repulsion before adding the electron and hence fluorine has unexpectedly low magnitude of first electron affinity.

FACTORS AFFECTING MAGNITUDE OF FIRST ELECTRON AFFINITY

There are various factors affecting the magnitude of first electron affinity including:

(i) Size of an atom
(ii) Effective nuclear charge of an atom
(iii) Electronic configuration of an atom

(i) Atomic size

As the size of an atom become small, nucleus of the atom will have greater tendency of attracting extra electron toward itself and therefore higher amount of energy is released in the process of adding the extra electron and hence greater electron affinity is obtained and vice - versa.

Here again I'm insisting!

Fluorine has unexpectedly low magnitude of first electron affinity despite of its very small atomic size (and also very high electronegativity) because its atomic size is so small that there is very large repulsion force existing between outer and inner electron making difficult to add electron to it. So extra energy must be adsorbed to overcome the repulsion before adding the electron and hence in overall, less energy is released in the addition process of electrons leading to its low electron affinity.

(ii) Effective nuclear charge

As the magnitude of effective nuclear charge increases, the tendency of an atom to attract the extra electron also increases making the process of adding the electron more thermally fovoured and hence high electron affinity of the atom. Furthermore when there is large **screening effect,** the effective nuclear attractive force is lowered and hence the electron affinity becomes small.

(iii) Electronic configuration of an atom

Atoms with stable electronic configuration have low electron affinity while those of less stable electronic configuration have high electron affinity. For example:

Group IIA elements have practically zero electron affinity (numerically it is large positive energy) due to (apart from other factors of large atomic size and small effective nuclear charge) their stable electronic configuration of completely filled valence orbital

e.g. $\mathrm{Be} \rightarrow [\mathrm{He}]\, 2s^2$; $\mathrm{Mg} \rightarrow [\mathrm{Ne}]\, 3s^2$; $\mathrm{Ca} \rightarrow [\mathrm{Ar}]\, 4s^2$

Halogens (group VIIA) elements have highest electron affinity in each period because (apart from their small atomic radii and high effective nuclear charge) they have outermost electronic configuration of ns^2np^5 (where n is the outermost energy level) which need only one electron to attain stable electronic configuration of noble gases.

Group VA elements have unexpectedly low electron affinity despite of their small atomic radii and high nuclear charge because with outermost electronic configuration of ns^2np^3, they have all three of its valence p – orbitals singly occupied with electron which is stable electronic configuration of completely unpaired orbitals and hence less affinity to electrons.

Group VIIIA elements (noble gases) have practically zero electron affinity due to their stable doublet and octet electronic structure of completely paired orbitals.

TREND OF FIRST ELECTRON AFFINITY IN THE PERIODIC TABLE

After above discussion, now we can have conclusion on the trend of magnitude of first electron affinity in the periodic table.

Across the period: Generally (with few irregularities), first electron affinity increases as you go gross the period from left to right due to decrease in atomic size and increase in effective nuclear attractive force to the same direction.

Down the group: Generally (with few irregularities), first electron affinity decreases on descending the group due to increase in atomic size and increase in screening effect to the same direction.

Example

From each set three chemical species, choose the one with lowest electron affinity and one with greatest electron affinity

(a) $\mathrm{Ge}, \mathrm{Si}, \mathrm{C}$

(b) Cl, $\mathrm{Cl}^-, \mathrm{Cl}^+$

Answer:

(a) Greatest electron affinity: C

Lowest electron affinity: Ge

(b) Greatest electron affinity: Cl^+

Lowest electron affinity: Cl^-

PRACTICE EXERCISE 5

Question 1

Arrange F, Cl, Br and I in order of increasing electron affinity

Question 2

Why noble gases have zero electron affinity?

Question 3

Which one of the following pairs of elements would have higher electron gain enthalpy?

(a) Phosphorous or sulphur
(b) Fluorine or chlorine

In each case give reason for our choice

Chapter 6

INTRODUCTION TO COMPLEXES

INTRODUCTION

Complex *is an addition product which does not lose its identity in solution and behaves as one entity that consists of the central metal atom (or ion) and several ligands bonded to it by dative bond.*

- One important distinguishing feature between complex and simple salt is that: ***while simple salt lose its identity in solution, complex does not; why?***

Reason:

In simple salts, anions are bonded to cations by ionic bond. Thus simple salts are usually ionic compounds whose great property is to exist as ions not as molecules. Hence in aqueous solution the salts tend to ionises (dissociates) to give cations and anions.

That is bout simple salts (or double salts), what bout complexes?

In complexes, anions or neutral molecules are so strongly bonded to central metal atom (or ion) by dative bond which is covalent whose great property to exist as molecule and not as ions. Thus the covalent bond between central metal atom and anions (or neutral molecule) cannot be separated in aqueous solution and even in normal chemical reaction.

Complex formation explains why NaCN is poisonous while $\mathbf{Na_4\,[Fe(CN)_6]}$ is not:

A solution of sodium cyanide in water, is deadly poison due to presence of cyanide ions which block the oxygen – carrier capacity of haemoglobin in red blood cells because sodium cyanide (NaCN) being simple salt ionises in solution according to the following equation:

$$\mathrm{NaCN} \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+(aq)} + \underset{\textbf{Poison}}{\mathrm{CN^-(aq)}}$$

While $\mathrm{CN^-}$ in $[\mathrm{Fe(CN)_6}]^{4-}$ are not free in solution and instead are bonded to $\mathrm{Fe^{2+}}$ so strongly by dative covalent bond in the complex ion formation. $[\mathrm{Fe(CN)_6}]^{4-}$ occurs in solution as a single ion and, therefore, does not give the reactions of individual ions, $\mathrm{Fe^{2+}}$ and $\mathrm{CN^-}$. If so the compound ($\mathrm{Na_4}\,[\mathrm{Fe(CN)_6}]^{4-}$) is dissolved in water, the resulting solution contains $\mathrm{Na^+}$ and $[\mathrm{Fe(CN)_6}]^{4-}$.

$$\mathrm{Na_4[Fe(CN)_6](s)} \xrightarrow{\mathrm{H_2O(l)}} 4\,\mathrm{Na^+\,(aq)} + [\mathrm{Fe(CN)_6}]^{4-}\,\mathrm{(aq)}$$

What is complex compound?

Complex compound *is the neutral (uncharged) substance that has at least one of its ions consisting of an addition product which does not lose its identity in solution and behaves as one entity that consist of central metal atom (or ion) and several ligands bonded to it by dative bond.* **So any compound that at least one of it ions is the complex, is regarded as the complex compound**. As the complex is formed by dative bonds which is also known as coordination bond, **complex compounds are also known as coordination compounds.**

Central metal atom (or ion)

This is the metallic atom or ion which is capable of accepting lone pair from ligands during complex formation.

Conditions for an atom to act as central metal atom are:

(i) High cationic charge

- This enables the ion to exert enough nuclear attractive force to hold lone pair of ligands.

(ii) Small cationic (or atomic) radius

- This enables the effective nuclear attractive force to reach the lone pair of ligands easily.

(iii) Presence of empty orbitals

- This acts as a room of lone pair of ligands.

The reader should understand that: The first two conditions are for the same purpose of holding ligands. So it is not necessary for the atom (or ion) to have them simultaneously one atom (or ion) may be neutral (or possessing lower charge) but still acting as central metal atom (or ion) if the atom (or ion) has very small radius. The third condition is necessary, no atom (or ion) with no empty orbitals can coordinate with ligands in complex formation.

- Cations of strong electropositive metals do not satisfy the first two conditions and therefore strong electropositive metals do not form complexes. Only weak electropositive metals can form complexes.

Ligands

Ligands *are species which contain non metallic atom or ion with lone pair(s) so that they can donate the lone pair to central metal atom (or ion) during complex formation.*

Depending on their charges, ligands can be classified into two categories, namely:

- Neutral ligands
- Charged ligands

Neutral ligands *are species with zero charge which contain non metallic atom with lone pair(s) so that they can donate the lone pair to central metal atom or ion during complex formation.*

Examples:

H_2O whose name is **aqua**

CO whose name is **carbonyl**

NO whose name is **nitrosyl**

NH_3 whose name is a**mm**ine (double 'm' in a**mm**ine insists the ligand is derived from a**mm**onia so don't confuse it with a**m**ine which has single 'm')

$H_2N-CH_2-CH_2-NH_2$ or **en** whose name is **ethylenediamine**

$H_2N-NH_2(N_2H_4)$ whose name is **hydrazino**

CH_3NH_2 whose name is **methylamine**

N_2 whose name is **dinitrogen**

O_2 whose name is **dioxygen**

C_5H_5N whose name is **pyridine**

Charged ligands *are negatively or positively charged species possessing atom with lone pair which can be donated to central metal (or ion) during complex formation*.

Examples of negatively charged ligand

F^- whose name is **fluoro**

Cl^- whose name is **chloro**

Br^- whose name is **bromo**

I^- whose name is **iodo**

CN^- $(\leftarrow C\equiv N)$ whose name is **cyano**

$-N=C:$ whose name is **isocyanato**

$OH^-(HO^-)$ whose name is **hydroxo**

$-S-C\equiv N$ whose name is **thiocyanato**

$- N = C = S$ whose name is **isothiocyanato**

O^{2-} whose name is **oxo**

O_2^{2-} whose name is **peroxo**

CO_3^{2-} whose name is **carbonato**

SO_3^{2-} whose name **sulphito**

SO_4^{2-} whose name is **sulphato**

NO_3^- whose name is **nitrato**

NO_2^- whose name is **nitro**

$ONO-$ $(O = N - O^-)$ whose name is **nitrito**

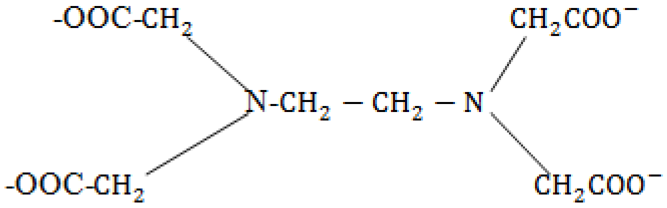
H^- whose name **hydrido**

CH_3COO^- whose name is **acetato**

NH_2^- whose name is **amido**

$S_2O_3^{2-}$ whose name is **thiosulphato**

$C_2O_4^{2-}$ or ox^{2-} whose name **oxalato**



Whose name is **ethylenediaminetetracetato** which is commonly denoted as $EDTA^{4-}$. It has charge of -4.

Examples of positively charged ligands

Positively charged ligands are not common. Below are some examples of them.

$^-NH_2NH_3^+$ whose name is **hydrozonium**

NO_2^+ whose name is **nitronium**

NO^+ whose name is **nitrosonium**

The student should note that: Being electrons (lone pair) donor, ligands acts as Lewis base while central metal atom (or ion) acts as Lewis acid as it accepts electrons from ligands during complex formation.

Ligands can also be classified into various categories depending upon the number of **coordination sites** in them. ***What is the coordination site?***

- **Coordination site** *is the atom in the ligand that donates its lone pair to the central metal atom (or ion) during complex formation.*

According to the number of coordination sites, ligands can be classified into the following categories, namely:

- Monodentate ligands
- Polydentate ligands

Monodentate ligand

This is a ligand which is attached to the central metal atom (or ion) by its only one atom in the molecule or ion thus contributing one dative bond only to the central metal ion or atom.

- Monodentate ligands are also known as **unidentate ligands**.

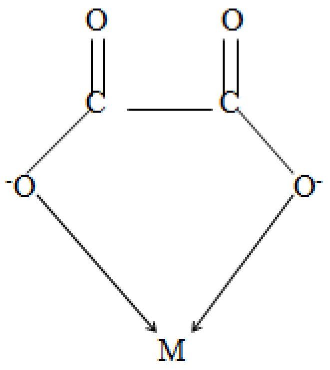
Among the mentioned neutral and charged ligands (in previous section) all ligands are monodentate except **en, EDTA** and **oxalato** only.

Polydentate ligand

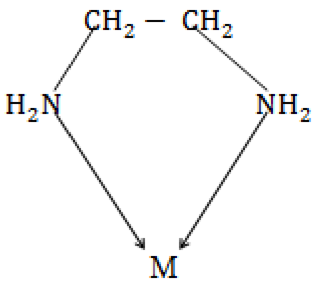
This is a ligand which makes use of more than one atom to form more than one coordinate (dative) covalent bond with the central metal ion (or atom). It may be:

- **Bidentate ligand** if it makes the use of two atoms. Examples are ethylenediamine (en) and oxalato.
- **Tridentate ligand** if it make the use of three atoms
- **Tetradentate ligand** if it makes the use of four atoms
- **Pentadentate ligand** if it makes the use of five atoms
- **Hexadentate ligand** if it makes the use of six atoms example EDTA

Majority of polydentate ligands are organic compounds which forms rings with central metal ion and so are called **chelating agent** e.g. oxalato and ethylenediamine.



Oxalato



Ethylenediamine

Where **M** is the central metal ion

Chelating agents *are polydentate ligands (like bidentate ligands e.g. oxalato and ethylenediamine) which are capable of forming rings (cyclic complex) with the central metal ion.*

Chelate *is the ring (cyclic) complex formed when polydentate ligands are bonded to central metal ion.*

Chelation *is the formation of a cyclic complex with polydentate ligands and central metal ion.*

Coordination and ionisation spheres

Coordination sphere *is the complex part of the compound which consists of central metal ion (or atom) and ligands bonded to it by dative bond enclosed in square brackets*.

- Thus in a compound $[\mathrm{Co}\ (H_2O)(NH_3)_5]Cl_3$, the coordination sphere is $[\mathrm{CO}\ (H_2O)(NH_3)_5]^{3+}$.

Ionisation sphere *are ions outside the coordination sphere.*

- Thus in the compound $[\mathrm{Co}\ (H_2O)(NH_3)_5]Cl_3$, the $Cl_3(3Cl^-)$, forms the ionisation sphere.

The coordination sphere is also knows as **inner coordination sphere** while ionisation sphere is also known as **outer sphere**

Coordination number

Coordination number *is the number of dative bonds the central metal ion (or atom) makes with ligands during complex formation.* It is also known as **coordination state**.

- Each monodentate ligand contributes coordination number of 1. **Thus for complex whose all of ligands are monodentate, coordination number is equal to total number of ligands in the complex**
  E.g. In $[Cu(H_2O)_4], H_2O$ being monodentate ligand, coordination number of copper in the complex is 4
- Each bidentate ligand contributes coordination number of 2. Thus for a complex whose all of ligands are bidentate, coordination number is twice the number of the ligands. E.g. in $[Cu(C_2O_4)_2]^{2-}, C_2O_4^{2-}$ being bidentate ligand, coordination number of copper in the complex is $2 \times 2 = 4$

TYPES OF COMPLEXES

Complexes can be grouped into three classes depending upon the nature of the charge they carry. The three classes are:

- Cationic complex
- Anionic complex
- Neutral complex

Cationic complex *is the complex ion that has net positive charge.* Example of complex cation is $[Cu(NH_3)_4]^{2+}$.

Anionic complex *is the complex ion that has net negative charge.* Example of complex anion is $[Cu(OH)_4]^{2-}$.

Neutral complex *is the complex that has no charge*. A good example of this is $[Ni(CO)_4]$

Labile and inert complexes

Depending on their reactivity, complexes can be classified into **labile** and **inert** complexes.

Labile complex *is the complex in which ligands are easily substituted by other ligands.* Most of complexes which contain H_2O(aqua) ligands like $[Cu(H_2O)_4]^{2+}$are labile complexes.

E.g. $[Cu(H_2O)_4]^{2+} + 4NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq) + 4H_2O(l)$

Labile complex

Inert complex *is the complex in which ligands are substituted slowly (by difficult) by other ligands.* Example of inert complex is any complex containing CN^- ligands like. $[NiCN_4]^{2-}$

E.g. $[Ni(CN)_4]^{2-} + 4\,H_2O \rightarrow$ No reaction

Inert complex

Homoleptic and heteroleptic complexes

Depending on the kind of ligands present in the complex, complexes can be classified into **homoleptic** and **heteroleptic** complexes.

Homoleptic complex *is the complex with all ligands identical*. For example, $[Cu(NH_3)_4]^{2+}$ with all ligands being ammines, it is homoleptic complex.

Heteroleptic complex *is the complex with non-identical ligands.* An example of heteroleptic complex is $[Co\,(OH_2)(NH_3)_5]^{3+}$.

EXPANSION OF VALENCE SHELL AND FORMATION OF COMPLEX

The most common coordination numbers of central metal atom in the complexes are 4 and 6. For elements in **representative groups**, coordination number of 4 is the result of sp^3 hybridisation of the central metal atom. To show coordination number of 6, the central metal atom (of **representative element**) must exploit two extra d-orbitals in sp^3d^2 hybridisation. *The ability of an atom to use d-orbitals in the bond formation apart from s and p hybridised orbitals* is known as the **expansion of valence shell**.

- The expansion of valence shell so as an atom to show coordination number of 6 is possible if:

(i) **An atom of the element has outermost energy level greater than 2** (so that it possesses d–subenergy level)

- Complexes like $[BF_6]^{3-}$ and $[Be(OH)_6]^{4-}$are not known because both boron and beryllium have outermost energy level of n = 2 which has no d–orbitals and hence they cannot expand their valence shell in sp^3d^2 hybridisation so as to exhibit coordination number of 6.

(ii) **Ligands are small in size**

- If ligands are of large size, the inner ligands in s and p orbitals will exert large steric hindrance thus making difficult for the central metal atom to hold ligands in far d–orbitals.
- Complex like $[AlF_6]^{3-}$ exists while $[AlI_6]^{3-}$ do not because I^- in the second complex being larger in size extert stronger steric hindrance than the smaller ligand, F^-.

NOMENCLATURE OF COMPLEX COMPOUNDS

Systematic naming of complexes is based on the system recommended by IUPAC. The rules are as follows:

General rule: **The name of a cation is written first followed by an anion.**

The cation in $[Cu(OH_2)_4]SO_4$ which is $[Cu(OH_2)_4]^{2+}$ must be named first followed by the name of SO_4^{2-} which is simple anion while in $Na_4[Fe(CN)_6]$, the simple cation, Na^+ is named first followed by the name of complex anion; it follows the same order as naming simple salt like KCl (potassium chloride).

A: NAMING OF COMPLEX CATIONS AND NEUTRAL COMPLEXES

Rule 1:

The ligands are named first and then the central metal ion (or atom)

According to latest IUPAC nomenclature (2005 version): Non- identical ligands are named according to alphabetical order regardless to their charges or numerical prefixes they carry. The alphabetical order is determined by the name of the ligand.

Rule 2:

The names of negative (charged) ligands end in o and the names of neutral ligands are written as such.

Common neutral ligands have special names. The name **aqua** is used for H_2O, **ammine**, (note the spellings, mm) for NH_3, **carbonyl** for CO, **nitrosyl** for NO, **ethylenediamine (en)** for

$H_2-N-CH_2-CH_2-NH_2$

Rule 3:

The number of each type of ligands is denoted by a Greek prefix such as di for two, tri for three, tetra for four, penta for five and hexa for six. Double vowels such as in "hexaaqua" and "pentaammine" are retained.

Rule 4:

In naming central metal ion (or atom), the ordinary name of the metal is used.

Rule 5:

The oxidation state of the metal is denoted by a roman numeral in parenthesis after the name of central metal ion e.g. ---Fe(II) if the oxidation state of iron in the complex is $+2$

Rule 6:

For bidentate ligands like ethylenediamine and oxalato the terms bis, tris and tetrakis are used instead of di, tri and tetra respectively and the group (name of the ligand) is enclosed in brackets.

E.g. (i) bis(ethylenediamine) instead of diethylenediamine.

(ii) tris(oxalato) instead of trioxalato

Very important to note:

Bis, tris and tetrakis are very important in avoiding ambiguity which sometimes arises on using normal prefixes. For example, one would use **di**ammine, for $(NH_3)_2$, but **bis**(methylamine), for $\mathbf{(CH_3NH_2)_2}$, to make a distinction from dimethylamine with the structure $\mathbf{CH_3NHCH_3}$ or $\mathbf{(CH_3)_2NH}$.

B: NOMENCLATURE OF COMPLEX ANIONS

All rules for naming complex cations or neutral complexes are followed except the name of the metal in central metal ion ends in **ate**, e.g. **cobaltate** for cobalt, **zincate** for zinc, **chromate** for chromium, **manganate** for manganese, **aluminate** for aluminium, **nickelate** for nickel etc. There are certain exceptions to the ending of the name of metal. For example:

Lead is named as **plumbate**

Iron is named as **ferrate**

Copper is named as **cuprate**

Silver is named as **argentate**

Gold is named as **aurate**

Tin is named as **stannate**

Boron is named as **borate** (and **not** boronate)

Example 51

Given with the following complex, $[CoBr_2(OH_2)_2]Cl$:

(a) Give its IUPAC name
(b) What is the coordination number of Co in the complex?

Solution

- The first step is to find out the oxidation state of Co in the complex
  - Let the oxidation state of Co be x

Then :

- H_2O being neutral ligand, its oxidation state is 0
- Br^- being charged ligand, its oxidation state is equal to the amount of the charge which is -1. Thus for two Br^-, the total oxidation state contributed by Br^- is $2 \times -1 = -2$
- Cl^- being free anion, its oxidation state is equal to the amount of its charge which is -1

- Using the fact that the summation of oxidation states in the whole compound is zero, the oxidation state cobalt can be found as follows: $x + 0 - 2 - 1 = 0$ or $x = 3$
- By naming ligand alphabetically, the name of $[Co(OH_2)_2Br_2]Cl$ is diaquadibromocobalt(III) chloride

Warning!

Don't forget to write complex name as **a single word**, a little space should be left between name of the cation and that of anion and not otherwise.

(b) Since both H_2O and Br^- are monodentate ligands, the coordination number of Co in the complex is equal to the total number of ligands.

Hence coordination number Co is 4.

Example 52

Given with the following complex: $[Ni(OH)_2(en)_2]$

(a) Give its IUPAC name
(b) What the coordination number is of nickel in the complex?

Solution

- Oxidation state contributed by 2en (ethylenediamine) $= 2 \times 0 = 0$
- Oxidation state contributed by $2OH^- = 2 \times -1 = -2$
- Let the oxidation state of Ni be x
- Then the complex being neutral;

$$x + 0 - 2 = 0 \text{ or } x = 2$$

- en being bidentate ligand, we cannot use diethylenediamine and we must use bis(ethylenediamine) instead.
- Naming ligands alphabetically, the name of the given complex become:
  bis(ethylenediamine)dihydroxonickel(II)

(b) en being bidentate ligand contribute $2 \times 2 = 4$ of coordination bonds while OH^- being monodentate contribute $2 \times 1 = 2$ bonds. Hence coordination number of Co is 6

Example 53

Given with the following complex compound:

$K[MnO_4]$ (Commonly written as $KMnO_4$)

(a) Give its IUPAC name
(b) What is the coordination number of manganese in the complex?

Solution

- Oxidation state contributed by $K^+ = +1$
- Oxidation state contributed by $4\ O^{2-} = 4 \times -2 = -8$
- Let the oxidation state Mn be x

Then $1 + x - 8 = o$ or $x = 7$

Thus the name of the compound is:

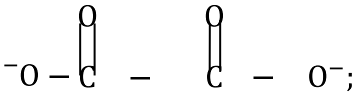
Potassium tetraoxomanganate(VII)

(In this case the central metal ion is found in complex anion, so its name must end with – ate)

(b) O^{2-} being monodentate ligands, $4O^{2-}$ contributed 4×1 or 4 coordination (dative) bonds to the central Mn^{7+}
Hence coordination number of manganese is 4

The student should note that: some students confuse that whenever the charge in ligand is

-2, then the ligand is bidentate; this is not true! For ligand with charge of -2 to a act as a bidentate, the atoms with lone pair must be bonded to different atoms like in $C_2O_4^{2-}$ whose

structure is 

$^{-}O - \overset{\overset{O}{\|}}{C} - \overset{\overset{O}{\|}}{C} - O^{-}$;

Ligands like O^{2-}, SO_4^{2-} or CO_3^{2-} (In SO_4^{2-}, the two O^- are bonded to the same sulphur atom while in CO_3^{2-}, the two O^- are bonded to the same carbon atom) are monodentate ligands although have charge of -2.

Furthermore, even if atoms with lone pairs (donor atoms) are bonded to different atoms, the donor atom must be far apart enough to allow simultaneous donation of electrons to central atom. Most of inorganic ligands like hydrazine are monodentate ligands even if they have two donor atoms because they incapable of forming relatively long chain like organic ligands. As a general rule, **only organic species are commonly acting as polydentate ligands.**

WRITING FORMULA OF COORDINATION COMPLEXES

According to IUPAC, the latest rules (**2005 version**) for writing formula of complexes can be summarised as follows:

Rule 1:

The formula of a coordination complex is written in a different order than its name. The chemical symbol of the metal central atom is written first. The ligands are written next.

Rule 2:

If there is more than one ligand, they are written in alphabetical order according to the first letter in their **chemical formula** (**NOT** their names). The first letter in the chemical formula of ligand must be the symbol of donor atom; for example as ligand, aqua is written (in formula of complex) as OH_2 and **not** H_2O because the donor atom is O and not H.

Rule 3:

The formula of the entire complex entity, whether charged or not, is enclosed in square brackets.

Rule 4:

If the coordination (complex) entity is negatively charged, the formula is preceded by the cation formula; i.e. it is written next to the cation formula.

Rule 5:

When ligands are polyatomic (consist of more than one atom), their formulae are enclosed in parentheses (even if only one ligand is present). Ligand abbreviations are also enclosed in parentheses.

Rule 6:

In a coordination compound's name, when one of the ions is simple, the number of atoms is not indicated with a prefix. Since it still has to be written in the formula, it is determined by balancing the overall charge of the compound. (For example, tetrafluorochromium(VI) chloride becomes $[CrCl_4]Cl_2$).

Example 54

Write the formula of amminetetraaquachromium(II)

Solution

Formula of the complex with given name is $[Cr(NH_3)(OH_2)_4]^{2+}$

Things to note from the above formula:

- Cr (central metal atom) is written before ligands
- N is donor atom in NH_3 while O is donor atom in H_2O.
- Because **N** (of NH_3) is before **O** (of OH_2) in the alphabetical order, ammine ligand is written before aqua ligand.
- Both H_2O and NH_3 being polyatomic ligands their formula are enclosed parentheses.

- The charge of $+2$ comes from the fact that the oxidation state of Cr is $+2$ and all ligands are neutrals thus making the net charge to be $+2$.

Example 55

Write the formula of amminesulphatochromium(II)

Solution

Formula of the complex with given name is $[Cr(NH_3)(OSO_3)]$

Example 56

Write formula of the following complex compounds:

(i) amminetetraaquachromium(II) sulphate (ii) potassium hexacyanoferrate(III)
(iii) triamminenitroplatinum(II) chloride

Solution

(i) $[Cr(NH_3)(OH_2)_4]SO_4$ (ii) $K_3[Fe(CN)_6]$ (iii) $[Pt(NH_3)_3(NO_2)]Cl$ (Here both ligands begin with N so the next letter is used whereby **H** of NH_3 is alphabetically before **O** of NO_2).

The reader should understand that:

In writing formula of complexes, it is generally accepted that it is more important to list the ligands correctly than to place them in order. This leniency is not applied to order of listing ligands in naming the compounds. Follow the rules carefully for naming compounds.

FURTHER WORKED EXAMPLES ON COMPLEXES

Example 57

How many moles of ions produced in solution when one mole of $[Co(NO_2)(NH_3)_5](NO_3)_2$ is dissolved in water?

Solution

Three moles, i.e. two moles of NO_3^- and one mole of $[Co(NH_3)_5]^{2+}$ ions are produced as the compound ionises according to the following equation:

$$[Co(NO_2)(NH_3)_5](NO_3)_2\,(aq) \rightarrow [Co(NH_3)_5NO_2]^{2+}(aq) + 2NO_3^-(aq)$$

Example 58

Explain how $[PtCl_2(NH_3)_2]$ and $[Pt(NH_3)_6]Cl_4$ will differ in their electrolytic conductance?

Solution

$[PtCl_2(NH_3)_2]$ is a neutral complex and so does not ionises in solution. Its electrolytic conductance is therefore zero. 1 mole of $[Pt(NH_3)_6]Cl_4$ ionises to form 1 mole of $[Pt(NH_3)_6]^{4+}$ and 4 moles of Cl^- ions. Its electrolytic conductance is therefore corresponds to 4 moles of Cl^-ions and 1 mole of $[Pt(NH_3)_6]^{4+}$

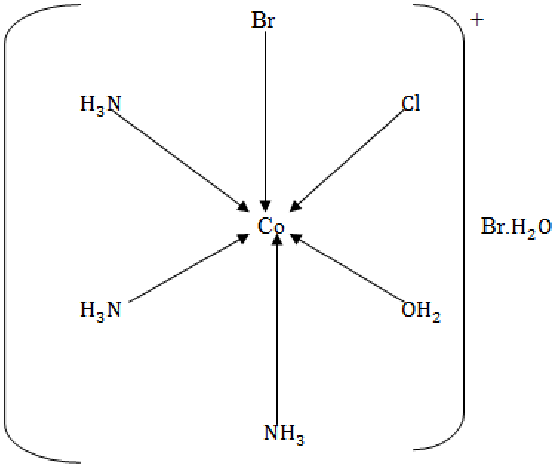
Example 59

Two compounds L and M have the same molecular formula of $Co(NH_3)_3(H_2O)_2Cl\,Br_2$. One male of L, readily loses 1 mole of water in a desicator while M does not lose any water under the same condition. An aqueous solution of L has a conductivity equivalent to that of a compound with two ions per formula unit. The conductivity of M(aq) corresponds to that of a compound with three ions per formula unit. When $AgNO_3$ solution is added to a solution of L, one mole of AgBr is precipitated per mole of L. A solution of M gives two moles of AgBr per mole of M. Give the structural formula of L and M and their IUPAC names.

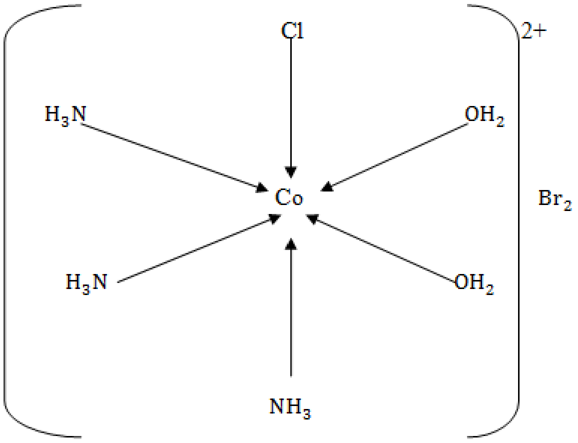
Solution

- Since L loses 1 mole of water easily, then 1 mole of H_2O is not a ligand i.e. it is loosely attached to the complex compound as water of crystallisation.

- Since L ionises to give two ions, then one mole of halide ions (Cl^- or Br^-) is present in the ionisation sphere, i.e. not ligand
- Since L precipitates one mole of AgBr then the halide ions cannot be chloride, Cl^-, it must bromide ion, Br^-
- Hence L is the compound with one Br^- and one H_2O of hydration in the ionisation sphere of the following structural formula:



- Since M does not lose water readily, then all the water (H_2O) molecules are directly attached to the central metal ions as ligands
- Since M ionises to give three ions, then two halide ions are present in the ionisation sphere, i.e. are not ligands
- Since M precipitates two moles of AgBr, then two halide ions must be Br^- ions
- Hence M is the compound with two Br^- ions only in the ionisation sphere of the following structural formula:



- Name of L is triammineaquabromochlorocobalt(III) bromide monohydrate
- Name of M is triamminediaquachlorocobalt(III) bromide

Example 60

In one experiment, 2.5×10^{-3}mol of a compound of formula $Cr(NH_3)_5Cl_3$ was dissolved in water and titrated with $0.1MAgNO_3$ solution. $50cm^3$ of $AgNO_3$was required for complete precipitation of free Cl^-. Give the ionic formula of the compound and name it.

Solution

- Number of mole $AgNO_3$ in $50cm^3$ of its solution
  $= \frac{50}{1000} \times 0.1mol = 5 \times 10^{-3}mol$
- $AgNO_3$ combines with Cl^- according to the following equation:
  $AgNO_3(aq) + Cl^-(aq) \rightarrow AgCl(s) + NO_3^-(aq)$

From the stoichiometry of the above equation, the mole ratio of $AgNO_3$ to Cl^- is 1:1

- Thus number of moles of Cl^- ions produced from 2.5×10^{-3}moles of the complex compound was also 5×10^{-3}moles.
- So 2.5×10^{-3} moles of $Cr\,(NH_3)_5Cl_3$ produces 5×10^{-3}moles of Cl^- in aqueous solution.
- Thus mole ratio of $Cr\,(NH_3)_5Cl_3$ to Cl^- is $2.5 \times 10^{-3} : 5 \times 10^{-3}$ or in its simplest form is 1:2 (dividing by 2.5×10^{-3} throughout)
- The simplest ratio suggests that $2Cl^-$ are in ionisation sphere according to the formula: $[CrCl(NH_3)_5]Cl_2$

Hence the compound has the following ionic formula $[CrCl(NH_3)_5]2Cl^-$

Name of the complex compound is: pentaamminechlorochromium(III) chloride

Example 61

$50cm^3$of a solution of 0.1M $[Co(SO_4)(NH_3)_5]$Br was mixed with $50cm^3$ of a solution of 0.1MKBr and the solution made up to $200cm^3$. What was $[Br^-]$

Solution

$[Co(SO_4)(NH_3)_5]$Br ionises according to the following equation:

$$[Co(SO_4)(NH_3)_5]Br \rightarrow [Co(SO_4)(NH_3)_5]^+ + Br^-$$

$$\frac{50}{1000} \times \mathbf{0.1mol} = \mathbf{5 \times 10^{-3}mol} \qquad \mathbf{5 \times 10^{-3}mol} \qquad \mathbf{5 \times 10^{-3}mol}$$

Thus number of moles of Br^- from the complex salt (compound) is 5×10^{-3}mol

KBr ionises according to the following equation:

$$KBr \rightarrow K^+ + Br^-$$

$$\frac{50}{1000} \times \mathbf{10^{-3}} \qquad \mathbf{5 \times 10^{-3}mol} \qquad \mathbf{5 \times 10^{-3}mol}$$

$= \mathbf{5 \times 10^{-3}mol}$

Thus number of moles of $Br^-$from the simple salt was also 5×10^{-3}mol

Whence the total number of moles of Br^-

$$= (5 \times 10^{-3} + 5 \times 10^{-3})moles = 1 \times 10^{-2}moles$$

Using [ ] = $\frac{n}{v}$

Then $[Br^-] = \frac{1 \times 10^{-2} \times 10^3}{200}M = 0.05M$

Hence molar concentration of Br^- was 0.05M

Example 62

$50cm^3$ of a solution of 0.1M $[CoBr(NH_3)_5]SO_4$ was mixed with $50cm^3$of a solution of 0.1MKBr and the solution made up to $200cm^3$. What was $[Br^-]$? Assume complete dissociation of the salt.

Solution

- Since Br^- in the complex, present in coordination sphere as ligand, the existence of Br^- ions in solution is accounted by KBr only.
  i.e. KBr → $K^+ + Br^-$; from which mole ratio of KBr to Br^- is 1:1

- Thus number of moles of Br^-

$$= \frac{50}{1000} \times 0.1\text{mol} \ = 5 \times 10^{-3}\text{mol}$$

Hence $[Br^-] = \frac{5 \times 10^{-3} \times 10^3}{200} = 0.025\text{M}$

Example 63

Given with the following complex compound:

$K_2[Cr_2O_7]$ (Its is commonly written as $K_2Cr_2O_7$)

(a) Give its IUPAC name
(b) What is coordination number of chromium in the complex?

Solution

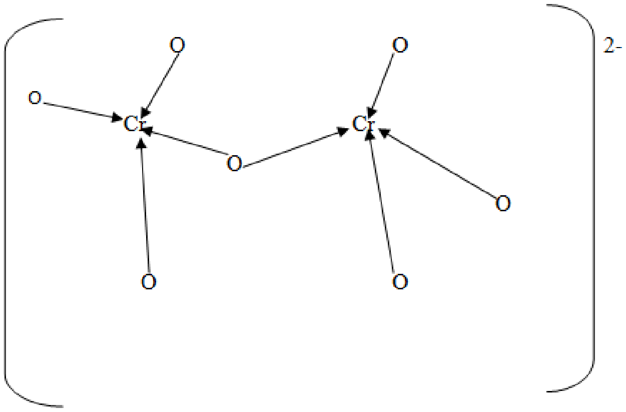
(a) Let oxidation state of chromium be *x*

Then $(2 \times 1) + 2x + (7 \times -2) = 0$ or $x = +6$

Thus the name of the compound is Potassium heptaoxodichromate (VI)

(Don't forget: the prefix di before the name of central metal ion because in this case there are two chromium ions acting as central metal ion)

(b) To understand coordination number of chromium, consider the structure of dichromate ion whose geometric shape consist of two tetrahedral units joined together through oxygen atom.



From above complex anion, it is clearly seen that each chromium ion form four coordination (dative) bonds with O^{2-} ligands.

Hence coordination number of chromium in the complex is 4

It should be noted that:

In the above complex, O^{2-} is known **bridging ligand** because it joins the two central metal ions.

Example 64

Given with the following complex compound:

$K_6[Co_2(CN)_{10}]$

(a) Name the compound
(b) What is the coordination number of cobalt in the complex

Solution

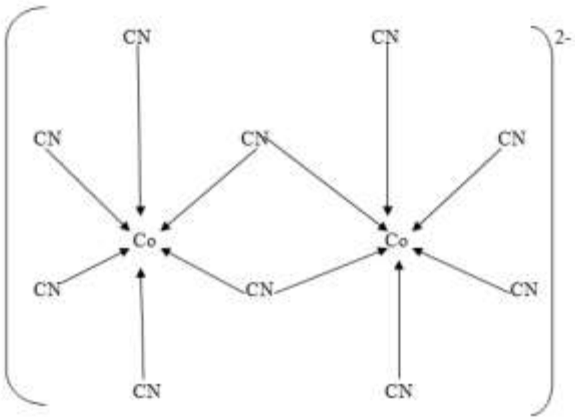
(a) Let oxidation state of Co be x

Then $6 + 2x - 10 = 0$ or $x = 2$

Thus the name of the complex compound is

Potassium decacyanodicobaltate(II)

(b) Consider structure of $[Co_2(CN)_{10}]^{6-}$ as shown below:



From the above structure of complex, it is clearly seen that each cobalt forms six dative bonds with CN^- ligands.

Hence the coordination number of Co is 6

Here the bridging ligand is CN^-.

Example 65

Name the following compounds indicating the coordination number of the central metal atom in each case.

(i) $Li[AlH_4]$
(ii) $[Cu(NH_3)_4(H_2O)_2]SO_4$
(iii) $K_2\ [CrO_4]$
(iv) $[Be(H_2O)_4]^{2+}$
(v) $[Be(OH)_4]^{2-}$
(vi) $[Cr(H_2O)_6]Cl_3$
(vii) $[CrCl(H_2O)_5]\ Cl_2.H_2O$
(viii) $[Ag(NH_3)_2]^+$
(ix) $[Ag(CN)_2]^-$
(x) $[Au(CN)_2]^-$
(xi) $[Fe(ox)_3]^{3-}$
(xii) $[Ni(en)_3]^{2+}$

Solution

(i) Lithium tetrahydridoaluminate(III). Coordination number of Al is 4
(ii) Tetraamminediaquacopper(II) sulphate. Coordination number of Cu is 6
(iii) Potassium tetraxochromate(VI) . Coordination number of Cr is 4
(iv) Tetraaquaberyllium(II) ion. Coordination number of Be is 4
(v) Tetrahydroxoberyllate(II) ion. Coordination number of Be is 4
(vi) Hexaaquachromium(III) chloride. Coordination number of Cr is 6
(vii) Pentaaquachlorochromium(III) chloride monohydrate. Coordination number of Cr is 6
(viii) Diamminesilver(I) ion. Coordination number of Ag is 2
(ix) Dicyanoargentate(I) ion.Coordination number of Ag is 2
(x) Dicyanoaurate(I) ion. Coordination number of Au is 2
(xi) Tris(oxalato)ferrate(III) ion. Coordination number of Fe is 6
(xii) Tris(ethylenediamine)nickel(II) ion. Coordination number of Ni is 6

Example 66

Write formula of the following complex compounds:

(i) Triamminetrichloroplatinum(IV) chloride
(ii) Potassium tetraaquadisuplhatochromate(III)
(iii) Tetraamminecopper(II) sulphate monohydrate
(iv) Potassium heptaoxodicromate(VI)
(v) Dichlorobis(ethylenediamine)chromium(III) nitrate

Solution

(i) $[PtCl_3(NH_3)_3]Cl$
(ii) $K\ [Cr(OH_2)_4(O_4S)_2]$

(iii) $[Cu(NH_3)_4]SO_4 . H_2O$
(iv) $K_2[Cr_2O_7]$
(v) $[CrCl_2(NH_2 - CH_2 - CH_2 - NH_2)_2]\ NO_3$

Example 67

Name the following complex compounds:

(i) $[PtCl_3(NH_3)_3]\ [CrCl_4(H_2O)_2]$
(ii) $[Ni\ (NH_3)_6]\ \ [Ni\ Cl_4]$
(iii) $[Fe\ (CO)_5]$
(iv) $[Cr\ (SO_4)(NH_3)_4\ ]\ ClO_4$
(v) $[Cr\ (SO_4)(NH_3)_4\ ]\ ClO_3$
(vi) $[Ag(NH_3)_2]ClO_2$
(vii) $[Cr\ (CO_3)(NH_3)_4]OCl$
(viii) $(NH_4)_3[Co(NO_2)_6]$
(ix) $[Co(ONO)(NH_3)_5]\ Cl_2$
(x) $[Pt\ Cl_6]^{2-}$
(xi) $[Ni\ (CN)_4]^{2-}$
(xii) $[Fe(EDTA)]^-$
(xiii) $NaVO_3$
(xiv) $[Cr\ Cl_2(H_2O)_4\ ]Cl . 2H_2O$

Solution

(i) **For complex cation:**
Let oxidation state of Pt be x
Then $x - 3 = 1$ or $x = 4$
For complex onion:
Let oxidation state of Cr be y
Then $y - 4 = -1$ or $y = 3$
Thus the name is triamminetrichloroplatinum(IV) diaquatetrachlorochromate(III)

(ii) Let the oxidation state of Ni be x
Then $x + 0 + x - 4 = 0$ or $x = 2$
Thus the name is: hexaamminenickel(II) tetrachloronickelate (II)
(iii) Pentacarbonyliron(0)
(iv) Tetraamminesulphatochromium(III) perchlorate
(v) Tetraamminesulphatochromium(III) chlorate
(vi) Diamminesilver(I) chlorite
(vii) Tetraamminecarbonatochromium(III) hypochlorite
(viii) Ammonium hexanitrocobaltate(III)
(ix) Pentaamminenitritocobalt(III) chloride
(x) Hexachloroplatinate(IV) ion
(xi) Tetracyanonickelate(II) ion
(xii) Ethylenediaminetetraacetatoferrate(III) ion
(xiii) Sodium trioxovanadate (V)
(xiv) Tetraquadichlorochromium(III) chloride dihydrate

Example 68

There are three distinct compounds with the same formula$(Cr(H_2O)_6Cl_3)$. One of these is violet in colour; the second is light green in colour and the third compound is dark green in colour. Their formula might be written as:

$[Cr(H_2O)_6]Cl_3$ (violet);

$[Cr\ Cl\ (H_2O)_5]Cl_2 . H_2O$ (Light green);

$[Cr\ Cl_2\ (H_2O)_4]Cl . 2\ H_2O$ (Dark green)

How would you distinguish the compound above chemically?

Solution

By titrating solution of $AgNO_3$ against an equal volume with an equal concentration of each of given compound then determining volume of $AgNO_3$ solution which is required for forming complete precipitate of AgCl:

- Light green compound need twice the volume needed by the dark green compound
- Violet compound need thrice the volume needed by the dark green compound

Careful is needed! Most of students distinguish those compounds by saying 'on ---------------------, dark green compound gives one mole of AgCl, light green compound give two moles AgCl and violet compound gives three moles AgCl'. That is true as far as the problem is not asked about distinguishing the given compounds. **The problem is; how can you recognize that; here there is one mole of AgCl and not two moles of AgCl l?** In distinguishing compounds we must choose the property we can observe either by eyes, nose (smell) or ear (hear).

PRACTICE EXERCISE 6

Question 1

(a) Define the terms:
  - (i) Coordinate bond
  - (ii) Coordination number

(b) Consider the complex $[Co(NH_3)_6]Cl_3$
  - (i) What is the oxidation state of cobalt in the compound?
  - (ii) Explain why chloride ions are not considered to be acting as ligands in this complex?
  - (iii) Give the formula of a complex ion of cobalt which does contain chloride ions acting as ligands.
  - (iv) Deduce the structural formula of the complex compound $CoCl_3.4NH_3$, in which cobalt has the same oxidation state and coordination number as in $[Co(NH_3)_6]Cl_3$.

Question 2

The ethanedioate ion, $C_2O_4^{2-}$, acts as bidentate ligand

(i) What is meant by the term bidentate ligand?

(ii) These ligands form an octahedral complex with iron (III) ions. Deduce the formula of this complex and draw its structure showing all the atoms

Question 3

Chloride ions form the tetrahedral complex ion $[AlCl_4]^-$ but fluoride ions form the octahedral complex ion $[AlF_6]^{3-}$. Suggest a reason for this difference.

Question 4

Name the following:

i. $K_4[Ni(CN)_4]$

ii. $(NH_4)_3[Fe(SCN)_6]$

iii. $Na_2[Ni(CN)_4]$

iv. $[Fe(ox)_3]^{3-}$

v. $[CoCl(NH_3)_5]Br_2$

vi. $[CrCl_2(OH_2)_4]Cl$

vii. $[Pt(NH_3)_2]Cl_2$

viii. $Na_2[MoCl_4O]$

Exercise 5

Write formulas for the following:

i. Sodium hexafluoroaluminate

ii. Pentaaquabromomanganese(III) sulphate

iii. Hexaamminechromium(III) nitrate

iv. Sodium tetrahydroxochromate(III)

v. Tetraamminecopper(II) pentacyanohydroxoferrate(III)

vi. Potassium diaquatetrabromovanadate(III)

EXAMINATION QUESTIONS FOR PART ONE

Question 1
SO_2 has low boiling point while sulphate (SO_4^{2-}) containing compounds do not. Explain.

Question 2
Between K_2CO_3 and Na_2CO_3 which one has higher melting point? Give reason.

Question 3
Magnesium has higher melting point than phosphorous. Explain.

Question 4
Between AlF_3 and $AlCl_3$ which one sublimes on heating?

Question 5
AlF_3 has higher melting point than $AlCl_3$. Explain.

Question 6
Na and K are metals but they can never used in construction of bridges. Explain.

Question 7
Na is soft metal while Mg is hard. Explain.

Question 8
Anhydrous aluminium chloride does not conduct electricity but its aqueous solution conducts. Explain.

Question 9
PCl_3 is covalent liquid but in aqueous solution it conducts electricity. Explain.

Question 10
Li^+ and K^+ are ions of group IA, but while K^+ is good conductor in aqueous solution Li^+ is poor conductor. Explain.

Question 11
Between molten Cl^- and I^-which one you consider to be better conductor of electricity? Give reason for your choice.

Question 12
AlF_3 can conduct electricity in molten state while $AlCl_3$ cannot. Explain.

Question 13
Molten NaCl conduct electricity while molten $AlCl_3$ does not. Explain.

Question 14
Electrolytic conduction of solid NaCl is not known although the chloride is almost purely ionic. Give reason for this.

Question 15
Atomic radius cannot be defined as the distance from a nucleus of an atom to the farthest electron from the nucleus i.e. to the valence shell. Give reasons for this.

Question 16
Below is the representation of two periods in a modern periodic table.

Period 2	Li	Be	B	C	N	O	F	Ne
Period 3	Na	Mg	Al	Si	P	S	Cl	Ar

Indicate the symbol which element you consider to be:
(i) The most reactive metal.
(ii) Most reactive non-metal.
(iii) The one with smallest atomic size.
(iv) The one with largest atomic size.
(v) In the same group as that of atomic number 31.

Question 17
What are the two factors that helped the classification of elements in the periodic table?

Question 18
Explain why potassium ion (K^+) is smaller than the chloride ion (Li^+) even though they have the same number of electrons.

Question 19
Give an account for this statement: Magnesium does not impart any colour to the flame while calcium in the same group does.

Question 20

Why don't atomic radii in the transition element series vary much?

Question 21

a) Explain the following:
  i. Periodicity
  ii. Polarising power

b) Account for the following phenomena
  i. The second ionisation energy of calcium is more than that of first and yet calcium forms $CaCl_2$ not $CaCl$. Why?
  ii. Water boils at $100°C$ but methane with comparable weight is a gas at room temperature and pressure.

Question 22

Explain the following:

i. Fluorine has lower electron affinity than chlorine.
ii. Na atom is larger than Na^+ ion but Cl atom is smaller than Cl^- ion in size.
iii. Be an Mg do not give colour to flame where other alkaline earth metals do so.

Question 23

Two atoms have electronic configurations $1s^2 2s^2 2p^6$ and $1s^2 2s^2 2p^6 3s^1$. The first ionisation energy of one is $2080 kJ/mol$ and that of the other is $496 kJ/mol$. Pair up each ionisation energy with one of the given electronic configurations. Justify your answer.

Question 24

Explain the following phenomenon:

i. Electron affinity of fluorine is anomalous.
ii. In period 2, the electron affinities of Be and N are positive

Question 25

Explain what will you observe when greenish copper(II) carbonate is heated strongly.

Question 26

Explain the following:

i. The size of Na^+ ion is larger than that of Mg^{2+} ion although both have the same number of electrons.
ii. Some compound of lithium have a partial covalent character.

Question 27

a) What is meant by
  i. Atomic (covalent) radius
  ii. Electronegativity
  iii. Polarisation
  iv. Polarising power

b) Consider the following ions: $F^-, Na^+, N^{3-}, O^{2-}$ and Mg^{2+}. Arrange them in order of:
  i. Increasing ionic size
  ii. Increasing polarising
  iii. Increasing polarisability

Question 28

First ionisation energy of beryllium is greater than first ionisation energy of boron but second ionisation energy of boron is greater than second ionisation energy of beryllium. Explain.

Question 29

Predict the trend in radius of the following ions $Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}$

Question 30

Explain the acidity for the following compounds and then arrange in increasing order NH_3, HF, H_2O

Question 31

Explain briefly the trends of the following properties in the periodic table:

i. Valence electrons
ii. Electron affinity
iii. Melting point
iv. Atomic radius

Question 32

In each of the following pairs, choose the ions with larger ionic radius and give the reasons:

i. K^+ and Na^+
ii. K^+ and Ca^{2+}
iii. K^+ and Cl^-
iv. Cu^{2+} and Cu^+

Question 33

a) Explain why second ionisation energy of sodium is much bigger than the first ionisation energy.
b) Given the following melting point. $Na = 98℃, Mg = 650℃$. Comment on the values given
c) Ionic size of the following isoelectronic atoms increase in the order

$Si^{4+} < Ca^{2+} < K^+ < S^{2-}$. Explain.

Question 34

a) Name the group and period to which each of the following elements belong
  i. The element having atomic number of 20.
  ii. The element having three unpaired electrons in the 2p-subshell of its atom.
  iii. The element having three electrons in the 3d-subshell of its atom.
b) Nitrogen has first ionisation potential more than oxygen. Explain.

Question 35

The atomic number of elements A, B, C, D and E are shown below:

${}_{11}A, {}_{15}B, {}_{16}C, {}_{17}D, {}_{24}E$

For each of the elements write electronic configuration in terms of s, p, d and f orbitals.

i. Classify the elements as s, p or d-block elements.
ii. Which element has the smallest ionisation energy (I.E)? give reasons for your answer.
iii. Which element can exhibit the oxidation state of -2 in its compound? explain
iv. What type of chemical bond will be formed when element A combines with element C? Explain?
v. Consider the process $M(g) + e \longrightarrow M^-(g)$ Where M represent one of the elements listed above (A, B, C, D or E). Which elements can undergo readily the process represented by equation (i) above? Explain

Question 36

Electronic affinity values for period three (3) elements are as follow:

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Electron affinity, EA(J/mol)	-75	$+42$	-47	-134	-75	-200	-354	$+29$

From the electron affinity energy values in the table answer the following questions

i. Why are the electron affinity energy values of magnesium and argon positive (endothermic) unlike those of the other period three (3) members?
ii. Why is the electron affinity value of phosphorous less exothermic than that of silicon despite being close to group VIIA elements which have most exothermic values of electron affinity?

Question 37

The element with atomic number 36 has exceptional high ionisation energy. Explain?

Question 38

Predict which of the following hydroxyl compounds is acidic and which is basic an aqueous solution $CsOH$, IOH

(Given Electronegativity values: $Cs = 0.7, O = 3.5, H = 2.1, I = 2.5$)

Question 39

Giving reason(s), suggest which atom/ion in a set has the smallest size.

a) O, F, Ne b) Na, Al c) Na, Cl, Si, Ar d) Na^+, Mg^{2+}, Al^{3+}

Question 40

Which of the following pairs is more covalent?

a) H_2O and H_2S
b) $BeCl_2$ and BCl_3

Question 41

Explain why KCl is known and has been prepared while KCl_2 is not known and has never been prepared.

Question 42

Given the elements X,Y,Z and W with atomic number of 19,11,37 and 20 respectively

a) Explain why W forms W^{2+} but X does not.

b) Suggest
   (i) Group
   (ii) Period
   (iii) Block for each element

c) Place the above elements in order of
   (i) Melting point
   (ii) Boiling point
   (iii) Ionisation energy
   (iv) Sublimation(atomisation) energy
   (v) Photo electric effect

Question 43

Explain why:

a) In aqueous solution Li^+ has lowest ionic mobility of all alkaline metals

b) First ionisation energy (potential) of calcium is higher than that of potassium but a second ionisation energy of potassium is higher compared to that of calcium

Question 44

Arrange the following ions according to increase in

i. Ionic size
ii. Hydration
iii. Mobility in their anhydrous(fused) state
iv. Mobility in aqueous solution

Ions :
   a) Na^+, Mg^{2+}, Al^{3+}
   b) Li^+, Na^+, K^+, Rb^+

Question 45

Study the table below:

ELEMENTS	SYMBOL	ATOMIC SIZE (A°)	IONIC SIZE(A°)
Beryllium	Be	0.017	0.0022
Magnesium	Mg	0.039	0.0047
Calcium	Ca	0.063	0.0073
Strontium	Sr	0.117	0.0095
Barium	Ba	0.229	0.103

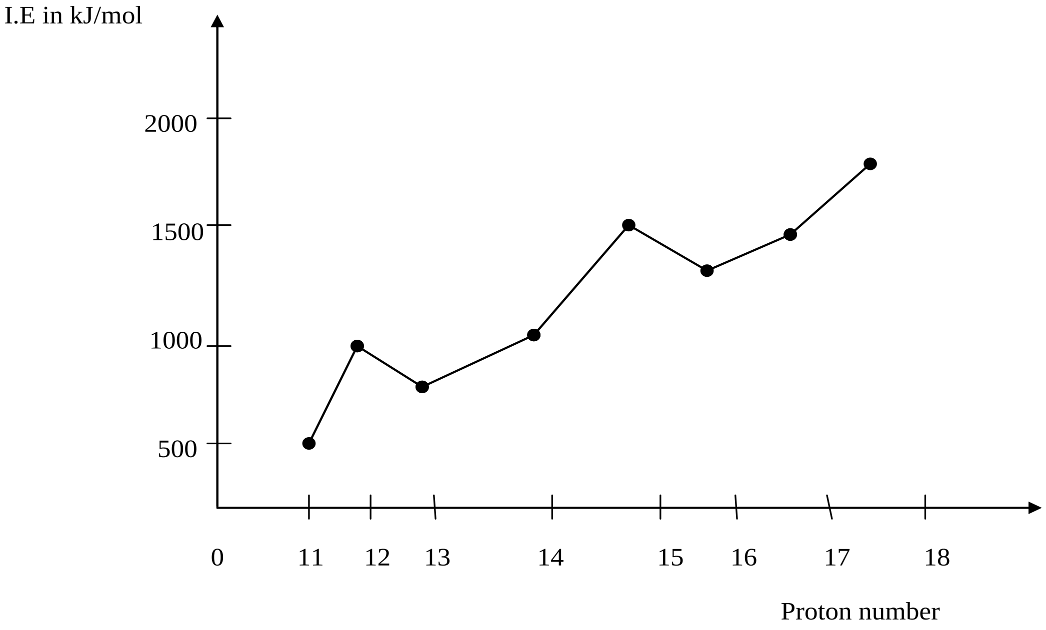
Account for the following observation:

i. Atomic size increase from Be to Ba
ii. In each case ionic radius is less than atomic radius

Question 46

a) Explain what is meant by the term first ionisation

b) The graph below show how first ionisation energy vary with proton number across the period (sodium to argon).



Explain :

- i. Why first ionisation energy increases overall across the period from sodium to argon?
- ii. Why first ionisation energy of sulphur is less than that of phosphorus?
- iii. Why first ionisation energy of aluminum is less than that of magnesium?

c) Use the graph in part (b) to explain why sodium and magnesium are metals while sulphur and chlorine are non-metals

d) Describe the bonding found in
  - i. Magnesium metal
  - ii. Solid magnesium chloride

Example 47

$[CoBr(NH_3)_5]SO_4$ and $[Co(SO_4)(NH_3)_5]Br$ are isomers:

(a) Which ions will these isomers yield in solution?
(b) What is the coordination number of cobalt in each isomer?
(c) Give two chemical tests that could be used to distinguish between them

Example 48

Silver nitrate solution reacts with the compound $[PtCl_3(NH_3)_3]Cl$ but cannot react with the compound $[Pt\,Cl_4(NH_3)_2]$. Explain.

Example 49

A solution containing 2.665g of $CrCl_3.6H_2O$ is passed through cation exchanger; the chloride ion obtained in solution was treated with excess of $AgNO_3$ to give 2.87g of AgCl, deduce the structure of the compound.

PART TWO

PERIODIC TREND IN PHYSICAL AND CHEMICAL PROPERTIES

Chapter 7

PERIOD 3

INTRODUCTION

The first two periods in the periodic table are not typical, why? This is because:

- The first period contain only two elements.
- The second period contains the top element of each group whose most of their properties are different compared to other fellow group members.

So Period 3 is the best for studying periodic trend.

Period 3 elements with their respective group numbers have been shown in the table below:

Group number	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
Period 3 element	Na	Mg	Al	Si	P	S	Cl	Ar
Outermost electronic structure	$3s^1$	$3s^2$	$3s^23p^1$	$3s^23p^2$	$3s^23p^3$	$3s^23p^4$	$3s^23p^5$	$3s^23p^6$

PHYSICAL PROPERTIES OF PERIOD 3 ELEMENTS

Physical properties in relation to their structures

Sodium magnesium and aluminium all have metallic structures. So their physical properties are well explained by their strengths in the metallic bond.

- Na being largest in size accompanied with only one valence electron, has weakest metallic bond of the three metals. Having weakest metallic bond, in most cases Na has smallest physical properties, e.g. lowest melting point of the three metals.

Compared to Na, Mg has much stronger metallic bond due to the following reasons:

(i) It has smaller metallic radius

(ii) Having two valence electrons, Mg forms two metallic bonds while sodium atom form only one metallic bond as it has only one valence electron

The above two factors explain why melting point (physical property) of Mg is much higher compared to Na

- ***The difference in strength of metallic bond between Al and Mg is not very large as expected like in the case of Mg and Na, why?***

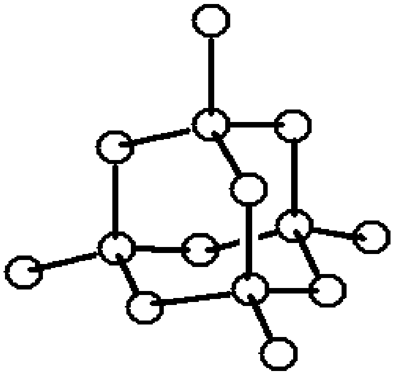
Reasons:

It was expected each aluminium atom to form three metallic bond as it has three valence electrons. This requires one $3s^-$ electron to be promoted to higher sub – energy level, $3P_y$ in hybridisation so as to form three unpaired electrons in three hybridized orbitals ($3s, 3p_y$ and $3p_z$). However Al being very small in size, its s^- electrons are strongly held by nuclear attractive force such that normal room temperature is not enough to promote the electron to higher sub-energy level and eventually there is neither hybridisation nor formation of three metallic bonds despite the fact that it has three valence electrons. ***So what is going to happen?***

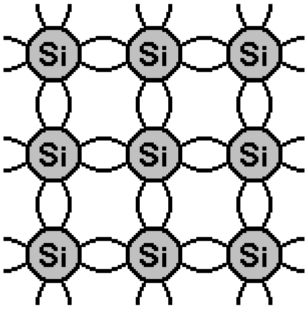
A pair of 3s electron of one aluminium atom fuses together with an empty orbital of another aluminum atom to form first metallic bond and two unpaired orbitals in the two aluminium atoms fuse together to form final and the second metallic bond. Hence **aluminium forms two metallic**

bonds only like magnesium and the only advantage aluminium have over magnesium on the strength of metallic bond is its smaller atomic radius. And this also accounts for the small difference on their melting point.

Silicon has a giant covalent structure (just like diamond). The structure is held together by strong covalent bonds in all three dimensions as shown below and this explain why silicon has highest melting point of all period 3 elements.



The **simplified form** of the structure is as follows:



Phosphorus, sulphur, chlorine and argon have simple molecular structures. The atoms in each of these molecules are held together by covalent bonds (except argon which does not form bond). They are held together by Van – der – Waals force of attraction whose strength increases with an increase in molecular weight. Therefore:

(i) Sulphur having molecular structure of S_8 whereby eight atoms are covalent bonded together, has greatest molecular weight as well as greatest Van – der – waals forces of attraction and hence largest melting and boiling point among the four

(ii) Sulphur is followed by phosphorous which has molecular structure of P_4 whereby four phosphorous atoms are bonded together.

(iii) Chlorine having molecular structure of Cl_2 (diatomic) comes after phosphorous while argon which exists as simple atom (monoatomic) is the last.

Conduction of electricity

Sodium, magnesium and aluminium being metals, have delocalised valence electrons which makes them to be good conductor of electricity. ***The conductivity of electricity increases as you go from sodium to magnesium to aluminium, why?***

This simply because *as you go across the period, number of valence electrons increases causing the increase in number of delocalised electrons in sea of electrons which are responsible for doing conduction of electricity*

- Silicon is semiconductor

- Phosphorous, sulphur, chlorine (non – metals) and argon do not conduct electricity at all because they have no delocalised electrons as result of their very high ionisation energy (despite the fact that they have greater number of valence electrons).

CHEMICAL REACTIONS OF THE PERIOD 3 ELEMENTS

Reaction with water

Strong electropositive metals liberate hydrogen gas with cold water or steam. Their reactivity to water is governed by:

- **Amount of atomisation energy** which depends on the strength of metallic bond; the weaker metallic bond the lower atomisation energy and hence higher reactivity of the metal to water.
- **Amount of ionisation energy.** The lower ionisation energy the higher reactivity of the metal to water.

Since both strength of metallic bond and amount of ionisation energy increases as you go across the period, the reactivity of metals towards water decreases in the same direction. So………………….!

Sodium has highest reactivity towards water of all metals in the period. It reacts with both cold water and steam.

With cold water: $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$

With steam: $2Na(s) + 2H_2O(g) \longrightarrow Na_2O(s) + H_2(g)$

Magnesium has low reactivity to water compared to sodium. It has very slight reaction with cold water, but reacts readily with steam.

With cold water: $Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(s) + H_2(g)$………………..slow

($Mg(OH)_2$ being insoluble is formed as very thin layer on the magnesium and this tend to stop further reaction)

With steam: $Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$……………………………fast

Formation MgO (instead of $Mg(OH)_2$ is explained by thermal decomposition of the hydroxide which would be formed i.e. talking about 'steam' is equivalent to application of heat to cold water. Heat evolved in the reaction (the reaction is exothermic) is another source of heat used in thermal decomposition of the hydroxide.

That is:

$Mg(s) + 2H_2O \rightarrow Mg(OH)_2(s) + H_2(g)$…………………………….(i)

Then $Mg(OH)_2(s) \underset{\Delta}{\rightarrow} MgO(s) + H_2O$………………………………………..(ii)

Taking (i) + (ii) and then combining and cancelling like terms to get overall reaction equation:

$$Mg(s) + H_2O \underset{\Delta}{\rightarrow} \underset{\textbf{White}}{MgO(s)} + H_2(g)$$

Aluminium does not react with cold water, ***why?***

Reason:

Being small in size, Al has very strong metallic bond leading to its large value of atomisation energy. With addition to very high net ionisation energy of Al to Al^{3+}, the activation energy of its reaction with water is very high making it uncreative to water.

However ***aluminium cannot react even with steam, why?***

Reason:

Under presence of heat (steam), $Al(OH)_3$which would be formed, undergo thermal decomposition yielding Al_3O_3 which is highly insoluble. The insoluble layer of Al_3O_3 formed over Al is passive, it resist further reaction between aluminium and steam (water).

Silicon does not react with cold water. But at red heat (very high temperature) it reacts with steam to produce silicon dioxide and hydrogen gas.

$$Si(s) + 2H_2O(g) \xrightarrow{\text{Strong heating}} SiO_2(s) + 2H_2(g)$$

Phosphorous and **sulphur** have no reaction with water

Chlorine dissolves in water and disproportionate in it to give a mixture of hydrochloric acid and chloric(I) acid (hypochlorous acid). The reason for this will be discussed in group VIIA (chapter 10).

$$Cl_2 + H_2O \rightarrow HCl + HOCl \text{..(i)}$$

In presence of sunlight, the hypochlorous acid decomposes to produce more hydrochloric acid and oxygen gas is evolved

$$2HOCl \xrightarrow{\text{U.V}} 2HCl + O_2 \text{..(ii)}$$

Then taking 2(i) + (iii) and combining and cancelling like terms to get overall reaction equation which is obtained when Cl_2 is bubbled through water under presence of sunlight.

$$2Cl_2 + 2H_2O \xrightarrow{\text{U.V}} 4HCl + O_2$$

Argon cannot react with either cold water or steam as expected!

Reactions with dilute HCl and dilute H_2SO_4

All strong electropositive metals which are above hydrogen in electrochemical series, liberates hydrogen gas with the dilute acids provided that the metal does not form an insoluble chloride or sulphate (insoluble layer formation over metal surface always prevent further reaction between the metals and acids). Trend of reactivity of metals over the acids is the same as that of over water. The reactivity tends to decrease as you go across the period from left to right.

Sodium and **magnesium** react with the dilute acids and hydrogen gas is evolved. The reactivity of Mg is moderate compared to that of Na.

$$2Na(s) + 2HCl\,(aq) \rightarrow 2NaCl\,(aq) + H2\,(g)$$

$$2Na(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2(g)$$

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

$$Mg(s) + H_2SO_4 \rightarrow MgSO_4(aq) + H_2(g)$$

Aluminium does not react with cold acids. It reacts if the acid is hot and moderately concentrated.

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

Silicon, **phosphorous**, **sulphur** and **chlorine** having more non – metallic in characters do not react with either dilute HCl or dilute $H_2\,SO_4$

Reactions with concentrated HNO_3 and concentrated H_2SO_4

Concentrated nitric acid and sulphuric acid are oxidising agents.

- Metals react giving the corresponding nitrate and sulphate. Some metals are rendered passive as they form insoluble protective oxide layer over the metal surface which prevents the metal from being attacked by the acid as the layer is incapable of being penetrated by the acid to the metal.

Sodium and **magnesium** react with both concentrated acids.

$$\mathrm{Na(s) + 2HNO_3(conc) \rightarrow NaNO_3(aq) + NO_2(g) + H_2O(l)}$$

$$\mathrm{2Na(s) + 2H_2SO_4(conc) \rightarrow Na_2SO_4(aq) + SO_2(g) + 2H_2O(l)}$$

$$\mathrm{Mg(s) + 4HNO_3(conc) \rightarrow Mg(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)}$$

$$\mathrm{Mg(s) + 2H_2SO_4(conc) \rightarrow MgSO_4 + SO_2 + 2H_2O}$$

In each case, the metals oxidised to their respective ions while sulphuric acid and nitric acid are reduced to SO_2 and NO_2 respectively.

Aluminium reacts with concentrated sulphuric acid according to the following equation:

$$\mathrm{2Al + 6H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3SO_2 + 6H_2O}$$

However the aluminium is rendered passive by concentrated nitric acid, why?

Reason:

With concentrated HNO_3, aluminium form very thin insoluble layer of Al_2O_3 over surface of the metal. The impervious protective oxide layer prevents further oxidation of the metal by the acid.

$$\mathrm{4Al + 12HNO_3\ (con) \rightarrow 2Al_2O_3 + 12NO_2 + 6H_2O}$$

The formation of Al_2O_3 in the above reaction instead of $Al(NO_3)_3$ which would be formed like in other cases of Na and Mg is due to decomposition of the nitrate caused by high degree of polarisation of the $Al(NO_3)_3$ brought about by very large polarising power of small in size and high charged Al^{3+} accompanied with large polarisability of the large anion, NO_3^-

Silicon does not react with both concentrated acids.

$$\mathrm{Si + HNO_3\ (conc) \rightarrow No\ reaction}$$

$$\mathrm{Si + H_2SO_4\ (conc) \rightarrow No\ reaction}$$

Phosphorous and **sulphur** reacts with both concentrated acids giving oxoacids (or oxide, in the case of reaction between sulphur and concentrated sulphuric acid).

$$\mathrm{P + 5HNO_3 \rightarrow H_3PO_4 + 5NO_2 + H_2O}$$

$$\mathrm{2P + 5H_2SO_4 \rightarrow 2H_3PO_4 + 5NO_2 + H_2O}$$

$$\mathrm{S + 6HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O}$$

$$\mathrm{S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O}$$

Most of non – metals react with the concentrated acids in this way i.e. they react with concentrated nitric acid and sulphuric acid to give oxoacid.

Concentrated nitric acid and concentrated sulphuric acid are not strong oxidising agents enough to oxidise chlorine which has also significant oxidising characters and hence chlorine does not react with both acids under normal conditions.

$$\mathrm{Cl_2 + H_2SO_4\ (conc) \rightarrow No\ reaction}$$

$$\mathrm{Cl_2 + HNO_3\ (conc) \rightarrow No\ reaction}$$

It should be noted that:

- **Sulphuric acid may act as:**
  (i) An **acid** when it is **diluted**
  (ii) An **oxidising agent** when it is **concentrated**

As the oxidising agent is commonly reduced to SO_2 (sometimes to H_2S if the reducing agent is very strong like HI)

(iii) **A dehydrating (drying) agent** when it is **concentrated**

- **Nitric acid may act as:**

(i) An **acid with some oxidising characters** when it is **diluted**

(ii) A **strong oxidising agent** when it is **concentrated**.

As the oxidising agent is commonly reduced to $\mathrm{NO_2}$ (sometimes to NO and even to $\mathrm{N_2}$ depending on the power of reducing agent it react with, whereby with stronger reducing agent, it tends to give reduction product with lower oxidation state of nitrogen)

Reactions with dilute NaOH

For **metals**, only amphoteric metals (weak electropositive metals) react with the hydroxide giving complexes and hydrogen gas.

- In period 3, only aluminium is amphoteric metal and is the only one which reacts in that way. Sodium and magnesium being strong electropositive metals do not react.

$$\mathrm{2Al + 2NaOH + 6H_2O \rightarrow 2Na[Al(OH)_4] + 3H_2}$$

$$\mathrm{Na + NaOH\ (dil) \rightarrow No\ reaction}$$

$$\mathrm{Mg + NaOH\ (dil) \rightarrow No\ reaction}$$

Silicon which is metalloid react according to the following equation:

$$\mathrm{Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2}$$

(Note: $\mathrm{NaOH + H_2O =}$ dilute NaOH

Non metals undergo disproportionation in dilute NaOH. So in the period 3, phosphorus, sulphur and chlorine being non – metals disproportionates in the hydroxide.

$$\mathrm{4P + 3NaOH + 3H_2O \rightarrow \underbrace{PH_3}_{Phosphine} + \underbrace{3Na\,H_2\,PO_2}_{Phosphinate}}$$

$$\mathrm{4S + 6NaOH \rightarrow 2Na_2S + Na_2S_2O_3 + 3H_2O}$$

Chlorine disproportionates depending on the condition:

With cold dilute NaOH, it disproportionates to chloride and hypochlorite and greenish yellow colouration of the chlorine disappear

$$\mathrm{Cl_2 + 2NaOH\ (dilute) \xrightarrow[cold]{} \underbrace{NaCl}_{Chloride} + \underbrace{NaOCl}_{hypochlorite} + H_2O}$$

With hot concentrated NaOH, it disproportionates to chloride and chlorite and greenish yellow colouration of the chlorine disappear.

$$\mathrm{3Cl_2 + 6NaOH\ (conc) \xrightarrow[hot]{} 5NaCl + NaClO_3 + 3H_2O}$$

PRACTICE EXERCISE 7

Question 1

Between sodium and magnesium, which one is stronger conductor of electricity? Explain.

Question 2

With help of chemical equations, give two properties which show regular trend as one go across the period 3.

Question 3

Complete the following reaction

(i) $\mathrm{Na(s) + H_2O(g) \rightarrow}$
(ii) $\mathrm{Si(s) + H_2O(l) \rightarrow}$
(iii) $\mathrm{Magnesium\ +\ concentrated\ sulphuric\ acid \rightarrow}$
(iv) $\mathrm{P + HNO_3(conc.) \rightarrow}$
(v) $\mathrm{S + NaOH \rightarrow}$

Question 4

(i) Aluminium does not react with cold water
(ii) Phosphorous react with concentrated sulphuric acid while chlorine does not, although both chlorine and phosphorous are found at the same period
(iii) Sulphur does not react with dilute sulphuric acid ; however it react readily when the acid is concentrated

Chapter 8
GROUP IA

INTRODUCTION

Elements of group IA which will be studied under this chapter with their respective electronic configuration are shown in the table below.

ELEMENT	SYMBOL	ATOMIC NUMBER	ELECTRONIC CONFIGURATION
lithium	Li	3	$[He]2s^1$
Sodium	Na	11	$[Ne]\ 3s^1$
Potassium	K	19	$[Ar]\ 4s^1$
Rubidium	Rb	37	$[Kr]5s^1$
Caesium	Cs	55	$[Xe]6s^1$
Francium	Fr	87	$[Rn]7s^1$

They have outermost electronic configuration of ns^1 where n is the outermost energy level. With the outermost sub energy level of s – sub energy level, group IA elements are found at s – block of modern periodic table. Francium is radioactive, so it will not be discussed.

Some important miscellaneous facts about group IA elements

Group IA elements are also known as alkali metals, why?

This is simply because; they dissolve readily in water (as result of their weak metallic bond existing between their atoms) to give strong alkaline solution (as result of their low electronegativities which make their hydroxide formed after dissolving the metals in water to be strong basic).

Alkali metals are silvery coloured because they are so large in atomic size accompanied with low ionisation energy that normal radiant energy from the sun is enough to excite their valence electrons to higher energy level and on returning to ground state they radiate energy with wavelength within visible atomic spectrum which can be detected by eyes.

Alkali metals and their salt impart characteristic colour to the flame, i.e. they give positive flame test.

- This is because; having large atomic and cationic size, electrons in alkali metals are weakly held by nuclear attractive force. So on heating an alkali metal or its ion (the ion is present in a salt) in a flame, the electrons are excited easily to higher energy level and on returning to ground state, the electrons emit radiation energy with wavelength in visible spectrum and eventually a characteristic colour is observed. ***Why colours imparted by alkali metals to flame are different?***
- This is due to the fact that, alkali metals have different atomic and ionic (cationic) radii. As you descend the group IA, their sizes are found to decrease and electrons become less attracted by nuclei making the amount energy required to excite the electrons to decrease. So amount of energy absorbed in exciting electrons and hence the amount of energy emitted when electrons return to ground state decrease to the same direction. This difference in amount of radiation energy emitted cause the difference in the wavelength associated with the energy and hence the colour of flame changes.

Alkali metals (except lithium) exhibit photoelectric effect, why?

The phenomenon of ejection of electrons from a metal surface when the electromagnetic radiations are made to strike the metal, i.e. photoelectric effect depends on the size of ionisation energy of the metal. Alkali metals having small atomic radii accompanied with low ionisation energy eject electrons when exposed to light. ***Why lithium does not exhibit photoelectric effect?***

Lithium being on the top of group IA has smallest atomic radius accompanied with highest ionisation energy of all alkali metals. Thus radiation energy from the light is not enough to knock out electrons from its surface as the electrons are firmly held by its nucleus.

Melting and boiling points of alkali metals are very low and decrease as you go down the group because as you descend the group there is gradual decrease in strength metallic bond as result of increase in their metallic radii to the same direction.

Density of alkali metals increases as you go down the group IA because the increases in their masses as you descend the group outweighs the increase in volume (the increase in volume comes from the increase in atomic size) to the same direction. So as the density varies directly proportional to mass (and inversely proportional to volume) the density of alkali metals is found to increase as you descend the group.

REACTIVITY OF ALKALI METALS

Alkali metals are very reactive and very strong reducing agent, i.e. they are oxidised easily according to the following equation:

$$\mathrm{M(s)} \rightarrow \mathrm{M^+(aq)} + \mathrm{e}$$

The reaction takes place in three steps which are:

(i) **Atomisation:** In this step, the metal atom absorbs suitable amount of energy to form its corresponding gaseous atom. It is endothermic process and the energy absorbed in the process is known as **atomisation energy.**

$$\mathrm{M(s)} \rightarrow \mathrm{M(g)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots \Delta\mathrm{H} = +\mathcal{X}\mathrm{kJ/mol} = \text{Atomisation energy}$$

The process involves breaking of metallic bond and therefore the stronger metallic bond between metal atoms the greater atomisation energy required and vice – versa

(ii) **Ionisation:** In this step, the metal gaseous atom absorb suitable amount of energy to form its corresponding gaseous unipositive ion. It is also endothermic and the energy absorbed in the ionisation process is known as ionisation energy

$$\mathrm{M(g)} \rightarrow \mathrm{M^+(g)} + \mathrm{e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. \Delta\mathrm{H} = +\mathcal{X}\mathrm{kJ/mol} = \text{Ionisation energy}$$

(iii) **Hydration**: In this step, the gaseous ion is completely hydrated in water. It is exothermic process (cation attracts lone pair of oxygen in water and recall that always attraction is thermally fovoured which means that it must be exothermic process) and the energy evolved in the hydration process is known as **hydration energy.**

$$\mathrm{M^+(g)} \rightarrow \mathrm{M^+(aq)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \Delta\mathrm{H} = -\mathcal{X}\mathrm{kJ/mol} = \text{Hydration energy}$$

Smaller sized cation with higher charge has greater attraction to lone pair of oxygen in water molecules making the ion to become more hydrated and hence the hydration energy become greater and vice versa.

After above discussion, what can we conclude about reactivity of metals?

Reactivity of any element (or compound) towards a certain reaction is governed by the amount of **activation energy** which *is the minimum amount of energy required for the reaction to take place* (it is not governed by overall heat of reaction – don't confuse! Overall heat of reaction determines feasibility of a chemical reaction and not the rate of the chemical reaction). The lower activation energy means the reaction occur faster and vice – versa.

The activation energy of the reaction is result of energy required in all endothermic processes in the reaction. In the case of chemical reaction which involves oxidation of solid metal to form metal ions in aqueous solution, only two processes are endothermic which are:

- Atomisation of solid metal and
- Ionisation of gaseous metal atoms

Hydration of metal ions being exothermic process has nothing to do with activation energy and hence reactivity of metals.

So **Activation energy = Atomisation energy + Ionisation energy**

Compared to other metals, alkali metals:

- Have large metallic radii (accompanied with only one valence electron) leading to weak metallic bond between their atoms and eventually they have low atomisation energy
- Have low ionisation energy

Thus alkali metals are more reactive compared to other metals in the periodic table.

By comparing alkali metals themselves in the group IA:

- Strength of metallic bond decreases as you descend the group and hence their atomisation energy decreases in the same order.
- Ionisation energy decreases as you descend the group.

Thus alkali metals become more reactive as you go down the group IA.

Reaction of alkali metals with water

All of these metals react vigorously or even explosively with cold water. In each case, a solution of the metal hydroxide is produced together with hydrogen gas. They become more reactive towards water as you go down the group.

$$2M(s) + 2H_2O(l) \rightarrow 2MOH(aq) + H_2(g)$$

(The above equation applies to any of alkali metals; just replace the 'M' by symbol you want).

For example, $Na + 2H_2O \rightarrow 2NaOH + H_2$

That is about ordinary water, what about heavy water?

Although heavy water is chemically similar to ordinary water, chemical reactions of heavy water a slower than those of ordinary water.

Don't worry!

Chemical reactions of heavy water are completely similar to those of ordinary water, just replace H by D.

- For example , as we have seen H_2O react with sodium metal as per equation:

$$Na + 2H_2O \rightarrow 2NaOH + H_2$$

- To get corresponding reaction with heavy water (D_2O) just replace H (from above equation) with D as follows:

$$Na + 2D_2O \rightarrow 2NaOD + D_2$$

Similarly:

(i) $$CaO + D_2O \rightarrow Ca(OD)_2$$

(Compare with: $CaO + H_2O \rightarrow Ca(OH)_2$)

(ii) $$N_2O_5 + D_2O \rightarrow 2DNO_3$$

(Compare with: $N_2O_5 + H_2O \rightarrow 2HNO_3$)

(iii) $SO_3 + D_2O \rightarrow D_2SO_4$

(Compare with: $SO_3 + H_2O \rightarrow H_2SO_4$)

(iv) $CaC_2 + 2D_2O \rightarrow Ca(OD)_2 + DC \equiv CD$

(Compare with: $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + HC \equiv CH$)

(v) $AlCl_2 + 3D_2O \rightarrow Al(OD)_3 + 3DCl$

(Compare with: $AlCl_2 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$)

Reaction of alkali metals with dilute H_2SO_4 and dilute HCl

Being strong reducing agents, alkali metals liberate hydrogen gas from the dilute acids

$$2M(s) + H_2SO_4(aq) \rightarrow M_2SO_4(aq) + H_2(g)$$

$$2M(s) + 2HCl(aq) \rightarrow 2MCl(aq) + H_2(g)$$

Where M is any alkali metal

Again they become more reactive towards the acids as you descend the group IA.

REACTION OF ALKALI METALS WITH NITROGEN (NITRIDE FORMATION)

Among group IA elements, only lithium gives nitrides when heated wit nitrogen gas

$$N_2(g) + 6Li \underset{\Delta}{\rightarrow} 2Li_3N$$

The nitride hydrolyses in water, liberating **ammonia gas** which **is recognised by its choking smell**.

$$Li_3N + 3H_2O \rightarrow 3LiOH + NH_3$$

Why only Lithium?

Having smallest cationic size of all group IA elements, Li^+ exerts greatest force of attraction to N^{3-} resulting to greatest lattice energy of Li_3N which is large enough to compensate very large dissociation energy of $N_2(N \equiv N)$ and its net electron affinity in forming N^{3-} which is also very large (highly positive).

REACTION OF ALKALI METALS WITH HYDROGEN

Alkali metals react with hydrogen to form ionic hydrides. For example;

$$2Li(s) + H_2(g) \rightarrow 2LiH(s)$$

$$2Na(s) + H_2(g) \rightarrow 2NaH(s)$$

REACTION OF ALKALI METALS WITH HALOGENS

Alkali metals react violently with halogens to form halides. For example;

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

$$2K(s) + Br_2(l) \rightarrow 2KBr(s)$$

CHEMISTRY OF SELECTED COMPOUNDS OF ALKALI METALS

Oxides

Generally alkali metals are very reactive to oxygen yielding oxides and **have to be stored out of contact with air to prevent their oxidation.** Reactivity increases as you go down the group.

The metals form different classes of oxides depending on polarising power of the metal cation. They can form:

- Normal oxide, O^{2-} (simple one)
- Peroxide, O^{2-} (more complex)
- Superoxide, O_2^- (most complex)

It the cation has large polarising power, the peroxide or superoxide (complex oxides) are distorted to form normal oxide.

Lithium having ion (Li^+) of greatest polarising power of all group IA elements distort peroxide and superoxide ions, forming normal oxide only.

$$4Li(s) + O_2 \rightarrow 2Li_2O$$

Sodium has ion (Na^+) which has smaller polarising power than Li^+ but the polarising power is greater than all other remaining group numbers; so it cannot polarize peroxide but it can polarize superoxide ion. Thus sodium can form both normal oxide and peroxide but it cannot form superoxide. Normal oxide is formed at lower temperature while peroxide is formed at relative higher temperature.

$4Na + O_2 \rightarrow 2Na_2O$ (Normal oxide)

$2Na + O_2 \rightarrow Na_2O_2$ (Peroxide)

Potassium, rubidium, and **caesium** have ions which have very weak polarising power so they can form peroxide and superoxide. At low temperature, normal oxide is formed while peroxide is formed at relative higher temperature. When oxygen is present in excess at the higher temperature, superoxide is formed as major product. Example, for potassium:

$$4K(s) + O_2(g) \xrightarrow{180°C} 2K_2O(S)$$

$$2K(s) + O_{2(g)} \xrightarrow{300°C} K_2O_2(s)$$

$$K(s) + O_2(g, \text{excess}) \xrightarrow{300°C} KO_2(s)$$

All forms of oxides of alkali metals are basic. Being basic:

(i) They dissolve in water to give hydroxides which are basic

- **Normal oxides** give metal hydroxide only.

$$M_2O + H_2O \rightarrow 2MOH$$

Where M may be Li, Na, K, Rb or Cs

- **Peroxides** give metal hydroxide and hydrogen peroxide

$$M_2O_2 + 2H_2O \rightarrow 2MOH + H_2O_2$$

Where M may be Na, K, Rb or Cs

- **Superoxides** give metal hydroxide, hydrogen peroxide and oxygen gas is evolved.

$$2MO_2 + 2H_2O \rightarrow 2MOH + H_2O_2 + O_2$$

Where M may be K, Rb, Cs or Fr

(ii) They are capable of reacting with dilute acids like dilute HCl

- **Normal oxides** give salt and water only.

$$M_2O + 2HCl \rightarrow 2MCl + H_2O$$

Where M may be any alkali metal

- **Peroxides** give salt and hydrogen peroxide only.

$$M_2O_2 + 2HCl \rightarrow 2MCl + H_2O_2$$

Where M may be any alkali metal except Lithium

- **Superoxides** give salt, hydrogen peroxide and oxygen gas is evolved

$$2MO_2 + 2HCl \rightarrow 2MCl + H_2O_2 + O_2$$

Where M may be any alkali metal except lithium and sodium

Hydroxides

Hydroxides of alkali metals are strong basic. The basic strength of the hydroxides increases as you descend the group IA due to the fact that in the same direction there is:

- Decrease in electronegativity of the metals and
- Increase in ionic characters of the hydroxide (as result of decrease in degree of polarisation)

Being basic, hydroxide of alkali metals:

React with dilute acids like HCl (aq) to give salt and water only

$$MOH + 2HCl \rightarrow MCl_2 + H_2O$$

Where M may be any alkali metal

React with acidic oxide like CO_2

$$2MOH + CO_2 \rightarrow M_2CO_3 + H_2O \text{...(i)}$$

If CO_2 present in excess, bicarbonate is formed:

That is $M_2CO_3 + H_2O + CO_2 \rightarrow 2MHCO_3$...(ii)

Or by taking (i) + (ii):

$$MOH + CO_2 \rightarrow MHCO_3$$

Where M may be any alkali metal

- Both carbonates and bicarbonates of alkali metals are soluble in water. Solubility of carbonates increase as you descends the group. Lithium being at the top of the group, its carbonate is slightly soluble while all other carbonates are highly soluble in water.

High solubility of sodium carbonate (or any other carbonate of alkali metal) in water, explains why **sodium hydroxide cannot be used to test carbon dioxide like calcium hydroxide (lime water)**

In the case of lime water ($Ca(OH)_2$), the hydroxide reacts with carbon dioxide gas (CO_2) to give the insoluble $CaCO_3$ which appears as white precipitate (that is lime water turns milky).

$$Ca(OH)_2 + CO_2 \rightarrow \underset{\textbf{White precipitate}}{CaCO_3} + H_2O$$

While Na_2CO_3 being soluble, the reaction between CO_2 and NaOH does not give an observable change (for the reaction to act as chemical test, it must give a change we can observe i.e. the change we can see by eyes, we can smell or we can hear).

$$\underset{\textbf{Soluble}}{2NaOH} + CO_2 \rightarrow \underset{\textbf{Soluble}}{Na_2CO_3} + H_2O$$

It should be noted that:

Alkali metals can react with:

- **Oxygen** to form their corresponding oxides, then
- **Water** can react with the formed oxide to give hydroxide, finally
- **Carbon dioxide** can react with the given hydroxide to give carbonate

The bolded words (oxygen, water and carbon dioxide) are components of **moist air** found in the atmosphere. So **exposing any alkali metal to moist air, will lead to the series of reaction to form carbonate of alkali metals.** To avoid this, **alkali metals are always stored in inert hydrocarbon solvent like kerosene oil which prevents them from coming in contact with moist air.**

Hydrides

Alkali metals combine with hydrogen gas to give ionic hydride. Having large electronegativity difference with alkali metal being much more electronegative than hydrogen, the hydrides tend to react with water to give hydroxides which are basic and hydrogen gas is evolved.

$$2MH + 2H_2O \rightarrow 2MOH + H_2$$

Where M is any alkali metal

THEMAL STABILITY OF COMPOUNDS OF ALKALI METALS

Under this heading we are going to discuss on ability of compounds of alkali metals to exist at certain temperature or after being heated without undergoing thermal decomposition. Compounds which will be examined are.

- Hydroxides
- Bicarbonates
- Carbonates
- Nitrates

Hydroxides

Generally thermal stability of compounds of alkali metals increases as you descend the alkali group, why?

As you go down the group, there is an increase in cationic radius leading to a decrease in polarising power and the increase in degree of polarisation and hence thermal stability of compound of alkali metals increase as you go down the group IA.

Generally compounds of alkali metals have very high thermal stability due to their low degree of polarisation caused by small polarising power of large sized cations accompanied with only single charge. Lithium being on the top of the group IA, its hydroxide is the only one which decomposes on heating. Hydroxides of other alkali metal do not decompose on heating.

That is $2LiOH \underset{\Delta}{\rightarrow} Li_2O + H_2O$

While $MOH \underset{\Delta}{\rightarrow}$ No reaction

Where M may be any alkali metal except Li

Carbonates

Generally carbonates of alkali metals are thermally stable. Their thermal stability decreases as you go down the group whereby lithium being on the top of the group, its carbonate is the only one which decomposes on heating to give its corresponding oxide and CO_2 which appears as effervescence of colourless gas which turns lime water milky. On heating carbonates of other alkali metals do not decompose.

That is $Li_2CO_3 \underset{\Delta}{\rightarrow} Li_2O + CO_2$

While $M_2CO_3 \underset{\Delta}{\rightarrow}$ No reaction

Bicarbonates

Here:

- **Solid** lithium bicarbonate is highly thermally unstable such that only room temperature is enough to decompose it. So **the solid lithium bicarbonate (or lithium hydrogencarbonate) does not exist at room temperature. It only exists in aqueous solution due to stabilization of the hydration process.**

That is $2LiHCO_3(s) \xrightarrow[\text{Room temperature}]{} Li_2CO_3 + CO_2 + H_2O$

While $LiHCO_3\ (aq) \xrightarrow[\text{Room temperature}]{}$ No reaction.

The aqueous lithium bicarbonate decomposes after application of heat.

$$2LiHCO_3\ (aq) \underset{\Delta}{\rightarrow} Li_2CO_3 + CO_2 + H_2O$$

- Bicarbonate of other alkali metals exists in both solid form and aqueous form. However on heating, they tend to decompose according to the following equation:

$$2MHCO_3 \underset{\Delta}{\rightarrow} M_2CO_3 + CO_2 + H_2O$$

Where M is alkali metal

Nitrates

As result of very large polarisability of NO_3^- nitrate of all alkali metals decompose on heating.

- Nitrates of alkali metals except lithium, decompose to give the nitrite (which is more thermally stable than nitrate as the smaller NO_2^- has smaller polarisability than NO_3^-) and oxygen gas.

$$2MNO_3 \underset{\Delta}{\rightarrow} 2MNO_2 + O_2$$

Where M is any alkali metal except Li

You should be able to remember that Li^+ having greatest polarising power of all alkali ions, the $LiNO_2$ (lithium nitrite) is capable of undergoing further decomposition to Li_2O. Thus for $LiNO_3$:

$2LiNO_3 \underset{\Delta}{\rightarrow} 2LiNO_2 + O_2$ …………………………………….. (i)

Then $4LiNO_2 \underset{\Delta}{\rightarrow} 2Li_2O + 4NO + O_2$……………………………….. (ii)

Finally $2NO + O_2 \rightarrow 2NO_2$……………………………………………. (iii)

Taking 2(i) + (ii) + 2(iii), then combining and cancelling like terms, gives the following overall reaction equation:

$$4LiNO_3 \underset{\Delta}{\rightarrow} 2Li_2O + 4NO_2 + O_2$$

Thus lithium nitrate undergo thermal decomposition to give lithium oxide, oxygen gas and **brown fumes of nitrogen dioxide**.

COMPLEX FORMATION ABILITY OF ALKALI METALS

You should be able to recall that generally a metal atom can act as a central metal atom thus being able to form complex if has the following features:

- **High cationic charge**

- This enables the ion to exert enough nuclear attractive force to hold lone pair of ligands.

- **Small cationic radius**

- This enables the effective nuclear attractive force to reach the lone pair of ligand easily.

- **Presence of empty orbitals**

- This acts as a room of lone pair of ligands.

Alkali metals have neither high cationic charge (they have only single cationic charge) nor small cationic radii so they cannot hold ligands and hence becoming unable to form complexes.

Inability of alkali metals to form complex explains why alkali metals do not react with dilute sodium hydroxide (or any other strong alkaline solution). Weak electropositive (amphoteric) metals react with dilute sodium hydroxide through complex formation.

DIFFERENCES BETWEEN LITHIUM AND OTHER ALKALI METALS

Generally every first member (on top) of each group in period table has anomalous behaviour from other group members due to the fact that being on the top of the group, these elements have:

- Small size of atoms and their ions
- High electronegativity
- High ionisation energy
- No availability of d – orbitals

The anomalous properties of Lithium include:

(i) In most cases, lithium has greatest physical property than other alkali metals. For example;

- Lithium is hard while other alkali metals are soft.
- Lithium has exceptionally high melting and boiling point.

(ii) Lithium reacts with oxygen to give normal oxide only. Other alkali metals can give different types of oxides, from normal oxides, peroxides to superoxides

(iii) Lithium can combine with nitrogen to give lithium nitride while other alkali metals cannot.

$$6\mathrm{Li} + \mathrm{N_2} \underset{\Delta}{\rightarrow} 2\mathrm{Li_3N}$$

While $\mathrm{M} + \mathrm{N_2} \rightarrow$ No reaction

Where M may be any alkali metal except Li

(iv) Compounds of Lithium are less thermal stable compared to compounds of other alkali metals. For example;

- Hydroxide of lithium decomposes on heating while hydroxides of other alkali metals do not.

$$2\mathrm{LiOH} \underset{\Delta}{\rightarrow} \mathrm{Li_2O} + \mathrm{H_2O}$$

While $\mathrm{MOH} \underset{\Delta}{\rightarrow}$ No reaction

- Carbonate of lithium decomposes on heating while carbonates of other alkali metals do not.

$$Li_2CO_3 \underset{\Delta}{\rightarrow} Li_2O + CO_2$$

While $M_2CO_3 \underset{\Delta}{\rightarrow}$ No reaction

- Nitrate of lithium decompose to lithium oxide on heating while nitrate of other group members decompose to nitrite.

$$4LiNO_3 \underset{\Delta}{\rightarrow} 2Li_2O + 4NO_2 + O_2$$

While $MNO_3 \underset{\Delta}{\rightarrow}$ No reaction

(v) Compounds of lithium are more covalent in characters while those of other alkali metals are strongly ionic.

- LiCl is soluble in organic solvent (covalent character) while chlorides of other alkali metals are insoluble (ionic character).
- The hydroxide, carbonate and fluoride of lithium are sparingly soluble in water (covalent character) while those of other alkali metals are highly soluble (ionic character).
- Lithium hydroxide is relatively weaker base compared to hydroxides of other alkali metals.

(vi) Lithium chloride forms hydrated crystals ($LiCl.2H_2O$) in aqueous solution while other group members form anhydrous chloride crystals.

DIAGONAL RELATIONSHIP BETWEEN LITHIUM AND MAGNESIUM

Diagonal relationship *is the similarity in properties between the first element in a group and the second element in the next group.* This is because the members have:

(i) Similar polarising power

(ii) Similar atomic radius

(iii) Similar electronegativity values

(iv) Similar effective nuclear charge

Lithium and magnesium show diagonal relationship like:

(i) They both form hydrated chlorides ($LiCl.2H_2O$ and $MgCl_2.6H_2O$) which are deliquescent.

(ii) They both combine with oxygen gas to form normal oxide only (Li_2O and MgO).

(iii) They both react with nitrogen gas forming nitrides which react with water liberating ammonia.

(iv) Hydroxides, carbonates of both lithium and magnesium decompose on heating

(v) Nitrates of both lithium and magnesium decompose in similar way on heating (they both give oxide, nitrogen dioxide gas and oxygen gas)

(vi) Solid bicarbonates of both lithium and magnesium do not exist.

In each property listed above you must be able to give the respective chemical equation if any.

Be careful!

For the similarity to be regarded as the diagonal relationship, the property must be also anomalous property of the first element (in this case lithium). As an example, you **cannot** say *'both lithium and magnesium form basic oxide'* is diagonal relationship between the two elements. Although it is true that oxides of both lithium and magnesium are basic, but the similarity is not regarded as diagonal relationship because the formation of basic oxide is the property that all alkali metals exhibit. So to insist; diagonal relationship is the **anomalous property** of the first element in a group which is similar to the second element in the next group.

PRACTICE EXERCISE 8

Question 1

Explain the following:

(i) Lithium does not exhibit photoelectric effect while other alkali metals do.
(ii) Melting of sodium is greater than that of potassium.
(iii) Alkali metals are good reducing agents.
(iv) Solid lithium bicarbonate does not exist.
(v) Alkali metals do not react with dilute $NaOH$.

Question 2

Complete the following reactions:

(i) $Rb + D_2 \rightarrow$
(ii) $Li_3N + H_2O \rightarrow$
(iii) $CsO_2 + H_2O \rightarrow$
(iv) $KOH + SiO_2 \rightarrow$
(v) $NaHCO_3 \underset{\Delta}{\rightarrow}$
(vi) $KNO_2 \underset{\Delta}{\rightarrow}$

Question 3

Give reason (s) for the following:

(i) Alkali metals are stored in kerosene.
(ii) Potassium carbonate is soluble water while lithium carbonate is not.
(iii) Potassium reacts violently with chlorine gas.
(iv) Although potassium is very reactive, does not react with nitrogen.
(v) Lithium and magnesium show diagonal relationship.

Question 4

Arrange hydroxides of alkali metals in order of:

(i) Increasing their basic strength
(ii) Increasing their thermal stability

Question 5

Properties of lithium are anomalous. Justify this statement.

Chapter 9
GROUP IIA

INTRODUCTION

Elements group IIA which will be studied under this chapter with their respective electronic configurations are shown in the table below.

ALKALI METAL	SYMBOL	ATOMIC NUMBER	ELECTRONIC CONFIGURATION
Beryllium	Be	4	$[He]2s^2$
Magnesium	Mg	12	$[Ne]3s^2$
Calcium	Ca	20	$[Ar]4s^2$
Strontium	Sr	38	$[Kr]5s^2$
Barium	Ba	56	$[Xe]6s^2$
Radium	Ra	88	$[Rn]7s^2$

They have outermost electronic configuration of ns^2 where n is the outermost energy level. With the outermost sub energy level of s - sub energy level, group IIA elements are found at s - block of modern periodic table.

Note: radium being radioactive its properties will not be discussed**.**

Some important miscellaneous facts about group IIA elements

Group IIA elements are also known as alkaline earth metals, why?

This is because oxides of group IIA elements which were known before the elements were discovered are basic (alkaline) when combine with water. These oxides were termed as **'earths'** (by early chemists) and the term applies to any substances that are insoluble in water and resistant to heating – the properties shared by the oxides of group IIA elements.

It is important to understand that:

The old fashioned names of alkaline earths were:

- **Beryllia** for BeO
- **Magnesia** for MgO
- **Lime** for CaO
- **Strontia** for SrO
- **Baryta** for BaO

At ancient times those five **'earths'** were thought to be elements. When 'earths' are dissolved in water, they are generally give basic (alkaline) solution and hence the name **alkaline** earth. Some authors mislead by relating the term 'earth' and the **earth crust** by concluding that they are earth metals because they are found naturally on earth crust in form of their oxides (other say silicates); that is misconception! Group IIA elements are not only elements which are found naturally on the earth crust. There are also many other metals like aluminium, iron etc whose compounds are found on the earth crust.

To insist here: *the term '**earth'** is an old term applied by early chemists to non – metallic substances that are insoluble in water and resistant to heating.*

Earth metals (alkaline earth metals) are silvery – gray coloured (you should be able to give an explanation on this).

Flame colouration

Alkaline earth metals below magnesium impart colour to the flame. ***Why beryllium and magnesium do not impart colour to the flame?***

Reason:

Unlike other alkaline earth metals, Be and Mg do not impart colour to the flame because their atomic size are so small that their electrons are strongly bound to the nucleus. They need a large amount of energy for excitation process to higher energy levels which is not available in a Bunsen flame. So they do not impart colour to the flame and hence Be, Mg and their compounds give negative flame test.

Melting and boiling points of alkaline earth metals are higher compared to those of alkali metals, why?

This is because; the earth metals have stronger metallic bond between their atoms as:

- They have smaller metallic radii
- With two valence electrons, each atom contributes two electrons in the metallic bond while alkali metals contribute only one electron.

CHEMICAL REACTIONS OF ALKALINE EARTH METALS

Reaction with water

Generally reactivity of earth metals increases as you descend the group due to a decrease in net ionisation energy (M to M^{2+}) to the same direction.

Understand!

Unlike in alkali metals where their reactivity were governed by both ionisation energy and atomisation energy; in earth metals, atomisation energy has little influence in the explaining the trend in reactivity because the difference of atomisation energy for group IIA elements is small and show irregular trend. So the reason of trend shown by earth metals in their reactivity is dominated by the factor of the net ionisation energy.

Beryllium has no reaction with water or steam even at read heat. There are two reasons for this (one extra reason apart from that of very large ionisation energy of Be).

- **Be has very large net ionisation energy in forming Be^{2+}**

- This makes impossible for it to react with **cold** water.

- **Be form very strong resistant thin layer of beryllium oxide over its surface which resist further reaction of the beryllium**

- This explains why Be does not react with **steam** even after application of strong heating.

That is $Be(s) + H_2O(g) \underset{\Delta}{\rightarrow} BeO(s) + H_2(g)$

The oxide layer is formed as very thin layer which is insoluble and the layer is impervious protective layer which lowers the reactivity of the Be by preventing steam to react with underlying Be.

Hence in overall:

$Be + H_2O(g) \rightarrow \text{No reaction}$ (Negligible amount of Be react to form the thin layer)

It should be noted that:

The formation to impervious protective oxide layer by Be is just like in the aluminium case studied earlier in period 3 (chapter 7).

Magnesium burns in steam to produce white magnesium oxide and hydrogen gas. It cannot react with cold water.

$$\mathrm{Mg(s)\ +\ H_2O(\mathbf{g})\ \rightarrow\ MgO(s)\ +\ H_2(g)}$$

But $\mathrm{Mg(s)\ +\ H_2O(\mathbf{l})\ \rightarrow\ No\ reaction}$

(However clean magnesium ribbon has a very slight reaction with cold water, although reaction is very slow and after its start, the reaction soon stops because the magnesium hydroxide formed is almost insoluble in water and form a barrier on the magnesium preventing further reaction).

Calcium, strontium and **barium** can react with cold water to give hydroxide and hydrogen gas.

$$\mathrm{M(s) + 2H_2O(l) \rightarrow M(OH)_2(aq) + H_2(g)}$$

Where M may be $\mathrm{Ca, Sr}$ or Ba

Reactions with dilute HCl and dilute H_2SO_4

As usual, generally the reactivity increases as you descend the group.

With dilute HCl:

Beryllium does not liberate hydrogen gas due to its low oxidation potential caused by its very high net ionisation energy of Be to $\mathrm{Be^{2+}}$

$$\mathrm{Be(s)\ +\ HCl(aq)\ \rightarrow\ No\ reaction}$$

Other members liberate hydrogen gas

$$\mathrm{M + HCl\ \rightarrow\ MCl_2 + H_2}$$

Where M is $\mathrm{Mg, Ca, Sr}$ or Ba

With dilute H_2SO_4:

Like in the case of dilute HCl, **Beryllium** does not liberate hydrogen gas from dilute $\mathrm{H_2SO_4}$

$$\mathrm{Be + H_2SO_4\ \rightarrow No\ reaction}$$

Magnesium reacts to liberate hydrogen gas

$$\mathrm{Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)}$$

Calcium, strontium and barium do not react with dilute sulphuric acid although they are stronger reducing agents (generally more reactive) than magnesium, why?

Reason: $\mathrm{Ca, Sr}$ and Br form insoluble sulphates which prevent further reaction of the metals.

It should be noted that:

The solubility of group IIA sulphates decrease on descending the group because the cation become less hydrated due to an increase in cationic size to the same direction and hence the hydration energy become less sufficient to overcome the lattice energies .

Reactions with concentrated HNO_3 and concentrated H_2SO_4

Beryllium is rendered passive by both acids.

The rest of members react like metals.

$$\mathrm{M(s) + 4HNO_3(conc) \rightarrow M(NO)_3(aq) + 2NO_2(g) + 2H_2O(l)}$$

$$\mathrm{M(s) + 2H_2SO_4(conc) \rightarrow MSO_4(aq\ or\ s) + SO_2(g) + 2H_2O(l)}$$

Where M is Mg, Ca, Sr or Ba

Contradiction!

Although sulphates of calcium, strontium and barium are insoluble, the metals still have reaction with concentrated sulphuric acid, why?

Reason:

Concentrated H_2SO_4 is so strong oxidising agent that can erode the insoluble sulphate layer to react with inner (underlying) metal, i.e. in other words, sulphate fail to prevent further reaction of concentrated H_2SO_4 due to large oxidising power of the acid.

Reactions with dilute of NaOH

Beryllium being amphoteric metal, react with NaOH(aq) according to the following equation:

$$\mathrm{Be(s) + 2NaOH + 2H_2O \rightarrow Na_2[Be(OH)_4] + H_2(g)}$$

Other group members being strong electropositive metals do not react with the dilute solution.

$$\mathrm{M(s)} + \underbrace{\mathrm{NaOH + H_2O}}_{\text{Dilute NaOH}} \rightarrow \text{No reaction}$$

Where M is Mg, Ca, Sr or Ba

Reaction with nitrogen (nitride formation)

Unlike alkali metals whereby only lithium is capable of combining with nitrogen to form nitride, all alkali earth metals are capable of combining with nitrogen to form nitride because:

- They have smaller cationic radius and
- Higher cationic charge (they are dipositive while alkali metals form unipositive ion)

The above factors make ions of earth metals to have greater attraction to N^{3-} and hence larger lattice energy (of the nitride) which is enough to compensate large dissociation energy $N_2(N \equiv N)$ and net electron affinity in of N to N^{3-}.

$$\mathrm{3M + N_2 \rightarrow M_3N_2}$$

Where M is any alkaline earth metal

Like lithium nitride, nitride of alkaline earth metals hydrolyse in water to evolve ammonia gas

$$\mathrm{M_3N_2 + 6H_2O \rightarrow 3M(OH)_2 + 2NH_3}$$

Where M is any alkaline earth metal

Reaction of alkali metals with halogens

Group IIA elements react with halogens to form ionic halides except for beryllium which form covalent halides.

$$\mathrm{Ca(s) + F_2(g) \rightarrow CaF_2(g)}$$

$$\mathrm{Mg(s) + Cl_2(g) \rightarrow MgCl_2(g)}$$

$$\mathrm{Be(s) + Cl_2(g) \rightarrow BeCl_2(g)}$$

CHEMISTRY OF SELECTED COMPOUNDS OF EARTH METALS

Oxides

Generally oxides of group IIA are basic, except BeO which is amphoteric. These oxides of group IIA metals do not react so readily with water or acids because the larger charge density on the cation holds the O^{2-} ion more firmly implying high lattice energy for the oxides.

Beryllium is reluctant to burn unless it is in the form of dust or powder form which has greater surface area for the reaction to take place and hence the rate of reaction is increased.

- Beryllium has very strong (but very thin) layer of beryllium oxide on its surface, and this prevents any new oxygen getting at the underlying beryllium to react with it. It forms normal oxide only. (High yield of BeO is obtained by other methods like heating of $Be(OH)_2$).

$$2Be(s) + O_2 \rightarrow 2BeO(s)$$

BeO is amphoteric, can react with both acids and bases depending on the strength of acid or bases it react with.

E.g. **with strong base like NaOH, it acts as an acid**

$$BeO + 2NaOH + H_2O \rightarrow Na_2\,[Be(OH)_4]$$

Or after dehydration the equation become.

$$BeO + 2NaOH \rightarrow \underset{\textbf{Salt}}{Na_2BeO_2} + \underset{\textbf{Water}}{H_2O}$$

With strong acid like HCl, it acts as a base

$$BeO + 2HCl(aq) \rightarrow BeCl_2 + H_2O$$

Magnesium and **calcium** reacts with oxygen to form normal oxides only which are basic

$$2M(s) + O_2(g) \rightarrow 2MO(s)$$

Where M may be Mg or Ca

Being basic, MgO and CaO react with acids but they cannot with other basic solution. For example:

$$MgO + 2HCl \rightarrow MgCl_2 + H_2O$$

$$CaO + SiO_2 \rightarrow CaSiO_3$$

Strontium and **barium**, apart from normal oxide they can also form peroxides if they are heated with oxygen. Strontium needs high pressure while barium needs just normal heating.

That is $2M + O_2 \rightarrow 2MO$ (normal oxide)

Where M is Br or Ba

But $Sr(s) + O_2(g) \xrightarrow{\text{high pressure,heating}} SrO_2$ (strontium peroxide)

And $Ba(s) + O_2(g) \xrightarrow{\text{normal pressure,heating}} BaO_2$ (Barium peroxide)

Oxides at Br and Ba are basic. Being basic:

(i) **They dissolve in water to give hydroxide which are basic**

$$MO + H_2O \rightarrow M(OH)_2$$

$$MO_2 + 2H_2O \rightarrow M(OH)_2 + H_2O_2$$

Where M is Sr or Ba

(ii) They reacts with acidic solution like HCl(aq)

$$MO + 2HCl \rightarrow MCl_2 + H_2O$$

$$MO_2 + 2HCl \longrightarrow MCl_2 + H_2O_2$$

Where M is Sr or Ba

Hydroxides

Earth metals form hydroxides whose solubility in water increases on descending the group because in that direction they become more ionic as result of decrease in their degree of polarisation.

- Basic strengths of hydroxides of earth metals increase as you go down the group.

Beryllium hydroxide ($Be(OH)_2$) is amphoteric. It can react with both acids and bases depending on their strengths.

With strong bases like $NaOH(aq)$, it acts as an acid;

$$Be(OH)_2 + 2NaOH \rightarrow Na_2[Be(OH)_4]$$

Or after the dehydration the more stable form of beryllate is formed and the equation for the reaction becomes:

$$Be(OH)_2 + 2NaOH \rightarrow Na_2BeO_2 + 2H_2O$$

(i.e. $H_2BeO_2 + 2NaOH \longrightarrow Na_2BeO_2 + 2H_2O$)

With strong acids like HCl(aq), it acts as a base;

$$Be(OH)_2 + 2HCl \rightarrow BeCl_2 + 2H_2O$$

Hydroxides of remaining group members are basic. Being basic:

- They reacts with acidic solution like $HCl(aq)$ give salt and water

$$M(OH)_2 + 2HCl \rightarrow MCl_2 + 2H_2O$$

Where M may be Mg, Ca, Sr or Ba (and of course Be)

- They reacts with acidic oxide like CO_2

$$M(OH)_2 + CO_2 \rightarrow MCO_3 + H_2O$$

Where M may be Mg, Ca, Sr or Ba.

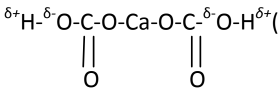
Carbonate of earth metals are insoluble in water and this justifies the use of calcium hydroxide (lime water) as a chemical test of CO_2.

$$Ca(OH)_2 + CO_2 \rightarrow \underset{\textbf{White precipitate}}{CaCO_3} + H_2O$$

However the precipitates dissolve to give clear solution again if the carbon dioxide is present in excess due to formation of calcium bicarbonate which is soluble.

$$Ca(OH)_2 + 2CO_2(g) \rightarrow Ca(HCO_3)_2(aq)$$

The solubility of calcium bicarbonate is explained by its ability of forming hydrogen bonding with water molecules as its structure suggests.



$$^{\delta+}H-^{\delta-}O-\underset{\underset{O}{\|}}{C}-O-Ca-O-\underset{\underset{O}{\|}}{C}-^{\delta-}O-H^{\delta+}$$

(Polarity in O-H of $Ca(HCO_3)_2$ accounts for its ability of form hydrogen bonding)

Hydrides

- Beryllium hydride is unstable.
- Other members combine with hydrogen gas giving ionic hydrides, MH_2. Therefore they react with water to give basic hydroxide and hydrogen gas.

$$MH_2(s) + H_2O(l) \rightarrow M(OH)_2 + 2H_2(g)$$

Where M is Mg, Ca, Sr or Ba

Carbides

Carbides *are binary ionic compounds which are formed between carbon and another element which is stronger electropositive than the carbon.*

- The most common form of carbide ion is $\mathbf{C_2^{2-}}$with the following structure: $\ominus\, \mathbf{C} \equiv \mathbf{C}\, \ominus$

However the structure become unstable if the carbide is combined with cation of large polarising power, why?

Reason:

When cation of large polarising power is brought near to the carbide ion, it tends to attract negatively charged electrons including electrons in $C \equiv C$. As a result the triple bond breaks and the negative charge is no longer distribute in the two carbons, the charge concentrate to the carbon which is nearer to the cation and eventually the carbide ion, C^{4-} is formed. In one sentence we can summarize that: *Cation of large polarising power, distort (polarizes) the more complex carbide ion, $\boldsymbol{C_2^{2-}}$ into simpler carbide ion, $\boldsymbol{C^{4-}}$.*

What is the effect of this distortion?

The first simple effect we can recognize easily is the difference in the chemical formula of carbides. For example:

- Beryllium being on the top of group IIA elements, its cation has greatest polarising power in the group. This makes chemical formula of its carbide to be Be_2C which contain the distorted carbide ion, C^{4-}. *What about other carbides?*
- Polarising power of rest of the group members is not large enough to distort the complex carbide ion, C_2^{2-} and hence they form carbide with the chemical formula MC_2 where M is any group IIA element, e.g. CaC_2 for **calcium carbide.**

What is the effect of the difference of carbide structures on their hydrolysis?

If the compound contain the complex carbide ion, C_2^{2-}, with C≡C in the anion, it hydrolyse in water to give ethyne, $C_2H_2(HC \equiv CH)$.

- Therefore carbides of all group IIA elements except beryllium, hydrolyse in water to give **ethyne (acetylene)**.

That is $MC_2 + 2H_2O \longrightarrow M(OH)_2 + C_2H_2$

Where M may be any group IIA element except beryllium

- For example, when calcium carbide is heated with water, ethyne is formed.

$$CaC_2 + 2H_2O \underset{\triangle}{\rightarrow} Ca(OH)_2 + C_2H_2$$

If the compound contain the distorted carbide ion, C^{4-} like in beryllium carbide, Be_2C, methane will be formed in the hydrolysis.

$$Be_2C + 2H_2O \underset{\triangle}{\rightarrow} 2BeO + CH_4$$

(For the same reason of greater polarising power of Be^{2+}, $Be(OH)_2$ which would be formed undergo decomposition to give BeO as indicated in the above reaction equation while hydrolysis of carbides of other members ends with hydroxides e.g. $Ca(OH)_2$).

Chlorides

Hydrolysis of chlorides

- $BeCl_2$ being covalent, hydrolyse in water according to the following equation:

$$BeCl_2 + 2H_2O \rightarrow Be(OH)_2 + 2HCl$$

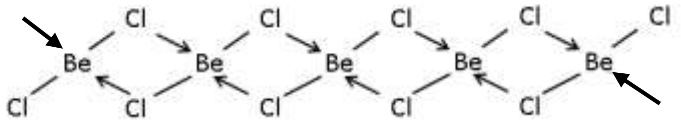
In small amount of water (drops of water), ***white fumes of hydrogen chloride gas*** *is observed while in large amount of water the gas dissolves resulting to formation of acidic solution (hydrochloric acid)*

- Chlorides of other group members are ionic, so they do not hydrolyse in water. They just dissolve in water to give their respective ions in the neutral solution.

Molecular structure of chlorides

Except $BeCl_2$, chlorides of earth metals have crystalline structure of oppositely charged ions of cations and anions. Giant ionic bond present in them make their melting and boiling point very high.

- The covalent chloride, $BeCl_2$, polymerises to $(BeCl_2)_n$ where n is the degree of polymerisation.



The chloride is able of undergoing polymerization due to the following reasons:

(i) Beryllium has empty p–orbitals which act as the room of lone pair of neighbour chlorine atom from neighbour chloride molecule.

(ii) Beryllium has very small size which enables it to exert enough nuclear attractive force to hold lone pair of the chlorine atoms in the empty orbitals.

Note: $BeCl_2$ is not the only chloride with empty orbitals. Many other chloride they have empty orbitals but they do not polymerise due to lack of the second factor.

Magnesium from $MgCl_2$ in sea water

One of the sources of magnesium is sea water. In sea water, magnesium exists in magnesium chloride which is soluble. ***How magnesium is recovered from sea water?***

Magnesium is recovered from sea water by firstly **liming** the chloride. By introducing liming material like calcium hydroxide into sea water, the insoluble magnesium hydroxide is formed.

$$\underset{\textbf{In sea water}}{MgCl_2} + \underset{\textbf{lime water}}{Ca(OH)_2} \rightarrow \underset{\textbf{precipitate}}{Mg(OH)_2} + CaCl_2$$

The insoluble $Mg(OH)_2$ precipitate out and concentrated hydrochloric acid is introduced into the precipitate. The hydroxide being basic reacts with the acid to form $MgCl_2$ again according to the following equation:

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$$

The magnesium chloride is electrolysed in Down's cell and finally pure magnesium deposits at cathode.

At cathode: $Mg^{2+}(aq) + 2e \rightarrow Mg(s)$

SOME IMPORTANT APPLICATIONS INVOLVING EARTH METALS

Mg^{2+}, Ca^{2+} and hardness of water

In contrast to **soft water**, **hard water** *is water that contains cations with charge of +2, especially* Ca^{2+} *and* Mg^{2+}. Hardness of water may be **temporary hardness** or **permanent hardness.**

Temporary hardness *is a type of water hardness caused by presence of soluble calcium bicarbonate and magnesium bicarbonate.*

- These bicarbonate yields Ca^{2+} and Mg^{2+} in the solution thus making the water hard.

Permanent hardness *is a type of water hardness caused by presence of calcium and magnesium sulphates or chlorides in the water.*

Effect of hard water in soap ability of making lather

With hard water, soap solutions form a white precipitate which is known as soap scum instead of producing lather, why?

This effect arises because the Mg^{2+} and Ca^{2+} destroy the **surfactant properties** of the soap by forming the **soap scum** which appears as a solid precipitate. *A major component of such scum is calcium (or magnesium) stearate which arises from sodium stearate.* The ***sodium stearate*** **is the main component of the soap.**

$$2C_{17}H_{35}COONa + Ca^{2+} \rightarrow (C_{17}H_{35}COO)_2Ca + 2Na^{+}$$

Sodium stearate (from soap) **calcium stearate**

Hardness can thus be defined as *the soap - consuming capacity of a water sample* ***or*** *the capacity of precipitation of soap as a characteristic property of water that prevents the leathering of soap*

It should be noted that:

Soapyless detergents do not consist of stearate or COO^{-} group (they contain OSO^{4-} or SO^{4-}group) and therefore do not form such scum and hence not affected by hardness of water. This is different to **soapy detergents** which contain COO^{-} group and for that reason, ***soapyless detergents form lather with hard water while soapy detergents do not.***

Hard water and formation scale

Another side effect of hard water is that: it forms solid deposits that clog plumbing. These deposits called **"scale"** are composed mainly of:

- **Calcium carbonate** ($CaCO_3$)
- $CaCO_3$ (of course and $MgCO_3$) are formed from thermal decomposition of their corresponding bicarbonates.
- **Magnesium hydroxide**
- **Calcium sulphate**

The resulting builds up of scale results to the following:

- It restricts the flow of water in pipes.
- In boilers, the deposits impair the flow of heat into water, reducing the heating efficiency and allowing the metal boiler components to overheat. This overheating can lead to failure of the boiler.

Softening hard water

Main principle of treating hardness of water is precipitating out Mg^{2+} and Ca^{2+}. This can explore two kinds of reactions:

(i) *Thermal decomposition reaction* or (ii) *ion exchange reaction*

The choice of a method to apply in treating hard water depends on whether the hardness is temporary or permanent.

(i) Treating temporary hardness:

Temporary hardness may be treated by either:

- Boiling hard water
- Lime softening

Boiling hard water explore thermal decomposition reaction whereby **bicarbonates of Mg and Ca being thermally unstable, decompose to their respective insoluble carbonates** thus precipitating (removing) out Mg^{2+} and Ca^{2+} and hence hardness is lowered by large amount.

$$Ca(HCO_3)_2(aq) \underset{\Delta}{\rightarrow} CaCO_3(s) + CO_2(g) + H_2O$$

$$Mg(HCO_3)_2(aq) \underset{\Delta}{\rightarrow} MgCO_3(s) + CO_2(g) + H_2O$$

Lime softening explore ion – exchange reaction where liming material like $Ca(OH)_2$ is introduced into hard water, precipitating magnesium hydroxide, $Mg(OH)_2$ and calcium carbonate.

$$Mg(HCO_3)_2(aq) + Ca(OH)_2(aq) \rightarrow Mg(OH)_2(s) + Ca(HCO_3)_2(aq) \text{ ……………..(i)}$$

$$Ca(HCO_3)_2(aq) + Ca(OH)_2 \rightarrow 2\,CaCO_3(s) + 2H_2O(l) \text{ ………………………………(ii)}$$

From the above (first) reaction equation and the original hard water

It should be noted that:

Among the two methods, explained above, lime softening method has greater efficiency, why?

Reason: Magnesium carbonate ($MgCO_3$) is more soluble than magnesium hydroxide($Mg(OH)_2$), so boiling temporary hard water will successfully precipitate out Ca^{2+} to large extent leaving some Mg^{2+} (of $MgCO_3$) in the solution. However using lime softening precipitates $Mg(OH)_2$ and $CaCO_3$ both of which are highly insoluble in water and hence both Ca^{2+} and Mg^{2+} will successfully precipitate out to large extent.

(ii) Treating permanent hardness

In contrast to temporary hardness, ***permanent hardness cannot be treated by boiling, why?***

There are two reasons for this:

- Calcium and magnesium sulphate (and chlorides) which cause permanent hardness are thermally stable. They do not decompose easily on heating to give insoluble products.
- The chlorides and sulphates of calcium and magnesium become more soluble as the temperature increases.

So ***how permanent hardness is removed?***

This is done by using the method which is known as **lime - soda process,** the method which explore ion – exchange reaction. In lime soda process, the water is treated by combination of **slaked lime,** $Ca(OH)_2$ and **soda ash,** Na_2CO_3.

- $Ca(OH)_2$ of slaked lime is moderately soluble in water. Hence it can dissociate in water to give one Ca^{2+} ion and two OH^- ions for each unit of $Ca(OH)_2$ that dissolve. The OH^- ions react with Mg^{2+} ion in the water to form the insoluble precipitate, $Mg(OH)_2$. The Ca^{2+} ions are unaffected by this reaction.

$$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$$

- Ca^{2+} ions are removed from water by CO_3^{2-} of soda ash, Na_2CO_3

$$Ca^{2+}(aq) + \underbrace{CO_3^{2-}(aq)}_{\textbf{From soda ash}} \rightarrow CaCO_3(s)$$

So $Ca(OH)_2$ (lime) removes Mg^{2+} while Na_2CO_3 (soda ash) removes Ca^{2+}.

Ba^{2+} as a test for $SO_4^{2-}, CO_3^{2-}, SO_3^{2-}$ and $C_2O_4^{2-}$

Solutions containingBa^{2+}, usually $\mathbf{BaCl_2}$ and $\mathbf{Ba(NO_3)_2(aq)}$ are used in **anionic test** of presence of $SO_4^{2-}, CO_3^{2-}, SO_3^{2-}$ or $C_2O_4^{2-}$ in the salt.

SO_4^{2-} gives a white precipitate of $BaSO_4$ which is insoluble in hydrochloric acid.

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

Then $BaSO_4(s) + HCl(g) \rightarrow$ No reaction

CO_3^{2-} give white precipitate of $BaCO_3$ which is soluble in hydrochloric acid evolving CO_2(g) with the acid like any other carbonate. The evolved CO_2 appears as effervescence of colourless gas which turns lime water milky.

$$Ba^{2+}(aq) + CO_3^{2-}(aq) \rightarrow BaCO_3(s)$$

Then $BaCO_3(s) + 2HCl(aq) \rightarrow BaCl_2(g) + CO_2(g) + H_2O(l)$

SO_3^{2-} (Sulphite) gives a white precipitate of $BaSO_3$ which is soluble in hydrochloric acid evolving sulphur dioxide gas (SO_2) with the acid. SO_2 is colourless gas with smell like that of burnt matches.

That is $Ba^{2+}(aq) + SO_3^{2-}(aq) \rightarrow BaSO_3(s)$

Then $BaSO_4(s) + 2HCl(aq) \rightarrow BaCl_2(aq) + SO_2(g) + H_2O(l)$

$C_2O_4^{2-}$ gives a white precipitate of BaC_2O_4 which is soluble in hydrochloric acid with no evolution of gas.

$$Ba^{2+}(aq) + C_2O_4^{2-}(aq) \rightarrow BaC_2O_4(s)$$

Then $BaC_2O_4(s) + 2HCl(aq) \rightarrow BaCl_2(aq) + H_2C_2O_4(aq)$

$MgSO_4$ in a test to distinguish between Na_2CO_3 and $NaHCO_3$

Solution of magnesium sulphate is useful in distinguishing Na_2CO_3 from $NaHCO_3$.

When $MgSO_4(aq)$ is added to $Na_2CO_3(aq)$, a white precipitate of $MgCO_3$ is formed

$$MgSO_4(aq) + Na_2CO_3(aq) \rightarrow \underbrace{MgCO_3(s)}_{\textbf{Insoluble}} + Na_2SO_4(aq)$$

When $MgSO_4(aq)$ is added to $NaHCO_3(aq)$, there is no formation of the precipitate.

$$MgSO_4(aq) + 2NaHCO_3(aq) \rightarrow \underbrace{Mg(HCO_3)_2(aq)}_{\textbf{Soluble}} + \underbrace{Na_2SO_4(aq)}_{\textbf{Soluble}}$$

However; the precipitate will be formed if the solution is boiled.

$$Mg(HCO_3)_2 \underset{\Delta}{\rightarrow} MgCO_3(s) + CO_2(g) + H_2O(g)$$

THERMAL STABILITY OF COMPOUNDS OF EARTH METALS

Compared to compound of alkali metals, compound of earth metals are less thermally stable due to their greater degree of polarisation brought about my greater polarising power of smaller sized and higher charged of earth metals cations.

Carbonates of earth metals decompose on heating to form their corresponding oxides.

$$MCO_3(s) \underset{\Delta}{\rightarrow} MO(s) + CO_2(g)$$

Hydroxides of earth metals decompose on heating to form their corresponding oxides.

$$M(OH)_2(s) \rightarrow MO(s) + H_2O(g)$$

Nitrates also form oxides on heating.

$$2M(NO_3)_2(s) \underset{\Delta}{\rightarrow} 2MO(s) + 4NO_2(g) + O_2(g)$$

Solid bicarbonates of earth metals are highly thermal unstable such that they do not exist. The bicarbonates exist in aqueous solution only.

$$M(HCO_3)_2(s) \xrightarrow[\text{room temperature}]{} MCO_3(s) + CO_2(g) + H_2O(l)$$

While $MHCO_3(aq) \xrightarrow[\text{room temperature}]{}$ No reaction

In aqueous solution, bicarbonates will not decompose unless the solution is boiled

$$MHCO_3(aq) \underset{\Delta}{\rightarrow} MCO_3(s) + CO_2(g) + H_2O(g)$$

Where M may be any earth metal.

COMPLEX FORMATION ABILITY OF EARTH METALS

Generally alkaline earth metals do not form complexes. However Beryllium being on the top of group IIA has smallest cationic radius and hence can form complexes

- In complexes, Be show coordination number of 4 e.g. in $[Be(CN)_4]^{2-}$. It cannot show coordination number of 6 like some other metals, **why?**

When beryllium forms Be^{2+} ion, it loses the two electrons in the 2s orbital. That leaves all orbitals in outermost energy level (n = 2) empty. The four orbitals (one s – orbital and three p–orbitals) hybridize to make four equal sp^3 hybridized orbitals and hence showing coordination number of 4. To show coordination number of 6, it needs to use other two d-orbitals in sp^3d^2 hybridisation. But the outermost energy level, $n = 2$ has no d – sub energy level thus making impossible for Be to **expand its valence shell** and hence it cannot exhibit coordination number of 6.

DIFFERENCES BETWEEN BERYLLIUM AND OTHER GROUP MEMBERS

(i) In most cases, beryllium has greater physical properties than other group members like:

- It has exceptionally high melting and boiling point.
- It is harder than other group members.

(ii) It does not react with water while other members do.

(iii) It forms mainly covalent compounds like $BeCl_2$ while other members form mainly ionic compounds.

(iv) Its chloride ($BeCl_2$) hydrolyse in water while chlorides of other members do not.

(v) Its oxide and hydroxide (Beo and $Be(OH)_2$) are amphoteric while oxides and hydroxides of other members are basic.

(vi) It can form complex while other group members do not.

(vii) Its carbide (Be_2C) react with water producing methane while carbides of other group members produce ethyne.

(viii) Molecules of its chloride $(BeCl_2)$, can undergo association to form polymer while chlorides of other group members do not undergo association.

(ix) It cannot combine directly with hydrogen gas to form hydride while other group members do.

DIAGONAL RELATIONSHIP BETWEEN BERYLLIUM AND ALUMINIUM

(i) They both rendered passive by concentrated nitric acid.
(ii) They both have amphoteric oxides and hydroxides.
(iii) They both form covalent chlorides which hydrolyse in water.
(iv) They both form chlorides whose molecules can undergo association. Beryllium chloride associates to polymer while aluminium chloride associates to dimer.

$$nBeCl_2 \xrightarrow{\text{Polymerise}} (BeCl_2)_n$$

$$2AlCl_3 \xrightarrow{\text{Dimerise}} Al_2Cl_6$$

(v) They both do not react with water (cold water or steam).
(vi) They both react with aqueous solution of sodium hydroxides NaOH(aq), producing hydrogen gas and the complex.
(vii) They both form complexes.
(viii) They both have carbides $(Be_2C$ and $Al_4C_3)$ which react with water giving methane, CH_4.

$$Be_2C + 2H_2O \underset{\Delta}{\rightarrow} BeO + CH_4$$

$$Al_4C_3 + 6H_2O \underset{\Delta}{\rightarrow} Al_2O_3 + 3CH_4$$

(**Note**: Like in hydrolysis of Be_2C, another stable product of hydrolysis of Al_4C_3 is not $Al(OH)_3$, it is oxide of aluminium unlike in hydrolysis of carbides of other group IIA elements which give hydroxides. Just to remind you; this is due to greater polarising power of Al^{3+}, $Al(OH)_3$ undergoes thermal decomposition easily to Al_2O_3).

PRACTICE EXERCISE 9

Question 1

Why group IIA elements are also known as alkaline earth metals?

Question 2

Account for the following:

(i) Solid bicarbonates of alkaline earth metals are not known.
(ii) Barium has greater melting point that caesium.
(iii) Beryllium does not react with either cold water or steam.
(iv) Methane is formed when beryllium carbide is hydrolysed.
(v) Although calcium is more reactive than hydrogen, does not react with dilute sulphuric acid.

Question 3

With help of chemical equation; explain the following:

(i) Strontium does not react with dilute sulphuric acid but it reacts when the acid is concentrated.
(ii) Among earth metals only beryllium reacts with dilute sodium hydroxide.
(iii) Beryllium oxide is amphoteric while other oxides of earth metals are basic.
(iv) Unlike alkali metals, earth metals react with nitrogen.
(v) Unlike carbonate of alkali metals, carbonates of earth metals decompose on heating.

Question 4

Explain difference between chloride of beryllium and chlorides of other earth metals.

Question 5

Explain briefly similarities between beryllium and aluminium under the following headings:

(i) Chlorides
(ii) Oxides
(iii) Carbonates
(iv) Carbides

Question 6

This question concern the chemistry of group IIA metals Mg to Ba.

An aqueous solution of group IIA metal chloride XCl_2, forms a white precipitate when dilute aqueous sodium hydroxide is added. A separate sample of the solution of XCl_2 does not form a precipitate when dilute aqueous sodium sulphate is added. An aqueous solution of different group IIA metal chloride, YCl_2, does not form a precipitate when dilute aqueous sodium hydroxide is added. A separate sample of the solution YCl_2 forms a white precipitate when dilute aqueous sodium sulphate is added. Suggest identities for the group IIA metals X and Y. write equations, including state symbols, for the reaction which occur

Chapter 10

GROUP VIIA

Group VIIA elements are also known as **halogens** reflecting their ability of combining easily with metals to give salts. They are all non – metals.

- Halo means **salts** and **gen** comes from the word '**gennen**' which means **creator**. So **halogen** means **salt creator**.

Group VIIA elements have outermost electronic configuration of ns^2np^5 and hence they are found at p – block of modern periodic table.

Group VIIA elements with their respective electronic configurations are shown in the table below:

ELEMENT	SYMBOL	ATOMIC NUMBER	ELECTRONIC CONFIGURATION
Fluorine	F	9	[He] $2s^2$ $2p^5$
Chlorine	Cl	17	[Ne] $3s^2$ $3p^5$
Bromine	Br	35	[Ar] $3d^{10}$ $4s^2$ $4p^5$
Iodine	I	53	[Kr] $4d^{10}$ $5s^2$ $5p^5$
Astatine	At	85	[Xe] $4f^{14}$ $5d^{10}$ $6s^2 6p^5$

Note: Astatine is a very rare element and it is radioactive with very short half life disintegrating to give smaller element. So there is not that much known about this element and hence it will be omitted in our discussion.

OXIDATION STATES OF HALOGENS

Group VIIA elements have common oxidation state of -1.

- **Fluorine being most electronegative element in the periodic table** has fixed oxidation state of -1 only.
- Other members may show higher oxidation states like:
  - $+1$ e. eg. in $HOCl$
  - $+3$ e. g. in $HOCl_2$
  - $+5$ e. g. in $NaClO_3$
  - $+6$ e. g. in Cl_2O_6
  - $+7$ e. g. in $HClO_4$

Maximum oxidation state for halogen is $+7$ which is obtained when all seven valence electrons of halogen participate in the bond formation.

- Compounds of halogen in which the halogen has maximum oxidation of +7 are known as **perhali compounds**. Examples of perhali compounds include:
  - $HBrO_4$ (Perbromic acid)
  - $NaBrO_4$ (sodium perbromate)
  - $KClO_4$ (potassium perchlorate)

- Generally ions containing halogen, chlorine for example, in different oxidation states have different special names:
  - Cl^- is known as chloride
  - ClO^- is known as hypochlorite (similarly hypobromite for BrO^- etc)
  - ClO_2^- is known as chlorite (similarly bromite for BrO_2^- etc)
  - ClO_3^- is known as chlorate (similarly bromate for BrO_3^- etc)
  - ClO_4^- is known as perchlorate (similarly perbromate for BrO_4^- etc)

MELTING AND BOILING POINT OF HALOGENS

Halogens exist as diatomic with simple molecular structure.

- That means their intermolecular forces attraction is governed by Van-der-Waals dispersion forces which increases with an increase in molar mass.

As you go down the group, molar mass of halogens, X_2, tend to increase leading to the increase in Van-der-Waals forces of attraction and hence melting and boiling point increase in the same order. This can be easily verified by looking to their physical states at room temperature.

- **Fluorine** and **chlorine** are **gases**. This is because; having lower molar mass than other group members, fluorine and chlorine have weaker Van – der – Waals force of attraction. With weak Van-der- waals forces of attraction, both melting and boiling point of the elements is so small that room temperature is enough to melt and even to boil them and hence they become in gaseous state at room temperature.
- **Bromine** is **liquid**. This is because, having relatively greater molar mass compared to fluorine and magnesium, bromine has relatively strong Van-der-Waals forces of attraction leading to its higher boiling point while melting point is still somehow small (however it is still greater than those of fluorine and chlorine) such that room temperature is enough to melt the bromine but it is not enough to boil it, that is why it remains to be in liquid state at room temperature.
- **Iodine** is **solid**. This is because, iodine molecule has larger molar mass and stronger Van-der-Waals forces of attraction than F_2, Cl_2 and Br_2. Thus it has both high melting point and high boiling point such that room temperature is not enough to boil and even to melt the iodine and therefore it becomes solid at room temperature.

TREND IN BOND DISSOCIATION ENERGY FOR HALOGEN MOLECULES

All halogens exist as diatomic molecule (X_2) at room temperature.

- So during the chemical reaction, the halogen molecule must first dissociated to its corresponding gaseous atoms according to the following equation:

$$X_2 \rightarrow 2X \quad \Delta H = +\mathcal{X}\,\text{kJ/mol} = \text{Dissociation energy}$$

Ability of the molecule to undergo dissociation depends on the strength of the bond holding atoms together in the molecule. Also the strength of the bond depends on the bond length.

- Strength of the bond decreases with an increase in bond length. With the longer bond, the bond dissociation energy become smaller as the bond become weak as result of large bond length.

On another hand, bond length depends on sizes of atoms bonded together.

- As the size of atoms become bigger, bond length become large and therefore the bond dissociation energy become small.

Atomic sizes of halogens like in any other group, increases as you go down the group.

- So after above short discussion we can conclude that: **generally bond dissociation energy of halogen molecules decrease as you go down the halogen group.**

From the above conclusion, we are expecting fluorine molecule to have greatest bond dissociation energy since its atomic size is smallest in the group.

- However ***experimental results show that bond dissociation energy of chlorine molecule is greater than that of fluorine molecule, why?***

The irregularity is explained by repulsion of lone pairs of fluorine atom keeping in the mind that each fluorine atom has three lone pairs making a total of six lone pairs in the fluorine molecule. ***How these lone pairs have effect on the strength of F-F bond hence on the amount of bond dissociation energy?***

Fluorine being very small in size, the bond length in fluorine molecule is so short that the lone pairs of the two bonded fluorine atoms become very close to each other. As a result of this, large repulsion occurs between the two bonded fluorine atoms. The bond formed between the fluorine atoms which are under repulsion is very weak and hence can be broken by smaller amount of energy than that would be expected in absence of the repulsion.

What about other halogen molecules?

As you move down the group, atomic size and bond length increases. The lone pair of the bonding atoms becomes widely separated away from each other and hence the factor of repulsion becomes minor.

- Therefore after fluorine, chlorine molecule has maximum bond dissociation energy and after that the energy starts to decrease regularly as you go down the group. This is illustrated in the table below which show experimental values for dissociation energy of halogens.

ELEMENT	DISSOCIATION ENERGY IN KJ/mol
$F - F$	142
$Cl - Cl$	250
$Br - Br$	190
$I - I$	164

OXIDISING POWER OF HALOGENS

Generally halogens are good oxidising agents.

- In oxidising other species, halogens themselves get reduced to their corresponding halide ion.

$$X_2 + 2e \rightarrow 2X^-(aq) \text{……………………..Reduction}$$

Where X is halogen

The easier the halogen undergoes reduction, the stronger oxidising agent it becomes.

Trend of the oxidising power down the group

Oxidising power of halogens increases on descending the halogen group. To understand the reason of the trend we must first understand, what change halogens undergo when they oxidise other species.

- As mentioned earlier, in oxidising other species, halogen themselves undergo reduction according to the following equation:

$$\mathbf{X_2(g, l\,or\,s) + 2e \rightarrow 2X^-(aq)}$$

- The change may be thought to take place in three steps.

(i) Atomisation of the molecule

- For fluorine and chlorine being gases it involves dissociating X- X bond only. Bromine molecule being liquid the atomisation process involves firstly absorption energy required to convert it from liquid to gaseous state before doing dissociation while iodine molecule being solid, the atomisation process requires greater energy to convert it from solid to gaseous state before doing dissociation. The energy absorbed in the atomisation process is known as **atomisation energy**. It increases as you go down the group.

(ii) Gaining of electrons by gaseous atom

- After atomisation, the gaseous atoms gain electron from reducing agent to form their corresponding gaseous ions. It is exothermic process of halogens as each atom gains one electron only to form $X^-(g)$. So the electron is attracted making the process exothermic. The energy evolved in the process is known as **electron affinity**. Fluorine has lower electron affinity than chlorine which has maximum electron affinity in the group and after chlorine the electron affinity starts to fall gain.

(iii) Hydration of gaseous ion

- Finally the gaseous ion gets hydrated. Here smaller ion is hydrated more making the process more exothermic (remember hydration process exothermic). The energy evolved in the process is known as **hydration energy** and therefore hydration energy decreases as you go down the group because in that direction ions get bigger and hence less hydrated.

After above three steps, overall heat of reaction ΔH can be found by using the following equation:

$$\Delta H = \text{atomisation energy} + \text{electron affinity} + \text{hydration energy}$$

If the overall heat of reaction is smaller (more negative or less positive), the element is then said to have greater oxidising power and vice – versa.

Fluorine versus chlorine

Here there is a bit contradiction because chlorine has greater (more negative) electron affinity than fluorine. But both atomisation energy and hydration energy are in favour of fluorine.

- Both elements being gases;

  $\text{Their atomisation energy} = \frac{1}{2} \times \text{Dissociation energy.}$

And as explained earlier, dissociation energy of fluorine is lower than that of chlorine. Hence fluorine has smaller (less positive) atomisation energy than chlorine

- Fluorine being smaller in size, it more hydrated and hence it has greater (more negative) hydration energy than chlorine.

Therefore: *Lower atomisation energy and greater hydration of fluorine than chlorine, explains why the former (fluorine) has greater oxidising power despite the fact that the later (chlorine) has greater (more negative) electron affinity.*

After chlorine, no more contradiction; atomisation energy increase (become more positive) as you go down the group, both electron affinity and hydration energy decreases (become less negative) on descending the group making overall heat of reaction to increase (become less negative or more positive) in the same order and hence oxidising power is found to decrease in the same direction.

Justification of decreasing the oxidising power on descending the group VIIA

The fact can be justified by using **displacement reaction.**

- Halogens above the group displaces (oxidises) below member from their salts while the below members cannot displace the above members. For example:

(i) When chlorine is introduced into a beaker containing solution of sodium bromide, **reddish brown colouration of bromine** is observed suggesting the bromide ions have been oxidised according to the following equation:

$$\mathrm{Cl_2(g) + 2NaBr(aq) \rightarrow 2NaCl(aq) + Br_2}$$

Ionically: $\mathrm{Cl_2 + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2}$

Reduction half reaction: $\mathrm{Cl_2 + 2e \rightarrow 2Cl^-}$ (chlorine undergoes reduction, thus acting as an oxidising agent).

Oxidation half reaction: $\mathrm{2Br^-(aq) \rightarrow Br_2 + 2e}$ (bromine undergo oxidation)

But when iodine is introduced in the same beaker containing aqueous solution of sodium bromide no change is observed, suggesting that the iodine is incapable of oxidising the bromide ions.

$$\mathrm{I_2 + 2NaBr} \rightarrow \text{No reaction}$$

(ii) When chlorine gas is bubbled into a beaker containing aqueous solution of potassium iodide, **dark brown colouration of iodine** is observed suggesting that the iodide have been oxidised according to the following equation:

$$\mathrm{Cl_2 + 2KI(aq) \rightarrow 2KCl(aq) + I_2}$$

Or ionically: $\mathrm{Cl_2 + 2I^- \rightarrow 2Cl^-(aq) + I_2}$

But when iodine is introduced into a beaker containing aqueous solution of potassium chloride, no change is observed suggesting that the iodine is incapable of oxidising the chloride ions.

To conclude:

- Chlorine has the ability to take electron from both bromide ions and iodide ions thus oxidising them. Bromine and iodine cannot get those electrons back from the chloride ions formed.
- That means that chlorine is more powerful oxidising agent than either bromine or iodine
- Also bromine can remove electrons from iodide ions to give iodine and the iodine cannot get them back from the bromide ions formed. That implies that bromine is more powerful oxidising agent than iodine.
- This all means that oxidising power of halogens tend to decrease on descending the halogen group.

It should be noted that:

From above discussion of the justification by employing displacement reaction, fluorine has been deliberately excluded, why?

This is because; fluorine is very strong an oxidising agent. It oxidises water to oxygen (or ozone if fluorine present in excess) and so it is impossible to do simple solution reactions with it.

$$\mathrm{2F_2 + 2H_2O \rightarrow 4HF + O_2}$$

So any attempt to make a chemical reaction with solution of salt of other halogens, the fluorine tends to react violently with water in the solution instead of oxidising the halide ions in the solution.

Justification of oxidising power of halogens in their reaction with metals of variable oxidation state

Due to their oxidising characters, halogens combine with metals of variable oxidation state to give compounds in which the metals have their higher oxidation state suggesting that the metals have been oxidised to their higher oxidation state by halogen.

- For example, iron burns in halogen vapour to give iron (III) halides. Iodine having weaker oxidising power is the only halogen which give iron (II) iodide, i.e. it is only capable of oxidising the iron as far as the +2 oxidation state.

$$2Fe(s) + 3F_2(g) \xrightarrow[cold]{} 2FeF_3(s)$$

Pale green

$$2Fe(s) + 3Cl_2(g) \underset{\Delta}{\rightarrow} 2FeCl_3(s)$$

Black (turn to reddish – brown in presence of water)

$$2Fe(s) + 3Br_2(g) \underset{\Delta}{\rightarrow} 2FeBr_3(s)$$

Reddish brown

But $Fe + 2I_2(g) \underset{\Delta}{\rightarrow} FeI_2(s)$

Grey

What would happen if a solution containing iron (II) ions is used instead of solid iron metal?

This time, we can only talk about the reactions of chlorine, bromine and iodine. Wherever you have solution, fluorine will react with water.

Chlorine and **bromine** are strong enough oxidising agents to oxidise Iron (II) to Iron (III). In the process, the chlorine is reduced to chloride ions and the bromine to bromide ions.

$$2Fe^{2+} + Cl_2 \rightarrow 2Fe^{3+} + 2Cl^-$$

Green **Reddish – brown**

$$2Fe^{2+} + Br_2 \rightarrow 2Fe^{3+} + 2Br^-$$

Green **Reddish - brown**

Iodine is not a strong enough oxidising agent to oxidise Iron (II) ions, so there is no reaction.

$$Fe^{2+} + I_2 \rightarrow \text{No reaction}$$

But it should be noted that:

Iron (III) ions are strong enough oxidising agents to oxidise iodide ions to iodine.

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$$

To insist…!

The ability of halogens to form compound with higher oxidation state of the metal with variable oxidation state is maximum for fluorine and minimum for iodine.

- With chromium which has variable oxidation state up to +6, fluorine is the only halogen which can form hexavalent compound with the chromium, i.e. CrF_6 while other halogens like chlorine ends with trivalent like $CrCl_3$.

Justification of greatest oxidising power of fluorine

(i) With chromium and manganese, fluorine is the only halogen which can give fluoride in highest oxidation states of the metals which are $+6$ and $+7$ respectively thus forming CrF_6 and MnF_7. Other halogens like chlorine do not form compounds like $CrCl_6$ and $MnCl_7$.

(ii) Fluorine is the only halogen which can liberate oxygen from water confirming that the **oxygen from water has been oxidised** from -2 (in H_2O) to 0 (in O_2).

$$2F_2 + 2H_2O \rightarrow 4HF + O_2$$

(In excess of fluorine, Ozone, O_3 is produced instead of O_2)

- Other halogens **disproportionates** in water according to the following equation:

$$X_2 + H_2O \rightarrow HOX + HX$$

(In each compound, H_2O and HOX, oxidation state of oxygen remains unaltered – it is -2).

(iii) With concentrated alkaline solution of like $NaOH$ and KOH, fluorine is the only halogen which can liberate oxygen from the alkali confirming that **oxygen in the alkaline solution has been oxidised form -2 to 0**

$$2F_2 + 4NaOH \rightarrow 4NaF + O_2 + 2H_2O$$

- Other halogens disproportionate depending on conditions (Reaction equations for this will be given in next section)

(iv) No halogen can displace fluorine ions, F^- from its solution.

e.g. $NaF(aq) + X_2 \rightarrow$ No reaction

Where X may be Cl, Br or I

DISPROPORTIONATION OF HALOGENS IN ALKALINE SOLUTION

Halogens disproportionate in alkaline solution depending on the conditions

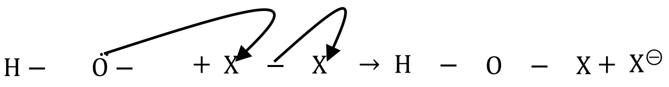
(i) The **reaction with cold dilute alkaline solution**

Generally $X_2 + 2OH^- \rightarrow XO^- + X^- + H_2O$

The reaction takes place in two steps:

First step:

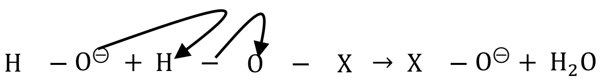
In this step, hydroxyl group as Lewis base donate its lone pair to empty d- orbital in one of halogen atom. This is followed by heterolytic bond cleavage of X – X bond.



$$H - \ddot{O} - + X - X \rightarrow H - O - X + X^{\ominus}$$

Second step:

H-O-X reacts with HO^- like any acid-base reaction.



$$H - O^{\ominus} + H - O - X \rightarrow X - O^{\ominus} + H_2O$$

Thus ignoring arrows, the reaction equation in two steps may be rewritten as follows:

$X_2 + OH^- \rightarrow HOX + X^-$……………………………………..(i)

$HOX + OH^- \rightarrow XO^- + H_2O$……………………………………(ii)

Overall reaction equation is obtained by taking (i) + (ii) and then simplifying to give the following equation:

$$X_2 + 2OH^- \rightarrow XO^- + X^- + H_2O$$

What is the important thing have we learned from the above mechanism?

The first step involves participation of empty d – orbital which is responsible for accepting lone pair from the Lewis base(HO^-). That means that if the element has no empty orbital, the reaction in the first step will not occur and hence the overall reaction will not occur also. That is what we are expecting to occur in fluorine.

With outermost energy level of $n = 2$ which has no d - sub energy level, fluorine has no empty d – orbitals. So fluorine cannot disproportionate like other halogens.

However fluorine has greatest oxidising power thus making possible for it to oxidise the hydroxide to oxygen gas. The alkaline must be very concentrated to avoid a chemical reaction between fluorine and water which will occur if the solution is dilute (has large amount of water).

$$2F_2 + 4OH^- \rightarrow 4F^- + O_2 + 2H_2O$$

Examples of disproportionation of halogens in cold dilute alkaline solution

(i) Chlorine disproportionates in cold dilute potassium hydroxide to form hypochlorite and chloride and its greenish – yellow colouration disappear.

$$Cl_2 + 2KOH(dil) \underset{cold}{\longrightarrow} KCl + KClO + H_2O$$

(ii) Bromine disproportionates in cold dilute sodium hydroxide to form sodium hypobromite and sodium bromide.

$$Br_2 + 2NaOH(dil) \underset{cold}{\longrightarrow} NaBrO + NaBr + H_2O$$

(ii) The **reaction with hot concentrated alkaline solution**

Recall in cold and dilute condition:

$X_2 + 2OH^- \rightarrow XO^- + X^- + H_2O$……………………………………(i)

In hot and concentrated condition, the XO^-, undergoes further disproportionation according to the following equation:

$3XO^- \rightarrow XO_3^- + 2X^-$……………………………………………….(ii)

Overall reaction equation is obtained by taking 3(i) + (ii) and then simplifying to give the following equation:

$$3X_2 + 6OH^- \rightarrow XO_3^- + 5X^- + 3H_2O$$

For example:

(i) $3Cl_2 + 6KOH(conc) \underset{Hot}{\longrightarrow} KClO_3 + 5KCl + 3H_2O$

(ii) $3Br_2 + 6NaOH(conc) \underset{Hot}{\longrightarrow} NaBrO_3 + 5NaBr + 3H_2O$

SOLUBILITY OF HALOGENS

(i) Solubility in organic solvents

The halogens are much more soluble in organic solvent like hexane than they are in water (polar solvent). Both hexane and halogens are non–polar molecules (remember; like dissolves like) attracted to each other by Van-der-Waals dispersion forces.

- That means that the attractions (between hexane molecules and between halogen molecules) are similar to the new attractions made when two substances mix.

(ii) Solubility in water

Fluorine reacts violently with water to give hydrogen fluoride gas (or a solution of hydrofluoric acid depending on the amount of water) and oxygen gas (or Ozone in presence of excess fluorine). So thinking about its solubility in water is pointless.

$$2F_2 + 2H_2O \rightarrow 4HF + O_2$$

Or in excess fluorine: $3F_2 + 3H_2O \rightarrow 6HF + O_3$

Chlorine, bromine and **iodine** all dissolve in water to some extent but they do not show any pattern (see the table below).

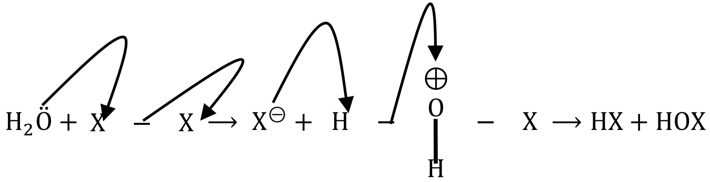
Element	**Solubility in mol/dm^3**
Chlorine	0.091
Bromine	0.21
Iodine	0.0013

Chlorine reacts with water to some extent to give a mixture of hydrochloric acid and hypochlorous acid. The reaction is reversible.

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

The forward reaction is disproportionation whereby oxidation state of chlorine change from 0 in Cl_2 to -1 (reduction) in HCl and to +1 (oxidation) in HOCl.

The reaction is thought to follow the following mechanism



Again the role of empty d – orbital is very important for the halogen to react in that way. Fluorine for example cannot disproportionate in water because it has no empty d – orbital.

Bromine and iodine react with water in similar way, but to a much lesser extent.

E.g. $Br_2 + H_2O \rightleftharpoons HOBr + HBr$

(iii) Solubility of iodine in potassium iodide solution

Although iodine is only slightly soluble in water, it dissolves readily in potassium iodide solution to give a **dark red – brown solution.**

- This is due to the fact that, iodine combine with iodide ions and form complex ions, I_3^- which are soluble

$$I_2 + KI \longrightarrow \underset{\textbf{Soluble}}{K^+[I_3]^-}$$

Or ionically $I_2 + I^- \longrightarrow \underset{\textbf{Soluble}}{[I_3]^-}$

SELECTED COMPOUNDS OF HALOGENS

Oxides

Fluorine is the only element which has a neutral oxide, F_2O.

- This is because in F_2O, fluorine is more electronegative than oxygen

Other oxides of halogens are acidic.

- **For chlorine:**

$$Cl_2O + H_2O \longrightarrow 2HOCl$$

$$Cl_2O_6 + H_2O \longrightarrow HClO_4 + HClO_3$$

$$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$$

- **For bromine:**

$$Br_2O + H_2O \longrightarrow 2HOBr$$

$$2BrO_3 + H_2O \longrightarrow HBrO_3 + HBrO_4$$

- **For iodine:**

$$I_2O_4 + H_2O \longrightarrow HIO_2 + HIO_3$$

$$I_2O_5 + H_2O \longrightarrow 2HIO_3$$

$$I_2O_7 + H_2O \longrightarrow 2HIO_4$$

- The oxides of iodine are solids at room temperature and are salt like.

Hydrogen halides, HX

Thermal stability of hydrogen halides

Here we are talking the ability of hydrogen halide to resist decomposition to its constituent elements when it is heated.

- When heated, hydrogen halides may decompose to their constituent elements according to the following equation:

$$2HX \underset{\Delta}{\rightarrow} H_2 + X_2$$

The ability of hydrogen halide to undergo decomposition depends on the bond energy of $H - X$ bond.

- If H – X bond is weak, the bond will break easily on heating and hence the halide is said to have low thermal stability.
- On other hand, the bond strength depends on the bond length of $H - X$ bond. The longer bond has weaker bond strength and vice – versa.

As the atom gets bigger, the bond length also increases.

- The atom get bigger on descending the group and therefore bond length of $H - X$ bond increases in the same order and hence thermal stability of halogens decreases as you go down the group VIIA.

Hydrogen fluoride and **hydrogen chloride** are very stable to heat. They do not split up into hydrogen and fluorine or chlorine again if heated to any normal laboratory temperature.

Hydrogen bromide splits slightly into hydrogen and bromine on heating and **hydrogen iodide** splits to an even greater extent.

So the pattern of thermal stability of hydrogen halides is as follows:

$$\xrightarrow[\textbf{Decrease in thermal stability}]{\mathbf{HF}>HCl>HBr>HI}$$

It should be understood that:

- Hydrogen fluoride is the only halide in the group which has enough hydrogen bonding to account for its properties.

- That is because fluorine is most electronegative element in the group; the fact which makes H-F bond most polar.

- **Presence of strong hydrogen bonding between molecules of hydrogen fluoride is an added advantage; HF has on its thermal stability.**

So we can conclude that HF has exceptionally high thermal stability due to the following reasons:

- It has very strong hydrogen bond holding its molecules together.
- Bond enthalpy (energy) of H – F bond is very high

Challenging!

Now the question is ***why F − F bond energy was unexpectedly low and now H – F bond energy is still high?***

Here the reason is very simple to understand!

- This is simply because there is no any lone pair in hydrogen atom and therefore no repulsion between lone pairs in the two bonded atoms like in F – F bond whereby each fluorine atom has three lone pairs.

Warning!

Talking hydrogen bonding as the only factor which determine thermal stability of hydrogen halides it totally misconception! There is no significant hydrogen bonding in all HCl, HBr and HI. So it is completely wrong to account their properties by using hydrogen bonding – HF is only hydrogen halide which has significant hydrogen bonding which can affect its properties.

Melting and boiling point of hydrogen halides

Again hydrogen fluoride, HF, is the only hydrogen halide whose melting and boiling point can be explained by using hydrogen bonding. Melting and boiling point of other hydrogen halides are explained by Van-der-Waals dispersion forces of which increases with an increase in molar mass. Generally hydrogen halides are colourless **gases** at room temperature.

- **Hydrogen fluoride** has unexpectedly high boiling point (despite the fact that it has lowest molar mass of all hydrogen halides in the group) due to that strong hydrogen bonding holding its molecules together. In fact, **hydrogen fluoride can condense to liquid on cool day**. It is only hydrogen halide which can do this as its boiling point (20℃ or 293K) is actually very close to room temperature (25℃ or 298K).

- Boiling point of other hydrogen halides increases with the increase in molecular weight which increases on descending the group.

Thus the trend of boiling point of hydrogen halides is as follows:

$$\xrightarrow[\textbf{Increase in boiling point}]{\mathbf{HCl}<HBr<HI<HF}$$

That is the boiling point is maximum at HF, after that HCl has minimum and thereafter it starts to increase regularly as you go down the group due to increase in molecular weight leading to increase in Van – der – Waals dispersion forces in the same order.

Acidic strength of hydrogen halides

According to the Bronsted – Lowry definition; an acid is a proton donor.

- Hydrogen halides are acids because they can donate protons to other species. With water, they react according to the following equation:

$$HX + H_2O \longrightarrow H_3O^+ + X^-$$

In donating hydrogen proton, the $H - X$ bond must break and therefore the $H - X$ bond enthalpy determines the strength of the acid.

- If the $H - X$ bond is weak, the bond will break easily and the halide will be strong acid.

As we have discussed earlier, the strength of $H - X$ bond decreases as you go down the group and hence acidic strength of hydrogen halide increase as you go down the group.

That is $\xrightarrow[\textbf{Increase in acidic strength}]{\mathbf{HF} < HCl < HBr < HI}$

However if we look in detail on their strength, hydrofluoric acid has abnormally low acidic strength.

- While all other hydrogen halides are very strong acids, ionizing completely in water, hydrofluoric acid is very weak acid (it acidic strength is similar to those of organic acid like ethanoic acid). This suggests that there is more reason accounting to its lower acidic strength apart from that of high bond enthalpy of $H - F$ bond. **What is that reason?**
- This is because for HF, there is very strong hydrogen bonding between un–ionised hydrogen fluoride molecule and water molecules. This costs quite a lot of energy to break and does not occur in the other hydrogen halides.

Reducing power of hydrogen halides

When dissolved in water, hydrogen halides, HX ionises to give halide ions, X^-.

- These halide ions can be oxidised to give their corresponding neutral molecules thus acting as reducing agent (don't forget reducing agent undergo oxidation in the redox reaction)

That is $2X^-(aq) \rightarrow X_2 + 2e$

As the halide ion become bigger, its electrons become weakly held by nuclear attractive force making easier for the halide to donate its electrons and hence the halide become stronger reducing agent.

- The size of halide ions increases as you go down the halogen group.

So after that short discussion we can conclude that:

Reducing power of hydrogen halides increases on descending the halogen group.

Justification on the increase of reducing power of hydrogen halides on descending the halogen group

This can be justified by considering the reaction between hydrogen halides and concentrated sulphuric acid which is good oxidising agent.

(i) $HF + H_2SO_4(conc) \rightarrow$ No reaction

(ii) $HCl + H_2SO_4(conc) \rightarrow$ No reaction

- So HF and HCl are not strong reducing agent enough to be oxidised by concentrated sulphuric acid.

(i) $2HBr + H_2SO_4(conc) \rightarrow Br_2 + SO_2 + 2H_2O$

- Here H_2SO_4 is reduced by HBr whereby oxidation state of sulphur is reduced from +6 (in H_2SO_4) to +4 (in SO_2) and HBr become oxidised to Br_2.

(ii) $8HI + H_2SO_4(conc) \rightarrow 4I_2 + H_2S + 4H_2O$

- In this case, H_2SO_4 is more reduced by HI than HBr does as the oxidation state of sulphur is much more reduced from +6 in H_2SO_4 to -2 in H_2S. HI has been oxidised to I_2.

The reader should understand that:

In presence of very strong oxidising agent like potassium permanganate, even HCl can be oxidised to Cl_2 and this explains why hydrochloric acid should not be used as an acidic medium in redox titration involving potassium permanganate. They react according to the equation shown below thus interfering measurement of correct volume of $KMnO_4$ which is exactly used to oxidise the intended reducing agent in the titration.

$$2MnO_4^- + 10Cl^- + 16H^+ \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$$

Effect of reducing characters of hydrogen halides in their preparation by the reaction between ionic halide and concentrated sulphuric acid

When ionic halide like sodium chloride is allowed to react with concentrated sulphuric acid, the concentrated sulphuric acid donates a hydrogen ion, H^+ to a chloride ion to make hydrogen chloride.

That is $NaCl + H_2SO_4(conc) \longrightarrow NaHSO_4 + HCl$

It is possible to prepare hydrogen chloride in that way because the chloride cannot be oxidised by the acid as we have seen earlier.

$$HCl + H_2SO_4 \rightarrow \text{No reaction}$$

But ***what will happen if the similar method is employed in the preparation of hydrogen bromide or hydrogen iodide?***

As we have seen in the previous section, both HBr and HI are capable of reacting with concentrated H_2SO_4 due to their high reducing power so the reaction will not end with either HBr or HI as intended.

- **For preparation of HBr, the following reactions occur:**

$$NaBr + H_2SO_4(conc) \rightarrow NaHSO_4 + HBr \text{……………………..(i)}$$

Then $2HBr + H_2SO_4(conc) \rightarrow Br_2 + SO_2 + 2H_2O$ ………………..(ii)

Overall reaction equation: Take 2(i) + (ii) and simplify,

$$2NaBr + 3H_2SO_4(conc) \rightarrow 2NaHSO_4 + Br_2 + SO_2 + 2H_2O$$

If NaBr present in excess, Na_2SO_4 is formed and not $NaHSO_4$ as per equation;

$$2NaBr + 2H_2SO_4(conc) \rightarrow Na_2SO_4 + Br_2 + SO_2 + 2H_2O$$

- Thus no HBr! The HBr which would be formed has been oxidised by concentrated H_2SO_4 to Br_2.
- **For preparation of HI, the following reactions occur:**

$$NaI + H_2SO_4(conc) \rightarrow NaHSO_4 + HI \text{………………………………………(i)}$$

Then $8HI + H_2SO_4(conc) \rightarrow 4I_2 + H_2S + 4H_2O$ ………………………………………(ii)

Overall reaction equation: Eliminate HI by taking 8(i) + (ii) and simplify to get,

$$8NaI + 9H_2SO_4(conc) \rightarrow 8NaHSO_4 + 4I_2 + H_2S + 4H_2O$$

Or in excess NaI;

$$8NaI + 5H_2SO_4(conc) \rightarrow 4Na_2SO_4 + 4I_2 + H_2S + 4H_2O$$

Again no HI! The HI which would be formed has been oxidised by concentrated H_2SO_4 to I_2.

So………………? ***If we cannot prepare HBr and HI by above method, how do we solve the problem?***

To overcome the problem, the concentrated phosphoric (V) acid is employed instead of concentrated sulphuric because the phosphoric (V) acid is not an oxidising agent.

That is $NaBr + H_3PO_4(conc) \rightarrow NaH_2PO_4 + HBr$

Then $HBr + H_3PO_4\ (conc) \rightarrow$ No reaction

And $NaI + H_3PO_4\ (conc) \rightarrow NaH_2PO_4 + HI$

Then $HI + H_3PO_4\ (conc) \rightarrow$ No reaction

Inter – halogen compounds

Halogens have a tendency of combining among themselves to form compounds which are called **inter-halogen compounds.**

- In forming inter-halogen compound, a large atom acts as central atom while small atoms become outer atoms. The common coordination numbers for the big atom (central atom) are 3 and 5.

For example:

(i) $3F_2 + Cl_2 \rightarrow 2ClF_3$ or $5F_2 + Cl_2 \rightarrow 2ClF_5$

(ii) $3Br_2 + I_2 \rightarrow 2IBr_3$ or $5Br_2 + I_2 \rightarrow 2IBr_5$

IDENTIFYING METAL HALIDES

All metal halides (except for metal fluoride) will react with silver ions in an aqueous solution to form a precipitate of silver halide. The identification is done in the following procedures:

1. Some dilute nitric acid is added to the halide solution to remove any basic impurities like carbonate and hydroxides.

That is $CO_3^{2-}(aq) + 2HNO_3(aq) \rightarrow 2NO_3^-(aq) + CO_2\ (g) + H_2O(l)$

And $OH^-(aq) + HNO_3(aq) \rightarrow NO_3^-(aq) + H_2O(l)$

No ambiguity!

If these impurities ($OH^-$and CO_3^{2-}) remained in the solution, they would react (like halide ions) with silver ions (added in second procedure) to form a precipitate of $AgOH$ or Ag_2CO_3. This would result into ambiguity on the identification of precipitating agent.

- So in one sentence; The introduction of dilute HNO_3 avoids the formation of $AgOH$ and Ag_2CO_3 precipitates which would interfere the experimental result.

2. Silver nitrate solution (which contains silver ions) is added to the halide solution.

- The halide ions will react with silver ions to form insoluble silver halide which appears as a precipitate

$Ag^+(aq) + F^-(aq) \rightarrow AgF\ (s)$ (No precipate)

Soluble

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl\ (s)$ (White precipate)

$Ag^+(aq) + Br^-(aq) \rightarrow AgBr\ (s)$ (Light yellow or creamy precipate)

$Ag^+(aq) + I^-(aq) \rightarrow AgI\ (s)$ (Yellow precipate)

- Colours of the three precipitates of silver halides are similar; it might be difficult to make clear distinction by eyes. To be more sure with the identification; further test is performed by adding aqueous ammonia to the precipitate.
- Silver halide with relative higher degree of ionic characters, will form easily soluble complex with aqueous ammonia and therefore the halide appear to dissolve in aqueous ammonia. Keeping in mind that polarisability of halide ion increases as the anionic radius increases from Cl^- to I^- which in turn makes AgCl to have lowest degree of polarisation and therefore more ionic while AgI behave in opposite to AgCl; observations after adding aqueous ammonia to silver halides will be as follows:

- White precipitate of AgCl dissolves in **dilute** ammonia solution to give clear solution due to formation of soluble complex.

$$AgCl(s) + 2NH_3 \rightarrow \underset{\textbf{Soluble}}{[Ag(NH_3)_2]Cl}$$

Here silver chloride being relatively more ionic has enough concentration of Ag^+ to enable formation of significant amount of the complex.

- Creamy precipitate of AgBr does not dissolve in dilute ammonia solution but dissolves in **concentrated** ammonia solution to give clear solution due to formation of soluble complex.

$$AgBr(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]Br$$

- Yellow precipitate of AgI does not dissolve in both dilute and concentrated ammonia solution.

$$AgI(s) + 2NH_3 \rightarrow \text{No reaction}$$

Here silver iodide being highly covalent in characters has no enough concentration of Ag^+ to enable formation of complex with aqueous ammonia.

CYANIDE ION, CN^- AS PSEUDO HALIDE

If non – halide anion has size which does not differ much to that of halide ions so that the anion resembles to halides in many aspects, the anion is then known as **pseudo halide** (**'pseudo'** comes from Greek word **'pseudes'** meaning **'fake** or **'false'**).

- CN^- is pseudo halide and resembles to halides in the following ways:

(i) Both have an oxidation state of -1

(ii) Both have a high affinity to metals forming salts with them, e.g. $KCN, KCl, NaCN, NaBr$ etc.

(iii) Both act as ligand in complex formation, e.g. $[COF_6]^{3-}$,$[Co(CN)_6]^{3-}$, $[CUCl_4]^{2-}$, $[CU(CN)_4]^{2-}$.

(iv) CN^-form HCN when its salt react with strong acid like halides which gives hydrogen halides with strong acids.

$$KCN + HCl \rightarrow KCl + HCN$$

$$KCl + H_2SO_4(conc) \rightarrow KHSO_4 + HCl$$

$$KBr + H_3PO_4(conc) \rightarrow KH_2PO_4 + HBr$$

(v) CN^- undergo oxidation similar to halide ions

$$2CN^- \rightarrow (CN)_2 + 2e$$

And $2X^- \rightarrow X_2 + 2e$ where X is halogen

(vi) CN^- forms $(CN)_2$ which undergo disproportionation in alkaline medium like the halogens (formed after oxidation of halide ions)

$$(CN)_2 + 2OH^- \rightarrow CN^- + OCN^- + H_2O$$

$$X_2 + 2OH^- \rightarrow X^- + OX^- + H_2O$$

(vii) The CN^- forms precipitates with $Ag^+(aq)$ and $Pb^{2+}(aq)$ like the halide ions

(viii) Their hydride are acidic, i.e. both HCN and HX are acidic

METALIC CHARACTERS OF IODINE

Like in any group, metallic characters increases on descending the group.

- Iodine being at the bottom side of group VIIA has some metallic characters (although it is generally non – metal). Some metallic characters of iodine include:

(i) Iodine is solid of room temperature reflecting its high melting point and boiling point

(ii) Iodine has lustrous structure (it is shiny black)

(iii) Iodine can conduct electricity at temperature just above its melting point

(iv) Iodine can exist as I^+ (unipositive charged cation).

- The compound ICl and ICN when electrolysed using platinum electrode, they give I_2 on the cathode and Cl_2 and $(CN)_2$ on the anode respectively suggesting the following dissociation:

$$ICN \rightarrow I^+ + CN^- \quad \text{and} \quad 2ICl \rightarrow I^+ + ICl^-$$

(v) Iodine can exist as I^{3+} (tripositive charged cation)

- The compounds $(CH_3COO)_3I$ and ICl_3 on being electrolyzed give I_2 on the cathode and CH_3COO^- and Cl_2 respectively on the anode suggesting the following dissociation:

$$(CH_3COO)_3I \rightarrow 3CH_3COO^- + I^{3+} \quad \text{and} \quad ICl_3 \rightarrow I^{3+} + 3Cl^-$$

ANOMALOUS BEHAVIOUR OF FLUORINE

(i) It is the most electronegative and strongest oxidising agent.

(ii) It has fixed oxidation state of -1. Other halogens may have higher oxidation state $(+1, +3, +5, +6, +7)$

(iii) No oxoacid of fluorine exist. Other halogens can have oxoacid of formula, HOX, HXO_2, HXO_3 and HXO_4.

(iv) It combines with silver to form AgF which is ionic and soluble in water. Other halogens form silver halides $(AgCl, AgBr, AgI)$ which are covalent and sparingly soluble

(v) It combines with hydrogen to from HF which has abnormally high boiling point while other halogens form hydrogen halides which have low boiling point.

(vi) It liberates oxygen gas from water while other halogens disproportionate in water.

$$2F_2 + 2H_2O \rightarrow 4HF + O_2$$

$$X_2 + H_2O \rightarrow HOX + HX$$

Where X may be Cl, Br or I

(vii) Dissociation energy of fluorine is unexpectedly low and does not follow the trend of dissociation energy of other halogens.

(viii) It combine with hydrogen to form HF which dissolve in water to give very weak acidic solution while other halogens forms hydrogen halides which dissolve in water to give strong acidic solution.

(ix) It forms neutral oxide (F_2O) while other halogens form acidic oxide.

(x) It liberates oxygen from strong alkaline solution like $NaOH$ and KOH while other halogens disproportionate in the alkaline solution.

PRACTICE EXERCISE 10

Question 1

Give at least one example of compounds of halogens in the following oxidation states:

(i) $+1$ (ii) $+2$ (iii) $+6$ (iv) $+7$

Question 2

Briefly explain the trend of melting and boiling point halogens.

Question 3

Give reasons for highest reactivity of fluorine.

Question 4

Justify the following:

(i) Oxidising power of halogens decreases on descending the halogen group.
(ii) Halogens are good oxidising agents.
(iii) Reducing power of halogens increases on descending the halogen group.
(iv) Among halogens, fluorine is strongest oxidising agent.

Question 5

Unlike other halogens, fluorine liberates oxygen from NaOH. Explain

Question 6

Complete the following reactions:

(i) $\mathrm{Cl_2 + KOH(conc) \rightarrow}$
(ii) $\mathrm{F_2(excess) + H_2O \rightarrow}$
(iii) $\mathrm{I_2O_4 + H_2O \rightarrow}$
(iv) $\mathrm{FCl + H_2O \rightarrow}$

EXAMINATION QUESTIONS FOR PART TWO

Question 1

Solid PCl_5 has unexpectedly high melting point. Explain.

Question 2

HCl can conveniently prepared by the reaction between concentrated sulphuric acid and NaCl but the similar methods cannot be applied for preparing HI. Explain.

Question 3

With help of chemical equations give two properties which show regular trend as you descend the group VII.

Question 4

Hydrochloric acid should not be used as an acidic medium in redox titration of potassium permanganate against iron(II) sulphate. Explain.

Question 5

Concentrated sulphuric acid should not be used to dry hydrogen sulphide gas. Explain.

Question 6

Dilute sulphuric acid has no action on copper but concentrated sulphuric acid reacts readily with the metal. Explain.

Question 7

Concentrated sulphuric acid should not be used in redox titration of potassium permanganate against $FeSO_4$. Explain.

Question 8

Nitric acid attacks metals but aluminium containers are used to transport concentrated nitric acid. Explain.

Question 9

Concentrated nitric acid renders aluminium passive. Explain

Question 10

Explain why temporary hardness can be treated by just heating?

Question 11

When binary compound of Aluminium and carbon is hydrolyzed, methane is formed. Explain.

Question 12

PCl_5 is more reactive than PCl_3. Explain.

Question 13

Magnesium is recovered from sea water by liming. Explain.

Question 14

Pentavalent compounds of phosphorus like PH_5 exist while pentavalent compounds of Nitrogen like NH_5 are not known. Explain.

Question 15

Ammonia has an exceptionally high solubility in water. Explain.

Question 16

Anhydrous magnesium chloride cannot be prepared by just heating its hydrated salt ($MgCl_2.6H_2O$) to remove water of crystallisation. Explain.

Question 17

A reaction between aqueous sodium hydroxide and carbon dioxide gas cannot be used as a chemical test of CO_2. Explain.

Question 18

Explain what will you observe when carbon dioxide is added to a beaker containing solution of calcium hydroxide.

Question 19

Complete and balance the following reactions:

(i) $NO_2(g) + H_2O(l) \rightarrow$

(ii) $Co(s) + H_2O(g) \rightarrow$

(iii) $Na_2O(s) + H_2O(g) \rightarrow$

(iv) $Rb_2O_2 + H_2O(l) \rightarrow$

Question 20

On heating hydrated Barium chloride($BaCl_2.2H_2O$) gives anhydrous barium chloride while hydrated magnesium chloride ($MgCl_2.6H_2O$) gives basic magnesium chloride ($Mg(OH)Cl$) and hydrogen chloride (HCl) gas. Explain.

Question 21

Explain what you will observe when concentrated hydrochloric acid is added to a beaker containing solution of lead (II) chloride.

Question 22

Arrange the following compounds: HF, HCl, HI and HBr in order of:

(i) Increasing boiling point.

(ii) Increasing acidic strength starting with the strongest acid.

Question 23

Aluminium chloride is a good Lewis acid. Explain.

Question 24

Copper metal resists attack by both dilute sulphuric acid and hydrochloric acid, but reacts with dilute nitric acid. Explain.

Question 25

Complete and balance the following equations:

(i)$Li_3N(s) + HCl(aq) \longrightarrow$ (iii) $Rb_2O(s) + H_2O(l) \longrightarrow$

(ii) $NaH(s) + H_2O(l) \longrightarrow$ (iv) $Cs_2O_2(s) + H_2O(l) \longrightarrow$

Question 26

Comment, with the help of chemical equations where necessary, on the following concepts: Iron (II) chloride cannot be prepared by heating iron fillings in a stream of chlorine gas.

Question 27

With Chromium, fluorine form CrF_6 while chlorine does not. Explain.

Question 28

Explain why iodine is sparingly soluble in water but readily soluble in a concentrated solution of potassium iodide.

Question 29

Give an account for the following facts: Alkali earth metals have greater tendency to form complexes than alkali metals.

Question 30

Give an account for this statement: Magnesium does not impart any colour to the flame while calcium in the same group does.

Question 31

Melting and boiling points of alkaline earth metals are higher than those of alkali metals. Give an account for this.

Question 32

Hard water becomes soft when washing soda ($Na_2CO_3.10H_2O$) is added. Explain.

Question 33

Mercury (II) iodide is readily soluble in potassium iodide solution but not in water. Explain.

Question 34

When water is sprayed into dry mixture of sulphur dioxide and hydrogen sulphide, a yellow solid is formed. Explain.

Question 35

Effervescence of colourless gas is obtained when ammonium chloride solution is added to a warm aqueous solution of sodium nitrite. Explain.

Question 36

What happens when solid ammonium chloride is heated?

Question 37

Calcium carbonate is insoluble in water but dissolves in the presence of dissolved carbon dioxide. Explain.

Question 38

Write a balanced chemical equation and expected observation when dilute hydrochloric acid is added to powder egg shells.

Question 39

Unlike other halogens, fluorine liberates oxygen from cold water. Explain.

Question 40

Write the chemical formula for the following:

(i) Iodic (VII) acid dihydrate

(ii) Bromic acid

(iii) Perbromic acid

Question 41

The cyano (CN^-) has about the same size as Br^-. Hence CN^- is pseudo halide, resembling the halide in many aspects. List five ways in which cyanide ion resembles halide ions.

Question 42

Write a balanced chemical equation and expected observation when magnesium nitride is dissolved in water.

Question 43

Aluminium metal does not react with hot water or steam. Explain.

Question 44

What will you observe when chlorine gas is bubbled through a beaker containing solution of NaBr.

Question 45

Explain what happens when chlorine is introduced into solution containing iodide ions (I^-)

Question 46

Consider the series of elements of period 3 in the periodic table:

Na, Mg, Al, Si, P, S and Cl, which one has the:

(i)smallest ionisation energy?(ii)highest metallic character?(iii)highest non-metallic character?(iv)smallest electronegativity?(v)highest melting point?

Question 47

Account for the following chemical phenomena; Alkali metals are good reducing agents.

Question 48

The elements of group IA of the periodic table form a well marked family of closely related elements. By choosing four chemical properties briefly justify this comment.

Question 49

Write equations to summarize the following reactions

i. $\text{sodium hydride} + \text{water} \longrightarrow$
ii. $\text{phosphine} + \text{water} \longrightarrow$
iii. $\text{magnesium nitride} + \text{water} \longrightarrow$

Question 50

(i) If element A is a very strong reducing agent and element B is a very strong oxidising agent, then explain giving reasons which of the two elements has smaller atomic radius.

(ii) Element Q and R have the following first electron affinities, $+575\text{kJ/mol}$ and -364kJ/mol respectively. With reasons state which element has higher reducing power than the other.

Question 51

Suggest an explanation for each of the following statement

i. Only lithium reacts with nitrogen to form nitride
ii. On heating, lithium nitrate forms an oxide whereas the nitrates of other metals in group IA form nitrites
iii. Lithium form only one oxide whereas each of the other alkali metals form at least two oxides

Question 52

Explain the following:

(i) Sulphur has higher boiling point than phosphorous.
(ii) Phosphorous has higher boiling point than chlorine.
(iii) HF is liquid while other hydrogen halides are gases.
(iv) F_2 and Cl_2 are gases, Br_2 is liquid, I_2 is solid.

PART THREE

EXTRACTION OF METALS

Chapter 11

INTRODUCTION TO EXTRACTION OF METALS

Metals occur in nature sometimes in **free** or **native state** or in most cases in the form of chemical combination, in their compounds which are associated with impurities. The natural material in which the metal or their compounds occur in the earth is known as mineral. Thus **a mineral** *is a naturally occurring material present in earth's crust which contains metal in free state* or *in combined state*.

A mineral may contain few or many earthy impurities. When a mineral contains sufficient amount of a metal in combined state, from which it can be readily and profitably separated on commercial scale, then the mineral is said to be an **ore** of the metal.

Thus **ore** *is a chosen* ***mineral*** *of a metal, from which metal is extracted profitably on a large scale, in pure form.*

So you will be correct if you will say that; all ores are minerals, but all minerals are not ores.

- For example, **clay** and **bauxite** are two minerals of aluminium, but aluminium, can be profitably extracted only from bauxite and not from the clay. Hence bauxite is an ore of aluminium, while clay is just a mineral.
- You should be aware with the fact that, the two terms; ore and minerals have very little difference in their meaning and people commonly use the two interchangeably. However that does not eliminate the little difference between the two terms.

Generally the ores can be:

(i) **Sulphide ores** like CuS (Copper sulphide), PbS (Galena) and HgS (Cinnabar)
(ii) **Carbonate ores** like $CaCO_3$ and $PbCO_3$
(iii) **Oxide ores** like Fe_2O_3(Haematite), and $Al_2O_3.2H_2O$ (Bauxite)

Extraction of metal *is the process of obtaining pure metal from its* ***ore***. It has subtle difference to **metallurgy** which *is the entire operation, involving all the physical and chemical processes in the extraction of metal from its ore.*

GENERAL STEPS IN EXTRACTION OF METALS

Generally extraction of metals involves the following common stages:

(i) **Mining** and **concentration** of the ore.

(ii) **Conversion of concentrated ore into their metallic oxide (roasting/calcination)**

(iii) **Reduction** of the metal compound to the metal

(iv) **Purification (Refining)** of the metal.

Concentration of the ore

The ore is generally associated with rock impurities like clay, sand etc. These impurities are called **gangue**. In the **concentration of the ore** or **ore dressing** gangue are removed as much as possible so as to get almost pure ore. Thus the percentage of pure ore in the concentrated ore is larger than that in the original ore.

Concentrating the ore *simply means getting rid of as much of the unwanted rocky material (impurities) as possible before the ore is converted into the metal.*

In some cases this is done **chemically**, for example:

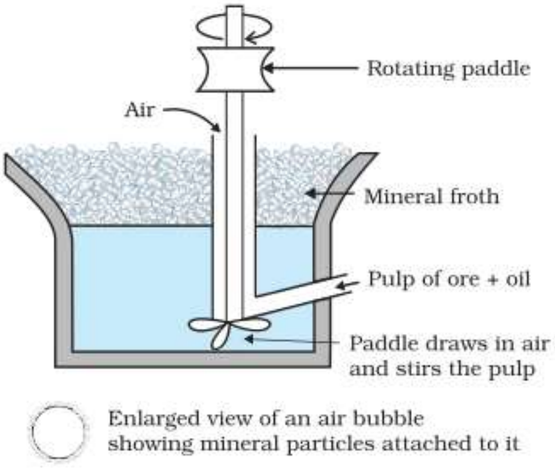
- Pure aluminium oxide is obtained from the aluminium chief ore (bauxite) by a process involving a reaction with sodium hydroxide.

- Some copper ores can be converted into copper (II) sulphate solution by leaving the crushed ore in contact with dilute sulphuric acid for long time. Copper can then be extracted from the copper (II) sulphate solution.

In many cases, it is possible to separate the metal compound from unwanted rocky material (impurities) by **physical means**. Depending on the ore, different physical methods of concentration are used. They include:

- **Gravity separation process** or **hydraulic washing:** This method is especially suitable for heavy 'oxide' ores like haematite (ore of iron), tinstone (ore of tin), etc. In this, the powdered ore is placed on a sloping floor (or platform) and washed by directing on it a strong current of water. The lighter sandy and earthy impurities are washed away; while the heavier ore particles are left behind.
- **Magnetic separation:** This method is meant for separating magnetic impurities from nonmagnetic ore particles, e.g., tinstone (a tin ore) in which tinstone is non- magnetic; while impurities iron, manganese and tungstates are magnetic.

- **Froth floatation:** This method is used to extract sulphide ores. The ore is first crushed and then treated with something will bind to the particles of the metal compound that you want and make those particles insoluble in water. **Pine oil** is often used for this purpose; it binds to the sulphide ore particles, but not the impurities (unwanted rocky material). The powdered ore (treated with pine oil) is then added to the tank containing water and a foaming agent (a soap or detergent of some kind), and air is blown through the mixture to make a lot of bubbles. Because they are water – repellent (insoluble), the coated particles of the metal sulphide tend to be picked up by the air bubbles, float to the top of the tank, and rest of the impurities stay in the tank.



Froth flotation process is especially suitable for sulphide ores like zinc blende (ZnS), and copper pyrites ($CuFeS_2$). This process is based on the fact that the sulphide ore particles are only moistened by oil; while those of oxide, and other earthy impurities are moistened only by water.

Conversion of the concentrated ores into their metallic oxides

Ore containing sulphides or carbonates are converted to oxide ores because it is easier to reduce oxide of the metal than the sulphide or carbonate and hence it becomes easier extract metals from oxides rather than directly from the sulphides or carbonates. The methods of conversion are:

1. **Roasting:** In this process, the metal ore is heated in the presence of air. The method applies for ores containing sulphide.

$$\mathrm{Cu_2S + O_2 \underset{\Delta}{\rightarrow} 2Cu_2O + 2SO_2}$$

2. **Calcination:** When the ores are heated in the absence of air, the process is known as calcination. This is used only for carbonate ores.

$$\mathrm{CaCO_3 \underset{\Delta}{\rightarrow} CaO + CO_2}$$

$$\mathrm{PbCO_3 \underset{\Delta}{\rightarrow} PbO + CO_2}$$

$$\mathrm{ZnCO_3 \underset{\Delta}{\rightarrow} ZnO + CO_2}$$

Reduction

In this step, the metal compound is reduced to get the metal.

- There are various types of reduction processes involved in the extraction of metal. This includes:

1. **Chemical reduction of oxide by using carbon as coke or charcoal**

- For example, zinc is obtained from ZnO by reducing with coke.

2. **Chemical reduction of oxide by carbon monoxide, CO gas**

- For example, iron is obtained from $\mathrm{Fe_2O_3}$ reducing it by CO gas.

3. **Chemical reduction by using a more reactive metal (thermite process)**

- For example chromium is produced by reducing $\mathrm{Cr_2O_3}$ using a more reactive metal, aluminium.

4. **Self reduction (Auto reduction)**

- For example in copper extraction;

$$\mathrm{Cu_2S(s) + \ 2Cu_2O(s) \longrightarrow 6Cu(s) + \ SO_2(g)}$$

5. **Electrolytic reduction**

- It used in extraction of very active metal (e.g. $\mathrm{K, Na, Ca, Mg}$ and Al) by electrolysing their fused compounds like chlorides and oxides.

- It is the **strongest method of reduction** of the five.

Purification of the metal

This can be done various ways, for example through **electrolysis refinery process.**

GANGUE, FLUX AND SLAG

Gangue *is the term used for all the earthy impurities associated with the ore of the metal.*

- These need to be removed in the extraction. For example **in iron ore, sand (SiO_2) is the main gangue.**

Flux *refers to the compound added during extraction, which reacts with a non fusible (high melting point) gangue and form a fusible (molten) product called **slag.***

- The slag (molten substance) can then be removed by simple physical methods.

The term **'slag'**, *refers to the easily fusible product formed between gangue and flux.*

To have better understanding of the three terms consider the following example:

- In the blast furnace for extraction of iron, the limestone $CaCO_3$ is added. This decompose to give the flux, CaO (a basic oxide) which reacts with sand, SiO_2 (gangue – acidic oxide) and forms a fusible slag, $CaCO_3$

$$\underset{\textbf{Gangue}}{SiO_2} + \underset{\textbf{Flux}}{CaO} \longrightarrow \underset{\textbf{Slag}}{CaSiO_3}$$

(Note: SiO_2 is acidic oxide while CaO is basic oxide. So the above reaction is acid-base reaction).

ROASTING VERSUS CALCINATION

Roasting is a chemical process where a sulphide ore is strongly heated in a current of oxygen gas (air) to oxidise the ore. It occurs at higher temperature, higher than the melting point of the ore.

Calcination *is heating of the ore, in absence of air to decompose it or drive (remove) volatile matter.* It occurs at temperature lower than the melting point of the ore.

For example:

Roasting: $2ZnS + 3O_2 \underset{\Delta}{\rightarrow} 2ZnO + 2SO_2$

Calcination: $ZnCO_3 \underset{\Delta}{\rightarrow} ZnO + CO_2 \uparrow$

The two processes are similar in the manner that: **they both change the ore to become porous for easy reduction.**

Differences between roasting and calcinations are summarised in the table below:

	ROASTING		**CALCINATION**
01	The ore is heated in presence of air	01	The ore is heated in absence of air
02	It occurs at temperatures, higher than melting point of the ore	02	It occurs at temperatures lower than the melting point of the ore
03	It is oxidation reaction	03	In most cases, it is decomposition reaction
04	It applies for sulphide ore only	04	It applies in various king of ore e.g. carbonates, hydrated oxides etc.

RELATIONSHIP BETWEEN MODE OF EXTRACTION AND THE POSITION IN THE ELECTROCHEMICAL SERIES

- At the top most part of the electrochemical series, metals are extracted by electrolysis of their fused (molten) salt (as these metals are very powerful reducing agents, common reductants are useless!). For example, extraction of aluminium from bauxite.
- On descending the series, extraction by **thermite process** is used. For example, extraction of chromium and manganese whereby aluminium is always used for the reduction.
- Lower down the series, extraction by normal reducing agent is possible. The reductants include carbon (C), carbon monoxide (CO) and hydrogen gas (H_2). For example, extraction of Cu, Ni, Fe, Zn and Pb.

However ***hydrogen gas is not commonly used in the process, why?***

This is simply because hydrogen gas is **expensive** and **explosive with air** to give water vapour.

- At the bottom most part of the series, metals are least reactive so that they have very low tendency of combining with other elements to make compounds.

\- So it is possible to find the metals free in nature. For example, extraction of mercury (Hg), Gold (Au) and silver (Ag).

Relationship between the mode of extraction and the periodic table

Groups IA to group IIIA are extracted by electrolysis (not simple reduction) of their fused chlorides.

\- Here we have three important questions to ask ourselves!

(i) **Why not by simple reduction?**
(ii) **Why chlorides?**
(iii) **Why fused?**

Why not by reduction?

There are three reasons for this:

1. Because groups IA to IIIA metals are stronger reductants than the common reductants used like carbon (coke) and carbon monoxide.
2. Being very reactive, the metals (of group IA to group IIIA) would react with some of the reductants. For example aluminium react with carbon to form aluminium carbide.
3. Even if reduction was possible e.g. by carbon, it would require very large amount of energy and therefore would be uneconomical.

Why chlorides?

There are also three reasons for this:

1. The chlorides have relatively low melting point and therefore they can easily be melted (fused).
2. The chlorides are highly ionic and can easily be electrolysed as they have low discharge potentials.
3. The chlorides are purest (can be crystallised in the purest form).

Why fused?

This is because, if would be aqueous chlorides, H^+ would be discharged in preference to the metal (H^+ has lower discharge potential than the metals of group IA to IIA).

SIDE EFFECTS OF EXTRACTION OF METALS IN THE ENVIRONMENT

Extraction of metals causes various environmental problems in mining and transporting the raw materials and processing them. The problems include:

(i) Loss of landscape

- This is due to mining, processing, transporting and the size of plant needed.

(ii) Atmospheric pollution

- This includes greenhouse effect and acid rain involved in these operations.

(iii) Disposal of unwanted material

- This may cause serious health hazard because some material are poisonous.
- The disposal also cause water pollution

(iv) Noise pollution

- This results from transportation of ore, operation of the plant and transportation of finished metal.

Advantages of recycling over extraction of metals

Some metals like iron, aluminium and copper can be recycled. This has various more advantages than if the used metals would be disposed and continue depending on extraction of fresh metals only. Some advantages include.

(i) Saving of raw material and energy by not having to first extract the metal from its ore

(ii) Avoiding the pollution problems in the extraction of the metal from its ore

(iii) It overcome a problem of not having enough space to dump the used or unwanted metal if it would not recycled

(iv) Offsetting (although to minor extent) energy and pollution costs in collecting and transporting the recycled metal.

PRACTICE EXERCISE 11

Question 1

Differentiate the following terms:

(i) Extraction of metal and metallurgy
(ii) Ore and mineral
(iii) Roasting and calcinations

Question 2

Outline five ways of reducing metal compound to get the metal

Question 3

(a) Define the following terms:
  (i) Gangue
  (ii) Flux
  (iii) Slag
(b) How the three terms define in (a) above are related?

Question 4

Why metals which are found in the top of electrochemical series, are extracted by electrolysis?

Question 5

Why hydrogen is not commonly used in the process of reducing metal compound into metal?

Chapter 12

EXTRACTION OF SELECTED METALS

EXTRACTION OF ALUMINIUM

Chief ore

The usual aluminium ore is **bauxite**

- Bauxite is hydrated aluminium oxide, $Al_2O_3.XH_2O$ where X is 2 or 3
- The ore is always contaminated with iron oxides, silicon dioxide (SiO_2) and titanium dioxide (TiO_2)

Other ores include:

- **Corundum,** Al_2O_3
- **Cryolite**, $Na_3[AlF_6]$

Concentration of ore – the Bayer process

This is done by **chemical means**. Crushed bauxite is treated with moderately concentrated sodium hydroxide solution of temperature range of 140°C to 240°C and pressure of about 35 atmospheres.

- *High pressure is necessary to keep the water in the sodium hydroxide solution liquid at temperature above 100°C.*
- With the hydroxide, only Al_2O_3 and SiO_2 will react. Other impurities will remain unreacted at solid state.

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \xrightarrow[3VAtm]{140^oC-240^oC} 2Na[Al(OH)_4]$$

$$SiO_2(s) + 2NaOH(aq) \longrightarrow Na_2SiO_3(aq) + H_2O(l)$$

(i) The mixture is then filtered

- **Filtrate** is the mixture of Na_2SiO_3 and $Na[Al(OH)_4]$
- **Residue** are other impurities (oxides of iron and TiO_2)

(ii) Separating the mixture of $Na[Al(OH)_4]$ and Na_2SiO_3

This is done by adding $CO_2(g)$

- $2Na[Al(OH)_4]\,(aq) + CO_2(g) \longrightarrow 2Al(OH)_3\,(s) + Na_2CO_3\,(aq) + H_2O(l)$
- Na_2SiO_3 does not react
- The mixture is then filtered to get residue and filtrate

- The residue is $Al(OH)_3$
- The filtrate is Na_2SiO_3 (and of course Na_2CO_3 formed in the above reaction).

(iii) Regeneration of Al_2O_3

This is simply done by heating $Al(OH)_3$ whereby the hydroxide undergo thermal decomposition

$$2Al(OH)_3\,(s) \underset{\Delta}{\rightarrow} \underset{\textbf{Pure}}{Al_2O_3(s)} + 3H_2O(g)$$

Electrolysis

Al_2O_3 is dissolved in molten cryolite ($Na_3[AlF_6]$) and electrolysed by using **carbon (graphite) electrodes.** The pure aluminium (Al) is obtained at cathode.

- At cathode: $Al^{3+} + 3e \rightarrow Al(s)$………………………………..(i)
- At anode: $2O^{2-} \rightarrow O_2(g) + 2e$……………………………….(ii)

It should be noted that:

- **The anodes used in the electrolytic cell must be constantly replaced** because oxygen gas is produced by the discharge of oxide ions at the graphite (carbon) anodes.

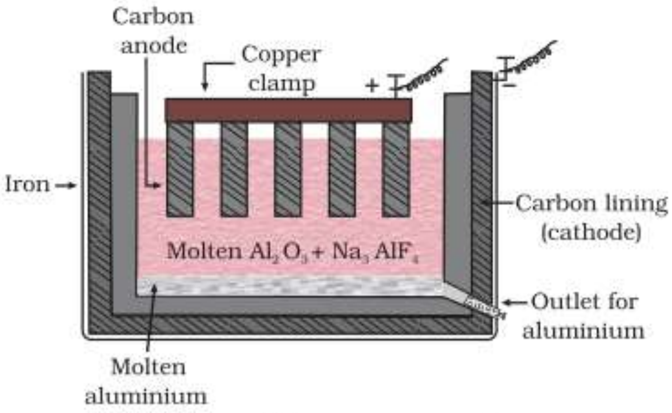
- The oxygen gas oxidises carbon (graphite) anodes to carbon dioxide and so they have to be replaced.

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

- **Al_2O_3 is not always used in electrolysis on its own without dissolving in the cryolite, $Na_3[AlF_6]$** due to the following reasons:

(i) Aluminium oxide has too high melting point (2045°C) to be used on its own, when mixed with cryolite, the melting point is lowered to about 900°C.

(ii) Even if it would be possible to get molten Al_2O_3 at such high temperature, the oxide has considerable (significant) covalent tendencies and would not conduct electricity well.



Electrolytic cell for extraction of aluminium

Uses of aluminium in relation to its properties

(i) **Low density and strength** make aluminium ideal for construction of aircraft, lightweight vehicles, and ladders.

(ii) **Easy shaping and corrosion resistance** make aluminium a good material for drink cans and roofing materials.

(iii) **Corrosion resistance and low density** leads to its use for greenhouses and window frames.

(iv) **Good conduction of heat** leads to its use for boilers, cookers and cookware.

(v) **Good conduction of electricity** leads to its use for overhead power cables hung from pylons *(low density gives it an advantage over copper).*

(vi) **High reflectivity** makes aluminium ideal for mirrors, reflectors and heat resistant clothing for fire fighting.

EXTRACTION OF COPPER

Chief ore

This is **copper pyrites, $CuFeS_2$**

Other ores include:

Copper Glance, Cu_2S

Malachite, $2CuCO_3.Cu(OH)_2$

Concentration of the ore

This is done by **froth floatation** (by using **pine oil** as explained earlier)

Roasting

The concentration ore is heated in a limited supply of air where the following reactions occur.

(i) $2Cu\,FeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$

(ii) $2Cu\,FeS_2 + 4O_2 \rightarrow Cu_2S + 2FeO + 3SO_2$

The roasted product is then mixed with limited supply of air and heated.

- Conversion of iron (II) sulphide, FeS into iron (II) oxide, FeO occur and some of the copper (I) sulphide, Cu_2S are conversed into Cu_2O

That is $2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$

And $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

The mixture is now consisting of FeO, Cu_2O and unreacted Cu_2S.

Smelting

To remove FeO from the mixture, the mixture product is mixed with SiO_2 and heated strongly, the slag of $FeSiO_3$ is formed which is removed (poured out) easily from the mixture

$$FeO + SiO_2 \underset{\Delta}{\rightarrow} FeSiO_3(slag)$$

- Cu_2O and Cu_2S do not react

Reduction

Auto – reduction between Cu_2S and Cu_2O occurs.

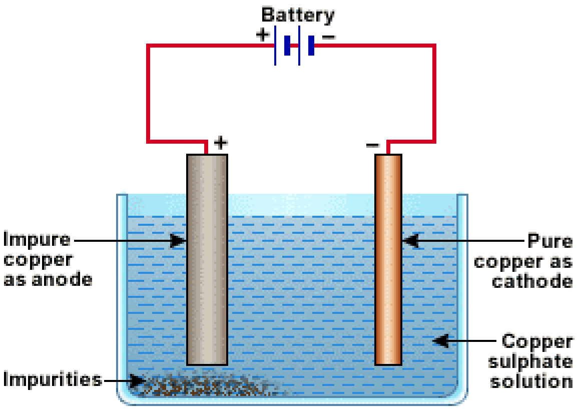
$$Cu_2S + 2Cu_2O \rightarrow 6Cu(s) + SO_2$$

− Copper formed in the auto-reduction, is known as **blister copper**.

Purification

This is done by **electrolysis refinery process** where impure copper is made the anode and pure copper is made the cathode

- The **electrolyte used is solution of copper (II) sulphate, $CuSO_4$(aq) acidified with dilute sulphuric acid H_2SO_4**.



Experimental set up for the electrolytic refining of copper.

Electrode reactions

At the cathode, copper(II) ions (Cu^{2+}) are deposited as copper metal.

$$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$$

At the anode, copper goes into solution as copper(II) ions (Cu^{2+})

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e$$

For every copper ion that is deposited at the cathode, in principle another one goes into solution at the anode. The concentration of the solution should stay the same.

- That means there is a transfer of copper from the anode to the cathode. The cathode gets bigger as more and more pure copper is deposited; the anode gradually disappears.

In practice, it isn't quite as simple as that because of the impurities involved.

What happens to the impurities?

Any metal in the impure anode that is below copper in the electrochemical series (reactivity series) doesn't go into solution as ions. It stays as a metal and falls to the bottom of the cell as an "anode sludge", together with any unreactive material left over from the ore. The anode sludge will contain valuable metals such as silver and gold.

Uses of copper

- **Copper is used to pipe water supplies.** The metal is also used in **refrigerators and air conditioning systems.**
- **Computer heat sinks** are made out of copper as copper is able to absorb a high amount of heat.
- **Magnetrons,** found in microwave ovens, contain copper.
- **Vacuum tubes and cathode ray tubes** both use copper.
- Some copper is added to **fungicides and nutritional supplements.**
- As a good conductor of electricity, copper is used in **copper wire, electromagnets and electrical relays and switches.**
- Copper is a great **water-proof roofing material**. It has been used for this purpose since ancient times.
- Copper is sometimes combined with nickel to make a **corrosion resistant material that is used in shipbuilding.**
- Copper is used in **lightning rods.** These attract lightning and cause the electrical current to be dispersed rather than striking, and possibly destroying, a more important structure.

- Copper(II) sulphate is used to **kill mildew**.
- Copper is often used to **colour glass**. It is also one component of ceramic glaze.
- Many **musical instruments,** particularly brass instruments, are made out of copper.

EXTRACTION OF TIN

Chief ore

This is **Cassiterite** (**tinstone**), SnO_2

Concentration of ore

The powdered tin stone is concentrated by gravity separation through washing with running water, which removes lighter siliceous (silicon containing) matter and the magnetic impurities like wolframite (consisting of iron and manganese tungstate) are separated from tin stone by magnetic separators.

Roasting of the ore

The concentrated ore is heated in a current of air when impurities like sulphur and Arsenic are removed as volatile SO_2 and As_2O_3. Iron and copper pyrites change to their oxides and sulphates.

Leaching and washing

The roasted ore is treated with water when $CuSO_4$ and $FeSO_4$ are washed away from the main ore. Further lighter ferric oxide is washed away leaving behind heavier ore particles known as **black tin** (SnO_2) containing 60 to 70% tin.

Smelting

Black tin is mixed with carbon and smelted in a **reverberatory furnace**. The ore is reduced to tin while SiO_2 is removed as slag.

$$SnO_2 + 2C \xrightarrow[1200℃]{} Sn + 2CO$$

$$CaCO_3 \xrightarrow[\Delta]{} CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow CaSiO_3(\text{slag})$$

Molten metal is cast into blocks. It is known as **block tin** and contains about 99.5% of metallic tin.

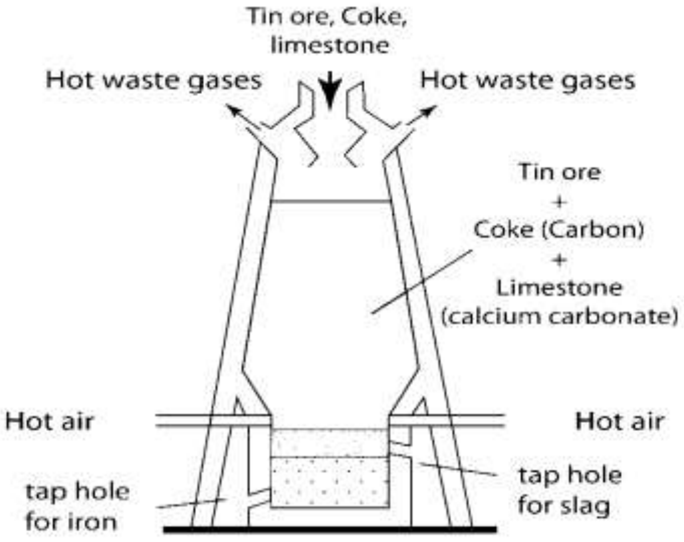


Figure: Reverberatory furnace

Purification

The metal is purified by:

- **Liquation**

The easily fusible tin melts away and less fusible impurities are left behind.

- **Electrolytic refining**

In this method, **impure tin is made anode** and a thin sheet of **pure tin is made the cathode**. Electrolyte consists of H_2SiF_6, tin sulphate and sulphuric acid.

- On passing current, **tin is dissolved from anode and gets deposited on the cathode**.
- Electrolytic method is applied for the need of obtaining tin with very high purity.

EXTRACTION OF OTHER METALS

In this part we are going to discuss extraction of some metals which although they are not mentioned in the current syllabus, you will find very useful to understand them.

EXTRACTION OF IRON

Chief ore

This is the **haematite $\mathbf{Fe_2O_3}$**

Other ores are:

- Siderite, $FeCO_3$
- Iron pyrites, FeS_2
- Magnetite, Fe_3O_4

It should be noted that:

Due to its many uses and large need, even minerals of iron with lower percentage of the metal like siderite, iron pyrites and magnetite are used in extraction of the metal and hence also they become useful ores of iron.

Concentration of ore

This can be done by a **magnet.**

- After the ores have been grinded, washed with water, they are passed into a large magnetic field whereby compounds of iron being paramagnetic are attracted towards the metal.

Roasting and calcination of the ore

The **concentrated sulphide ore (iron pyrites)** is heated in excess of air to give Fe_2O_3

$$\underset{\textbf{Iron pyrite}}{4FeS_2} + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

(Note: In limited supply of air, FeO is formed instead of Fe_2O_3)

The concentrated carbonate ore (siderite, $FeCO_3$) is calcinated to give Fe_2O_3 after treating the product with oxygen gas (from air).

That is $FeCO_3(s) \underset{\Delta}{\rightarrow} FeO(s) + CO_2(s)$

Then $4FeO(s) + O_2(g) \rightarrow 2Fe_2O_3(s)$

It should be noted that:

Roasting is useful if the ore is iron pyrite and calcination is useful for siderite. So if you are restricted to use iron pyrite only, the calcination stage does not appear and if you are asked to use siderite only, the roasting stage does not appear.

Smelting-reduction

The calcinated and roasted products are fed in the blast furnace with coke (carbon), $CaCO_3$ and SiO_2 (SiO_2 present as an impurity in the ore).

- The following reaction takes place:

(i) $2C(s) + O_2(g \longrightarrow) 2CO(g)$ (Reductant)

(ii) $CaCO_3(s) \underset{\Delta}{\rightarrow} CaO(s) + CO_2(g)$

(iii) $CaO(s) + SiO_2(s) \rightarrow CaSiO_3(s)(slag)$

- So the impurity, SiO_2 being acidic oxide reacts with the basic oxide, CaO (CaO is the product of thermal decomposition of the limestone, $CaCO_3$) to form molten calcium silicate, $CaSiO_3$ which is easily removed from the blast furnace as slag.
- The molten slag forms a layer above the molten iron and it has two purposes:

1. It forms a layer above molten iron, so it prevents the iron from getting oxidised to iron oxide.
2. The formation of slag removes the impurity silicon dioxide.

(iv) Fe_2O_3 is reduced by CO(g)

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(molten) + 3CO_2(g)$$

(v) Fe_3O_4 (magnetite) is reduced by carbon (coke)

$$Fe_2O_4(s) + 4C(s) \rightarrow 3Fe(molten) + 4CO(g)$$

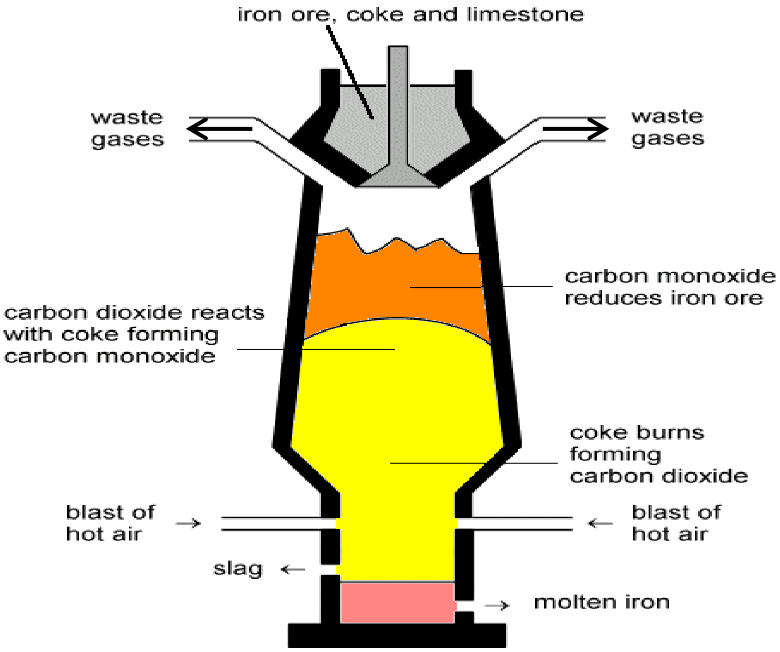


Figure: Blast furnace for extraction of iron

Types of Iron

Pig Iron

This is the iron produced in the blast furnace. It is the cheapest form of iron. It has impurities such as Si, P and S.

- Hard, brittle
- Not malleable and ductile
- Gets rusted easily
- Can be melted and made into *cast iron*.

Wrought iron

It is the purest form of iron. It has 0.2% carbon. It is manufactured by heating pig iron with FeO.

- Stronger than pig iron
- Malleable and ductile

Steel

An alloy of iron (interstitial compound) containing 0.5% to 1.5% carbon. Steel is tough and hard, malleable and ductile. By adding nickel and chromium, **stainless steel** is obtained.

EXTRACTION OF LEAD

Chief ore

This is **galena**, **PbS**

Other ores include:

Cerussite, $PbCO_3$

Anglesite, $PbSO_4$

Concentration of the ore

This is done by **froth floatation**.

Roasting

The concentrated ore is heated in air where different products (PbO and $PbSO_4$) are formed depending the relative concentration of the ore and air (oxygen)

(i) $2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$

(ii) $PbS(s) + 2O_2(g) \rightarrow PbSO_4(s)$

Smelting

Conversion of $PbSO_4$ into PbO is done by heating the roasted product in the presence of $CaCO_3$ and SiO_2.

The following reaction occurs:

(i) $CaCO_3(s) \underset{\Delta}{\rightarrow} CaO(s) + CO_2(g)$

(ii) $PbSO_4(s) + SiO_2(g) \rightarrow SO_3(g) + PbSiO_3(s)$

(iii) $PbSiO_3(s) + CaO(s) \rightarrow CaSiO_3(slag) + PbO(s)$

(iv) $CaO(s) + SiO_2(s) \rightarrow CaSiO_3(slag)$

Reduction

The smelted product is mixed with carbon (coke) in a limited supply of air and then heated.

- Reduction by C, CO and auto reduction also occurs.
  (i) $PbO(s) + C(s) \rightarrow Pb(s) + CO(g)$
  (ii) $PbO(s) + CO(s) \rightarrow Pb(s) + CO_2(g)$
  (iii) $2PbO(s) + PbS(s) \rightarrow 3Pb(s) + SO_2(g)$……………auto reduction

Refinery (purification)

This is done by electrolysis where impure lead (Pb) is made the anode and pure lead is made the cathode

- Here the **electrolyte is the mixture of $Pb[SiF_6]$ and $H_2[SiF_6]$**
  - At the anode: $Pb(s) \rightarrow Pb^{2+} + 2e$
  - At the cathode: $Pb^{2+} + 2e \rightarrow Pb(s)$

Hearth hazards of lead

Exposure to lead or having the increased level of lead in the body, may lead to serious health hazards. *The medical conditions caused by increased level of the heavy metal, lead in the body are known as* ***lead poisoning*** *or* ***plumbism***. Below are some health problems which are caused by lead poisoning.

(i) Renal system

Kidney damage occurs with exposure of high level of lead

(ii) Cardiovascular system

Lead exposure is associated with high blood pressure and there is a connection between lead exposure and coronary heart diseases and heart rate variability

(iii) Reproductive system

Lead affects both male and female reproductive system

(iv) Nervous system

Lead affects the **peripheral nervous system** and **central nervous system**

- Peripheral nervous system effects are more prominent in adults
- Central nervous system effects are more prominent in children

EXTRACTION OF MANGANESE

Chief ore

This is **pyrolusite, MnO_2**

Other ores of manganese include:

Psilomelane, $(Ba, H_2O)_2Mn_5O_{10}$

Rhodochrosite, $MnCO_3$

Extraction process

- The free metal can be obtained from the ore by reduction with aluminium in **thermite process.**
- It is followed by distillation of manganese in vacuum.

- The reaction between manganese (IV) oxide and finely powdered aluminium is explosive; therefore the oxide is first converted to Mn_3O_4 by heating it strongly in air.

That is $3MnO_2(s) \rightarrow Mn_3O_4(s) + O_2(g)$

Then $3Mn_3O_4(s) + 8Al(s) \rightarrow 4Al_2O_3(s) + 9Mn(s)$

EXTRACTION OF NICKEL

Chief ore

This is **NiS** (**millerite**) contaminated with **$CuFeS_2$ impurity.**

Concentration of the ore

- This is done by **froth floatation.**

Roasting

The concentrated ore is heated in excess of air and the following reactions occur:

(i) $2NiS(s) + 3O_2(g) \rightarrow 2NiO(s) + 2SO_2(g)$

(ii) $CuFeS_2(s) + 3O_2(g) \rightarrow CuO(s) + FeO(s) + 2SO_2(g)$

The mixture is now is consisting of CuO, FeO and NiO

Smelting

The roasted product is mixed with $CaCO_3$ and SiO_2 and heated strongly to form slags which are poured out from the mixture leaving NiO and CuO.

That is $CaCO_3(s) \underset{\Delta}{\rightarrow} CaO + CO_2(g)$

$$\left.\begin{array}{l} FeO + SiO_2 \rightarrow FeSiO_3 \\ CaO + SiO_2 \rightarrow CaSiO_3 \end{array}\right\} \textbf{Slag}$$

Bessemerisation

The smelted product is mixed with dilute sulphuric acid in a Bessemer (container).

- **CuO being more basic than NiO,** reacts according to the following equation:

$CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$

- NiO does not react

The resulting mixture is filtered to get residue and filtrate.

- Residue is NiO(s)
- Filtrate is $CuSO_4(aq)$

Reduction

NiO is reduced to nickel by the reaction with carbon in form of coke (hydrogen gas can also be used).

$NiO + C \rightarrow Ni + CO$

Purification (Mond process)

This is done through complex formation.

- The reduced product is mixed with CO(g) and heated to 50°C

$$\mathrm{Ni(s) + 4CO(g)} \xrightarrow[50°\mathrm{C}]{} \mathrm{[Ni(CO)_4]}$$

- Impurities do not react.
- There after the isolated complex, $\mathrm{[Ni(CO)_4]}$ heated to 150°C to regenerate the nickel.

$$\mathrm{[Ni(CO)_4]} \xrightarrow[150°\mathrm{C}]{} \mathrm{Ni(s) + CO(g)}$$

EXTRACTION OF CHROMIUM BY THERMITE PROCESS

Chief ore

This is the **chromite ore, $\mathbf{FeCr_2O_4}$** which is the **mixed oxide of FeO** and $\mathbf{Cr_2O_3}$

Concentration of the ore

This is done by **froth floatation**

- After grinding the ore and washing it with water to remove earthy materials solution of potassium cyanide, KCN (aq) is added followed by pine oil. The ore is skimmed off.

Formation of $\mathbf{Na_2CrO_4}$

The concentrated ore is mixed with $\mathrm{Na_2CO_3(aq)}$ in presence of $\mathrm{O_2(g)}$ to form $\mathrm{Na_2CrO_4}$

$$\mathrm{4FeCr_2O_4(s) + 8Na_2CO_3(aq) + 7O_2(g) \rightarrow 2Fe_2O_3(s) + 8Na_2CrO_4(aq) + 8CO_2(g)}$$

− The product mixture is now $\mathrm{Fe_2O_3(s)}$ and $\mathrm{Na_2CrO_4(aq)}$

The mixture is then filtered to get residue and filtrate

- Residue is $\mathrm{Fe_2O_3(s)}$
- Filtrate is $\mathrm{Na_2CrO_4}$(aq)

Formation of $\mathbf{Na_2Cr_2O_7}$

To the filtrate, $\mathrm{Na_2CrO_4}$(aq), dilute sulphuric acid is added.

$$\mathrm{2Na_2CrO_4(aq) + H_2SO_4(aq) \rightarrow Na_2Cr_2O_7 + Na_2SO_4(aq) + H_2O(l)}$$

- The salts, $\mathrm{Na_2Cr_2O_7(aq)}$and $\mathrm{Na_2SO_4(aq)}$ are then separated by **fractional crystallisation** *(fractional crystallisation is performed by heating the solution and then allowing it to cool down. The salt which is less soluble crystallizes out first).*

Formation of $\mathbf{Cr_2O_3}$ (reduction by Carbon)

The $\mathrm{Na_2CrO_2O_7}$ is mixed with carbon and heated to form $\mathrm{Cr_2O_3}$

$$\mathrm{Na_2\,CrO_2O_7 + 2C} \xrightarrow[\Delta]{} \mathrm{Cr_2O_3 + Na_2CO_3 + CO}$$

Reduction by aluminium

$\mathrm{Cr_2O_3}$ is mixed with Al and heated strongly

$$\mathrm{Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3}$$ ……………………Thermite processes

It should be noted that:

- Chromium can also be produced as an alloy with iron by reduction of chromite with carbon in electric furnace. The alloy is known as **chrome steel.**

$$\mathrm{FeO.Cr_2O_3(s)(or\ Fe\,Cr_2O_4) + 4C(s) \xrightarrow{\text{electric arc}} \underbrace{(Fe + 2Cr)(l)}_{\textbf{Alloy}} + 4CO(aq)}$$

- The alloy produced in that way has a high carbon content.

When low carbon content required in the alloy chromite is reduced with silicon instead of carbon

$$\mathrm{FeO.Cr_2O_3(s) + 2Si(s) \underset{\Delta}{\rightarrow} (Fe + 2Cr) + 2\,SiO_2}$$

EXTRACTION OF ZINC

Chief ore

This is the **blende, ZnS.**

Another ore is Calamine, $\mathrm{ZnCO_3}$

Concentration of the ore

This is done by **froth floatation**

Roasting of the ore

Zinc blend, ZnS is heated in excess air to convert all ZnS to ZnO.

$$\mathrm{2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(g) + 2SO_2\,(g)}$$

Reduction of the oxide

The oxide is reduced to metal by heating it with **excess coke.**

$$\mathrm{ZnO(s) + C(s) \rightarrow Zn(s) + CO(g)}$$

Why is the addition of excess coke essential in the reduction of zinc oxide, ZnO?

This is because, in limited amount of carbon (coke), there is formation of $\mathrm{CO_2}$ which reacts with Zn(s) to regenerate ZnO

That is $\mathrm{CO(g) + O_2(air) \rightarrow CO_2(g)}$

Then $\mathrm{CO_2 + Zn \rightleftharpoons ZnO + CO}$

But in presence of excess coke, the carbon react with $\mathrm{CO_2}$ and hence the reaction between $\mathrm{CO_2}$ and Zn does not occur

$$\mathrm{CO_2 + C \longrightarrow 2\,CO}$$

In one sentence only:

Excess coke is added to prevent formation of CO_2 which will cause reversible reaction where ZnO is reformed.

PRACTICE EXERCISE 12

Question 1

Answer the following questions related to extraction of aluminium;

(i) Give the common and IUPAC name and formula of the chief ore.
(ii) Explain the process of concentration of the ore.
(iii) Explain how electrolysis of concentrated ore is done?
(iv) In the process of electrolysis of concentrated ore, why the anode used in the electrolytic. cell must be constantly replaced?

Question 2

Describe the process of extraction of tin.

Question 3

Explain the following:

(i) In extraction of aluminium, Al_2O_3 is not always used in electrolysis on its own without dissolving in $Na_3[AlF_6]$.
(ii) Concentration of aluminium ore is done at high pressure.
(iii) The roasting process is un-avoidable in the extraction of copper.

EXAMINATION QUESTION FOR PART THREE

Question 1

Copper has been extracted from ancient times but aluminium is recently extracted. Explain.

Question 2

Explain why extraction of group IA elements is done by electrolysis and not by using reducing agents.

Question 3

a) Give at least four ores of ion.

b) Describe all the stages of extraction of ion from iron pyrites.

c) Outline the uses of different types of steel in everyday lives.

Question 4

Describe extraction of copper metal from copper pyrites.

Question 5

Members of group IA → group IIIA of periodic table are normally extracted by electrolysis of their fused chlorides.

i. Explain why electrolysis is done and not reduction?

ii. Explain why chlorides are used and not any other compound?

Question 4

a) List at least four uses of aluminium.

b) List at least four hazards of lead.

Question 5

a) Mention any four ores of copper

b) Explain briefly the extraction of copper under the following headings using one of ores mentioned in (a) above:

  i. Froth flotation
  ii. Roasting of an ore
  iii. Removal of FeO as an impurity
  iv. Auto-reduction

c) List down three uses of copper in our day to day's life.

Question 6

Alkaline metals are extracted by electrolysis of the fused ore and not by reduction process. Explain why?

i. Fused materials are used and not aqueous solutions.

ii. Alkaline metals are not extracted by reduction process.

iii. Chlorides in most cases are used as ores for extraction of alkaline metals and not oxides.

Question 7

Briefly explain the extraction of aluminium from its principle ore, bauxite($Al_2O_3 \cdot 2H_2O$).

Question 8

Outline the extraction of lead from its sulphide ore.

Question 9

a) Copper has been used from ancient times but aluminium has been extracted commercially only recent times. Explain

b) Describe the electrolytic purification of copper the headings

   i. The chemical nature of electrodes

   ii. The chemical nature of the electrolyte

   iii. The redox reactions involved

Question 10

a) Give the names and formulae of three common ores from which each of the following elements are extracted.

   i. Aluminium
   ii. Manganese

b) One of the above two named elements is used in the extraction of the other. Use equations to show how this extraction occurs for a named ore.

c) Compare and contrast the chemistry of these two elements in:

   i. Formation and nature of ions

   ii. Reaction with air or oxygen

   iii. Nature of their chlorides

   iv. Nature of their oxide

Question 11

a) What is the chief ore of zinc?

b) Outline methods of extraction of the metal from zinc ore

c) Why is the addition of excess coke essential in the reduction of zinc oxide (ZnO)?

Question 12

Elements in group I and group II are normally extracted by electrolysis of their fused chlorides. Explain why?

PART FOUR

CHEMISTRY OF SELECTED COMPOUNDS OF METALS

Chapter 13

OXIDES

Oxides are binary compound of oxygen with another element. They are formed when oxygen is combined with one element only and hence the term oxide.

CLASSIFICATION OF OXIDES

Depending upon the oxidation state of oxygen in binary compound, oxides are divided into the following categories:

(i) Normal oxides

These are oxides in which oxidation state of oxygen is -2. For example; MgO, SO_2, N_2O and NO_2.

When the normal oxide contain excess of less electronegative element (or in other words, less quantity of oxygen) than the expected 'normal' oxide the oxide is then known as **suboxide**; for example boron suboxide, B_6O, and carbon suboxide, C_3O_2. In suboxides, the oxidation state of oxygen is still -2 while that of less electronegative becomes less than the common one. Suboxides are unstable and they are few.

(ii) Peroxides

These are oxides in which oxidation state of oxygen is -1. For example, H_2O_2, Na_2O_2, K_2O_2 and BaO_2

(iii) Superoxides

These are oxides in which oxidation state of oxygen is $-\frac{1}{2}$. For example, KO_2, RbO_2, CsO_2 and FrO_2

It should be noted that:

F_2O is the only oxide in which oxidation state of oxygen is positive (+2).

- It may be regarded as the special class of oxide which does not fall in either of the above mentioned types.

Types of normal oxides

All peroxides and superoxides are basic as they are formed with strong electropositive metals only whose cations have weak polarising power. So among three **major categories** of oxides (normal oxides, peroxides and superoxides), only normal oxides can further divided into various types depending upon acid-base characters.

Depending on acid-base characters, normal oxides may be classified into:

(i) Acidic oxides
(ii) Basic oxides
(iii) Amphoteric oxides
(iv) Neutral oxides

(i) Acidic oxides

- They are oxides of metalloids and non-metals (except non-metal monoxides).
- They are covalent.
- Most of them are gases.
- They react with basic solution to give salt and water.
- They also react with basic oxide.
- Acidic oxides combine with water (unless the oxide is water insoluble like SiO_2) to give acids and hence they are also known as **acid anhydrides**.

- For example:

(i) $SO_2 + H_2O \rightarrow \underset{\text{Sulphorous acid}}{H_2SO_3}$

SO_2 is thus termed as sulphorous anhydride.

(ii) $SO_3 + H_2O \rightarrow H_2SO_4$

SO_3 is thus known as sulphuric anhydride.

Example: $CO_2, NO_2, SO_2, SO_3, SiO_2$ etc.

(ii) Basic oxides

- They are oxide of strong electropositive metals.
- They react with acids.
  - With acidic solution they give salt and water.
  - Being basic, they react with acidic oxide too.
- They are ionic and hence they are solid.
- They are insoluble in water except group IA oxides.
- If soluble in water, basis oxides react with water produce hydroxides. These are therefore known as **basic anhydrides**.

Examples: Na_2O, K_2O, CaO, MgO etc.

(iii) Amphoteric oxides

- They are oxides of weak electropositive metals.
- Their corresponding hydroxides are amphoteric too.

Understand that: Metals which form amphoteric oxides are metals which can form complex with OH^-.

Examples: $Al_2O_3, BeO, ZnO, PbO, SnO$ etc.

(iv) Neutral oxides

Neutral oxides are oxides which show neither acidic nor basic properties. Thus, they do not form salts when reacted with bases or acids.

- They are monoxides of non-metals (oxides of non-metals with single oxygen atom in a molecule).
- They are covalent.
- They are gases except water (H_2O) which is liquid

Examples: CO, NO, N_2O and F_2O

However although CO and F_2O are commonly regarded as neutral oxides;

- In fact, CO is very, very slightly acidic. **It does not react with water,** but it will react with hot concentrated sodium hydroxide solution to give a solution of sodium methanoate.

$$NaOH(conc) + CO \underset{\Delta}{\rightarrow} HCOONa$$

- F_2O reacts very slowly with hot water to give acidic solution.

$$F_2O(g) + H_2O(l) \underset{Hot}{\longrightarrow} 2HF(aq) + O_2(g)$$

Water is exceptional!

H_2O may be regarded as both amphoteric oxide and neutral oxide.

- It undergo self ionisation as per the following equation;

$$H_2O + H_2O \longrightarrow OH^- + H_3O^+$$

Thus:

- Water undergoes self-ionisation to give both H_3O^+ (representing acidic character) and OH^- (representing basic character), therefore acting as amphoteric oxide.
- Water undergoes self-ionisation to give equal concentration of H_3O^+ and OH^-, therefore acting as neutral oxide.

Compound oxides

Compound oxides or **mixed oxides** are metallic oxides and they behave as if they are made up of two oxides, lower and higher oxides of the same metal. For example:

(i) **Red lead oxide (Pb_3O_4)** which may be thought as an oxide mixture of lead (II) oxide and lead (IV) oxide.
That is $Pb_3O_4 = 2PbO + PbO_2$

(ii) **Ferro-ferric oxide (Fe_3O_4)** which may be thought as an oxide mixture of iron (II) oxide and iron (III) oxide.
That is $Fe_3O_4 = \underset{\textbf{Ferrous oxide}}{FeO} + \underset{\textbf{Ferric oxide}}{Fe_2O_3}$

CHEMICAL REACTIONS OF OXIDES

Reaction with water

Only **soluble** oxides dissolve in (react with) water to give acidic, basic or amphoteric solution depending upon type of oxide. Neutral oxides do not react with water.

For basic oxide:

- **Normal oxides** give hydroxide only.

$$O^{2-}(s) + H_2O(l) \rightarrow 2OH^-$$

- **Peroxides** give hydroxide and hydrogen peroxide.

$$O_2^{2-}(s) + 2H_2O \rightarrow 2OH^- + H_2O_2$$

- **Superoxides** give hydroxide, hydrogen peroxide and oxygen gas.

$$O_2^-(s) + 2H_2O \rightarrow 2OH^- + H_2O_2 + O_2$$

For amphoteric oxide: Amphoteric oxides react like normal oxides. For example;

$$Fe_2O_3(s) + 3H_2O \longrightarrow 2Fe(OH)_3(s)$$

For acidic oxide: Soluble acidic oxides dissolve in water to give oxoacids where oxidation state of the element which forms oxide remains unchanged. For example;

$SO_2 + H_2O \longrightarrow H_2SO_3$ (Oxidation state of S is +4 in both sides)

$SO_3 + H_2O \longrightarrow H_2SO_4$(Oxidation state of S is +6 in both sides)

$N_2O_5 + H_2O \longrightarrow 2HNO_3$(Oxidation state of N is +5 in both sides)

$N_2O_3 + H_2O \longrightarrow 2HNO_2$(Oxidation state of N is +3 in both sides)

What if there is no oxoacid of an element in the same oxidation state as that in corresponding oxide?

If this occurs, then the oxide undergoes disproportionation in water to give mixture of oxoacids. For example, in NO_2, oxidation state of nitrogen is +4 and there is no oxoacid of nitrogen in which oxidation state of N is +4. Writing HNO_3 only will imply that an electron is lost, or writing HNO_2 only will imply that an electron is created; all of which are impossible. To make sure that electrons are conserved, the oxide will give the mixture of the two oxoacids.

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

Similarly; $Cl_2O_6 + H_2O \longrightarrow HClO_4 + HClO_3$ (There is no oxoacid of chlorine in oxidation state of +6)

Reaction with acid

Basic, amphoteric and compound oxides react with acidic solution to give salt. Acidic and neutral oxides do not give salt with acidic solution.

For basic oxide:

- **Normal oxides** give salt and water. For example, with dilute sulphuric and hydrochloric acid;

$$O^{2-} + 2HCl(aq) \longrightarrow 2Cl^{-}(aq) + H_2O$$

$$\text{Or}\quad CaO + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O$$

$$O^{2-} + H_2SO_4(aq) \longrightarrow SO_4^{2-}(aq) + H_2O$$

$$\text{Or}\quad Na_2O + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + H_2O$$

- **Peroxides** give salt and hydrogen peroxide. Again with dilute sulphuric and hydrochloric acid;

$$O_2^{2-} + 2HCl(aq) \longrightarrow 2Cl^{-}(aq) + H_2O_2$$
$$O_2^{2-} + H_2SO_4(aq) \longrightarrow SO_4^{2-}(aq) + H_2O_2$$

- **Superoxides** give salt, hydrogen peroxide and oxygen gas. For example;

$$2O_2^{-} + 2HCl(aq) \longrightarrow 2Cl^{-}(aq) + H_2O_2 + O_2$$
$$2O_2^{-} + H_2SO_4(aq) \longrightarrow SO_4^{2-}(aq) + H_2O_2 + O_2$$

For amphoteric oxides: Amphoteric oxides react like normal oxides. For example;

$$ZnO + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2O$$

For compound (mixed) oxide:

On treatment with an acid, compound oxides give a mixture of salts.

For example, $Fe_3O_4 + 8HCl \rightarrow \underset{\textbf{Ferric chloride}}{2FeCl_3} + \underset{\textbf{Ferrous chloride}}{FeCl_2} + 4H_2O$

The red lead oxide (Pb_3O_4) would react according to the following equation:

$Pb_3O_4 + 8HCl \rightarrow 2PbCl_2 + PbCl_4 + 4H_2O$ …………………… (i)

However $PbCl_4$ is unstable, it tends to decompose into $PbCl_2$ as per equation:

$PbCl_4 \rightarrow PbCl_2 + Cl_2$ …………..……… (ii)

And the correct overall reaction equation becomes (by taking (i) + (ii))

$$Pb_3O_4 + 8HCl \rightarrow 3PbCl_2 + Cl_2 + 4H_2O$$

Similarly;

$$Pb_3O_4 + 4HNO_3 \underset{\text{Boil}}{\longrightarrow} 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

(Here formation of lead(IV) oxide is explained by the decomposition of lead(IV) nitrate which would be formed together with lead(II) nitrate))

Reaction with basic solution

Only acidic and amphoteric oxides react with basic solution to give salt. Neutral and basic oxides do not react with basic solution.

For acidic oxide: Acidic oxides give salt with basic solution. For example;

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$

$$SiO_2 + 2KOH \longrightarrow K_2SiO_3 + H_2O$$

$$SO_2 + Ca(OH)_2 \longrightarrow CaSO_3 + H_2O$$

$$SO_3 + Mg(OH)_2 \longrightarrow MgSO_4 + H_2O$$

For amphoteric oxide: Amphoteric oxides give salt with strong basic solution. For example;

$$\mathrm{ZnO + 2NaOH(aq) \longrightarrow Na_2ZnO_2 + H_2O}$$

The reaction takes place via complex formation as per equation;

$$\mathrm{ZnO + 2NaOH(aq) + H_2O \longrightarrow Na_2[Zn(OH)_4]}$$

Then the complex undergoes dehydration to give final product;

$$\mathrm{Na_2[Zn(OH)_4] \xrightarrow[-2H_2O]{} Na_2ZnO_2 + 2H_2O}$$

Hence **for metal oxide to act as amphoteric, the metallic ion in the oxide must able to form complex with OH^-.** To insist; **only metals which can form complex with OH^-, can form amphoteric oxide.**

Reaction between oxides

Acidic oxides react with basic oxides to give salt. Neutral oxides (except water which give hydroxides or oxoacids with soluble oxides) do not react with other oxides. For example;

$$\mathrm{CaO + SiO_2 \longrightarrow CaSiO_3}$$
$$\mathrm{K_2O + SO_2 \longrightarrow K_2SO_3}$$
$$\mathrm{Na_2O + CO_2 \longrightarrow Na_2CO_3}$$

PREPARATION OF OXIDES

Direct method

This is done by direct heating of an element with oxygen.

- Many metals and non-metals burn rapidly when heated in oxygen (or air) producing their oxides. For example:

$$\mathrm{2Mg + O_2 \underset{\Delta}{\rightarrow} 2MgO}$$
$$\mathrm{2Ca + O_2 \underset{\Delta}{\rightarrow} 2CaO}$$
$$\mathrm{4Li + O_2 \underset{\Delta}{\rightarrow} 2Li_2O}$$
$$\mathrm{S + O_2 \underset{\Delta}{\rightarrow} SO_2}$$
$$\mathrm{P_4 + 5O_2 \underset{\Delta}{\rightarrow} P_4O_{10}}$$

However the reader should understand that: ***Although metals below lithium (in group IA) react readily with oxygen, their normal oxides are normally not prepared by direct method, why?***

This is simply because the metals may form peroxides (and even superoxides for metals below sodium) apart from normal oxide!

- To avoid formation of peroxides and superoxides, normal oxides of those metals are prepared by reducing their nitrite or nitrate by free metal. For example;

$$\mathrm{2NaNO_3 + 10Na \longrightarrow 6Na_2O + N_2}$$

Indirect method

This can be:

(i) By reaction of oxygen with compound at high temperature. For example:

$$\mathrm{2PbS + 3O_2 \underset{\Delta}{\rightarrow} 2PbO + 2SO_2}$$
$$\mathrm{2ZnS + 3O_2 \underset{\Delta}{\rightarrow} 2ZnO + 2SO_2}$$

Similarly: $\mathrm{C_2H_5OH + 3O_2 \underset{\Delta}{\rightarrow} 2CO_2 + 3H_2O}$

or $\mathrm{C_4H_8 + 6O_2 \underset{\Delta}{\rightarrow} 4CO_2 + 4H_2O}$

(ii) By thermal decomposition of certain compounds like hydroxides, carbonates and nitrates

$$MgCO_3 \underset{\Delta}{\rightarrow} MgO + CO_2$$
$$2Ca(NO_3)_2 \underset{\Delta}{\rightarrow} 2CaO + 4NO_2 + O_2$$
$$Cu(OH)_2 \underset{\Delta}{\rightarrow} CuO + H_2O$$

(iii) By oxidation of some elements with nitric acid

$$2Cu + 8HNO_3 \underset{\Delta}{\rightarrow} 2CuO + 8NO_2 + 4H_2O + O_2$$
$$Sn + 4HNO_3 \underset{\Delta}{\rightarrow} SnO_2 + 4NO_2 + 2H_2O$$

Similarly: $C + 4HNO_3 \underset{\Delta}{\rightarrow} CO_2 + 4NO_2 + 2H_2O$

USES OF OXIDES

Below are some uses of metallic oxides.

In extraction of metals

- Significant number of useful ore oxides from which their respective metal are extracted. For example, bauxite is the oxide of aluminium ($Al_2O_3.XH_2O$) is used for extracting aluminium and haematite (Fe_2O_3) for iron.
- Furthermore metallic oxides like CaO and FeO are useful in removing gangue (earthy impurities) in blast furnace. For example, CaO is used to eliminate sand, SiO_2 (gangue) as slag.

In soil liming

Calcium oxide and magnesium oxide are good liming materials which are used to eliminate excess acid in the soil. They also increase fertility of the soil.

As oxygen source

Peroxides especially sodium peroxide is used in confined spaces (for example in emergency breathing devices on submarines) because it absorbs carbon dioxide and liberates oxygen at the same time.

$$2Na_2O_2(s) + 2CO_2(g) \longrightarrow 2Na_2CO_3(s) + O_2(g)$$

In manufacture of glass

Several metals oxides like trilead tetraoxide (Pb_3O_4), manganese(IV) oxide, calcium oxide, sodium oxide, etc., are used in the glass industry.

As catalysts

Some metal oxides are very useful catalysts for important chemical reactions. As an example, both manganese(IV) oxide and copper(II) oxide may be used to catalyse thermolysis of potassium chlorate to give potassium chloride and oxygen gas.

PRACTICE EXERCISE 13

Question 1

Classify the following oxides as acidic, basic amphoteric or neutral oxides

(i) P_4O_{10} (ii)CuO (iii) N_2O (iv) CaO (v) SrO_2 (vi) BeO

Question 2

State whether the following elements will be more likely to form acidic, basic, amphoteric or neutral oxide

(i) Alkali metals (ii) Halogens (iii) p-block metals (iv) semi-metals (v) d-block metals

Question 3

Giving at least one example in each case, define the following terms:

(i) Normal oxide (ii) Peroxide (iii) Superoxide (iv) Mixed oxide

Question 4

Complete the following reactions:

(i) $CaO + SiO_2 \rightarrow$
(ii) $Al_2O_3 + CO_2 \rightarrow$
(iii) $BrO_3 + H_2O \rightarrow$
(iv) $KO_2 + H_2SO_4(aq) \rightarrow$
(v) $Rb_2O_2 + HNO_3(aq) \rightarrow$
(vi) $Fe_3O_4 + H_2SO_4(aq) \rightarrow$

Question 5

With help of chemical equation, explain whether KO_2 can efficiently prepared by direct method or not?

Question 6

With help of chemical equation, briefly explain two uses of metal oxides.

Chapter 14

HYDROXIDES

Hydroxide is the chemical compound that contains hydroxyl ($-\mathbf{OH}$) radical. The term refers to especially inorganic compounds. Organic compounds with hydroxyl group as functional group are known as alcohols. However strictly speaking, hydroxides of non-metals and metalloids do not contain ionisable hydroxyl group, so the term hydroxide is commonly used to represent hydroxides of metal which may ionise to give hydroxide ion ($\mathbf{OH^-}$).

TYPES OF HYDROXIDES

Depending upon acid-base characters, hydroxides may be classified into:

- Acidic hydroxide
- Basic hydroxide and
- Amphoteric hydroxide

Acidic hydroxides: These are hydroxide of non-metals and metalloids. They are also termed as oxoacids or oxyacids because their acidic hydrogen is bonded to oxygen (in OH). For example, H_3BO_3 (which may be written as $B(OH)_3$) and H_2SO_4 (which may be written as $SO_2(OH)_2$).
Basic hydroxides: These are hydroxide of strong electropositive metals. They are basically ionic. S-block metals (except Be) form this kind of hydroxide.
Amphoteric hydroxide: These are hydroxide of weak electropositive metals which may show both acidic and basic characters. They have high degree of polarisation of ionic characters. So they are basically ionic characters with significant degree of covalent characters. Most of p and d-block metals form this kind of hydroxide.

PERIODIC TREND ON ACID-BASE CHARACTERS OF HYDROXIDES

The hydroxide of an element will behave either as an acid or as a base depending on electronegativity of the element. Hydroxides of strong electronegative elements are acidic while those of strong electropositive elements are basic. Since electronegativity is the periodic property, it is not a surprise for acid-base characters of hydroxides to show regular trend in the periodic table too!

Periodic trend across the period

As explained earlier in the introduction part, electronegativity increases across the period. This simple fact means that as you go across the period hydroxides become acidic. This can clearly be justified by using hydroxides of period 3 as shown in the **chapter 4**; nothing is new!

- We can use hydroxides of period 2 for justification too (see the table below).

Period 2 element	Li	Be	B	C	N	O	F
Hydroxide	$LiOH$	$Be(OH)_2$	H_3BO_3	H_2CO_3	HNO_2 or HNO_3	Not present	Not present
Acid-base character	Base	Amphoteric	Acid	Acid	Acid	−	−

Periodic trend down the group

As you go down the group electronegativity decreases thus making hydroxide basic. Furthermore as you go down the group, hydroxides of metals become more ionic, therefore more ionisation and hence higher basic strength for hydroxide.

- We are going to verify the statement that "hydroxides become more basic as you descent the group" by looking into hydroxides of group IIIA.

Hydroxides of group IIIA

Hydroxides of group IIIA and their acid-base character are shown in the table below.

ELEMENT	SYMBOL	ATOMIC NUMBER	HYDROXIDE	ACID-BASE CHARACTER
Boron	B	5	H_3BO_3	Acid
Aluminium	Al	13	$Al(OH)_3$	Amphoteric
Gallium	Ga	31	$Ga(OH)_3$	Amphoteric
Indium	In	49	$In(OH)_3$	Base
Thallium	Th	81	$Tl(OH)_3$ or $TlOH$	Base

The above trend on basic strength is also a good verification of the fact that; metallic characters increase as you go down the group.

- The first hydroxide, boric acid (H_3BO_3) being acidic react with basic solution like NaOH but it has no action to another acidic solution.

$$H_3BO_3 + 3NaOH \rightarrow Na_3BO_3 + 3H_2O$$

- $Al(OH)_3$ and $Ga(OH)_3$ being amphoteric, can react with both acids and bases.

As acids, they react with strong bases like NaOH(aq)

$$\text{E.g. } Ga(OH)_3 + 3NaOH \rightarrow \underbrace{Na_3[Ga(OH)_6]}_{\textbf{Unstable}} \xrightarrow[-3H_2O]{} \underbrace{Na_3GaO_3}_{\textbf{Stable}} + 3H_2O$$

Thus after dehydration, the equation can be rewriten as follows giving the stable product:

$$\text{E.g.} \quad \underbrace{H_3GaO_3}_{\textbf{Acid}} + \underbrace{3NaOH}_{\textbf{base}} \rightarrow \underbrace{Na_3GaO_3}_{\textbf{salt}} + \underbrace{3H_2O}_{\textbf{water}}$$

As bases, they react with strong acids like HCl(aq)

$$\text{E.g.} \quad \underbrace{Ga(OH)_3}_{\textbf{Base}} + \underbrace{HCl}_{\textbf{acid}} \rightarrow \underbrace{GaCl_3}_{\textbf{salt}} + \underbrace{3H_2O}_{\textbf{water}}$$

- Hydroxides of indium and thallium being basic, can react with acidic solution like HCl(aq) but they have no action on another basic solution.

$$\text{E.g. } \underbrace{TlOH}_{\textbf{Base}} + \underbrace{HCl}_{\textbf{Acid}} \rightarrow \underbrace{TlCl}_{\textbf{Salt}} + \underbrace{H_2O}_{\textbf{Water}}$$

THERMAL STABILITY OF HYDROXIDES OF METALS

Thermal stability of hydroxides depends on their degree of polarisation:

- Hydroxides with low degree of polarisation, are strong ionic and therefore do not decompose on heating. Alkali metals (except lithium) form this kind of hydroxide. As an example;

$$KOH \xrightarrow[\Delta]{} \text{No reaction}$$

- Hydroxides with high degree of polarisation are thermally unstable. They do decompose on heating to give their corresponding oxide and water. Hydroxides of earth metals, p and d-block metals form this kind of hydroxide. As an example;

$$Zn(OH)_2 \xrightarrow[\Delta]{} ZnO + H_2O$$

- If the hydroxide has very high degree of polarisation, it will be highly thermally stable such that even room temperature will be enough to decompose it and hence that hydroxide will not exist. For example, AgOH cannot be prepared in the laboratory for this reason. Any attempt to prepare AgOH results to Ag_2O as result of decomposition of the hydroxide.

$$2AgOH \xrightarrow[\text{room temperature}]{} Ag_2O + H_2O$$

PREPARATIONS OF HYDROXIDE OF METALS

Metal hydroxides may be prepared direct method or indirect method.

Direct method

Direct method employs displacement reaction and hence it is also known as **displacement method**. It is used to prepare **soluble hydroxide** of **very reactive metals** by direct reaction with water. The bolded words are conditions for direct method to be applied. Most of metal hydroxides are insoluble except hydroxides of alkali metals and those of earth metals below calcium ($Mg(OH)_2$ is insoluble while $Ca(OH)_2$ is only slightly soluble).

- These metals which form soluble hydroxides are also very reactive (Don't misunderstand! There are some other reactive metals which are able displace hydrogen from dilute acids but their hydroxides are insoluble. That means that 'all soluble hydroxides are hydroxides of reactive metals but there are some reactive metals which form insoluble hydroxide).
- Because there is no unreactive metal which can form soluble hydroxide, in one sentence we may conclude that:

  Direct method is used to prepare soluble hydroxides.

  For example;

$$Na + H_2O \longrightarrow NaOH + H_2$$

$$Ba + H_2O \longrightarrow Mg(OH)_2 + H_2$$

Indirect method

Indirect is used to prepare insoluble hydroxides. It employs **double decomposition reaction** whereby two soluble compounds (one of them must contain the required cation and another must be hydroxide) react to give one soluble compound and another insoluble compound (hydroxide) which appears as **precipitate** and hence the method is also known as **precipitation method** or **double decomposition method**. The hydroxide is obtained as residue after filtration.
For example;

$$MgCl_2(s) + 2KOH \longrightarrow Mg(OH)_2 + 2KCl$$
$$FeCl_2(s) + 2NaOH \longrightarrow Fe(OH)_2 + 2NaCl$$

But $2AgNO_3(aq) + 2NaOH(aq) \longrightarrow Ag_2O(s) + 2NaNO_3(aq) + H_2O(l)$ **(Due to thermal instability of AgOH, Ag_2O is formed instead of the expected hydroxide)**

USES OF METAL HYDROXIDES

Below are some uses of metal hydroxides.

Manufacture of soap

Soaps are chemical salts of long chain carboxylic acid. This is done by reaction between strong basic solution and ester (fats and oils). The reaction is known as saponification. NaOH and KOH are commonly used for this purpose.

For detailed discussion of manufacture and cleansing action of soap, refer to another book in series titled Advanced Organic Chemistry.

Soil liming

Calcium hydroxide is a cheap alkali which can be used in large quantities to treat acid soils. The alkali neutralises the excessive soil acidity, just like any alkali reacts with an acid, to form salt and water.

Extraction of metals

Sodium hydroxide is used in extraction of aluminium from bauxite.

Manufacture of bleach

Sodium hydroxide and calcium hydroxide are commonly used for this purpose. To show bleaching action, first the hydroxide is reacted with chlorine to form hypochlorite. The hypochlorite is good oxidising agent; it oxidises the dye and therefore bleaching it.

$$2NaOH + Cl_2 \longrightarrow NaCl + \underset{\substack{\uparrow \\ \textbf{Bleaching agent}}}{NaOCl} + H_2O$$

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow CaCl_2 + \underset{\substack{\uparrow \\ \textbf{Bleaching agent (commonly known as bleaching powder)}}}{Ca(OCl)_2} + 2H_2O$$

Then $ClO^-_{\text{(from bleaching agent)}} + \underset{\textbf{Coloured}}{dye} \longrightarrow \underset{\textbf{Colourless}}{(dye + O)} + Cl^-$

Softening of hard water

Calcium hydroxide is used in the softening of temporary hard water.

$$Ca(OH)_2(aq) + \underset{\textbf{Temporary hardness}}{Ca(HCO_3)_2(aq)} \longrightarrow 2CaCO_3(s) + 2H_2O(l)$$

PRACTICE EXERCISE 14

Question 1

Explain the following:

(i) Copper (II) hydroxide undergoes thermolysis while potassium hydroxide does not.
(ii) Silver hydroxide cannot be prepared in the laboratory.
(iii) Insoluble hydroxides cannot be prepared by direct method.

Question 2

Complete the following reactions:

(i) $\mathrm{Sr(s)} + \mathrm{H_2O(l)} \rightarrow$
(ii) $\mathrm{Cu(s)} + \mathrm{H_2O(l)} \rightarrow$
(iii) $\mathrm{B(OH)_3} + \mathrm{HCl} \rightarrow$
(iv) $\mathrm{Cu(OH)_2} + \mathrm{NaOH} \rightarrow$
(v) $\mathrm{AgNO_3} + \mathrm{KOH} \rightarrow$

Question 3

Explain how basic strength of hydroxides vary on descending the group in the periodic table.

Question 4

Briefly, explain at least three uses of metal hydroxides.

Chapter 15

CARBONATES AND BICARBONATES

Carbonates and bicarbonates (or hydrogenbicarbonates) are salts of carbonic acid. Bicarbonate ion is formed in the first step of ionisation of carbonic acid while carbonate ion is formed after second step of the ionisation (when all two hydrogen atoms in the carbonic acid have been ionised). So when only one hydrogen atom in carbonic acid is replaced by metal, the result is metal bicarbonate and when all two hydrogen atoms are replaced by metal, the result is metal carbonate.

$$\underset{\textbf{Carbonic acid}}{H_2CO_3} \longrightarrow \underset{\textbf{Bicarbonate ion}}{HCO_3^-} + H^+ \quad \text{(First step)}$$

$$\underset{\textbf{Bicarbonate ion}}{HCO_3^-} \longrightarrow \underset{\textbf{Carbonate ion}}{CO_3^{2-}} + H^+ \quad \text{(Second step)}$$

THERMAL STABILITY OF CARBONATES AND BICARBONATES

Both carbonate and bicarbonate having large size have very large polarisability. Bicarbonate ion having larger size than carbonate ion has greater polarisability. As result:

- Solid carbonates of metals with cation of **very** large polarising power do not exist at room temperature. These carbonates have **very** large degree of polarisation such that even the room temperature is enough to decompose the carbonate to oxide. For example, solid aluminium carbonate, beryllium carbonate and iron(III) carbonate do not exist for this reason.

$$BeCO_3(s) \xrightarrow[\text{room temperature}]{} BeO(s) + CO_2(s)$$

$$Al_2(CO_3)_3(s) \xrightarrow[\text{room temperature}]{} Al_2O_3(s) + 3CO_2(s)$$

$$Fe_2(CO_3)_3(s) \xrightarrow[\text{room temperature}]{} Fe_2O_3(s) + 3CO_2(s)$$

- Solid carbonates of metals with cation of large polarising power decompose on heating. These carbonates still have large degree of polarisation (that is why they undergo thermolysis) but they are thermally stable enough to exist at room temperature. However bicarbonates of these metals do not exist in solid form; they exist in aqueous solution only.

$$MgCO_3(s) \underset{\Delta}{\rightarrow} MgO(s) + CO_2(g)$$

But $$Mg(HCO_3)_2(s) \xrightarrow[\text{room temperature}]{} MgCO_3(s) + CO_2 + H_2O(g)$$

- Solid carbonates of metals with cation of small polarising power do not decompose on heating. These carbonates have small degree of polarisation such that normal heating is not enough to decompose them. These metals also form stable solid bicarbonates at room temperature, however due to large polarisability of bicarbonate ion, these bicarbonate decompose on heating. Only alkali metals (except lithium) form carbonates and bicarbonates of this nature. As an example;

$$K_2CO_3(s) \underset{\Delta}{\rightarrow} \text{No reaction}$$

But $$2KHCO_3(s) \underset{\Delta}{\rightarrow} K_2CO_3(s) + CO_2 + H_2O(g)$$

PREPARATIONS OF CARBONATES AND BICARBONATES

Neutralisation method

Both carbonates and bicarbonates are commonly prepared by neutralisation reaction. This is done by passing carbon dioxide (acidic oxide) to alkaline solution. The formation of carbonate or bicarbonate depend on whether alkaline solution or carbon dioxide present in excess.

- If the alkaline solution present in excess, carbonate is formed.

$$2OH^- + CO_2 \longrightarrow CO_3^{2-} + H_2O$$

For example;

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

- If the carbon dioxide solution present in excess, bicarbonate is formed.

$$OH^- + CO_2 \longrightarrow HCO_3^-$$

For example;

$$NaOH + CO_2 \longrightarrow NaHCO_3$$

$$Ca(OH)_2 + 2CO_2 \longrightarrow Ca(HCO_3)_2$$

This reaction is possible because carbonate is still good base, so it can undergo further reaction with dissolved carbon dioxide to give bicarbonate. However, although the bicarbonate is still basic too, it does not undergo further reaction with carbon dioxide because bicarbonate is too weak base to react with carbon dioxide.

$$CO_3^{2-} + CO_2 + H_2O \longrightarrow 2HCO_3^-$$

Or because mixture of CO_2 and H_2O give carbonic acid, H_2CO_3, the equation can alternatively be written as;

$$CO_3^{2-} + H_2CO_3 \longrightarrow 2HCO_3^-$$

Precipitation method

Only insoluble carbonate may be prepared by **double decomposition precipitation reaction**. All bicarbonates are soluble (because bicarbonate ion may interact with water through hydrogen bonding), so they are not prepared by this method. Insoluble carbonates which can be prepared by this method are all carbonates except carbonates of alkali metals (except $LiCO_3$) and ammonium carbonate which are soluble. As an example;

$$CaCl_2(aq) + Na_2CO_3(aq) \longrightarrow CaCO_3(s) + 2NaCl(aq)$$

USES OF CARBOATES AND HYDROGENCARBONATES

As industrial bases

- Na_2CO_3 (commonly known as washing soda or soda ash) is mainly used for this purpose. For example, soda ash can be used to increase the alkalinity in swimming pools, helping to ensure the proper pH balance of the water.

As baking powder

- $NaHCO_3$ is mainly used for this purpose.

$NaHCO_3$ (baking soda) is used as leavening agent to raise things like cookies, cakes because it decomposes to CO_2 and water upon heating. This makes the cookies porous and palatable.

In fire extinguisher

- Bicarbonate are good fire extinguisher because they decompose to produce carbondioxide gas and the reaction is endothermic.
- Again $NaHCO_3$ is commonly used for this purpose.

In production of quick lime

- Calcium carbonate undergoes thermolysis to give calcium oxide (quick lime) in lime kilns. The reaction is very useful in the manufacture of cement.

$$CaCO_3(s) \underset{\Delta}{\rightarrow} CaO(s) + CO_2(g)$$

The quick lime is further used in the preparation of slaked lime, $Ca(OH)_2$, which has very important agricultural uses like liming of soil to eliminate excessive acidity in the soil.

In softening hard water

Sodium carbonate (washing soda) is commonly used for this purpose.

In making glass

Again sodium carbonate (of course and calcium carbonate as you are soon going to see below) is commonly used for this purpose.

- Sodium carbonate's most important use is in the chemical make-up of glass. When heated at very high temperatures, combined with sand (SiO_2) and **calcium carbonate ($CaCO_3$),** and cooled very rapidly, sodium carbonate can be used to form a transparent non-crystalline material, commonly known as glass.

In soil liming

Calcium carbonate ($CaCO_3$) and mixture of calcium carbonate and magnesium carbonate known as dolomite (CaMg$(CaCO_3)_2$), are carbonates which are commonly used for this purpose.

PRACTICE EXERCISE 15

Question 1

Iron (III) carbonate is not known. Explain.

Question 2

Effervescence of colourless gas is observed when silver nitrate is mixed with sodium bicarbonate. Explain.

Question 3

Explain at least three uses of salts of carbonic acid.

Question 4

Complete the following reactions:

(i) $\mathrm{Na_2CO_3 + H_2CO_3 \rightarrow}$

(ii) $\mathrm{CuCO_3} \underset{\Delta}{\rightarrow}$

(iii) $\mathrm{Cs_2CO_3} \underset{\Delta}{\rightarrow}$

(iv) $\mathrm{Mg(HCO_3)_2 + 2CO_2 \rightarrow}$

Chapter 16

SULPHATES

Sulphates are compounds containing a polyatomic anion with the empirical formula SO_4^{2-}. They are salts of sulphuric acid and many are prepared from that acid. As it is derived from sulphuric acid which is very strong acid, SO_4^{2-} is very weak base.

SOLUBILITY OF SULPHATES

All sulphates are soluble except sulphate of lead (II), calcium, strontium, barium, mercury(II) and silver.

- Solubility of sulphates depends on relative amount of lattice energy and hydration energy. If the hydration energy is greater than lattice energy, then the sulphate will readily dissolve in water and if the hydration energy is small, the sulphate will not dissolve readily.

HYDROLYSIS OF SULPHATES

Sulphates with significant degree of covalent characters undergo cationic hydrolysis to give acidic solution. These 'covalent' sulphates have high degree of polarisation and they always contain cations of large polarising power which come from weak base.

- Most of sulphates of p and d-block metals form this kind of sulphate. For example;

$$Al_2(SO_4)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 6H^+ + 3SO_4^{2-}$$

$$CuSO_4 + 2H_2O \longrightarrow Cu(OH)_2 + 2H^+ + SO_4^{2-}$$

$$Fe_2(SO_4)_3 + 6H_2O \longrightarrow 2Fe(OH)_3 + 6H^+ + 3SO_4^{2-}$$

$$ZnSO_4 + 2H_2O \longrightarrow Zn(OH)_2 + 2H^+ + SO_4^{2-}$$

On another hand, strong ionic sulphates do not hydrolyse in water. These ionic salts contain cations from strong base which have small polarising power. Alkali and earth metals (except beryllium) form this kind of sulphates. As an example;

$$Na_2SO_4 + H_2O \longrightarrow \text{No reaction}$$

THERMAL STABILITY OF SULPHATES

Sulphates with high degree of polarisation undergo thermal decomposition (thermolysis) to give their corresponding oxides. The trend is similar to that of hydroxides, that is sulphates of earth metals, p and d-block metals decompose on heating whereby as the degree of polarisation become higher, the decomposition temperature (*temperature at which the compound decomposes*) becomes lower.

Generally; $$SO_4^{2-} \underset{\Delta}{\rightarrow} O^{2-} + SO_3$$

For example; $$Al_2(SO_4)_3 \underset{\Delta}{\rightarrow} Al_2O_3 + 3SO_3$$

$$MgSO_4 \underset{\Delta}{\rightarrow} MgO + SO_3$$

$$ZnSO_4 \underset{\Delta}{\rightarrow} ZnO + SO_3$$

Sulphates of alkali metals (except lithium) do not decompose on heating. As an example;

$$M_2SO_4 \underset{\Delta}{\rightarrow} \text{No reaction}$$

Where M is any alkali metal except lithium.

PREPARATION OF SOLUBLE SULPHATES

Displacement method

This method is also known as **direct method** or **excess metal method**. Metals which are stronger reducing agent (more reactive) than hydrogen, displace (reduce) hydrogen from dilute H_2SO_4 and themselves get oxidised to their respective sulphate

Generally;

$\text{Metal} + H_2SO_4(\text{dil}) \rightarrow \text{Sulphate} + H_2$

For example; $Mg(s) + H_2SO_4(\text{dil}) \rightarrow MgSO_4(aq) + H_2(g)$

The method is suitable if the following conditions are met:

(i) The metal must be stronger reducing agent than hydrogen

- Metals which meet this condition are found above hydrogen in the electrochemical series.
- Metals below hydrogen in the electrochemical series are not strong reducing agent enough to reduce in dilute acids and therefore these metals will not get oxidised to their sulphate.
- For example, copper being weaker reducing agent than hydrogen, does not react with dilute H_2SO_4 and hence the displacement method is not suitable for preparation of $CuSO_4$

That is: $Cu(s) + H_2SO_4(\text{dil}) \rightarrow \text{No reaction}$

However!

If the acid is concentrated, even metals which are weaker reducing agent than hydrogen give suphate due to oxidising characters of sulphuric acid.

$$Cu(s) + 2H_2SO_4(\text{conc.}) \rightarrow CuSO_4 + SO_2 + 2H_2O$$

(ii) The sulphate of the metal must be soluble

- Even reactive metals (which are stronger reducing agent than hydrogen) may not react with dilute H_2SO_4 if they form insoluble sulphate which prevents further reaction.
- For example, $CaSO_4$ cannot be prepared by the displacement method despite the fact that calcium is stronger reducing agent than hydrogen due to formation of insoluble $CaSO_4$ which resists further reaction.

That is; $Ca(s) \; + H_2SO_4(\text{dil}) \rightarrow \text{No reaction}$

But $Ca(s) + HCl(\text{dil}) \rightarrow CaCl_2(aq) + H_2(g)$

(Here $CaCl_2$ can be prepared by displacement method because it is soluble).

Other insoluble sulphates which cannot be prepared by displacement method are $PbSO_4, SrSO_4, BaSO_4$ $HgSO_4$, and Ag_2SO_4

(iii) The metal must be moderately reactive

- The metal may meet above two conditions but still its sulphate cannot be prepared by displacement method if the metal is so reactive that its reaction with dilute H_2SO_4 cause an explosion thus making unsafe to conduct the experiment in the laboratory.
- For example sulphate of group IA elements like K_2SO_4 and Na_2SO_4 are usually not prepared by the displacement method due to this reason.

Memorise MAZIT!

Magnesium, **A**luminium, **Z**inc, **I**ron and **T**in (MAZIT) are only metals which are commonly used to prepare soluble sulphate by displacement method.

Neutralisation method

This method is used to make sulphate of metals which are either very reactive or less reactive than hydrogen (Pure reactive metal would cause an explosion while less reactive metal would give no reaction with the dilute H_2SO_4).

Neutralisation method employs acid-base neutralisation reaction.

- The base may be oxide, hydroxide, carbonate or bicarbonate of the metal which will react with dilute H_2SO_4 to give sulphate of the metal.
- For example if the metal is potassium; then:

$K_2O + H_2SO_4 \rightarrow K_2SO_4 + H_2O$
$2KOH + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O$
$K_2CO_3 + H_2SO_4 \rightarrow K_2SO_4 + CO_2 + H_2O$
$2KHCO_3 + H_2SO_4 \rightarrow K_2SO_4 + 2CO_2 + 2H_2O$

PREPARATION OF INSOLUBLE SULPHATE

To prepare insoluble sulphate, **precipitation method** is always used. In preparing insoluble sulphate by precipitation method; one soluble salt must contain wanted cation and another soluble salt must contain wanted anion and then through double decomposition reaction the required insoluble salt is formed.

- For example, if we want to prepare $PbSO_4$, then we may use $Pb(NO_3)_2$ (soluble and contain the wanted Pb^{2+}) and Na_2SO_4 (soluble and contain the wanted SO_4^{2-}). Thus the two compounds will react in double decomposition reaction to give the wanted $PbSO_4$ as per equation:

$$Pb(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow PbSO_4(s) + 2NaNO_3(aq)$$

Other insoluble suphates which prepared by precipitation method are $BaSO_4$, $BrSO_4$, $PbSO_4$, $HgSO_4$, $CaSO_4$ and Ag_2SO_4.

USES OF SULPHATES

Some uses of metal sulphates are explained below.

In brown ring test

Iron(II) sulphate is used to test presence of nitrate by giving brown compound ($[Fe(H_2O)_5NO]SO_4$) which appears as a brown ring.

- In the testing experiment, the iron(II) sulphate is added to the solution of nitrate, e.g. sodium nitrate mixed with sulphuric acid where the following series of chemical reactions occur:

Firstly the mixture of the nitrate and sulphuric acid gives nitric acid.

$$NaNO_3(aq) + H_2SO_4(aq) \longrightarrow NaHSO_4(aq) + HNO_3(aq)$$

Produced nitric acid is then reduced to nitrogen monoxide by some of the iron(II) sulphate while the sulphate get oxidised to iron(III) sulphate.

$$6FeSO_4(aq) + 2HNO_3(aq) + 3H_2SO_4(aq) \longrightarrow 3Fe_2(SO_4)_3(aq) + 4H_2O(l) + 2NO(g)$$

Finally, the nitrogen monoxide (produced in the above equation) reacts (**ligand substitution reaction**) with more iron(II) sulphate to give the brown ring of $[Fe(H_2O)_5NO]SO_4$.

$$[Fe(H_2O)_6]SO_4(aq) + NO(g) \longrightarrow [Fe(H_2O)_5NO]SO_4(aq) + H_2O$$

Or ionically; $[Fe(H_2O)_6]^{2+}(aq) + NO(g) \longrightarrow \underset{\textbf{brown}}{[Fe(H_2O)_5NO]^{2+}(aq)} + H_2O(l)$

Don't get confused!

In aqueous solution, Fe^{2+} coordinates with water to form complex, $[Fe(H_2O)_6]^{2+}$ and therefore writing $FeSO_4(aq)$ is the same as writing $[Fe(H_2O)_6]SO_4(aq)$.

In making of plaster of Paris

Plaster of Paris is the commercial name for calcium sulphate hemihydrate, $CaSO_4.\frac{1}{2}H_2O$, (alternatively may be written as $(CaSO_4)_2.H_2O$). It is made by partial dehydration of gypsum, $CaSO_4.2H_2O$, through heating to temperature ranged from 100°C to 150°C in most cases.

$$2CaSO_4.2H_2O(s) \xrightarrow[100℃-150℃]{} (CaSO_4)_2.H_2O(s) + 3H_2O(g)$$

Among many other uses, plaster of Paris is used in surgery to maintain joints in a fixed position and in dentistry for taking impressions.

- These applications exploit the fact that calcium sulphate forms a moldable paste upon hydration and hardens as a hemihydrate. It is also convenient that calcium sulphate is very poorly soluble in water, so structures do not dissolve.

In agriculture

- Potassium sulphate is used as potassic fertilizer.
- Copper(II) sulphate is used in spraying vines and potatoes to kill moulds which would harm plants.

In making dyes

- Iron(II) sulphate is used with **gallic acid** (3,4,5-trihydroxybenzoic acid) in the manufacture of ink.
- Copper(II) sulphate is used in the manufacture of certain green pigments.

In medicines

Sulphates are widely used in medicines. For example:

- Sodium sulphate is used in treatment of hypercalcemia (abnormally high level of calcium in the blood).
- Magnesium sulphate for short term relief of constipation.
- Iron(II) sulphate for treating anemia.
- Zinc sulphate for the treatment of certain skin diseases.

PRACTICE EXERCISE 16

Question 1

Solution of sodium sulphate is neutral while that of zinc sulphate is acidic. Explain

Question 2

Effervescence of colourless gas is obtained when sodium carbonate is introduced into a beaker containing solution of copper (II) sulphate. Explain

Question 3

Complete the following reactions:

(i) $CaSO_4 \underset{\Delta}{\rightarrow}$
(ii) $K_2SO_4 \underset{\Delta}{\rightarrow}$
(iii) $Rb_2SO_4 + H_2O \rightarrow$
(iv) $BeSO_4 + H_2O \rightarrow$
(v) $NaHCO_3(aq) + H_2SO_4(aq) \rightarrow$

Question 4

With help of chemical equation(s), explain how you would distinguish solution of potassium sulphate and potassium nitrate by using ferrous sulphate.

Question 5

Outline three uses of sulphates.

Chapter 17

CHLORIDES

Chlorides are chemical compound containing chlorine whereby chlorine is more electronegative atom in the compound. Chlorides of metals contain negatively charged chloride ion, $\mathbf{Cl^-}$, (and of course, positively charged metallic ion) and therefore these chlorides are salts. Most of chlorides are salts.

STRUCTURE OF CHLORIDES

Chlorides with low degree of polarisation are highly ionic. They exist in crystalline ionic lattice of oppositely charged ions (cations and anions). Metals of group IA and IIA (except Beryllium) form this kind of chloride. These metals (s-block metals) have cation of small polarising power because have large cationic radius accompanied with low charge.

Oppositely, chlorides with high degree of polarisation are covalent. In large part, they exist as molecules. Most of metals in p and d-block form this kind of chloride because their cations have large polarising power.

Association of molecules of chlorides

Since chlorine is small in size, it exerts weak steric hindrance. Weak steric hindrance of chlorine means that it is possible for metallic atom (or ion) of one chloride molecule to form bond with chlorine of neighbour chloride molecule thus leading to association between the two chloride molecules. For this to occur, the metallic ion must have the following features:

- It must have **empty orbital** in sub-energy level which is closer to nucleus.
- The empty orbital is **the room of lone pair** of chlorine from neighbour chlorine molecule; and it must be closer to nucleus to ensure that nuclear attractive force (which hold lone pair) reach to the empty orbital easily.
- It should have **high cationic charge** to ensure that there is enough nuclear attractive force **to hold the lone pair**.
- It should have small **cationic radius** to ensure that the nuclear attractive force reach empty orbital easily so as **to hold the lone pair**.

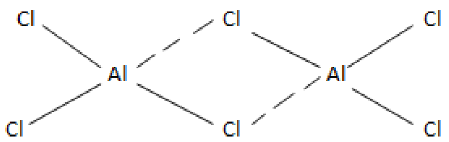
You should be able to notice that:

- The last two conditions are for the same purpose of holding lone pair in the empty orbital. So even chloride with metallic ion of low cation charge (like $\mathrm{Be^+}$) may undergo association if and only if the ion has very small cationic radius. Or the metallic ion may have high cationic charge but still its chloride does not undergo association if the ion has very large ionic radius.
- The last two conditions confirm that the chloride has high degree of polarisation. So the association is for covalent chlorides.

To have better understanding of the concept of association, consider structure of $\mathrm{AlCl_3}$.

With electronic configuration of $[\mathrm{Ne}]\ 3s^2 3p_x^1\, p_y^0\, p_z^0$, Al must undergo sp^2 hybridisation to form three unpaired hybridised orbitals(in $[\mathrm{Ne}]\ 3s^1 3p_x^1\, p_y^1\, p_z^0$) which are free to combine with other three monovalent atoms like chlorine thus forming compounds like $\mathrm{AlCl_3}$. This leaves p_z orbital empty.

- Due to presence of an empty orbital; two molecules of $\mathrm{AlCl_3}$ may undergo association in the vapour phase to form a **dimer,** i.e. each molecule of $\mathrm{AlCl_3}$ may welcome lone pair of chlorine atom from its neighbour molecule of $\mathrm{AlCl_3}$ thus forming the dimer (see the figure in the next page).



Things to note from dimerisation of $AlCl_3$

$AlCl_3$ undergoes dimerisation and not polymerisation like $BeCl_2$, why?

Unlike $BeCl_2$ (studied in chapter 9), $AlCl_3$ can undergo association to maximum of two molecules only, this is because in $BeCl_2$ there are two empty orbitals, p_y and p_z which enable the molecules of $BeCl_2$ to associate to infinite thus forming a polymer while $AlCl_3$ having one p_z empty orbital only ends to the dimer.

Dimerisation of molecules of $AlCl_3$ is possible in vapour phase and not in solid phase, why?

This is because, in vapour (gas) phase, molecules are moving randomly thus giving the possibility of having good orientation for Al of one molecule of $AlCl_3$ to form bond with Cl from another (neighbour) molecule of $AlCl_3$

Dimerisation of $AlCl_3$ is possible in organic solvent but not in aqueous solution, why?

Being covalent, $AlCl_3$ can dissolve in organic solvent. As its molecules in the solution are moving freely there is possibility of having good orientation of making bond between Al and Cl of neighbour molecule of $AlCl_3$. However in aqueous, solution aluminium chloride hydrolyses giving acidic solution.

In aqueous solution: $AlCl_3(s) + 3H_2O(l) \rightarrow Al(OH)_3 + 3H^+(aq) + 3Cl^-(aq)$

To finish with; the reader should understand that **similar explanation for dimerisation in $AlCl_3$ may be used to explain dimerisation in $FeCl_3$.**

HYDROLYSIS OF CHLORIDES

Only covalent chlorides hydrolyse in water to give acidic solution. Ionic chlorides do not hydrolyse in water. To justify this, we are going to look chlorides of group IA, IIA, IIIA, IVA and VA.

Chlorides of group IA

Chlorides of this group have very low degree of polarisation. As result, they are strong ionic and therefore they do not hydrolyse in water. When they dissolved in water, they just form neutral solution.

$$MCl + H_2O \longrightarrow \text{No reaction}$$

Where M is any group IA element

For example;

$NaCl(s) + 6H_2O \rightarrow \text{No reaction}$

or $NaCl(s) + 6H_2O \rightarrow Na^+(aq) + Cl^-(aq)$

Chlorides of group IIA

Here only $BeCl_2$ undergoes complete hydrolysis to give acidic solution. This is because, being on the top of the group, Be^{2+} has smallest cationic radius making it to have strongest polarising power and hence highest degree of polarisation for $BeCl_2$ which make it to be covalent.

$$BeCl_2 + 2H_2O \longrightarrow Be(OH)_2 + 2HCl$$

$MgCl_2$ does not hydrolyse in cold water. But in steam undergoes partial hydrolysis.

$$MgCl_2 + H_2O(l) \longrightarrow \text{No reaction}$$

$$\mathrm{MgCl_2 + H_2O \longrightarrow Mg(OH)Cl + HCl}$$

Other chlorides, are strong ionic; they do not hydrolyse in either cold water or steam.

Chlorides of group IIIA

Chlorides of this group are highly covalent in characters, they hydrolyse in water. For example;

- $\mathrm{BCl_3}$ hydrolyse to give boric acid and $\mathrm{H_3BO_3}$ hydrochloric acid, HCl

$$\mathrm{BCl_3(l) + 3H_2O(l) \rightarrow H_3BO_3(aq) + 3HCl(aq)}$$

- $\mathrm{AlCl_3}$ gives $\mathrm{Al(OH)_3}$ and HCl

$$\mathrm{AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl}$$

Chlorides of group IVA

Group IVA elements can form **tetrachloride** or **dichloride** with chlorine

- *All group IVA elements can form tetrachloride,* MCl_4
- *Only tin and lead can form dichloride,* MCl_2 (Recall inert pair effect).

Tetrachlorides are all covalent, so they are hydrolysed in water. Carbon tetrachloride, $\mathrm{CCl_4}$, is the only tetrachloride which does not hydrolyse in water.

Why carbon tetrachloride (tetrachloromethane) does not hydrolyse in water?

Suppose a water molecule is going to react with the carbon tetrachloride:

- The reaction between $\mathrm{CCl_4}$ and water would have to start by water molecule attaching itself to the carbon (in $\mathrm{CCl_4}$) by using lone pair of oxygen in the water molecule. So the chlorine atom in $\mathrm{CCl_4}$ would get pushed off the carbon in the process by the incoming water molecule.

There are two problems with this:

First problem:

The chlorine are so bulky and the carbon atom so small, that the oxygen cannot easily get at the carbon atom. And even if it did, there will be a transition stage where there is considerable cluttering around the carbon atom before the chlorine atom breaks away completely.

- So there is going to be a lot of repulsion between the various lone pairs on all the atoms surrounding the carbon (each chlorine atom has three lone pairs while each water molecule has two lone pairs in its oxygen).
- That cluttering makes the transition state very unstable and very unstable transition state means very high activation energy for the reaction.

Second problem:

Also there is no a convenient empty orbital on the carbon that the oxygen lone pair can attach to. *What would happen if the empty orbital would be present?*

- It could attach before the chlorine starts to break away, that would be an advantage, **why?**

Forming a bond releases energy, and that energy would therefore be readily available for breaking a carbon – chlorine bond. But carbon having an outermost energy level of $n = 2$ which has no d – orbitals and all of its s and p orbitals have been occupied with electrons in $\mathrm{CCl_4}$, that is not possible

In summary: carbon tetrachloride does not hydrolyse due to the following reasons:

- It has so small atomic size that cannot allow the incoming water molecule to attach in it.
- It has no empty orbitals in its electronic structure

What about other tetrachloride like $SiCl_4$?

- Silicon atom is bigger and so there is more room around it for water molecule to attack and the transition state will be less cluttered.
- Also there are empty 3d orbitals available to accept lone pair from the water molecule.

Hence other tetrachloride like $SiCl_4$ hydrolyse in water.

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$$

$$GeCl_4 + 2H_2O \rightarrow GeO_2 + 4HCl$$

$$SnCl_4 + 2H_2O \rightarrow SnO_2 + 4HCl$$

$$PbCl_4 + 2H_2O \rightarrow PbO_2 + 4HCl$$

Don't forget:

Formation of white fumes of hydrogen chloride gas or hydrochloric acid solution depends on the amount of water:

- In small amount of water e.g. when the tetrachlorides are exposed in moist air, hydrogen chloride gas is formed.
- In large amount of water, the gas dissolves to give hydrochloric acid.

For dichlorides

- $SnCl_2$ undergo partial hydrolysis
  $SnCl_2 + H_2O \rightarrow Sn(OH)Cl + HCl$
- $PbCl_2$ is ionic, insoluble in water and therefore it does not hydrolyse in water
  $PbCl_2 + H_2O \rightarrow$ No reaction

Chlorides of group VA

The hydrolysis of this group depends on whether the chloride is **trichloride** or **pentachloride**.

For trichloride:

NCl_3 has peculiar behavior on hydrolysis.

- It reacts with water to give ammonia and hypochlorous acid.

$$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$$

PCl_3 hydrolyses to give phosphorous acid and hydrochloric acid

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

The reaction takes two steps:

First step: formation oxychloride

$$\underset{\textbf{Oxychloride}}{PCl_3 + H_2O \rightarrow POCl + 2HCl} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(i)}$$

Second step: Hydrolysis of oxychloride

$$\underset{\textbf{Phosphorous oxychloride}}{POCl + 2H_2O \rightarrow H_3PO_3 + HCl}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(ii)}$$

Overall reaction equation: take (i) + (ii) and simplify,

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

It should be understood that:

The oxychloride, POCl is capable of undergoing more hydrolysis because it is covalent. Despite the fact that ClO^{3-} is very strong electronegative radical, POCl is still covalent due to the fact that phosphorous, P being non–metal has high electronegativity also, making POCl covalent. If phosphorous would be electropositive, POCl would be ionic (ionic compounds do not hydrolyse in water) and the reaction would end at the first step only. Wait………..! You will see this in the case of $AsCl_3, SbCl_3$ and $BiCl_3$ below!

$\mathbf{AsCl_3}, \mathbf{SbCl_3}$ and $\mathbf{BiCl_3}$ have still significant degree of covalent characters to hydrolyse in water.

- They react with water to give oxychloride

$$MCl_3 + H_2O \rightarrow MOCl + 2HCl$$

Where M may be As, Sb or Bi

In this case As, Sb and Bi being more electropositive than phosphorous combined with very high electronegativity of oxychloride radical, ClO^{3-}, their oxychloride are ionic and hence they cannot undergo further hydrolysis. This is different to POCl which can undergo more hydrolysis to give H_3PO_3.

For pentachlorides:

Pentachlorides which exists are $PCl_5, AsCl_5$ and $SbCl_5$

- They are hydrolysed completely to the higher oxoacids

$$MCl_5 + 4H_2O \rightarrow H_3MO_4 + 5HCl$$

Where M may be P, As or Sb

Again the reaction takes in two steps:

First step: Formation of oxychloride

$$MCl_5 + H_2O \rightarrow MOCl_3 + 2HCl \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(i)}$$

Second step: Hydrolysis of oxychloride

$$MOCl_3 + 3H_2O \rightarrow H_3MO_4 + 3HCl \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(ii)}$$

Overall reaction: take (i) + (ii) and simplify,

$$MCl_5 + 4H_2O \rightarrow H_3MO_4 + 5HCl$$

It is interesting!

In this case even $AsOCl_3$ and $SbOCl_3$ are capable of undergoing more hydrolysis in spite of high electronegativity of oxychloride radical because with charge of +5, As^{5+} and Sb^{5+} have very large polarising powers which make oxychlorides to have very high degree of polarisation causing them to be covalent and hence they can hydrolyse in water.

PREPARATION OF CHLORIDES

Direct method

By direct chlorination of the metal: Most of elements react directly with chlorine to give their corresponding chlorides. For example;

$$Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$$
$$2Al(s) + 3Cl_2(g) \longrightarrow 2AlCl_3(s)$$

If the metal has variable oxidation state, chlorine being good oxidising agent will oxidise the metal to its higher oxidation state to form higher chloride. As an example;

$$2Fe(s) + 3Cl_2(g) \longrightarrow 2FeCl_3(s) \ \ (\textbf{Not } \mathbf{FeCl_2})$$

By displacement method: Metals which are stronger reducing agent (more reactive) than hydrogen, displace (reduce) hydrogen from dilute HCl and themselves get oxidised to their respective sulphate

Generally;

$$\text{Metal} + HCl(dil) \rightarrow \text{Chlorides} + H_2$$

For example; $Mg(s) + 2HCl(dil) \rightarrow MgCl_2(aq) + H_2(g)$

$$Fe(s) + 2HCl(dil) \rightarrow H_2(g) + FeCl_2(aq) \quad (\textbf{Not } \mathbf{FeCl_3})$$

The conditions required for this method are exactly the same as those of sulphate explained in the previous chapter.

Indirect method

By neutralisation method: This method is preferred for making chloride of metals which are either very reactive or less reactive than hydrogen (Pure reactive metal would cause an explosion while less reactive metal would give no reaction with the dilute HCl).

Neutralisation method employs acid-base neutralisation reaction.

- The base may be oxide, hydroxide, carbonate or bicarbonate of the metal which will react with dilute HCl to give chloride of the metal.
- For example if the metal is potassium; then:

$$K_2O + 2HCl \rightarrow 2KCl + H_2O$$

$$KOH + HCl \rightarrow KCl + H_2O$$

$$K_2CO_3 + 2HCl \rightarrow 2KCl + CO_2 + H_2O$$

$$KHCO_3 + HCl \rightarrow KCl + CO_2 + H_2O$$

By precipitation method: This method is preferred for making insoluble chloride like silver chloride.

$$AgNO_3(aq) + NaCl(aq) \longrightarrow AgCl(s) + NaNO_3(aq)$$

Other insoluble chlorides are lead(II) chloride and mercury(I) chloride. All other remaining chlorides are soluble.

USES CHLORIDES

In Downs' process

- This is the electrolysis of molten sodium chloride to produce sodium and chlorine gas.

$$2NaCl(l) \xrightarrow{\text{Electrolysis}} 2Na(l) + Cl_2(g)$$

In chlor-alkali process

- His process is useful in the production of NaOH.
- It involves electrolysis of brine solution (concentrated sodium chloride solution) to produce NaOH, H_2 and Cl_2

$$2NaCl(aq) + H_2O(l) \xrightarrow{\text{Electrolysis}} 2NaOH(aq) + H_2(g) + Cl_2(g)$$

In production of hydrogen chloride gas

- NaCl reacts with concentrated sulphuric acid to give hydrogen chloride gas

$NaCl(s) + H_2SO_4(conc) \rightarrow NaHSO_4(aq) + HCl(g)$………………… (i)

Then $NaCl(s) + NaHSO_4(aq) \rightarrow Na_2SO_4(aq) + HCl(g)$………….. (ii)

Overall reaction equation (by taking (i) + (ii))

$$2NaCl(s) + H_2SO_4(conc) \rightarrow Na_2SO_4(aq) + 2HCl(g)$$

In dehumidifiers and air conditioning

- $LiCl$ (and $LiBr$) is used in dehumidifiers because it is deliquescent (which in turn it is explained by small cationic radius of Li^+)
- It is also used in air conditioning because of its positive heat of solution.

In agricultural fertilizer

- For example, potassium chloride is used as potassic fertilizer to increase fertility of the soil in agriculture.

PRACTICE EXERCISE 17

Question 1

Can ferrous chloride be prepared by direct method? Explain.

Question 2

Can manganese (VII) chloride be prepared by direct method? Explain.

Question 3

Compare aluminium chloride and beryllium chloride.

Question 4

Explain what will you observe when drops of water are introduced into a beaker containing iron (III) chloride.

Question 5

Complete following reactions.

(i) $BCl_3 + H_2O(l) \rightarrow$
(ii) $NCl_3 + H_2O(l) \rightarrow$
(iii) $SiCl_4 + H_2O(l) \rightarrow$
(iv) $MgCl_2 + H_2O(g) \rightarrow$
(v) $BiCl_3 + H_2O(l) \rightarrow$

Chapter 18

NITRATES

Nitrates are compounds containing a polyatomic anion with the empirical formula NO_3^-. They are salts of nitric acid. As it is derived from nitric acid which is very strong acid, NO_3^- is very weak base. **All inorganic nitrates are soluble in water** because *they have low lattice energy due to large size of* NO_3^- *accompanied with only single charge while the hydration energy is very large due to possibility of* NO_3^- *to make hydrogen bonds with water molecules.*

HYDROLYSIS OF NITRATES

Nitrates with significant degree of covalent characters undergo cationic hydrolysis to give acidic solution. These 'covalent' nitrates have high degree of polarisation and they always contain cations of large polarising power which come from weak base.

- Most of nitrates of p and d-block metals form this kind of sulphate. For example;

$$Al(NO_3)_3 + 3H_2O \longrightarrow Al(OH)_3 + 3H^+ + 3NO_3^-$$

$$Zn(NO_3)_2 + 2H_2O \longrightarrow Zn(OH)_2 + 2H^+ + 2NO_3^-$$

On another hand, strong ionic nitrates do not hydrolyse in water. These ionic salts contain cations from strong base which have small polarising power. Alkali and earth metals (except beryllium) form this kind of nitrates. As an example;

$$KNO_3 + H_2O \longrightarrow \text{No reaction}$$

THERMAL STABILITY OF NITRATES

Nitrates with high degree of polarisation undergo thermolysis to give their corresponding oxides and also brown fumes of NO_2 are evolved in the process. Nitrates of earth metals, p and d-block metals decompose on this way.

Generally; $$4NO_3^- \underset{\Delta}{\rightarrow} 2O^{2-} + 4NO_2 + O_2$$

For example; $$4Al(NO_3)_3 \underset{\Delta}{\rightarrow} 2Al_2O_3 + 12NO_2 + 3O_2$$

$$2Cu(NO_3)_2 \underset{\Delta}{\rightarrow} 2CuO + 4NO_2 + O_2$$

Nitrates of alkali metals (except lithium) decompose to give nitrite and oxygen gas. They do not give oxide or brown fumes of NO_2 (You should be able to give reason for this).

$$2MNO_3 \underset{\Delta}{\rightarrow} 2MNO_2 + O_2$$

Where M is any alkali metal except lithium

PREPARATION OF NITRATES

Displacement method (Excess metal method)

Metals which are stronger reducing agent (more reactive) than hydrogen, displace (reduce) hydrogen from dilute HNO_3 and themselves get oxidised to their respective nitrates.
Generally;

$$\text{Metal} + HNO_3(\text{dil}) \rightarrow \text{Nitarate} + H_2$$

For example; $Mg(s) + 2HNO_3(\text{dil}) \rightarrow Mg(NO_3)_2(aq) + H_2(g)$

You should aware with the fact that: Due to oxidising character of dilute nitric acid, even less metals like copper and silver may react with the acid. However nitrogen monoxide gas is evolved as reduction product instead of hydrogen gas.

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

But if the acid is concentrated, the common reaction will occur like any other metal would do.

$$Cu(s) + 4HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

Neutralisation method

This method is used to make nitrate of metals which are either very reactive or less reactive than hydrogen (pure reactive metal would cause an explosion while less reactive metal would give no reaction with the dilute HNO_3).

Neutralisation method employs acid-base neutralisation reaction.

- For example if the metal is potassium; then:

$K_2O + 2HNO_3 \rightarrow 2KNO_3 + H_2O$
$KOH + HNO_3 \rightarrow KNO_3 + 2H_2O$
$K_2CO_3 + 2HNO_3 \rightarrow 2KNO_3 + CO_2 + H_2O$
$KHCO_3 + HNO_3 \rightarrow KNO_3 + CO_2 + H_2O$

USES OF NITRATES

The most important common uses of metal nitrates are in making fertilizers and making explosives.

In agricultural fertilizers

Nitrogen is among nutrients required by plants in large proportion and thus it said to be primary nutrient. Nitrates are commonly used nitrogenous fertilizer.

- Calcium nitrate, sodium nitrate and potassium nitrate (it also supply potassium which is primary nutrient too) are good examples of metal nitrates used to enhance soil fertility in agriculture.

The reason that nitrates are more preferred as nitrogenous fertilizer is their high solubility and biodegradability.

In making explosives

When a gas expands suddenly enough as to create a shock wave, an explosion occurs. After agricultural fertilizers, the second major application of nitrates is as oxidising agent like in explosives.

- Are used in explosives (e.g. in fireworks and gunpowder) because nitrates are very good oxidizing (combusting) agent (it plays the same role as oxygen) where the rapid oxidation of carbon compounds liberates large volumes of gases. To have better understanding of this, let us have a look at gunpowder as an example.

Gunpowder consists of a mixture of potassium nitrate (**saltpeter**), wood charcoal (carbon) and sulphur. The explosive effect of the nitrate arises from sudden production (by combustion of gunpowder) of a volume of gas which is very large and further expanded by heat of reaction which is exothermic.

- Gases which are produced in the combustion are mainly carbon dioxide, and nitrogen (with some carbon monoxide) according to the following equation;

$2KNO_3(s) + S(s) + 3C(s) \longrightarrow K_2S(s) + N_2(g) + 3CO_2(s)$

PRACTICE EXERCISE 18

Question 1

Give reason (s) of high solubility of nitrate in water.

Question 2

Explain what will you observe when silver nitrate is heated?

Question 3

Complete the following reactions:

(i) $Zn(NO_3)_2 \underset{\Delta}{\rightarrow}$
(ii) $NaNO_3 \underset{\Delta}{\rightarrow}$
(iii) $Cu(NO_3)_2 + H_2O \rightarrow$
(iv) $KNO_3 + H_2O \rightarrow$
(v) $KO_2 + HNO_3 \rightarrow$

EXAMINATION QUESTIONS FOR PART FOUR

Question 1

Aluminium carbonate does not exist i.e. it is never prepared in the laboratory. Explain.

Question 2

When a solution of $Ba(OH)_2$ is mixed with a solution of sulphuric acid (H_2SO_4), a white precipitate forms and its electrical conductivity decreases markedly.

(i) Write balanced equation for the reaction that occurred.

(ii) Account for the decrease in electrical conductivity.

Question 3

Effervescence of colourless gas is obtained when sodium hydrogen carbonate is added to copper (II) sulphate solution. Explain.

Question 4

How does calcium hydroxide react with:

(i) Carbon dioxide

(ii) Ammonium salt

(iii)Temporary hard water

Question 5

Write a balanced chemical equation for the following reactions:

(i) Excess carbon dioxide is bubbled in sodium hydroxide solution.

(ii) Excess sulphuric acid is added to sodium sulphate solution.

(iii) A white precipitate is observed when sodium sulphate solution is added to Barium chloride solution in the presence of hydrochloric acid.

Question 6

Sodium, Na, and aluminium, Al, are metals of period 3 but their chloride have different physical and chemical properties. Explain.

Question 7

Write a balanced chemical equation for the following reactions:

(i) Copper metal is warmed with excess concentrated H_2SO_4.

(ii) Sulphur reacts with dilute nitric acid.

(iii) Copper metal is warmed with excess concentrated HNO_3

Question 8

Use balanced equations to explain the following

i. When lead (II) nitrate solution is mixed with potassium chromate solution, yellow precipitate is obtained.

ii. Sodium hydroxide is unsuitable for precipitation of Zn^{2+} in aqueous solution.

iii. When aqueous $AgNO_3$ is added to a solution of $BaCl_2$ a white precipitate forms which dissolve in excess of aqueous NH_3.

Question 9

Write balance chemical equation and the expected observations for each of the following:

a) silver nitrate is heated

b) dilute nitric acid is added to an aqueous solution of sodium thiosulphate

c) a small amount of water is added to bismuth chloride solution followed by the addition of concentrated hydrochloric acid

Question 10

Solid lithium hydroxide is used in space vehicles to remove exhaled carbon dioxide from the living environment. What mass of gaseous carbon dioxide can be absorbed by 1kg of lithium hydroxide? (Atomic masses $\mathrm{Li} = 7, \mathrm{O} = 16, \mathrm{H} = 1, \mathrm{C} = 12$).

Question 11

A spray used to relieve the pain and swelling caused by insect stings contains aluminium sulphate, $\mathrm{Al_2(SO_4)_3}$, as its active ingredient. A 5g sample of the spray was dissolved in distilled water and an excess of aqueous barium chloride was added. The precipitate barium sulphate weighted 2.047g. Calculate the percentage of aluminium sulphate in the spray.

(Atomic masses: $\mathrm{Ba} = 137, \mathrm{Al} = 27, \mathrm{S} = 32, \mathrm{O} = 16$ and $\mathrm{Cl} = 35.5$).

Question 12

2.1g of the oxide of divalent metal X were dissolved in slightly excess of dilute HCl. On addition of excess $\mathrm{Na_2CO_3}$ to the mixture solution, insoluble carbonate was formed. After purification, drying and weighing, the mass of the insoluble carbonate was found to be 3.75g

i. Calculate the relative atomic mass of the metal X

ii. Identity element X

PART FIVE

TRANSITION ELEMENTS
AND
COMPLEXES

Chapter 19

TRANSITION ELEMENTS

INTRODUCTION

Transition elements *are those whose atoms or at least one of their ions have partially filled d orbitals*.

- They lie between s and p blocks of modern periodic table so they can be regarded as affecting a **transition** from electropositive elements of the s-block, on the one hand, to the more electronegative elements of p-bock on the other and hence the term 'transition elements'

The transition elements are placed in four series which are known as transition series.

- **First transition series** have incomplete 3d – orbitals
- **Second transition series** have incomplete 4d – orbitals
- **Third transition series** have incomplete 5d − orbitals
- **Fourth transition series** have incomplete 6d – orbitals

In this chapter we will concentrate on the first series so wherever we talk about 'transition element' the implication will be on transition elements of first series.

Transition elements versus d–block elements

The terms **transition element (or metal**) and **d – block element** are sometimes used as they mean the same thing.

- In actual sense they do not have the same meaning: there is a subtle difference between the two terms

d – block elements *are elements in periodic table which correspond to the d – sub energy levels filling of electron.* The first row of these is shown in the table below:

ELEMENT	SYMBOL	ATOMIC NUMBER	ELECTRONIC CONFIGURATION
Scandium	Sc	21	$[\mathrm{Ar}]\ 3d^1\ 4s^2$
Titanium	Ti	22	$[\mathrm{Ar}]\ 3d^2\ 4s^2$
Vanadium	V	23	$[\mathrm{Ar}]\ 3d^3\ 4s^2$
Chromium	Cr	24	$\mathbf{[Ar]\ 3d^5\ 4s^1}$
Magnesium	Mn	25	$[\mathrm{Ar}]\ 3d^5\ 4s^2$
Iron	Fe	26	$[\mathrm{Ar}]\ 3d^6\ 4S^2$
Cobalt	Co	27	$[\mathrm{Ar}]\ 3d^7\ 4s^2$
Nickel	Ni	28	$[\mathrm{Ar}]\ 3d^8\ 4s^2$
Copper	Cu	29	$\mathbf{[Ar]\ 3d^{10}\ 4s^1}$
Zinc	Zn	30	$[\mathrm{Ar}]\ 3d^{10}\ 4s^2$

You will notice that the pattern of filling is broken in both chromium and copper.

From above electronic structures of d- block elements:

- Zinc has the electronic structure of [Ar] $3d^{10}4s^2$ whereby all of its d – orbitals are paired with electrons. When it forms ions, it always loses two 4s electrons to give Zn^{2+} ion with the electronic structure of [Ar] $3d^{10}$ which also has no any unpaired d – orbital. Therefore both zinc and its ion has exactly paired d – orbitals and does not meet with the definition of transition element either. **Hence zinc is d – block element but is not transition element.**
- So strictly speaking, Zn (and of course, Cd and Hg) are just **post transition metals** but they are often referred to as transition metals because of similar properties.

What about the case of copper?

- By contrast to zinc, copper, [Ar] $3d^{10}4s^1$, forms two ions. In the Cu^+ ion, its electronic structure, [Ar] $3d^{10}$ has exactly filled d – orbitals. However, the more common, Cu^{2+} ion has the structure [Ar] $3d^9$ which has one unpaired d – orbital and therefore according to the definition of transition element, copper is transition element (although electronic configuration of its neutral atom has all of its d- orbitals paired with electrons)

The following single sentence provides good conclusion on relationship between transition element and d – block element:

All transition elements are d – block elements but not all d – block elements are transition elements.

SOME MISCELLANEOUS FACTS OF TRANSITION ELEMENTS

Metallic character

Transition elements are metals.

- The characteristic chemical properties of metals are based on the abilities of their atoms to lose one or more electrons under appropriate conditions to form positive ions (cations).

Atomic radii

Transition elements have almost the same atomic radii.

- This is because in transition elements, the increase in screening effect is enough to counterbalance with the increase in nuclear attractive force as you go across the period since the electrons are added to penultimate shell (unlike in s and p block elements where electrons are added to valence shell thus making the increase in nuclear attractive force to outweigh the increase in screening effect and hence their atomic radii is found to decrease as you across the period from left to right)
- Compared to s – block metals, d – block metals have smaller atomic radii

Conduction of electricity

Transition elements conduct electricity very well.

- Due to their low ionisation energy, transition metals have delocalised unpaired d–electrons which are responsible for conducting electricity.

Strength of metallic bond

Transition metals form very strong metallic bond between their atoms.

- They form stronger metallic bond than s – block metals because they have smaller metallic radii.

- Among transition elements themselves, strength of metallic bond increases with an increase in number of **unpaired d–electrons** (and of course unpaired s – electrons for chromium and copper).
- As the unpaired d – orbital electrons pair up, the strength of metallic bond decreases. Thus zinc having all of its 4s and 3d electrons paired, has weakest metallic bond.

Covalent bond formation

Since penultimate d - orbitals of transition metals are unpaired with electrons; it is possible that their incomplete d – orbitals overlap with each other to some extent to form d – d bonds which introduce **covalent bonding.**

- Hence unlike in s and p block metals, **in transition elements there is covalent bonding due to d – d overlapping** which indicates that there are stronger inter – atomic forces in transition metals.

Why s and p – block metals do not undergo covalent bonding?

This is simply because, all inner orbitals of s and p – block metals are completely filled with electrons.

Melting and boiling point

Compared to s- block metals, transition metals have higher melting and boiling point as they have stronger inter - atomic forces because:

- They have stronger metallic bond.
- They have ability of forming covalent bonds between their atoms due to d –d overlapping.

The two factors make transition metals to be **hard** and **brittle.**

For d – block elements themselves, zinc has lowest melting and boiling point because it has all of its d – orbitals paired with electrons and therefore:

- It has weakest metallic bond.
- It cannot undergo d – d overlapping and hence there is no covalent bonding formation in zinc

It should be noted that:

Mercury which is at third transition series has similar outermost electronic configuration to that of zinc with all s and d orbitals paired with electrons. Being below zinc in the periodic table, means it has larger atomic and cationic size.

- So combining with the fact, it has all of its d – orbitals paired with electrons, mercury has abnormally weak metallic bond
- Adding the fact that it cannot form covalent bonding through d – d overlapping, mercury has abnormally weak inter-atomic forces making it to have abnormally low melting and boiling point. That is why **mercury is liquid (liquid metal!) at room temperature**.

Reactivity of transition elements

Despite the fact that transition elements have larger hydration energy as they have smaller cationic radii than s – block metals, transition metals have relatively low reactivity compared to the s – block metals due to the following reasons:

(i) They have higher enthalpy of atomisation (atomisation energy)

The interatomic forces between transition metal atoms are very strong because of:

- Their small sizes which make them to have very strong metallic bonds.
- Presence of additional covalent bonding due to d – d overlapping.

The above factors make heat of atomisation of transition elements to be very high.

(ii) They have greater ionisation energy

Due to their smaller sizes and greater nuclear charges, ionisation energies of transition metals are higher than s – block metals.

Large atomisation and ionisation energy, lower oxidation potential and the reaction (oxidation) $\mathrm{M(s)} \rightarrow \mathrm{M^{n+}(aq)} +$ ne occur by more difficult than in s – block metals.

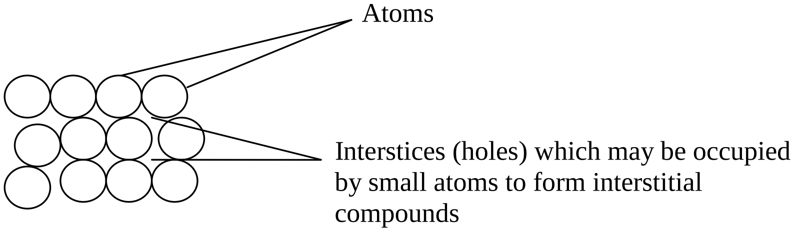
However:

Transition elements are generally still reactive, for example:

- With exception of copper, all transition metals (of first series remember!) react with dilute acid to liberate hydrogen gas.
- But with concentrated acids (concentrated HNO_3 and concentrated H_2SO_4) most of transition metals form a protective layer of oxide which resist further attack of the acids.

Formation of interstitial compounds

The transition metals form interstitial compounds *in which small sized atom like carbon, hydrogen, nitrogen and boron occupy the holes or interstices present in the metal lattice.*



The formation of interstitial compounds modifies the properties of transition metals.

- For example, steel which is interstitial compound for iron and carbon in harder than iron.

Alloy formation

Alloy formation is one of the most important properties of transition metals; **why transition metals?**

- Transition metals have metallic bonds in their crystal lattices in which metal cations are fixed in space and free electrons surround them. **The positions of some of the metal cations in a crystal lattice can easily be taken by other transition metals atoms because of their similar atomic and ionic radii and their property to form metallic bonds**.

The alloys formed by transition metals can be grouped into the following types:

(i) **Inter metallic alloys,** example brass (alloy of copper and zinc).

- Brass is also an example of solid solution.

It should be noted that:

They **alloys of mercury are known as amalgam**. For example an alloy of zinc and mercury is known as zinc amalgam.

(ii) **Interstitial alloys**, example steel (In which interstices in close packing of iron are occupied by carbon atoms as explained above in the 'interstitial compound formation')

GENERAL (SPECIAL) PROPERTIES OF TRANSITION ELEMENTS

Important special properties of transition elements to study here are:

(i) They form complexes
(ii) They have variable oxidation states
(iii) They have catalytic actions
(iv) They form coloured compounds
(v) They are paramagnetic

COMPLEX FORMATION ABILITY

Transition metals can form complexes because:

(i) They have empty orbitals in their electronic structure
(ii) They have small cationic size accompanied with high ionic charge

It should be noted that:

Other metals also form complex ion – it is not something that only transition metals do; however transition metals form a very wide range of complexes.

VARIABLE OXIDATION STATES

Transition elements exhibit variable oxidation state.

- The reason for the existence of variable oxidation states is **the tendency of penultimate electrons to enter into chemical bond formation because of the comparable (almost similar) energies of 4s and 3d orbitals.**

To have better understanding of the reason consider formation of chloride of calcium (non transition metal) and chloride of iron (transition metal).

First case: Formation of chloride of the non – transition metal, calcium

- Electronic structure of calcium is, $[\mathrm{Ar}]4\mathrm{s}^2$
- Stable chemical formula of calcium chloride is $\mathrm{CaCl_2}$, **why that? Why not CaCl or $\mathbf{CaCl_3}$**?
- If you tried to make CaCl (containing $\mathrm{Ca^+}$ ion) the overall process is slightly exothermic.
- By making a $\mathrm{Ca^+}$ ion so as to form $\mathrm{CaCl_2}$, instead, you have to supply more ionisation energy but a lot of more lattice energy is obtained also because there is much more attractive between chloride ions and $\mathrm{Ca^{2+}}$ ions than there is if you only have a $\mathrm{Ca^+}$ ions ($\mathrm{Ca^{2+}}$ has smaller sized and greater cationic charge than $\mathrm{Ca^+}$).

- Because the formation $\mathrm{CaCl_2}$ releases much more energy than making CaCl, then $\mathrm{CaCl_2}$ is more stable and hence it forms instead.

What about $\mathbf{CaCl_3}$?

- This time you have to remove third electron from calcium to form $\mathrm{Ca^{3+}}$ ion.
- The first two electrons come from 4s (in the outermost shell). The third one comes from the 3p (in the inner shell) which is much closer to the nucleus and therefore much more difficult to remove.

- So there is a large jump in ionisation energy between the second and third electron removed. Although again the lattice energy will increase but this time the increase is not enough to compensate for the extra ionisation energy and the overall process is very endothermic.
- In fact, $\mathrm{CaCl_3}$ does not exist!

Second case: Formation of chloride of transition metal, iron

Here there are changes in electronic structure of iron to make Fe^{2+} and Fe^{3+} ion.

Electronic structure is Fe is $[Ar]3d^6 4s^2$

Electronic structure of Fe^{2+} is $[Ar]3d^6$

Electronic structure of Fe^{3+} is $[Ar]3d^5$

The 4s orbital and the 3d orbitals have very similar energies

- There is not a huge jump in the amount of energy you need to remove the third electron compared with the first and second.

So in the iron case, the extra ionisation energy is compensated by the extra **lattice enthalpy (in solid $FeCl_3$)** or **hydration enthalpy (in aqueous $FeCl_3$)** evolved when Fe^{3+} compound is made.

The net effect of all this is that the overall enthalpy change is not vastly different whether you make, say, $FeCl_2$ or $FeCl_3$. That means that it is not too difficult to convert between the two compounds.

Trend shown on oxidation state by transition elements

With exception of zinc, all d- block elements of first row can form more than one stable oxidation state.

The maximum oxidation state shown by transition elements increases from scandium to manganese and then decreases to zinc, why?

Before manganese, the elements can ionise by losing all of their 4s and 3d electrons to attain stable electronic structure of Ar.

- Scandium can lose all two 4s electrons and one d-electron to show maximum oxidation state of +3 in Sc^{3+}
- Titanium can lose all two 4s electrons and two d-electrons to show maximum oxidation state of +4 in Ti^{4+}

Similarly:

Vanadium can lose a total of five electrons to show maximum oxidation state of +5, chromium can lose a total of six electrons to show maximum oxidation state of +6 and finally manganese can lose a total of seven electrons to show maximum oxidation state of +7.

- After manganese, atoms of transition elements starts to exert very strong effective nuclear attractive force to 3d and 4s orbitals due to increase nuclear charge which increases with an increase in number of protons. So……………………!

Eventually; elements after manganese cannot lose all d-electrons. For example; iron can lose a maximum of one d-electron only. With two 4s electrons, iron show stable oxidation state of +2 and +3 only in Fe^{2+} and Fe^{3+} respectively.

If so…………………*why zinc does not form Zn^{3+}?*

Among d – block elements of the first row, zinc has greatest nuclear charge so that its penultimate d electrons (and of course outer 4s electrons) are firmly held by nuclear attractive force and hence it can afford losing two 4s electrons only to form Zn^{2+} which has stable electronic structure of exactly full filled electronic configuration.

With exception of chromium and copper, the lowest stable oxidation state shown by transition elements is +2; chromium and copper show minimum oxidation state of +1, what is the reason for this pattern?

- With exception of chromium and copper, all transition elements have two 4s electrons in the outermost energy level, so on losing them in the ionisation they exhibit oxidation state +2
- On another hand chromium and copper have only one 4s electron, so in the ionisation they can lose that electron and therefore showing oxidation state of +1.

Stability of oxidation state

A compound is regarded stable if it exists at room temperature and is not oxidised by air, hydrolyzed by water or steam and does not disportionates at room temperature.

The stability of an oxidation state also depends upon the nature of elements combined with the transition metal.

- Since fluorine is the most electronegative element, the higher oxidation state of transition metals are more stable in fluorides.
- After fluorine, the most electronegative element is oxygen, so the higher oxidation state of transition metals are also stable when the metals are directly bonded to oxygen.

The stability of oxidation states can be compared by their electrode potential value: For example for Cu^{2+} and Cu^{+}, the comparison may be done as follows:

$$Cu^{2+}(aq) + 2e \rightarrow Cu(s) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots E^{\theta}_{red} = +0.34V$$

$$Cu^{+}(aq) + e \rightarrow Cu(s) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots E^{\theta}_{red} = +0.52V$$

The electrode (reduction) potential values indicates that Cu^{+} is more readily reduced to Cu(s) as it has larger value of the potential and hence Cu^{2+} or +2 oxidation state of copper is more stable than Cu^{+} (+1 oxidation state).

- Actually Cu^{+} is highly unstable and always disproportionate to Cu(s) and Cu^{2+}.

$$2Cu^{+} \rightarrow Cu^{2+} + Cu$$

Variation of ionic characters with oxidation states

Compounds of transition metals in lower oxidation state of +2 and +3 are mostly ionic compounds, why?

- This simply because, having lower oxidation state, the transition metal cation have lower charge thus they exert relatively smaller polarising power to the anion, as a result the compound which is made has lower degree of polarisation and hence become less in covalent characters (more ionic in characters)
- **Being more in ionic characters:**
  - *Chlorides of transition elements in their lower oxidation state do not normally hydrolyse in water.*

E.g. $TiCl_2 + H_2O \rightarrow$ No reaction

While $TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$

That is titanium (II) chloride does not hydrolyze in water while titanium (IV) chloride does. (Note: due to very large polarising power of Ti^{4+}, $Ti(OH)_4$ is not formed in the reaction as usual and TiO_2 is formed instead as the decomposition product of the hydroxide)

  - *Oxides of transition elements in their lower oxidation states are normally basic.* They usually dissolve in water to give solutions which have no reaction with other basic solution but have reaction with acidic solutions.

Oppositely, **Compounds of transition metals in higher oxidation state are mostly covalent compounds.** Being covalent in their characters:

- Chlorides (and other halides) hydrolyse in water
- Oxides are acidic

Justification of increase in covalent characters as oxidation state of transition metal increases by using oxides of chromium and manganese

Argument: *As degree of covalent characters in oxides increases, the acid – base characters of the oxides change from basic characters to acidic characters via amphoteric characters.*

(i) Chromium

Common oxides of chromium are:

(i) CrO in which oxidation state of chromium is +2

(ii) Cr_2O_3 in which oxidation state of chromium is +3

(iii) CrO_3 in which oxidation state of chromium is +6

The first oxide, chromium (II), CrO is basic. It dissolves in water to form strong basic solution which has no chemical reaction with other basic solutions but reacts with acidic solution.

For example: $CrO + H_2O \rightarrow Cr(OH)_2$

Then $Cr(OH)_2 + 2HCl \rightarrow CrCl_2 + 2H_2O$ but $Cr(OH)_2 + NaOH \rightarrow$ No reaction

The second oxide, chromium (III) oxide, Cr_2O_3 is amphoteric. It dissolves in water to give hydroxide which can react with both acidic and basic solution.

For example: $Cr_2O_3 + 3H_2O \rightarrow 2Cr(OH)_3$

$Cr(OH)_3$ as base: $Cr(OH)_3 + 3HCl \rightarrow CrCl_3 + 3H_2O$

$Cr(OH)_3$ as acid: $Cr(OH)_3 + 3NaOH \rightarrow Na_3[Cr(OH)_6] \xrightarrow[-3H_2O]{\text{Dehydration}} Na_3CrO_3 + 3H_2O$

Or $H_3CrO_3 + 3NaOH \rightarrow Na_3CrO_3 + 3H_2O$

The last oxide, chromium (VI) oxide, CrO_3 is acidic. It dissolves in water to form strong acidic solution which cannot react with other acidic solutions but reacts with basic solutions to give salt and water only.

For example: $CrO_3 + H_2O \rightarrow H_2CrO_4$

Then $H_2CrO_4 + 2NaOH \rightarrow Na_2CrO_4 + 2H_2O$ but $H_2CrO_4 + HCl \rightarrow$ No reaction

Conclusion

The first oxide with oxidation state of +2 is more ionic and therefore is basic. The second oxide with oxidation state of +3 is less ionic and therefore is amphoteric. The last oxide with oxidation +6 is covalent, that why is acidic. Hence degree of covalent of compounds of transition metals increases with an increase in oxidation state of the transition metals.

(ii) Manganese

Manganese has oxides in its oxidation state of $+2, +3, +4, +6$ and $+7$.

Manganese (II) oxide, MnO, is basic

- Being basic dissolves in water to give basic solution.

$$MnO + H_2O \rightarrow Mn(OH)_2$$

- Both MnO and $Mn(OH)_2$ reacts with acid but have no reaction with bases.

$$MnO + 2HCl \rightarrow MnCl_2 + H_2O$$
$$Mn(OH)_2 + 2HCl \rightarrow MnCl_2 + 2H_2O$$

Manganese (III) oxide, Mn_2O_3 is amphoteric

- Being amphoteric dissolve in water to give amphoteric hydroxide

$$Mn_2O_3 + 3H_2O \rightarrow 2Mn(OH)_3$$

- Both Mn_2O_3 and $Mn(OH)_3$ being amphoteric react with acids and bases

As acid: $Mn_2O_3 + 6HCl \rightarrow 2MnCl_3 + 3H_2O$
And $Mn(OH)_3 + 3HCl \rightarrow MnCl_3 + 3H_2O$
As base: $Mn_2O_3 + 6NaOH \rightarrow 2NaMnO_2 + H_2O$
And $Mn(OH)_3 + NaOH \rightarrow NaMnO_2 + 2H_2O$

Manganese (IV) oxide, MnO_2, manganese (VI) oxide, MnO_3 and manganese (VII) oxide which are acidic.

- Being acidic, they dissolve in water to give acidic solution.

$$MnO_2 + H_2O \rightarrow \underset{\textbf{Manganous acid}}{H_2MnO_3}$$

$$MnO_3 + H_2O \rightarrow \underset{\textbf{Manganic acid}}{H_2MnO_4}$$

$$Mn_2O_7 + H_2O \rightarrow \underset{\textbf{Permanganic acid}}{2HMnO_4}$$

- Being acidic, both oxides and their respective solution react with base but have no reaction with acids.

$$MnO_2 + 2NaOH \rightarrow Na_2MnO_3 + H_2O$$
$$MnO_3 + 2NaOH \rightarrow Na_2MnO_4 + H_2O$$
$$Mn_2O_7 + 2NaOH \rightarrow 2NaMnO_4 + H_2O$$
$$H_2MnO_3 + 2NaOH \rightarrow Na_2MnO_3 + 2H_2O$$
$$H_2MnO_4 + 2NaOH \rightarrow Na_2MnO_4 + 2H_2O$$
$$HMnO_4 + NaOH \rightarrow NaOH \rightarrow NaMnO_4 + H_2O$$

Examples of some transition elements with their possible ions in different oxidation states

(i) CHROMIUM

ATOM OR ION	ELECTRONIC CONFIGURATION	COMMENT
Cr	$[Ar]3d^5 4s^1$	
Cr^{2+}	$[Ar]3d^4$	Unstable and are easily oxidised to Cr^{3+}
Cr^{3+}	$[Ar]3d^3$	Common oxidation state of Cr in its compounds
Cr^{6+}	[Ar]	Oxidising

(ii) MANGANESE

ATOM OR ION	ELECTRONIC CONFIGURATION	COMMENT
Mn	$[Ar]3d^5 4s^2$	
Mn^{2+}	$[Ar]3d^5$	Common oxidation state of Mn in its compounds
Mn^{3+}	$[Ar]3d^4$	Unstable and disproportionate: $2Mn^{3+} \rightarrow Mn^{2+} + Mn^{4+}$
Mn^{4+}	$[Ar]3d^3$	Uncommon. Mainly found in MnO_2 (black)
Mn^{6+}	$[Ar]3d^1$	Uncommon. Mainly found in MnO_4^{2-} (**manganate**) e.g. K_2MnO_4
Mn^{7+}	[Ar]	Stable and oxidising e.g. MnO_4^-(**per**manganate)

(iii) COPPER

ATOM OR ION	ELECTRONIC CONFIGURATION	COMMENT
Cu	$[Ar]3d^{10}4s^1$	
Cu^+	$[Ar]3d^{10}$	Unstable and disproportionate: $2Cu^+ \rightarrow Cu^{2+} + Cu$
Cu^{2+}	$[Ar]3d^9$	Common oxidation state of Cu in its compounds

(iv) IRON

ATOM OR ION	ELECTRONIC CONFIGURATION	COMMENT
Fe	$[Ar]3d^6 4s^2$	
Fe^{2+}	$[Ar]3d^6$	Easily oxidised to Fe^{3+}
Fe^{3+}	$[Ar]3d^5$	Stable
Fe^{6+}	$[Ar]3d^2$	Uncommon. Mainly found in FeO_4^{2-}

(v) NICKEL

ATOM OR ION	ELECTRONIC CONFIGURATION	COMMENT
Ni	$[Ar]3d^8 4s^2$	
Ni^{2+}	$[Ar]3d^8$	Common oxidation state
Ni^{4+}	$[Ar]3d^6$	Oxidising

CATALYTIC ACTIONS

Many of transition metals and their compounds are often good catalysts. This is due to the following reasons:

- **They have variable oxidation state** so that they can form unstable intermediate products with the reactants.
- **They have large surface areas to absorb the reactants** on their surface and activate them in the process.

Examples of transition metals catalysts are:

- **Iron** in the Haber process
- **Nickel** in hydrogenation of unsaturated hydrocarbon

Examples of catalysts transition metal compounds are:

- **Vanadium (V) oxide, V_2O_5** in the contact process
- **Manganese (IV) oxide, MnO_2** in preparation of carbonyl compound by heating carboxylic acids.

FORMATION OF COLOURED COMPOUNDS

The transition metal ions or compounds are generally coloured in at least one if not all oxidation states.

- The colour formation is due to the presence of incomplete d–sub shell. The electrons can be excited from one orbital to another within the d- sub shell.
- The energy required to cause such d – d promotions of the electrons is within visible range for all transition elements.

Colour formation by transition elements is well explained by **crystal field theory** (also known as **ligand field theory**). According to crystal field theory, there are two conditions necessary for transition elements to form colour in their compounds.

(i) Presence of at least one d- orbital with unpaired electron.

(ii) Presence of chemical specie, called **ligand.**

Process of colour formation

The process of colour formation begins when ligand approaches the d-orbitals containing at least one unpaired electron.

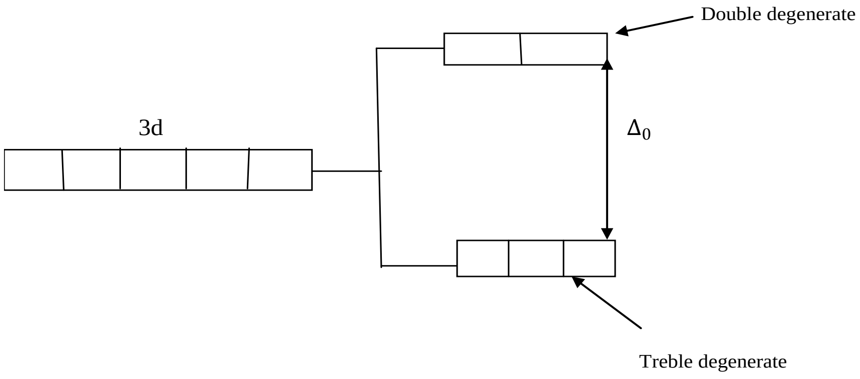
- The ligands exert electric field or repulsive force to electrons in **degenerated d-orbitals** of metal ion
- That raises the energy of the d–orbitals. However because of the way the d–orbitals are arranged in space, it does not raise all their energies by the same amount, instead it split them into two groups: **double degenerate** which has two d- orbitals and **treble degenerate** which has three d–orbitals.

Between double degenerate and treble degenerate which one has higher energy?

The way d–orbitals split depends on whether the complex is **octahedral** or **tetrahedral.**

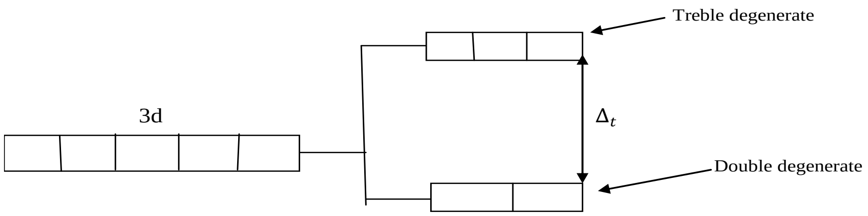
- *For* ***octahedral complexes*** *which have six simple ligands,* ***double degenerate*** *has always higher energy*. The difference of energy between the two degenerates is denoted as Δ_0(delta octahedral).

Splitting in octahedral complex



- *For* ***tetrahedral complexes*** *which have four simple ligands,* ***treble degenerate*** *has always higher energy*. The difference of energy between the two degenerates is denoted as Δ_t (delta tetrahedral)

Splitting of d–orbitals in tetrahedral complexes



What is the effect of splitting of d–orbitals in the colour formation?

When white light is passed through a solution containing the transition metallic ion, some of the energy in the light is used to promote (excite) an electron from the lower set of orbitals into a space in the upper set.

- Colour is seen as result of electrons returning from higher energy set of d–orbitals to lower energy set of d-orbitals as on doing so they tend to emit energy with wavelength within visible part of spectrum.
- In few words we can conclude that *d–d transition of electrons is the basis of colour formation in transition metal complexes.*

Why presence of unpaired d-orbital is necessary for the colour formation?

If all d-orbitals are filled up with electron, the d-electron must be promoted to a 4p-orbital (the next higher orbital which is empty). Because the energy level of the 4p orbitals is much higher than that of the 3d orbitals, photons of a very high energy are needed, i.e. ultra violet radiation and hence no visible light will be observed for those compounds whose all their d-orbitals (in central metal atom or ion) completely filled with electrons.

Factors affecting the colour of a transition metal complex

There are various factors affecting the amount of separation (difference in energy) between double and treble degenerate thus affecting amount of energy required for doing d–d transition of electrons and wavelength of the radiant energy emitted and therefore intensity of colour observed and hence formation of different colour by complexes. These factors include:

(i) The nature of ligand
(ii) The oxidation state of the metal
(iii) The coordination of the transition metal ion

(i) The nature of ligands

- Different ligands have different effects on energies of the d–orbitals of the central ion
- Some ligands have greater electron donating ability, therefore exerting strong electrical fields which cause large energy gap when d–orbitals split into two groups. Such ligands are termed as **strong ligands**.
- Large energy gap between double and treble degenerate means that large energy is required to excite electrons and therefore the large energy will be released also when electrons fall to the lower set of d-orbitals. Consequently the wave contained in the radiation energy will be possessing high energy with short wavelength and high frequency and hence the resulting colour will be **nearer to the violet colour** (recall: ROYGBIV in which 'violet' has greatest energy, 'red' has lowest) in visible spectrum and normally the colour will be **deep** and **intensive**.
- As strong ligands cause large energy gap between two sets of d – orbitals, a lot of energy is required to get electrons into the higher energy d– orbitals, the electrons will instead pair up in

the lower energy orbitals according to Aufbau principle; resulting in a complex that is called **'low spin'** (unreactive) complex because *it allows less electrons to stay unpaired*. **Strong ligands are therefore also known as ligands of low spin**.

Some ligands have weak electrical fields (as they have small electron donating ability), which cause small energy gap when d–orbitals split into two groups. Such ligands are known as **weak ligands.**

- Small energy gap between double and treble degenerate means that small radiant energy is required to excite electrons and therefore small energy will be released also when electrons fall to the lower energy set of d – orbitals. Consequently the waves contained in the radiation energy will be possessing low energy with long wavelength and low frequency and hence the resulting colour will be **nearer to the red colour** (again recall ROYGBIV) in visible spectrum and normally the colour will be **light** and **faint.**
- As weak ligands cause small energy gap between two sets of d–orbitals, it is simple to get electrons into the higher energy orbitals, the electrons will do so and remain unpaired (until there are more than five electrons) in accordance to Hund's rule, resulting in a **'high spin'** (reactive) complex because *there is a greater chance of having more unpaired electrons in the complex* and hence **weak ligands are also known as ligands of high spin**.

You should memorise that:

All ligands cause weak electrical filed strength; that is all ligands are weak except NO_2^-, CN^-, NH_3, amines e.g. en (ethylene diamine), SCN^- and CO which are strong ligands. For example:

$[Cu(H_2O)_4]^{2+}$ is light blue (cyan) while

$[Cu(NH_3)_4]^{2+}$ is dark blue

That is simply because; H_2O being weak ligand cause small energy of separation between double and treble degenerates of d–orbitals while NH_3 being strong ligand cause large energy gap. That means………………! You can finish it – up to now is more than simple for you!

(ii) Oxidation state of the metal

As the oxidation state of the metal increases, the amount of splitting of the d–orbitals also increases.

- So transition metal ions with higher charge (higher oxidation state) have large energy gap between double and treble degenerates and consequently the colour their complexes will be deep and intensive, nearer to violet while those with lower oxidation state will be light and faint, nearer to red colour in visible spectrum.
- For example in aqueous solution, Cr^{2+} ion is almost **light blue** while Cr^{3+} ion is hard to describe, something like **violet–blue–grey** colour.

(iii) The coordination of the ion

Splitting is greater if the complex ion is octahedral (with coordination number of 6) than if it is tetrahedral (coordination number of 4) and therefore the colour will change with change of coordination.

PARAMAGNETISM

Paramagnetism *is the tendency of a substance possessing some magnetic field to be attracted by another substance of higher magnetic field called* ***magnet.***

- The substance which exhibit paramagnetism is known as **paramagnetic material.**

Diamagnetism *is the tendency of a substance to possess zero magnetic fields so that it cannot be attracted by the magnet.*

- The substance which exhibit diamagnetism is known as **diamagnetic material.**

Transition elements are paramagnetic because they possess at least one unpaired electron – the important condition for a substance to exhibit paramagnetism, i.e. **the substance must possess at least one unpaired electron in order to show paramagnetic property.**

Why unpaired electron?

In orbitals electrons are spinning, i.e. are moving. Those electrons carry negative charge; so movement of electrons in the orbitals implies that there is movement of charges.

- *Movement of charges in the orbitals means small electric current is established in the orbitals which in turn establish small magnetic field.*

In paired orbital, electrons spin in opposite direction (Paul's exclusion principle). That means, magnetic field exerted by each electron in the orbital cancels each other since the magnetic field is the vector quantity.

- So *if all orbitals are paired up, the resultant magnetic field will be zero and hence the substance will be diamagnetic*

If a substance has greater number of unpaired electrons, the substance will possess stronger magnetic field and hence the substance will be stronger paramagnetic.

- Chromium with six unpaired electrons which is the maximum number of unpaired electrons for transition metals is the strongest paramagnetic for all the metals.

Actually, *elements which possess greater number of unpaired electrons have very large magnetic field electrons so that can be magnetized permanently*. These substances are known as **ferro–magnetic materials**. Example of ferromagnetic material is chromium, iron, cobalt, nickel or manganese.

Factors affecting paramagnetic property of transition elements

Paramagnetic property may be affected through:

(i) Ion formation (temperature rise)
(ii) Complex formation

(i) Ion formation

Rise of temperature may destroy paramagnetic property of the element. It may cause excitation of electrons and ionisation of the atoms by losing electrons

- Ionisation may occur to an extent of losing all unpaired electrons thus converting paramagnetic material into diamagnetic. For example with an electronic configuration of $[\mathrm{Ar}]3\mathrm{d}^1 4\mathrm{s}^2$ which has one unpaired d – electron, scandium is paramagnetic while Sc^{3+} which has electronic configuration of argon, has all electrons paired and hence it is diamagnetic

(ii) Complex formation

Introduction of strong ligands to the transition metal ion cause large energy of separation between two set of d – orbitals (double and treble degenerates).

- The large energy gap means that electron can no longer filled by Hund's rule, they must be filled in the d–orbitals by Aufbau principle. This decreases the chance of having unpaired electrons and hence paramagnetic property of the transition metal ion in the complex decreases also.

The situation is different when weak ligand is introduced into the transition metal ion.

- Weak ligand cause small energy of separation between two sets of d–orbitals, the electronic configuration of the ion is conserved as the small energy gap between the two sets (double and treble degenerates) allow to re-fill electrons by Hund's rule and hence the paramagnetic property of the transition metal ion in the complex is conserved also.

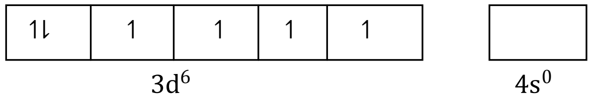
For example:

$[CO(NH_3)_6]^{3+}$ is diamagnetic while

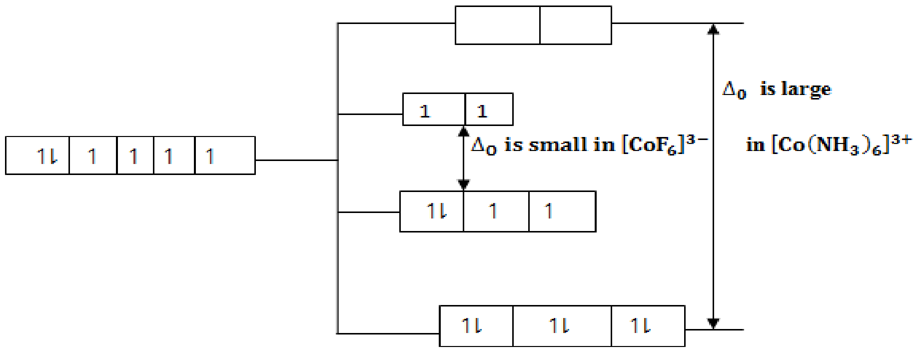
$[COF_6]^{3-}$ is paramagnetic

The reason of that difference in their magnetic property can be investigated as follows:

- Outermost electronic configuration of Co^{3+} is,



- After introduction of ligands in $[CO(NH_3)_6]^{3+}$ and $[COF_6]^{3-}$ the re- distribution of electrons become as follows (recall NH_3 is strong ligand while F^- is weak ligand).



So $[Co(NH_3)_6]^{3+}$ is diamagnetic because all electrons in Co^{3+} are paired after redistribution of electrons caused by NH_3 ligands which are strong (they exert a strong electric field causing large energy gap between treble and double degenerates making more suitable for electrons to be refilled by Aufbau principle) while $[CoF_6]^{3-}$ is paramagnetic due to presence of four unpaired electrons in 3d – orbitals. This is due to the fact that, F^- being weak ligand does not exert enough electric field to cause pairing of electrons in Co^{3+} of $[CoF_6]^{3-}$.

It should be noted that:

Oxidation state of the metal and **coordination of transition on metal ion** which affected the colour formation of complexes (as explained in the section of colour formation in this chapter) also affect paramagnetic property of transition metals.

- As they affect amount of energy gap between double and treble degenerates, they also affects re-distribution of electrons in the ion after introduction of ligands and therefore number of unpaired electron and hence they also affect paramagnetic property of the transition metal. (if you have not good memory on how these two factors affect the amount of energy gap between two sets of d-orbitals, go back to appropriate section on factors affecting colour formation for recalling)

EVIDENCES FOR ZINC NOT BEING TRANSITION METAL

With electronic configuration of $[\mathrm{Ar}]3\mathrm{d}^{10}4\mathrm{s}^{2}$ and its ion, $[\mathrm{Ar}]3\mathrm{d}^{10}$, neither neutral zinc atom nor Zn^{2+} ion has at least one unpaired d – orbital. Having all of its d-orbitals paired in its atom and ion which is the basic property for transition metal to show other transition metal properties, zinc has some properties which exclude it from the family of transition metals. These properties include:

(i) Both zinc and its compound are colourless (white)

- Having all d-electrons paired, d – d transition of electrons is not possible for zinc

(ii) It has fixed oxidation state of +2

- This is due to its highest nuclear charge and stable electronic configuration of completely paired electronic structure which is obtained after losing the two 4s electrons.

(iii) Zinc, its ion and its compounds are all diamagnetic

- This is simply because, neither of the three (zinc atom, zinc ion or zinc compounds) has at least one unpaired electron in zinc.

PRACTICE EXERCISE 19

Question 1

(a) Define:
  (i) Transition elements
  (ii) d-block metals
(b) What is the relation between two terms in (a) above?

Question 2

Explain the following:

(i) Transition metals are very good conductor of electricity.
(ii) Transition metals have very strong physical properties.
(iii) Transition metals do not react with cold water.
(iv) Transition metals have high ability of forming alloys.

Question 3

Explain why transition elements have variable oxidation state.

Question 4

Explain why Titanium (IV) chloride hydrolyses in water while Titanium (II) chloride does not.

Question 5

Chromium (II) oxide is basic while chromium (VI) is acidic. Explain.

Question 6

Complete the following reactions:

(i) $CrO_2(OH)_2 + NaOH \rightarrow$
(ii) $Mn(OH)_2 + NaOH \rightarrow$
(iii) $Mn_2O_7 + NaOH \rightarrow$
(iv) $MnO_2 + H_2SO_4 \rightarrow$
(v) $H_2MnO_4 + Cr(OH)_2 \rightarrow$

Question 7

Explain why transition metals and their compounds are good catalyst.

Question 8

By using crystal field theory, explain process of colour formation in compounds of transition metals.

Question 9

Explain factors affecting colour formation in transition metal complexes.

Question 10

Explain how some transition metal complexes are paramagnetic while others are diamagnetic.

Question 11

(a) Vanadium is a transition element. State three characteristics features of the chemistry of vanadium and its compounds.
(b) Predict, with a reason in each case, whether or not vanadium (IV) chloride would react with hexane or with ethanol.

Question 12

Explain how the colour of $[Co(NH_3)_6]Cl_3$ will differ to that of $[Co(NH_3)_4Cl_2]Cl$

Question 12

(a) When titanium dissolves in concentrated hydrochloric acid, the violet $[Ti(H_2O)_4Cl_2]^+$ ion is formed. Deduce the oxidation state and coordination number of titanium in this ion.
(b) Draw the structures of the two isomers of $[Ti(H_2O)_4Cl_2]^+$.

Chapter 20

COMPLEXES

In this chapter, we will discuss matters about complexes, mainly transition metal complexes. The discussion started at chapter 6. We are going to explore some matters which were not discussed in that chapter.

ISOMERISM IN COMPLEXES

In organic chemistry we learned that, **isomerism** *is the existence of compounds with the same molecular formula but differ in their structures or spatial arrangement of atoms in space.*

- In other words we can say that, *two or more compounds, radicals or ions that are composed of the same kinds and number of atoms but differ from each other in the arrangement of atoms is called isomerism.*

The isomerism is observed not only in organic compounds but complexes also because of the variety of bond types and the number of shapes possible.

- Like in organic chemistry, isomerism in complexes can be classified into two main categories:

(i) Structural isomerism
(ii) Stereo isomerism

(Structure and stereo isomerism are defined in the same way we did in organic chemistry – refer to another book in the series titled *Advanced organic chemistry*)

Structural isomerism is divided into four types: ionisation isomerism, hydrate isomerism, coordination isomerism and linkage isomerism while **stereo isomerism** is divided into geometric isomerism and optical isomerism, making a total of six types of isomerism in complexes which are:

(i) Ionisation isomerism
(ii) Hydrate isomerism
(iii) Co-ordination isomerism
(iv) Linkage isomerism
(v) Geometric isomerism
(vi) Optical isomerism

(i) Ionisation isomerism.

Ionisation isomers *are complex compounds which have the same composition (same molecular formula) but they give different ions in the solution.*

- The ionisation isomerism occurs when ligands in the same complex can be exchanges with the anions outside the co-ordination sphere.

A good example of ionisation isomers is bromopentaamminecobalt(III) sulphate and sulphatopentaamminecobalt (III) bromide

$[CoBr(NH_3)_5]SO_4$	and	$[CoSO_4(NH_3)_5]Br$
Bromopentaamminecobalt (III) sulphate		**sulphatopentaamminecobalt (III) bromide**
(Violet coloured)		**(Red coloured)**

The two isomers may be distinguished from each other by using solution containing Ba^{2+} like $BaCl_2$ or Ag^+ like $AgNO_3$. The reaction of the complex in solution with barium chloride and silver nitrate indicates the free anions in the complex compound.

- The **violet complex** in solution gives a *white precipitate of* $BaSO_4$ with barium chloride and no precipitate with silver nitrate. This implies that SO_4^{2-} ion is the anion in this complex compound
- The **red complex** in solution not give precipitate with barium chloride but form *yellow precipitate* with silver nitrate solution confirming that Br^-ion is the anion in this complex compound.

Other examples of ionisation isomers are:

- $[Pt(OH)_2(NH_3)_4]SO_4$ and $[PtSO_4(NH_3)_4](OH)_2$
- $[CoCl(NH_3)_5]SCNCl$ and $[CoSCN(NH_3)_5]Cl_2$
- $[CoNO_3(NH_3)_5]SO_4$ and $[CoSO_4(NH_3)_5]NO_3$
- $[PtCl_2(NH_3)_4]Br_2$ and $[Pt\,Br_2(NH_3)_4]Cl_2$

(ii) Hydrate isomers

Hydrate isomers *are complex compounds with the same composition but differ in number of water molecules present as ligands in the coordination sphere and as molecules of hydration in the ionisation sphere.*

- Actually, it is the special case of ionisation isomers whereby the ligand used for exchange in coordination sphere and ionisation sphere is water molecule(s)

Examples of hydrate isomers are:

- $[COCl(H_2O)(NH_3)_4]Br_2$ and $[CoBr_2(H_2O)(NH_3)_4]Cl\,.\,H_2O$
- $[CoCl(H_2O)(NH_3)_4]Cl_2$ and $[CoCl_2(NH_3)_4]Cl\,.\,H_2O$
- $[Cr(H_2O)_6]Cl_3$, $[CrCl(H_2O)_5]Cl_2.H_2O$ and $[CrCl_2(H_2O)_4]Cl.2H_2O$

(iii) Coordination isomers

Coordination isomers *are complex compounds with the same molecular formula but differ in ligands contained in central metal atom of complex cation and complex anion.*

- The coordination isomerism occurs when both cation and anion are complexes and the ligands can be exchanged between central metal atom of complex cation and complex anion.

Examples of co-ordination isomers are:

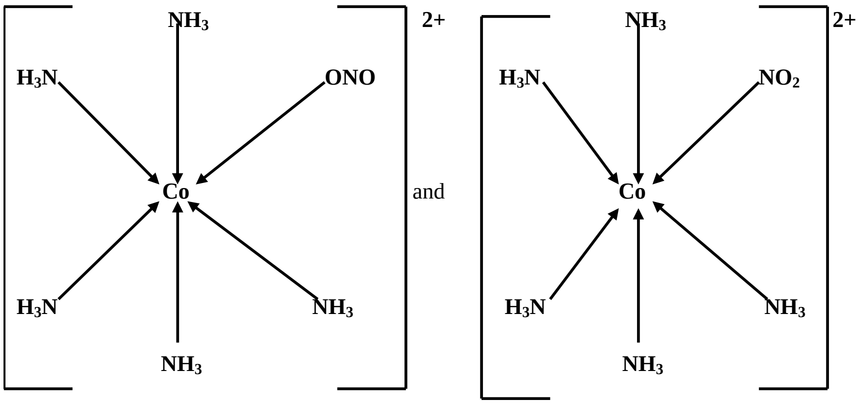
- $[Co(NH_3)_6]\,[Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$
- $[Co(en)_3]\,[Cr(CN)_6]$ and $[Cr(en)_3][Co(CN)_6]$
- $[Co(NH_3)_6][Cr(C_2O_4)_3]$ and $[Cr(NH_3)_6][Co(C_2O_4)_3]$

(iv) Linkage isomers

The linkage isomerism occurs when a monodentate ligand has two co-ordination sites, i.e. the ligand has two donor atoms. Ligands of this nature are known as **ambidentate ligands**.

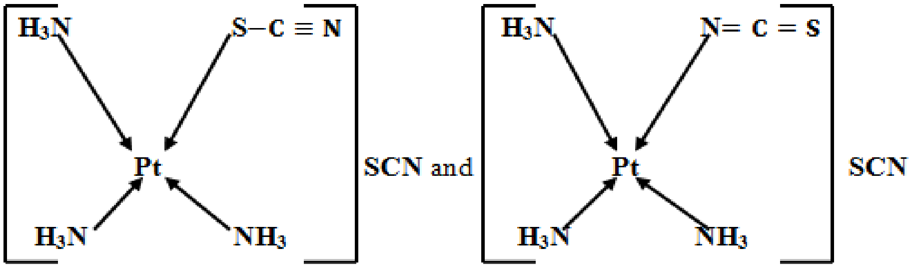
- For example, nitro group, NO_2 can bond to the central metal ion through nitrogen (nitro) or through oxygen (nitrito) and this results to linkage isomerism.

For example, nitritopentaamminecobalt (III) ion and nitropentaamminecobalt (III) ion. They have the following **geometric structure.**



Nitritopentaamminecobalt (III) ion (red) **nitropentaamminecobalt (III) ion (yellow)**

Another example of linkage isomers is thiocyanatotriammineplantium(II) thiocyanate, $[Pt(SCN)(NH_3)_3]SCN$ and isothiocyanatotriammineplatinum(II) thiocyanate, $[Pt(NCS)(NH_3)_3]SCN$.



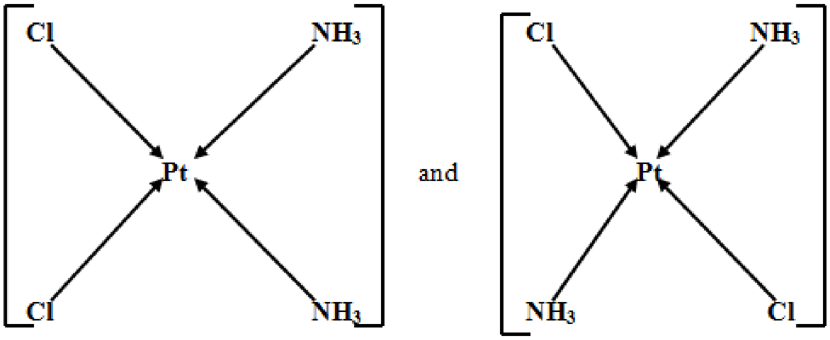
(v) Geometric isomers

The **geometric isomerism** *occurs when exchange of atoms or ions within the co-ordination sphere of the complex changes its geometry*

- It is possible in square planar and octahedral complexes and not tetrahedral complexes.

Geometric isomers exist in **cis** and **trans** forms.

- For example isomers of dichlorodiammineplatinum (II) ion are**:**



Cis-dichlorodiammineplatinum (II) ion **Trans-dichlorodiammineplatinum (II) ion**

(vi) Optical isomerism

The co-ordination compounds that are mirror images of each other but are not super-imposable are called **optical isomers** and the phenomenon is called optical isomerism.

LIGAND SUBSTITUTION (EXCHANGE) REACTION

Transition metal ions in aqueous solution form complex ions by bonding with water molecules.

- For example, nickel chloride dissolve in water due to the formation of hexaaquanickel(II) ion

$$\mathrm{NiCl_2(s) + 6H_2O(l) \rightarrow [Ni(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)}$$

So when we are talking about solution of nickel chloride, in reality we are talking about complex compound with the formula, $\mathrm{[Ni(H_2O)_6]Cl_2}$

Similarly:

- Solution of copper (II) sulphate is $\mathrm{[Cu(H_2O)_4]SO_4}$
- Solution of iron (III) chloride is $\mathrm{[Fe(H_2O)_6]Cl_3}$
- Analogously, aluminium having ability of forming complexes, the solution of aluminium chloride has the structure, $\mathrm{[Al(H_2O)_6]Cl_3}$ etc

Water ligands in the complexes can be easily substituted by other ligands hence the complexes containing water ligands are said to undergo ligand substitution reaction easily, i.e. are **labile complexes**.

By definition:

Ligand substitution reaction *is the chemical reaction which involves the replacement of the ligands attached to the central metal ion in the complex by other ligands.*

- Ligand substitution reaction is the general method for preparing transition metal complexes

Here below, are some example of ligand substitution reactions:

(i) If ammonia is added to the solution of nickel (II) chloride, the colour of the solution change from green to blue – violet due to replacement of water ($\mathrm{H_2O}$) molecules bonded to nickel by ammonia ($\mathrm{NH_3}$) molecules to form hexaamminenickel (II), $\mathrm{[Ni(NH_3)_6]^{2+}}$ ions.

$$\mathrm{[Ni(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \rightarrow [Ni(NH_3)_6]^{2+}(aq) + 6H_2O(l)}$$

- *The change of colour of the complex is explained by the fact that NH_3 molecules being ligands of low spin, cause larger energy gap between double and treble degenerates than H_2O molecules do. The greater energy gap means the colour which will be observed is nearer to violet (in ROYGBIV) which has higher energy and hence blue – violet colour of $[Ni(NH_3)_6]^{3+}$ is observed while in $[Ni(H_2O)_6]^{2+}$ the colour is relatively nearer to red because water ligands exerts weaker electric field to d – orbitals leading to smaller energy gap between double and treble degenerate.*

(ii) Tetraamminecopper(II) sulphate is prepared by adding ammonia solution.

$$\mathrm{[Cu(H_2O)_4]SO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4 + 4H_2O}$$

Or ionically, $\underset{\textbf{light blue}}{\mathrm{[Cu(H_2O)_4]^{2+}}} + \mathrm{4NH_3} \rightarrow \underset{\textbf{dark blue}}{\mathrm{[Cu(NH_3)_4]^{2+}}} + \mathrm{4H_2O}$

(iii) The yellow tetracyanonickelate(II) ion is prepared by mixing $\mathrm{[Ni(NH_3)_6]^{2+}}$ ions solution and sodium cyanide solution

$$\mathrm{[Ni(NH_3)_6]^{2+}(aq) + 4CN^-(aq) \rightarrow [Ni(CN)_4](aq) + 6NH_3(aq)}$$

- *In this case, CN^- ligands having larger size than NH_3 ligands, the Ni^{2+} ion can accommodate **four** CN^- ligands only, so the six NH_3 ligands are replaced by four CN^- ligands and coordination number of nickel change from 6 to 4*

(iv) If you add concentrated hydrochloric acid to a solution containing hexaaquacobalt(II) ion (for example, cobalt (II) chloride solution), the six water molecules are replaced by four chloride ions.

$$[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$$

(From$CoCl_2(aq)$) (from $HCl(aq)$)

- *The change of co-ordination number of cobalt is again explained by the size of ligands. Chloride ions are bigger than water molecules and there is not room to fit six of them around the central cobalt ion.*

It should be noted that:

Hexaaqua (even tetraaqua, sometimes) complex ions are always acidic, why?

This is because in complexes of the form of $[M(H_2O)_6]^{n+}$, each of the six water molecules are attached to the central metal ion via a co-ordinate bond using one of the lone pairs on the oxygen.

- When the lone pair is attracted to the central metal ion, the electrons in O – H bond of water H_2O, are attracted also towards the ion and therefore are pulled away from the O – H bond making the hydrogen atom in the bond (O – H) more positive polarised and hence becoming more acidic.

In comparison to 2+ ions, 3+ ions are more acidic because they exert stronger force of attraction to the lone pair and to electrons in O – H bond making the hydrogen more positive.

A good example of acidic character of hexaaqua ion is hexaaquairon(III) ion, $[Fe(H_2O)_6]^{3+}$.

- Being acidic, the ion can donate hydrogen proton to water to give hydroxonium ion, H_3O^+.

$$[Fe(H_2O)_6]^{3+} + H_2O \rightarrow [Fe(OH)(H_2O)_5]^{2+} + H_3O^+ \ldots\ldots\ldots\ldots\ldots\ldots\text{(i)}$$

(From $Fe^{3+}(aq)$e.g. $FeCl_3(aq)$)

Or $$[Fe(H_2O)_6]^{3+} + 2H_2O \rightarrow [Fe(OH)_2(H_2O)_4]^{+} + 2H_3O^+ \ldots\ldots\ldots\ldots\ldots\text{(ii)}$$

Or $$[Fe(H_2O)_6]^{3+} + 3H_2O \rightarrow [Fe(OH)_3(H_2O)_3] + 3H_3O^+ \ldots\ldots\ldots\ldots\text{(iii)}$$

The last reaction equation in (iii) gives a neutral complex. Because it has no charge, it does not dissolve in water to any extent and a precipitate is formed. The precipitate, is usually written in simple way as $Fe(OH)_3$ giving the same result as in cationic hydrolysis of Fe^{3+}as per equation:

$$Fe^{3+}(aq) + 3H_2O \rightarrow Fe(OH)_3 + 3H^+(aq)$$

In fact the above reaction equation (iii) is more appropriate way (but to some extent is more complex way) of explaining cationic hydrolysis of ions in the aqueous solution to give acidic solution

- Being acidic, the ion can react with alkaline solution like NaOH.

$$[Fe(H_2O)_6]^{3+} + OH^- \rightarrow [Fe(OH)(H_2O)_5]^{2+} + H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(i)}$$

$$[Fe(H_2O)_6] + 2OH^- \rightarrow [Fe(OH)_2(H_2O)_4]^{+} + 2H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(ii)}$$

$$[Fe(H_2O)_6] + 3OH^- \rightarrow [Fe(OH)_3(H_2O)_3] + 3H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(ii)}$$

Don't confuse:

The reaction between hexaaqua ions with alkaline solution is not ligand substitution reaction. ***The OH^- ions in the complex don not come from the alkaline solution!*** *They are formed after donation of hydrogen proton, H^+ by water ligands and water formed at the product side of the reaction equation are result of neutralization reaction, $H^+ + OH^- \rightarrow H_2O$.*

HYBRIDISATION AND GEOMETRIC SHAPES OF COMPLEX METAL IONS

In combination with crystal field theory (ligand field theory), the following points from valence bond theory may be helpful in determination of geometric shapes of complexes and making the work easier.

(i) The **octahedral** shape of transition metal complexes can be explained by $\mathbf{d^2sp^3}$ **hydridisation or** $\mathbf{sp^3d^2}$ **hybridisation**

(ii) The tetrahedral shapes of transition metal complexes can be explained by $\mathbf{sp^3}$ **hydridisation.**

(iii) The **square planar** shape of transition metal complexes can be explained by $\mathbf{dsp^2}$**hybridisation or** $\mathbf{sp^2d}$ **hybridisation.**

(iv) The **trigonal bipyramidal** shape of complex is explained by $\mathbf{dsp^3}$**hybridisation or** $\mathbf{sp^3d}$ **hybridisation.**

(v) **Inner d – orbitals** or **outer d – orbitals** of central metal ion can be involved in the hybridisation.

If the **inner d – orbitals** are involved in the hybridisation; then the complex is known as the **inner orbital complex** and if the **outer d - orbitals** are involved in the hybridisation; then the complex is known as the **outer orbital complex.**

It should be remembered that:

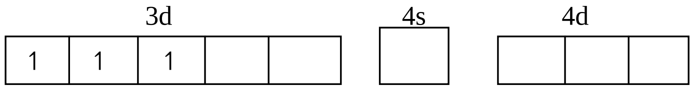
According to the crystal field theory, an introduction of ligands splits five d – orbitals into double and treble degenerates.

- The energy of separation of the two degenerates depends on whether the ligands have strong electric field strength (ligand of low spin) or weak electric field strength (ligands of high spin).
- Strong ligands cause large energy of separation between the two degenerates and always they cause re-distribution **(in most cases, pairing)** of electrons while weak ligands cause small energy of separation and they do not cause re-distribution of electrons.
- All ligands cause weak electrical filed strength; that is all ligands are weak except $\mathbf{NO_2^-}$, $\mathbf{CN^-}$, $\mathbf{SCN^-}$, $\mathbf{NH_3}$, **amines e.g. en (ethylene diamine) and CO** which are strong ligands.

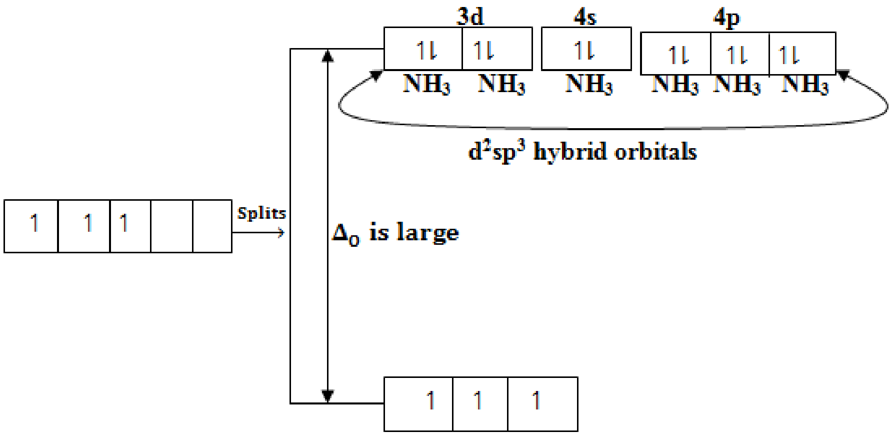
To have better understanding on hybridisation and geometric shapes of complexes of transition metals, let us have close look on the following cases of bonding in the various common complexes.

1. Bonding in hexaammine chromium (III) ion, $[\mathbf{Cr(NH_3)_6}]^{3+}$

Outer electronic configuration of $\mathrm{Cr^{3+}}$ is shown below:



After introduction of $\mathrm{NH_3}$ ligands in $[\mathrm{Cr(NH_3)_6}]^{3+}$

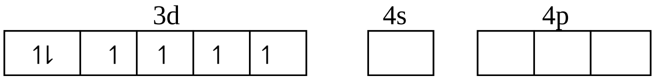


Thus the complex, $[Cr(NH_3)_6]^{3+}$:

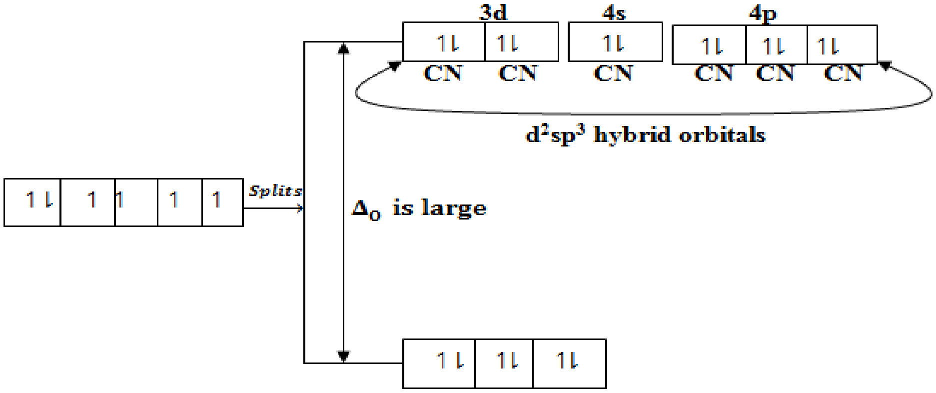
- Is formed by **d^2sp^3 hydridization**
- Is **paramagnetic** due to the presence of three unpaired 3d – electrons
- Has geometric shape of **octahedral** since it is formed by d^2sp^3 hydridization

2. Bonding in hexacyanoferrate (II) ion, $[Fe(CN)_6]^{4-}$

The outermost electronic configuration of Fe^{2+} is,



After introduction of CN^- ligands in $[Fe(CN)_6]^{4-}$



Thus the complex $[Fe(CN)_6]^{4-}$:

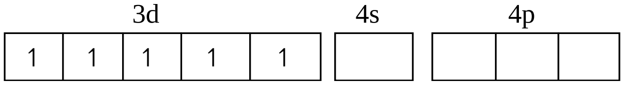
- Is formed **d^2sp^3 hydridisation** and hence it is **octahedral**
- The complex is **diamagnetic** because all electrons in Fe^{2+} are paired after redistribution of electrons due to introduction of strong ligands, CN^- ions.

It should be noted that:

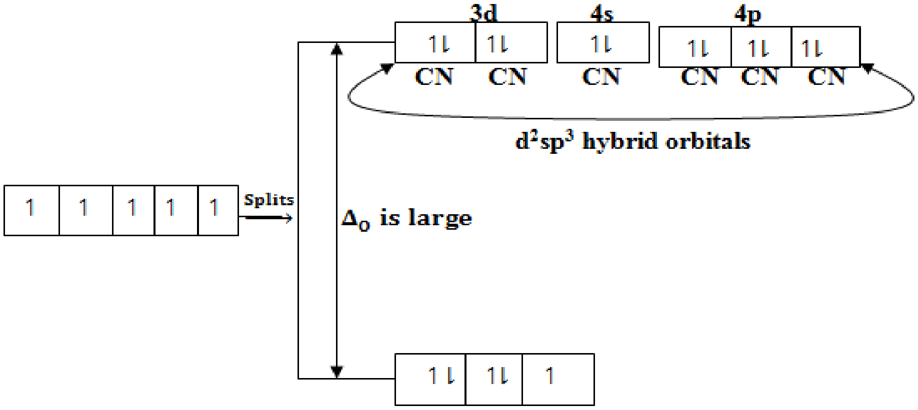
In the above two cases of $[Cr(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{4-}$, the complexes are **inner orbital complexes** because the inner 3d – orbitals are involved in hybridisation.

3. Bonding in hexacyanoferrate (III), ion $[Fe(CN)_6]^{3-}$,

Outermost electronic configuration of Fe^{3+} is;



After introduction of CN^- ligands in $[Fe(CN)_6]^{3-}$,

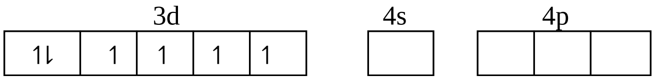


Thus the complex, $[Fe(CN)_6]^{3-}$:

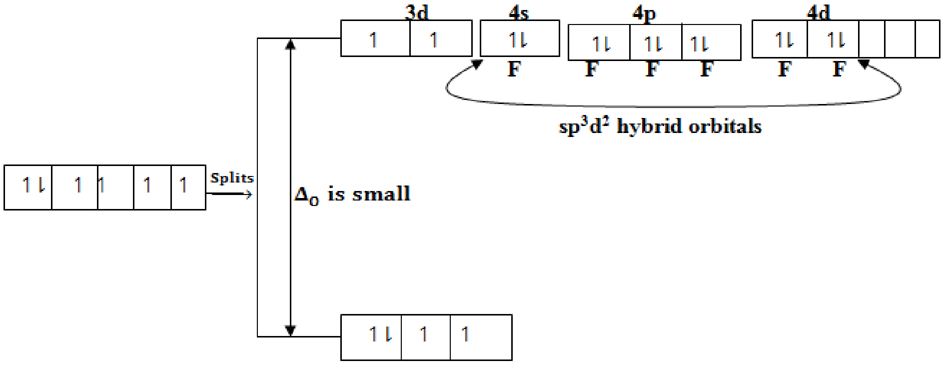
- Is formed by **d^2sp^3 hydridization** and hence it is **octahedral.**
- Is **paramagnetic** due to presence of one unpaired electron in 3d -orbital

4. Bonding hexafluoroferrate(II) ion, $[FeF_6]^{4-}$

The outermost electronic configuration of Fe^{2+} is;



After introduction of F^- ligands in $[FeF_6]^{4-}$



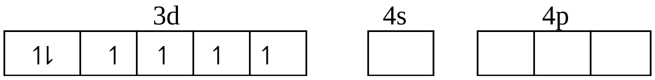
Thus the complex, $[FeF_6]^{4-}$:

- Is formed **sp^3d^2 hybridisation** and hence it is **octahedral**.
- Is **paramagnetic** due to presence of four unpaired electronic in 3d orbitals

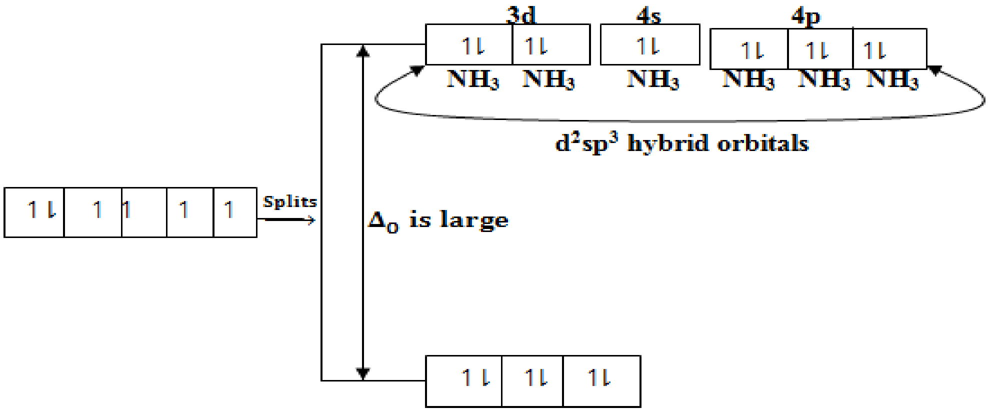
$[FeF_6]^{4-}$ is an example of ***outer orbital complex*** because the outer 4d – orbitals are involved in the hybridisation.

5. Bonding in hexaammine cobalt (III) ion, $[Co(NH_3)_6]^{3+}$

Outermost electronic configuration of Co^{3+} is;



After introduction of NH_3 ligands in $[Co(NH_3)_6]^{3+}$;

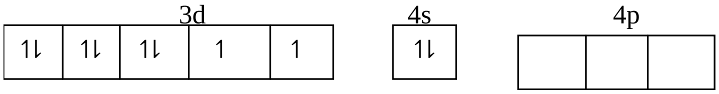


Thus the complex, $[CO(NH_3)_6]^{3+}$:

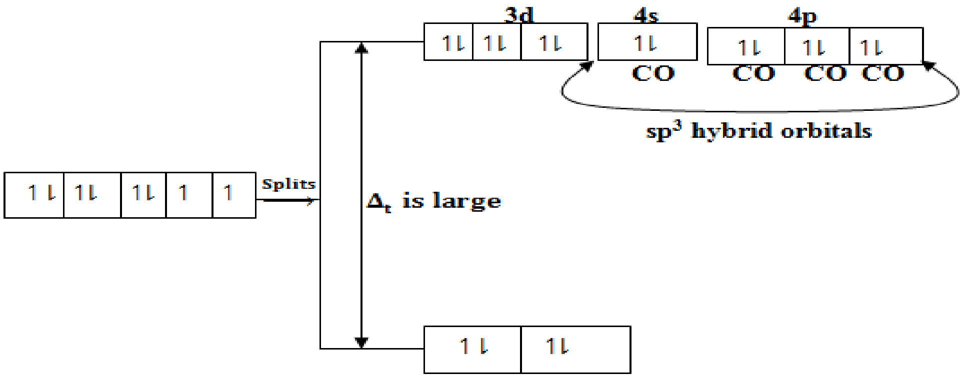
- Is formed by **d^2sp^3 hydridisation** and hence it is **octahedral**
- Is **diamagnetic** because all electrons in Co^{3+} are paired after redistribution of electrons brought about by strong ligand, NH_3

6. Bonding in tetracarbonylnickel(0), $[Ni(CO)_4]$

Outermost electronic configuration of Nickel is;



After introduction of CO ligands in $[Ni(CO)_4]$;



It should be noted that:

- $[Ni(CO)_4]$ being tetrahedral (has four CO monodentate ligands), the double degenerate has lower energy than treble degenerate.
- Due to strong electric field exerted by CO ligands, even the two 4s – electrons are paired up in unpaired 3d – orbitals.

After those few words, let us finish our work!

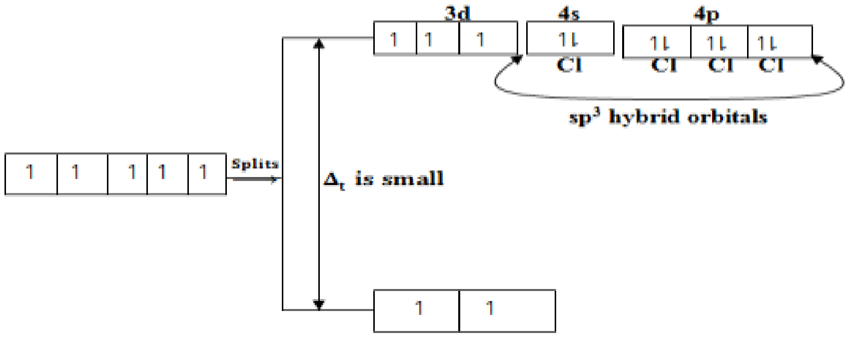
- The complex is formed by $\mathbf{sp^3}$ **hydridisation** and hence is **tetrahedral**
- The complex is **diamagnetic** because all electrons in Ni are paired after **redistribution** of electrons caused by strong ligand, CO.

7. Bonding in tetrachloromanganate(II) ion, $[\mathbf{MnCl_4}]^{2-}$

Outermost electronic configuration of Mn^{2+} is;

3d					4s	4p		
1	1	1	1	1				

After introduction of Cl^- ligands in $[MnCl_4]^{2-}$;



Here:

- Cl^- being weak ligand, does not cause pairing (redistribution of electrons).
- Again double degenerate has lower energy.

The complex, $[MnCl_4]^{2-}$

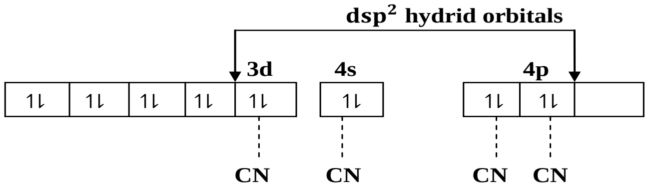
- Is formed by $\mathbf{sp^3}$ **hydridisation** and hence is tetrahedral
- Is paramagnetic due to presence of five unpaired electrons in 3d – orbitals

8. Bonding in tetracyanonickelate (II) ion, $[\mathbf{Ni(CN)_4}]^{2-}$

Outermost electronic configuration of Ni^{2+} is

3d					4s	4p		
1⇂	1⇂	1⇂	1	1				

After introduction CN^- ligands in, $[Ni(CN)_4]^{2-}$



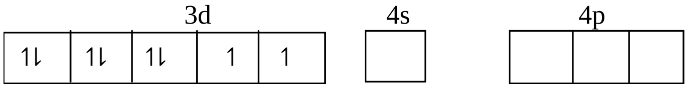
(CN^- being strong ligand cause pairing of all electrons in 3d – orbitals)

Thus:

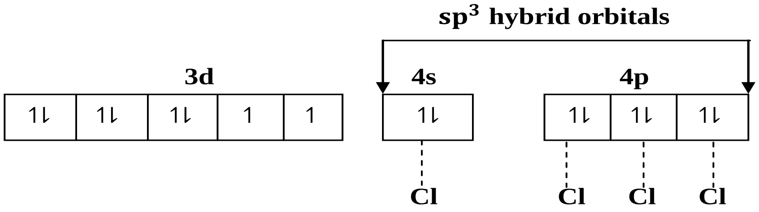
- The complex is formed by **dsp^2 hybridisation** and hence its geometric shape is **square planar**
- The complex is **diamagnetic** because all electrons in Ni^{2+} are paired after the redistribution caused by strong ligand, CN^-

9. Bonding in tetrachloronickelate(II) ion, $[NiCl_4]^{2-}$

Outermost electronic configuration of Ni^{2+} is;



After introduction of Cl^- ligands in $[NiCl_4]^{2-}$;

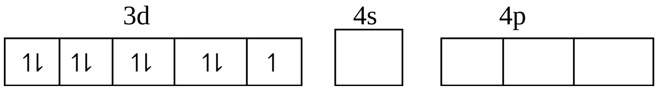


(Here Cl^- weak ligand, there is no pairing of electrons in Ni^{2+} like in the previous case)

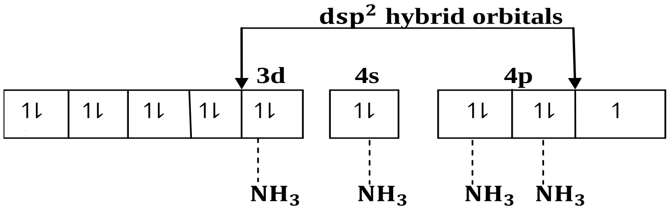
- The complex is formed by **sp^3 hybridisation** and hence its geometric shape is **tetrahedral.**
- The complex is **paramagnetic** due to presence of two unpaired 3d- electrons.

10. Bonding in tetraamminecopper(II) ion, $[Cu(NH_3)_4]^{2+}$

Outermost electronic configuration of Cu^{2+} is;



After introduction of NH_3 ligands in $[Cu(NH_3)_4]^{2+}$;

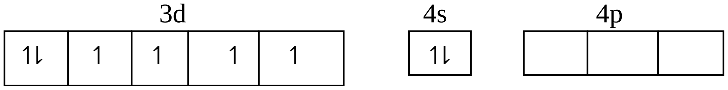


(Under presence of strong field ligand, an unpaired 3d – electron is promoted to an empty 4p – orbital to make one empty 3d – orbital available for dsp^2 hybridisation)

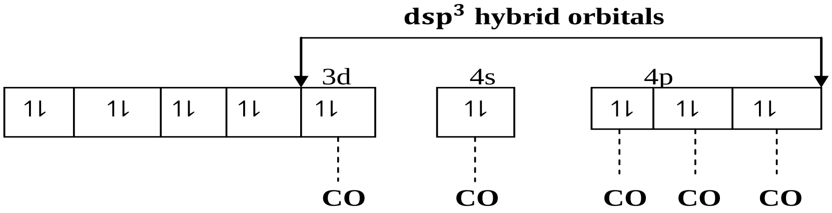
- The complex is formed by **dsp^2 hybridisation** and is **square planar**
- The complex is **paramagnetic** due to presence of one unpaired electron in 4p orbital.

11. Bonding in pentacarbonyliron(0), $[Fe(CO)_5]$

Outermost electronic configuration of Fe;



After introducing CO ligands in $[Fe(CO)_5]$;



(CO being strong field ligand, cause pairing of all available electrons, so as to allow dsp^3 hybridisation)

- The complex is formed by **dsp^3 hybridisation** and hence its geometry shape is **bipyramidal.**
- The complex is **diamagnetic**

FACTORS AFFECTINNG STABILITY OF COMPLEXES

The stability of a complex ion depends upon the following factors:

(i) Nature of central metal ion

The central metal ion form more stable complex ion if the ion has:

- Small cationic size
- High cationic charge

- Small cationic size accompanied with high cationic charge means high charge density of the ion leading to high ability of the ion in holding ligands.
- A metal ion in higher oxidation state is smaller in size than the metal ion in lower oxidation state and therefore forms more stable complex with the same ligand.

- Co^{3+} for example, form more stable complex than Co^{2+} with the same ligand

(ii) Nature of ligand

Greater the electron density of the donor atom of the ligand, more stable is the complex formed by it.

- In other word ligands which are better Lewis bases, i.e. ligands with greater basic strength form more stable complexes.

On another hand if the ligand is smaller in size, tends to form more stable complexes.

- Among, F^-, Cl^-, Br^- and I^-, F^- forms more stable complexes than other halogens e.g. while complex ion, $[CoF_6]^{-4}$ exists, similar complex for other halogens like $[CoCl_6]^{4-}$ does not exist. Instead they tend to form complex with Co^{2+} in lower coordination number of 4 e.g. $[CoCl_4]^{2-}$.

(iii) Formation of chelate

Always a chelate (complex ion involving polydentate ligands) is more stable than complex ions with only unidentate (monodentate) ligands.

- *The increase in stability of the complex which is obtained when water or other simple (monodentate) ligands are replaced by polydentate ligands like ethylenediamine (en) is known as* ***chelate effect.***

APPLICATION OF COMPLEX (COORDINATION) COMPOUNDS

Complex compounds have various applications including application in:

(i) Analytical chemistry

Formation of complexes by transition metal ions is used to detect metal cations to estimate metal cation gravimetrically volumetrically and colourimetrically.

(ii) Animal and plant

Complex compounds play an important role in number of processes occurring in nature.

- For example, chlorophyll present in plants is a coordination compound of magnesium, hemoglobin present in blood is coordination compound of iron (Fe^{2+}) and vitamin B_{12} is the complex of cobalt (Co^{3+}).

(iii) Extraction of metals

The unreactive metals like silver and gold are extracted from their ores through the formation of cyanide complexes. $[Ag(CN)_2]^-$ and $[Au(CN)_4]^-$.

(iv) Electroplating of metals

The complex compounds of silver and gold are used in electroplating baths for controlling deposition of metal ion.

- For example $K[Ag(CN)_2]$ is used in the electroplating of silver

(v) Chemotherapy (medicines)

Cis–dichlorodiammineplatinum (II) commonly known as **Cisplatin** is used as an anticancer drug.

Application of complex ion formation in cationic test of qualitative analysis experiment

In **qualitative analysis,** cations are divided in groups depending on the ease precipitation.

- Each group has particular reagent for causing that precipitation.

Group I: Ag^+, Hg^+ and Pb^{2+}

Chlorides of mentioned ions have very small solubility product, K_{sp}.

- So the mentioned ions need very small concentration of chloride Cl^- ions to precipitate their respective chlorides.
- The common useful reagent with ensures that small concentration of Cl^- ion for causing precipitation is **dilute hydrochloric acid, HCl.**

(i) $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$

(ii) $Hg^+(aq) + Cl^-(aq) \rightleftharpoons HgCl(s)$

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

The colour of the precipitates ($AgCl$, $HgCl$ and $PbCl_2$) is white

The use of dilute hydrochloric acid ensures small production of chloride, Cl^- ions. This has two advantages:

1. It differentiates cations of first group from other cations which need relatively greater concentration of chloride, Cl^- ions to form their respective precipitates.

2. It avoids formation of soluble complex, $[PbCl_4]^{2-}$which is formed in presence of greater concentration of chloride, Cl^- ions produced by concentrated hydrochloric acid (or excess HCl).

Silver chloride, AgCl can be distinguished from other chlorides by the following ways:

1. Adding excess of ammonia, NH_3 solution, it forms the soluble complex, $[Ag[NH_3]_2]^+$ while others chloride do not (the precipitate do not dissolve).
2. Adding solution of potassium cyanide, KCN it forms the soluble complex, $[Ag(CN)_2]^-$ while other chlorides do not.

Group II: $Cu^{2+}, Cd^{2+}, Sn^{2+}, Sn^{4+}, Sb^{3+}$, Bi^{3+} and Hg^{2+}

Sulphides of mentioned ions have very small solubility product, K_{sp}.

- So the mentioned cations need very small concentration of sulphide, S^{2-} ions to precipitate their respective sulphides.

How the production of the small concentration of sulphide, S^{2-} ions is ensured?

This is done by applying **hydrogen sulphide in the presence of dilute hydrochloric acid.**

- The two acids ionise in solution according to the following equations:

(i) $H_2S \rightleftharpoons 2H^+ + S^{2-}$

(ii) $HCl \longrightarrow H^+ + Cl^-$

The presence of strong acid, HCl which ionises completely in the solution, increase the concentration of H^+ shifting the equilibrium (i) to the left hand side, thereby decreasing concentration of sulphide S^{2-}. Hence only those sulphides (sulphides of second group cations) needing low concentration of sulphide, S^{2-} ions will precipitate.

Cu^{2+} and Cd^{2+} can be distinguished from the rest by using the solution of potassium cyanide, KCN whereby the cations are capable of forming their respective soluble complexes and hence their precipitates appear to dissolve.

$$Cu^{2+} + 4CN^- \longrightarrow [Cu(CN)_4]^{2-}$$

$$Cd^{2+} + 4CN^- \longrightarrow [Cd(CN)_4]^{2-}$$

Therefore CuS and CdS will not precipitate in presence of KCN(aq) while sulphide of other cations of second group precipitate.

Cu^{2+} can be distinguished from the rest by adding excess of ammonia, NH_3 solution whereby it forms the soluble complex, $[Cu(NH_3)_4]^{2+}$ which appears as deep blue solution.

- **Also in small adddition of concentrated hydrochloric acid, CuS does not precipitate due to the formation of $[CuCl_4]^{2-}$**

Group III: $Al^{3+}, Fe^{3+}, Fe^{2+}, Cr^{3+}$

Hydroxides of the mentioned cations have very small solubility product, K_{sp}.

- So the cations need very small concentration of hydroxide, OH^- ions to precipitate their respective hydroxides: **How this is achieved?**

Low concentration of hydroxide, OH^- ions is obtained by using the reagent which is **the mixture of ammonium chloride, NH_4Cl and ammonium hydroxide, NH_4OH solutions.**

- NH_4Cl solution being strong salt undergoes complete ionisation while NH_4OH solution being weak base undergoes partial ionisation.

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ ……………………………………….(i)

$NH_4Cl \longrightarrow NH_4^+ + Cl^-$ …………………………………….(ii)

NH_4^+ + ions from (ii) disturb the position of equilibrium in (i) by common ion effect, shifting the position of equilibrium to the left hand side, thus decreasing concentration of OH^- ions. Hence only those hydroxides (of third group) needing low concentration of hydroxide, OH^- ion will precipitate

- Al^{3+} and Cr^{3+} can be distinguished from the rest by adding excess solution of sodium hydroxide, NaOH.

- **White precipitate** of $Al(OH)_3$ dissolve to gives clear solution of $[Al(OH)_4]^-$ with NaOH(aq)
- **Green precipitate** of $Cr(OH)_3$ dissolve to give green solution of $[Cr(OH)_6]^{3-}$

- **Cr^{3+} can be also be distinguished from the rest** by adding excess solution of ammonia, $NH_3(aq)$

- Only $Cr(OH)_3$ dissolve to give green solution of $[Cr(NH_3)_6]^{3+}$

Tests of Fe^{2+} and Fe^{3+} (from $Fe(OH)_2$ and $Fe(OH)_3$

To test Fe^{2+}, the precipitate ($Fe(OH)_2$) is dissolved in dilute hydrochloric acid followed by addition of potassium hexacyanoferrate (III), $K_3[Fe(CN)_6]$

- With $K_3[Fe(CN)_6]$, Fe^{2+} gives deep blue solution. The colour is commonly known as **Turn bull's blue** . The colour is the result of formation of $\mathbf{K[Fe(Fe(CN)_6)]}$

That is: $Fe(OH)_2(s) + 2HCl(aq) \longrightarrow FeCl_2(aq) + 2H_2O(l)$

Then $$\underset{\textbf{(From FeCl}_2\textbf{)}}{Fe^{2+}} + \underset{\textbf{(from K}_3[\textbf{Fe(CN)}_6]\textbf{,)}}{[Fe(CN)_6]^{3-}} \longrightarrow \underset{\textbf{Turn bull's blue (deep blue)}}{[Fe(Fe(CN)_6)]^-}$$

Fe^{3+} can be tested by firstly dissolving the precipitate ($Fe(OH)_3$), then followed by addition of potassium hexacyanoferrate (II), $K_4[Fe(CN)_6]$ or ammonium thiocyanate, NH_4SCN

- **With $K_4[Fe(CN)_6]$,** Fe^{3+} gives deep blue solution of $K[Fe(Fe(CN)_6)]$. In this case the colour is commonly known as **Prussian blue** (to differentiate to the deep blue colouration formed in the case of Fe^{2+})
- With NH_4SCN, Fe^{3+} gives bloody red colouration of $[Fe(H_2O)_5SCN]^{2+}$

That is $Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$

Then $$\underset{\textbf{(From FeCl}_3\textbf{)}}{Fe^{3+}(aq)} + \underset{\textbf{(From K}_4\ [\textbf{Fe(CN)}_6]}{[Fe(CN)_6]^{4-}} \longrightarrow \underset{\textbf{Prussian blue (deep blue)}}{\left[Fe\left(Fe(CN)\right)_6\right]^-}$$

And $$\underset{\textbf{(From Fe}^{3+}\textbf{(aq))}}{[Fe(H_2O)_6]^{3+}} + SCN^- \longrightarrow \underset{\textbf{Bloody red colour}}{[Fe(H_2O)_5(SCN)]^{2+}}$$

Group IV: $Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}$

Compared to cations of second group, the above mentioned **cations need relatively greater concentration of sulphides, S^{2-} ions to precipitate their respective sulphides.**

How the greater concentration of sulphide ions is ensured?

- Greater concentration of sulphide, S^{2-} ions is obtained by using **ammonium sulphide, $(NH_4)_2S$ only or hydrogen sulphide, H_2S in the presence of ammonium hydroxide, NH_4OH solution**

(i) By using $(NH_4)_2S$

Ammonium sulphide, $(NH_4)_2S$ being strong salt ionises completely to give large concentration of S^{2-} ions according to the following equation:

$$(NH_4)_2S \longrightarrow 2NH_4^+ + S^{2-} \text{...(i)}$$

Sulphide of the fourth group cations, being slightly soluble, ionises according to the following equation:

$$M(s) \rightleftharpoons M^{2+}(aq) + S^{2-}(aq) \text{...(ii)}$$

Where M may be Ni, Co, Mn, or Zn

Ammonium sulphide, $(NH_4)_2S$ increases concentration of sulphide, S^{2-} ions, shifting the position of equilibrium in (ii) towards the left hand side and therefore forming precipitation of the sulphide. Hence **sulphides (of fourth group cations) needing large concentration of S^{2-} ions will precipitate**

(ii) By using H_2S in presence of NH_4OH

Both H_2S and NH_4OH being weak acid and weak base respectively, undergo partial ionisation in solution according to the following equation:

$$H_2S \rightleftharpoons 2H^+ + S^{2-} \text{..(i)}$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^- \text{......................................(ii)}$$

Hydrogen protons, H^+ from (i) combine with hydroxide, OH^- ions from (ii) to form water, H_2O according to the following equation:

$$H^+ + OH^- \longrightarrow H_2O$$

This decreases concentration of sulphide, S^{2-} ions, shifting the position of equilibrium in (i) towards the right had side by producing more sulphide, S^{2-} ions and **cations (of fourth group) needing large concentration of the sulphide, S^{2-} ions will precipitate**

*To distinguished the sulphides, the precipitates are firstly dissolved in mineral acids, (**to produce large concentration of Ni^{2+}, Co^{2+}, Mn^{2+}, or Zn^{2+} in the solution**) followed by:*

(i) Addition of NaOH(aq)

Zn^{2+} firstly give **white precipitate of** $Zn(OH)_2$ which dissolve in excess NaOH(aq) to give **clear solution** due to formation of $[Zn(OH)_4]^{2-}$

(ii) Addition of $NH_3(aq)$

- Zn^{2+} gives **clear solution** of $[Zn(NH_3)_4]^{2+}$
- Ni^{2+} gives **deep blue solution** of $[Ni(NH_3)_6]^{2+}$

(iii) Addition of concentrated HCl

Co^{2+} gives **blue solution** of $[CoCl_4]^{2-}$

Group V: Ca^{2+}, Ba^{2+}, Sr^{2+}

This is the only case where complex formation has no application on the **cationic test** (**Note:** All Ca^{2+}, Ba^{2+} and Sr^{2+} are incapable of making complexes).

Reagent used for test: Ammonium carbonate, $(NH_4)_2CO_3$

$$(NH_4)_2CO_3 \longrightarrow 2NH_4^+ + CO_3^{2-}$$

With the carbonate, all Ca^{2+}, Ba^{2+} and Sr^{2+} gives white precipitates of $CaCO_3$, $BaCO_3$ and $SrCO_3$ respectively.

PRACTICE EXERCISE 20

Question 1

Draw structures for each of the following species:

(i) $[Ni(CN)_5]^{3+}$
(ii) $[CO_2Cl_{10}]$
(iii) $[Fe(C_2O_4)_3]^{3-}$

Question 2

(a) Name the two shapes most commonly found in transition metal complex and state their bond angles.
(b) For each shape, suggest formula of nickel (II) complex having that shape.

Question 3

With help of an example, explain ligand substitution reaction.

Question 4

Complete and balance the following reactions:

(i) $[Cu(H_2O)_6]^{2+} + Cl^- \rightarrow$
(ii) $[Cu(CN)_4]^{2-} + H_2O \rightarrow$
(iii) $[Zn(NH_3)_6]^{2+} + CN^- \rightarrow$
(iv) $[Al(H_2O)_6]^{3+} + H_2O \rightarrow$

Question 5

With the help of an example, clearly distinguish between inner orbital complex and outer orbital complex.

Question 6

Show how the following complexes are formed through hybridization and for each case:

(a) State whether the complex is paramagnetic or diamagnetic
(b) State the geometric shape of the complex
  (i) $[Cu(H_2O)_4]^{2+}$
  (ii) $[Ni(NH_3)_6]^{2+}$
  (iii) $[Ni(CN)_4]^{2+}$
  (iv) $[Fe(H_2O)_6]^{3+}$
  (v) $[CoCl_4]^{2-}$
  (vi) $[Co(NH_3)_6]^{3+}$

Question 7

Deduce the formulae of the following complexes which contain only chloride ions as ligands:

(i) A tetrahedral complex ion of nickel (II)
(ii) An octahedral complex ion of titanium (VI)
(iii) A linear complex of copper (I)

EXAMINATION QUESTIONS FOR PART FIVE

Question 1

(a) Define a transition element.
(b) What is the general outer electronic configuration of a transition element?
(c) Why is copper considered a transition element?
(d) Why zinc is not considered a transition element?

Question 2

Why can transition metals act as catalysts?

Question 3

Give reasons for the following:

(i) Transition metal ions form complexes.

(ii) Transition metal salts are generally coloured.

(i)Transition elements have high enthalpy of hydration.
(ii)Transition metals form alloys.

Question 4

The first ionisation energy of copper is higher than those of alkali metals but second and third ionisation energies are lower.

Question 5

Zinc does not show oxidation state higher than two. Give reason for this.

Question 6

(a) A solution of hydrated copper (II) sulphate $CuSO_4.5H_2O$ has blue colouration. What species is responsible for this colour formation?

(b) When $C_2O_4^{2-}(aq)$ is added to a solution in (a) above. White precipitate is observed which dissolves into blue solution when excess $C_2O_4^{2-}(aq)$ is added. Explain this observation.

Question 7

Simple sugars like glucose and fructose are known as reducing sugars. Explain.

Question 8

Copper metal resists attack by both dilute sulphuric acid and hydrochloric acid, but reacts with dilute nitric acid. Explain.

Question 9

Copper (I) chloride is insoluble in water, and its molar mass in the vapour state is twice its expected value. Explain

Question 10

Copper (II) hydroxide is insoluble in sodium hydroxide solution but it is readily soluble in aqueous ammonia solution. Explain.

Question 11

While Copper (II) compounds manifest transition metal characteristics, Copper (I) compounds do not. Explain.

Question 12

Anhydrous Copper (II) sulphate is white, but when water is added to it, its solution is blue. Explain.

Question 13

Explain in terms of their electronic configuration, why Fe^{2+} ions are readily oxidised to Fe^{3+}but Mn^{2+} ions are not readily oxidised to Mn^{3+}.

Question 14

(i) Give the formula of a compound or ion containing manganese in an oxidation state of +7

(ii) How do you account for the existence of +7 oxidation state of manganese?

Question 15

Write down a balanced chemical equation for the following:

(i) Addition of excess ammonia solution to aluminium ion

(ii) Iron (III) oxide is heated with aluminium powder.

Question 16

Concentrated hydrochloric acid prevents precipitation of copper (II) sulphide from copper (II) silphide aqueous solution. Explain.

Question 17

A greenish aqueous salt solution of iron turned to brownish precipitate when sodium hydroxide solution was added and allowed to stand in air.

(i) What is the oxidation state of Fe in the brownish precipitate?

(ii) Why are the compounds of Fe coloured?

Question 18

Silver chloride salt is insoluble in water but readily soluble in aqueous ammonia. Explain.

Question 19

Silver chloride is soluble in ammonia while silver iodide is insoluble in ammonia. Explain.

Question 20

An aqueous suspension of chromium hydroxide. When boiled with sodium peroxide gives a yellow solution. Explain.

Question 21

Copper (I) ion rarely exists in aqueous solution. Explain.

Question 22

a) Describe what you would expect to observe on gradual addition of the excess of the following reagents to separate samples of solution containing copper (II) ions, $Cu^{2+}(aq)$

  i. Aqueous ammonia

  ii. Potassium iodide

Give the formula and names of all species produced

b) Explain the nature of the reaction with potassium iodide solution giving also a balanced overall chemical equation

Question 23

Both $[Co(CN)_6]^{3-}$ and $[CoF_6]^{3-}$ are octahedral complexes. Then what is the difference between the two ?

Question 24

With the help of a chemical equation, state what will you observe when iron (III) chloride is allowed to react with potassium hexacyanoferrate(II). What is the main practical use of the reaction?

Question 25

When potassium iodide solution is added to mercuric chloride solution, a precipitate which changes colour first but dissolve in excess of potassium iodide. Explain

Question 26

Effervescence of colorless gas is observed when sodium carbonate is added to an aqueous solution containing Fe^{3+}. Explain.

SOLUTIONS TO EXAMINATION QUESTIONS

PART ONE

Question 1

SO_4^{2-} being ionic compound there electrostatic force of attraction existing between oppositely charged ions (cations and anions) which is stronger than Van-der-Waals dispersion forces existing between SO_2 molecules which is covalent.

Question 2

K_2CO_3 has higher melting point.

Reason: K_2CO_3 is more ionic in characters as result of its lower degree of polarisation brought about by smaller polarising power of larger sized K^+.

Question 3

Mg being metal there is metallic bond existing between its atoms which is stronger than Van der Waals dispersion forces existing between phosphorous molecules which is non-metal.

Question 4

$AlCl_3$ sublimes on heating.

Reason: $AlCl_3$ is more covalent in characters as result of its higher degree of polarisation brought about by smaller sized and higher charged Al^{3+} .

Question 5

AlF_3 is more ionic in characters as result of its lower degree of polarisation brought about by smaller polarisability of smaller sized F^- thus making its melting point higher.

Question 6

Na and K have weak metallic bond existing between their atoms as result of their large metallic radii and few valence electrons (only one valence electron is available in each) thus making them soft accompanied with low density and high solubility in water.

Question 7

Mg has stronger metallic bond existing between its atoms as result of its smaller metallic radius and greater number of valence electrons (Mg has two valence electrons while Na has one valence electron) and hence the metal has higher melting point.

Question 8

In molten state $AlCl_3$ has no enough concentration of ions for doing electrolytic conduction as result of its high degree of covalent characters brought about by its high degree of polarisation. But in aqueous solution the salt undergo cationic hydrolysis yielding enough concentration of free ions (H^+**(aq)** and Cl^-**(aq)** from HCl**(aq))** which are responsible for electrolytic conduction.

i.e. $AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3H^+(aq) + 3Cl^-(aq)$

Question 9

In aqueous solution PCl_3 hydrolyse yielding enough concentration of H^+ and Cl^-ions which are responsible for electrolytic conduction

$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3H^+(aq) + 3Cl^-(aq)$

(H^+ and Cl^- ions are from HCl(aq) which is strong electrolyte)

Question 10

Lithium being on the top of the group IA its ion has greater degree of hydration in aqueous solution as result of its smaller cationic radius thus lowering its mobility as the ions become heavy and hence Li^+ ions are not free to move in aqueous solution which account for its poor conduction of electricity.

Question 11

Chloride ions (Cl^-) are better conductors.

Reason: Cl^- being smaller size has higher mobility in molten state and hence the ions are freer to move thus becoming better conductor.

Question 12

AlF_3 has more ionic characters as result of its lower degree of polarisation brought about by smaller polarisability of smaller sized F^- hence it has higher concentration of ions which account for its electrolytic conduction in molten state.

Question 13

$AlCl_3$ has greater degree of covalent characters brought about by its greater degree of polarisation caused by smaller sized and higher charged Al^{3+} and hence in molten state it has no enough concentration of ions which can conduct electricity like in molten NaCl.

Question 14

In solid form, Na^+ and Cl^- are not free to move so as to do electrolytic conduction.

Question 15

- Atoms exist in combined form which cannot be spitted to get a single isolated atom.
- Exact position of farthest electron cannot be determined.
- Atomic size is affected by nature of neighbour atoms.

Question 16

(i)Na (ii) F (iii) F **(F has smaller atomic size although it is at the left of Ne due to the difference in type of of bonds holding atoms together. F has a covalent radius while Ne has Van der Waals radius and generally Van der Waals radius is greater than covalent radius)** (iv) Na (v) B and Al(element with atomic number of 31 has electronic configuration of $[Ar]3d^{10}4s^24p^1$ with total number of valence electrons of $2 + 1 = 3$ hence the element must be in group IIIA).

Question 17

(i) Periodicity of outermost electronic configuration of elements.
(ii) Periodicity of properties of elements.

Question 18

Potassium has greater number of protons so there is a greater nuclear attractive force per electron in K^+ than in Cl^-.

Question 19

Calcium being below Magnesium in the group has a larger atomic size (radius) accompanied with lower ionisation energy so that its valence electrons are weakly held by nuclear attractive forces such that normal radiant energy from the sun is enough to excite these valence electrons (in Ca) and on returning to ground state the electrons emit energy with wavelength in visible spectrum unlike in Mg where electrons are firmly held by nuclear attractive force.

Question 20

For transition elements as atomic number increases an electron is added to the penultimate shell (in the inner d-orbitals) thus making increase in screening effect enough to counterbalance (offset) the increase in the nuclear attractive force.

Question 21

(b) (i)

- **In solid $CaCl_2$**, the increase in lattice energy is large enough to compensate the increase of the ionisation energy as Ca^{2+} (in $CaCl_2$) has greater attraction to Cl^- than Ca^+ (in CaCl).
- **In aqueous $CaCl_2$,** the increase in hydration energy is large enough to compensate the increase of the ionisation energy as Ca^{2+} has greater attraction to lone pair of oxygen of oxygen in water molecules making it to be more hydrated than Ca^+.

Hence $CaCl_2$ exists in both solid and aqueous form while CaCl does not.

(ii**) In water,** there are strong hydrogen bonding holding its molecules due to high electronegativity of oxygen atom accompanied with presence of two lone pairs in the atom while **in methane**, carbon is less electronegative without any lone pair thus making incapable for it to make hydrogen bonding; instead there is Van-der-Waals dispersion forces which is weaker intermolecular force of attraction than hydrogen bonding and hence methane has far lower boiling point, far below the room temperature.

Question 22

(i) Fluorine has so small atomic size that there is large repulsion between outer and inner electrons making difficult to add electron.

(ii) **In making Na^+,** an electron is removed from Na atom thus the remained fewer electrons in the ion experience greater effective nuclear attractive force.

In making Cl^-, an electron is added to Cl atom making electrons in the ion to experience smaller effective nuclear attractive force.

Question 23

- The atom with configuration of $1s^22s^22p^6$ has ionisation energy of 2080kJ/mol.
- The atom with electronic configuration of $1s^22s^22p^63s^1$ has ionisation energy of 496kJ/mol.

Justification

The first atom has greater ionisation energy due to the following reasons:

(i) With all of its orbitals are paired with electrons, the first atom has more stable electronic structure of completely paired electronic configuration.

(ii) The electron in the first atom is removed from the second shell while in the second atom, the electron is removed from the third shell which is of greater distance from the nucleus.

(iii) The 2p-electron which is to be removed from the first atom is screened by 4 electrons (two 2s-electrons and two 1s-electrons) while the 3s-electron to be removed from the second atom is screened by 10 electrons and therefore the ionisable electron in the first atom experience weaker screening effect

Question 24

(i) Due to its very small atomic size, it was expected fluorine to have greatest attraction to the added electron and hence greatest electron affinity. However the size of fluorine is so small that there is very large repulsion between its electrons (the small atomic size makes electrons to be very close to each other). This weakens the ability of fluorine to attract electrons and hence fluorine has unexpectedly lower electron affinity.

(ii) Be and N have very stable electronic configuration; the factor which weakens their ability to attract electrons thus making their affinities positive.

- With electronic configuration of $1s^2 2s^2$, Be has stable electronic structure of exactly full paired electronic configuration.
- With electronic configuration of $1s^2 2s^2 2p^6 2p_x^1 2p_y^1 2p_z^1$, N has stable electronic structure of completely half filled electronic configuration in its outermost p-subenergy level.

Question 25

The carbonate undergo thermal decomposition (due to its degree of polarisation) to give CO_2 which appears as effervescence of colourless gas which turns lime water milky.

$$CuCO_3(s) \underset{\Delta}{\rightarrow} CuO(s) + CO_2(g)$$

Question 26

(i) With 12 protons, Mg^{2+} ion exerts greater nuclear attractive force per electron than Na^+ which has fewer protons (11 protons).

(ii) Li^+ ion has large polarising power as result of its small cationic radius. So when it combines with the anion of large polarisability (large sized and/or highly negative anion), the compound formed must have large degree of polarisation and hence becoming highly covalent in characters; for example LiI is highly covalent.

Question 27

The given ions are isoelectronic with the same electronic configuration of Ne.

- Being isoelectronic, ionic sizes increase with a decrease in their ionic charges.

$$\underset{\text{Increase in ionic size}}{\underrightarrow{Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}}}$$

- Polarising power increases with a decrease in ionic size (Small ions in the isoelectronic series have high ionic charge which also make the ions to have large polarising power)

$$\underset{\text{Increase in polarising power}}{\underrightarrow{N^{3-} < O^{2-} < F^- < Na^+ < Mg^{2+}}}$$

- Polarisability increases with an increase in ionic size (and decrease in ionic charges)

$$\underset{\text{Increase in polarisability}}{\underrightarrow{Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}}}$$

Question 28

Electronic configurations of Be, B and of their respective unipositive ions:

$Be \rightarrow [He]2s^2$ $Be^+ \rightarrow [He]2s^1$

$B \rightarrow [He]2s^2 2p^1$ $B^+ \rightarrow [He]2s^2$

From above electronic configurations, it can be concluded that:

(i) First ionisation energy of Be (in converting Be to Be^+) is greater than that of B because:

- With all of its orbitals paired, Be has more stable electronic configuration
- The 2s-electron to be removed from Be experience weaker screening effect as it is shielded by two electrons (two 1s-electrons) only while in B, the 2p-electron is shielded by four electrons (two 1s-electrons and 2s-electrons)
- The 2p-electron to be removed from B is of greater distance from the nucleus than the 2s-electron in Be

(ii) Second ionisation energy of B (in converting B^+ to B^{2+} which is isoelectronic to Be^+) is greater than that of Be because once the first ionisation has taken place, B^+ has more stable electronic configuration of completely full paired electronic structure while the second electron in B is removed from unpaired orbital.

Question 29

The given ions are all belong to period IIA; therefore their radii increase on descending the group to give the following trend

$$\underset{\text{Increase in ionic radii}}{\underrightarrow{Be^{2+} < Mg^{2+} < Ca^{2+} < Sr^{2+}}}$$

Question 30

Acidity of hydrides depends on the electronegativity difference between the element which make the hydride and hydrogen. Strong electronegative atom form acidic hydride and less electronegative form basic (less acidic hydride).

(iii) NH_3 contains N which is least electronegative of the three (N, O, F). It is basic.

(iv) H_2O is amphoteric which has action with both acids and bases.

(v) HF contains F which is most electronegative of the three. It is acidic.

Therefore the trend becomes:

$$\underset{\text{Increase in acidic strength}}{\xrightarrow{NH_3 < H_2O < HF}}$$

Question 31

Valence electrons

Number of valence electrons increases as you go across the period from the left to right hand side while on descending the group, the number remains constant.

Electron affinity

This increases as you go across the period (from left to right) due to decrease in atomic size and decreases on descending the group due to increase in atomic size.

Melting point

Here the general trend is not clear:

For metals, melting point is found to increase as you go across the period (due to an increase in strength of metallic bond as number of valence electrons increases and atomic size decrease to the same direction) and decreases on descending the group (down the group, atomic size increases and therefore strength of metallic bond decreases)

For non-metals, there is no generalisation can be made for their trend of melting point across the period – it depends on the molecular structure of the element. However we are expecting molecular mass of non-metals to increase on descending down the group thus increasing Van-der-Waals dispersion forces and hence melting points of groups with non-metals, increase on descending the groups.

Atomic radius

Atomic radius decreases as you go across the period (from left to right) due to increase in effective nuclear attractive force and decreases as you go down the groups due to increase in screening effect as result of an increase in number of shells.

Question 32

(a) K^+ has larger ionic radius because it has greater number of shells (K^+ has 3 shells while Na^+ has 2 shells) making its outermost shell to experience stronger screening effect.

(b) K^+ has larger ionic radius because it has smaller nuclear attractive force per electron (in K^+, 19 protons attract 18 electrons while in Ca^{2+}, the same number of electrons is attracted by 20 protons).

(c) Cl^- has larger ionic radius because it has smaller nuclear attractive force per electron.

(d) Cu^+ has larger ionic radius because it has smaller nuclear attractive force per electron.

Question 33

(a) Na atom with electronic configuration of $[Ne]3s^1$ undergoes first ionisation to give Na^+ ion with electronic configuration of neon ($1s^22s^22p^6$). This makes the second ionisation energy much higher than the first because:

(i) Na^+ has stable electronic structure of completely full paired electronic configuration of noble gas (Ne)

(ii) There is much and suddenly increase of screening effect in Na^+ as the first electron is removed from the third shell (shielded by 10 inner electrons) while the second electron is removed from the second shell (shielded by only two electrons from inner shells)

(iii) The second electron is removed from Na^+, there is greater nuclear attractive per electron than Na atom from which first electron is removed

(b) There is stronger metallic bond in Mg as result of its smaller metallic radius accompanied with greater number of valence electrons than in Na, making Mg to have higher melting point.

(c) Due to increase in nuclear attractive force per electron as the ionic charges increases, the ionic size is found to decrease as the ionic charges increase.

Question 34

(i) Group IIA, period 4

(ii) Group VA, period 2

(Note: If the element has 3 unpaired 2p-electrons, also it must have two 2s-electrons making a total of five valence electrons and hence it must be at group VA).

(iii) Group 3B, period 4

Question 35

$${}_{11}A \rightarrow 1s^22s^22p^63s^1$$

$${}_{15}B \rightarrow 1s^22s^22p^63s^23p^3$$

$${}_{16}C \rightarrow 1s^22s^22p^63s^23p^4$$

$$_{17}\mathrm{D} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^5$$

$$_{24}\mathrm{E} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$$

A is s-block element **B** is p-block element **C** is p-block element

D is p-block element **E** is d-block element

- **A** being s-block metal has lowest ionisation energy due to its smallest nuclear charge.

Note: ionisation energy of d-block elements (d-block is between s and p blocks of periodic table) lies between those of s-block and p-block elements, i.e. the energy tends to increase as you go across the period from s-block to p-block via d-block.

- **C** because to attain octet structure of noble gas (argon), it must gain two electrons and this occurs when it combines with less electronegative atoms than itself, for example in Na_2C.
- **A** is s-block element, so it must be **strong electropositive metal** while C is p-block element which lacks only two electrons to get stable octet electronic structure of noble gas, argon and therefore it must be **non-metal** and hence the bond formed between A and C will be ionic
- **D** undergoes the process most readily.

This is because its electronic structure suggests that:

(i) **D has smallest atomic radius** (the p-block element with seven valence electrons, i.e. two 3s-electrons and five 3p-electrons – it must be in group VIIA in the same period 3 like A, B and D while E is at period 4; no factor can prevent it from being smallest atom of all given elements)

(ii) **D has unstable electronic configuration** needing one electron only to attain stable electronic structure of noble gas (argon)

The two factors make D to have highest electron affinity and hence the process $M(g) + e \rightarrow M^-(g)$ occurs most readily.

Question 36

(a) With electronic configuration of $1s^2 2s^2 2p^6 3s^2$ and $1s^2 2s^2 2p^6 3s^2 3p^6$ for Mg and Ar respectively, the two elements have very stable electronic structure of exactly full filled orbitals making difficult for them to gain electrons.

(b) With electronic configuration of $[Ne]3s^2 3p_x^1 3p_y^1 3p_z^1$, phosphorous has more stable electronic configuration of completely half filled electronic structure (all of its p-orbitals are singly occupied with electrons) making more difficult to add electron in it than in silicon.

Question 37

With electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$, the element has very stable electronic configuration of exactly full filled electronic structure. The stability leads to difficulty of removing an electron from an atom of the element. (Actually the element with atomic number of 36 is noble gas, krypton).

Question 38

Hydroxide will be acidic if the element which makes the hydroxide is more electronegative than hydrogen and will be basic if the element is less electronegative. Hence, **CsOH is basic** and **IOH is acidic**.

Question 39

(a) F

Reason: F has greater nuclear charge than O and its radius is covalent (like O). Although Ne has greater nuclear charge than F, it has larger size than F because it has Van-der-Waals radius which is larger than covalent radius found in F.

(b) Al

Reason: Al has greater nuclear charge, i.e. its valence shell experience greater effective nuclear attractive force and hence more contraction of shells.

(c) Cl

Reason: Cl has large nuclear charge and has covalent radius.

(d) Al^{3+}

Reason: Al^{3+} has greater nuclear attractive force per electron than the rest.

Question 40

(a) H_2S is more covalent because S is less electronegative than O, making $S-H$ bond less polar.

(b) BCl_3 is more covalent because B^{3+}having smaller size and higher charge, has greater polarising power than Be^{2+} and therefore BCl_3 has greater degree of polarisation than $BeCl_2$.

Question 41

The ionisation energy of K^+ to K^{2+} (in KCl_2) is too high to be compensated by either lattice energy in the solid KCl_2 or hydration energy in aqueous KCl_2 and hence the compound does not exist unlike KCl which has no such problem.

Question 42

(i) With electronic configuration of $[Ar]4s^2$, all two electrons of W are removed from the same shell and thus both first and second ionisation energy of W are small and hence it lose easily the two valence electrons to attain stable octet electronic structure of noble gas, Ar.

In X; with electronic configuration of $[Ar]4s^1$, the second electron has to be removed from inner shell which is closer to nucleus and experience weaker screening effect; and also after removing first electron, X^+ has very stable electronic configuration of noble gas (Ar) all of which make the second ionisation of X very high that cannot be attained in practice.

(ii) Electronic configuration of each element is as follows:

$X \rightarrow [Ar]4s^1$
$Y \rightarrow [Ne]3s^1$
$Z \rightarrow [Kr]5s^1$
$W \rightarrow [Ar]4s^2$

Hence:

- X, Y and Z are found at **group IA**
- W is found at **group IIA**
- X and W are found at **period 4**
- Y is found at **period 3**
- Z is found at **period 5**
- All X, Y, Z and W are found at **s-block** of modern periodic table

(iii)

$$\xrightarrow{W > Y > X > Z}$$

Decrease in melting point

$$\xrightarrow{W > Y > X > Z}$$

Decrease in boiling point

$$\xrightarrow{W > Y > X > Z}$$

Decrease in ionisation energy

$$\xrightarrow{W > Y > X > Z}$$

Decrease in sublimation energy

$$\xrightarrow{Z > X > Y > W}$$

Decrease in ability to show photoelectric effect

Question 43

- Having smallest ionic size, Li^+ ion is most hydrated and therefore become heaviest in aqueous solution of all ions of alkali metals.
- Electronic configuration of K, Ca and their respective unipositive ions are shown below:

$K \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
$Ca \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
$K^+ \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6$
$Ca^+ \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

From above electronic configurations, it can be concluded that:

- The first ionisation energy of Ca is greater than that of K because:

(i) It has greater nuclear charge due to presence of larger number of protons in Ca than in K
(ii) With all electrons paired, Ca has more stable electronic configuration than K

- The second ionisation energy of K is greater than that of Ca because:

(i) With electronic configuration of noble gas (Ar), K^+ has all of its orbitals paired with electrons which is very stable electronic configuration
(ii) The electron to be removed in K^+ is closer to the nucleus (it is in the third shell) than in Ca^+ where the second electron is removed from the same fourth shell as the first one
(iii) The electron to be removed in K^+ experience stronger screening effect than in Ca^+

Question 44

$$\xrightarrow{Al^{3+} < Mg^{2+} < Na^+}$$

Increase in ionic size

$$\xrightarrow{Na^+ < Mg^{2+} < Al^{3+}}$$

Increase in hydration

$$\xrightarrow{Na^+ < Mg^{2+} < Al^{3+}}$$

Increase in mobility in **anhydrous form**

$$\xrightarrow{Al^{3+} < Mg^{2+} < Na^+}$$

Increase in mobility in aqueous solution

Question 45

(i) Atomic size increase from Be to Ba due to an increase in number of shells on descending the group which in turn increase screening effect and hence the valence shell expand more
(ii) Ionic radius is less than atomic radius due to:

- Decrease in number of shells which goes with decrease in screening effect

- Increase in nuclear attractive force per electron and hence there is more contraction of shells in remaining fewer electrons of the ions.

Question 46

(c) With atomic number of 11 and 12 respectively, sodium and magnesium have low ionisation energy (below 800kJ/mol) making possible for them to ionise as positively charge easily which is the main characteristic of metal.

(d) (i) Being metal, the bond found in magnesium is metallic bond.
(ii) Magnesium is metal while chlorine (with very high ionisation energy from the graph which is above 800kJ/mol) is non-metal and therefore the bond formed between the two in the solid magnesium chloride is ionic bonding.

Question 47

(a) $[CoBr(NH_3)_5]SO_4$ yields $[CoBr(NH_3)_5]^{2+}$ and SO_4^{2-}
While $[Co(SO_4)(NH_3)_5]Br$ yield $[Co(SO_4)(NH_3)_5]^+$ and Br^-,

(b) Coordination number of cobalt in each complex is 6.
(c)
First test:
With an aqueous solution of $AgNO_3$, $[Co(SO_4)(NH_3)_5]Br$ yields a light yellow precipitate of insoluble AgBr while $[CoBr(NH_3)_5]SO_4$ does not.

Second test:

With barium chloride ($BaCl_2$) under presence of hydrochloric acid, $[CoBr(NH_3)_5]SO_4$ yields a white precipitate of insoluble barium sulphate ($BaSO_4$) while $[Co(SO_4)(NH_3)_5]Br$ does not.

Question 48

$[Pt\,Cl_4(NH_3)_2]$ has no free Cl^- ions in the ionisation sphere to combine with Ag^+ (from $AgNO_3$) as all of its Cl^- ions are directly bonded to the central metal ion in the coordination sphere as ligands by dative bond while in $[PtCl_3(NH_3)_3]Cl$, there is free Cl^- in the ionisation sphere which may combine with Ag^+ (from $AgNO_3(aq)$) yielding a white precipitate of AgCl

i.e. $[PtCl_3(NH_3)_3]Cl + AgNO_3 \rightarrow [Pt(NH_3)_5Cl_3]NO_3 + AgCl(aq)$

While $[Pt\,Cl_4(NH_3)_2] + AgNO_3 \rightarrow$ No reaction

Question 49

Molar mass of $CrCl_3 . 6\,H_2O = 266.5gmol^{-1}$

Using $n = \frac{m}{Mr}$;

Number of moles of $CrCl_3 . 6\,H_2O = \frac{2.665g}{266.5gmol^{-1}} = 0.01mol$

Molar mass of AgCl $= 143.5gmol^{-1}$

Then number of moles of AgCl produced

$$= \frac{2.87g}{143.5gmol^{-1}} = 0.02mol \text{ of } Ag^+$$

But Ag^+ (from $AgNO_3$) combines with Cl^- to form AgCl according to the following equation:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

From which mole ratio of Ag^+ to $Cl^-$is 1:1

Thus number of moles of Cl^- from 0.01mol of $CrCl_3 . 6\,H_2O$ was also 0.02mol

Whence 0.01mol of $CrCl_3 . 6H_2O$ produces 0.02mol of Cl^-

Or 1mol of $CrCl_3 . 6H_2O$ produces 2mol of Cl^-. This suggests the that one Cl^- is coordinated to central metal ion (Cr^{3+}) as ligand in the coordination sphere and $2Cl^-$ present in the ionisation sphere

- Cr^{3+} having common coordination number of six, $5H_2O$ must be also coordinated to it so that with one Cl^-, a total of six monodentate ligands are bonded to the ion and one H_2O remains as water of crystallisation.

Hence the structure of the compound is $[CrCl(H_2O)_5]Cl_2 . H_2O$.

PART TWO

Question 1

In solid state, PCl_5 exists in ionic form as $[PCl_4]^+[PCl_6]^-$ so there is strong electrostatic force of attraction between cation and anion and not weaker Van-der-Waals force of attraction between covalent bonded molecules of PCl_5 as expected.

Question 2

HI which would be formed is stronger reducing agent (than HCl) thus it oxidised by concentrated H_2SO_4 which has oxidising property to I_2.

$NaI + H_2SO_4\,(conc) \rightarrow NaHSO_4 + HI$

Then $HI + H_2SO_4\,(conc) \rightarrow H_2S + H_2O + I_2$

Thus overall reaction equation becomes;

$NaI + H_2SO_4\,(conc) \rightarrow NaHSO_4 + H_2O + I_2 + H_2S$

(Note: In excess, $NaI, NaHSO_4$ undergo further reaction to form Na_2SO_4)

While

$NaCl + H_2SO_4\,(conc) \rightarrow NaHSO_4 + HCl$

Then: $HCl + H_2SO_4\,(conc) \rightarrow$ No reaction

Question 3

(i) **Oxidising power of halogens (group VII elements) decrease as you descend the group VII.**

i.e. member above the group replaces below members from their salts e.g. Br_2 replaces (oxidises) I^- from its salts but not Cl^-
i.e $Br_2 + 2NaI \rightarrow 2NaBr + I_2$

(or ionically $Br_2 + 2I^- \rightarrow 2Br^- + I_2$)

BUT $Br_2 + NaCl \rightarrow$ No reaction.

(ii) **Reducing power of hydrogen halides increase as you descend the group VII.**

- This can be verified by considering action of concentrated H_2SO_4 on hydrogen halides.

i.e. (i) $HF + H_2SO_4\,(Conc.) \rightarrow$ No reaction

(ii) $HCl + H_2SO_4\,(Conc.) \rightarrow$ No reaction

(HF and HCl are not strong reducing agents enough to be oxidised by concentrated H_2SO_4)

(iii) $HBr + \overset{+6}{H_2SO_4}\,(Conc) \rightarrow Br_2 + \overset{+4}{SO_2} + H_2O$

(H_2SO_4 is reduced by HBr where by oxidation state of sulphur is reduced from +6 to +4)

(iv) $HI + \overset{+6}{H_2SO_4} \rightarrow I_2 + \overset{-2}{H_2S} + H_2O$

(H_2SO_4 is more reduced by HI than HBr does as the oxidation state of sulphur is reduced from $+6$ to -2)

Question 4

HCl contain Cl^- which has reducing property. So with $KMnO_4$ which is very strong oxidising agent the chloride is oxidised to Cl_2 thus interfering the measurement of correct volume of $KMnO_4$ which is exactly used to oxidise Fe^{2+} to Fe^{3+}.

i.e. $2MnO_4^- + 10Cl^- + 16H^+ \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$

Question 5

Concentrated sulphuric acid being good oxidising agent oxidises H_2S which is good reducing agent to sulphur and itself become reduced to SO_2 instead of removing water (drying) the gas.

i.e. $H_2SO_4\,(conc) + H_2S \rightarrow SO_2 + S + H_2O$

Question 6

Copper metal is not strong reducing agent enough to reduce (replace) hydrogen from the acid but concentrated H_2SO_4 being good oxidising agent oxidises Cu^{2+} and itself become reduced to SO_2.

i.e. $Cu + \text{Dilute } H_2SO_4 \rightarrow$ No reaction.

BUT $Cu + H_2SO_4\,(Conc.) \rightarrow CuSO_4 + SO_2 + H_2O$

Question 7

Concentrated H_2SO_4 is good oxidising agent so it tends to oxidise Fe^{2+} (from $FeSO_4$) to Fe^{3+} as $KMnO_4$ does thus interfering measurement of correct volume of $KMnO_4$ which is exactly used to oxidise Fe^{2+} to $Fe^{3+.}$

Question 8

Aluminium being good reducing agent is easily oxidised by oxygen from air to give strong impervious aluminium oxide layer which resists oxidation of concentrated HNO_3 .

i.e. $Al(s) + O_2 (g) \rightarrow Al_2O_3$

Then $Al_2O_3 + HNO_3$ (conc) → No reaction

Furthermore, wherever there a chance for aluminium to react with the acid, it is rendered passive by the acid through forming very thin but very strong protective oxide layer.

Question 9

With concentrated HNO_3, aluminium form insoluble layer of Al_2O_3 which resist further oxidation of the acid.

i.e. $4Al + 12HNO_3 (con) \rightarrow 2Al_2O_3 + 12NO_2 + 6H_2O$

Warning!

In this case, don't talk about the role of oxygen from air. The word "renders" in the question, restricts us to concentrate on the way concentrated nitric acid make aluminium passive.

Question 10

Temporary hardness of water are caused by $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ which are thermally unstable due to their high degree of polarisation. So on heating they precipitate (remove) their corresponding carbonates thus treating hardness.

i.e. $Mg(HCO_3)_2 \underset{\Delta}{\rightarrow} MgCO_3(s) + CO_2 + H_2O$

Or $Ca(HCO_3)_2 (aq) \underset{\Delta}{\rightarrow} CaCO_3(s) + CO_2 + H_2O$

Question 11

Binary compound of Aluminium and carbon is aluminium carbide which consists of highly distorted carbide ion (C^{4-}) ion brought about by very large polarising power of a small in size and high charged Al^{3+}. This makes the carbide to form methane, CH_4 on hydrolysis instead of ethyne, C_2H_2 which would be formed if the normal carbide ion, C_2^{2-} would be undistorted.

i.e. $Al_4C_3 + H_2O \underset{\Delta}{\rightarrow} Al_2O_3 + CH_4$

Question 12

PCl_5 has higher energy electronic configuration as it is formed by sp^3d hybridization while PCl_3 is formed by lower energy electronic configuration which is sp^3 hybridization.

Question 13

In sea water, magnesium exists in the form of magnesium chloride ($MgCl_2$) which is soluble. Thus introducing liming material like calcium hydroxide precipitate the insoluble magnesium hydroxide which in turn on addition of hydrochloric acid to the precipitate, $MgCl_2$ is formed again from which pure magnesium is obtained by electrolysis.

i.e. $MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$

Then $Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$

And finally; at the cathode: $Mg^{2+}(aq) + 2e \rightarrow Mg(s)$

Question 14

Nitrogen has no sub- energy level so as to undergo sp^3d hybridization which is necessary for formation of pentavalent compounds (Nitrogen cannot expand its valence shell) as its outermost energy level is $n = 2$ which has no d-sub-energy level unlike phosphorus which has outermost energy level of $n = 3$ which has d-sub-energy level.

Question 15

Ammonia (NH_3) molecules are capable of making very strong inter-hydrogen bonding with water molecules thus making its solubility very high.

Question 16

On heating $MgCl_2$ undergo partial hydrolysis with water molecules which is to be removed yielding basic magnesium chloride (Mg(OH)Cl) and hydrogen chloride (HCl) gas.

i.e. $MgCl_2.6H_2O \underset{\Delta}{\rightarrow} Mg(OH)Cl + HCl + 5H_2O$

Question 17

With solution of sodium hydroxide, carbon dioxide does not give any observable changes as it gives soluble sodium carbonate.

i.e. $CO_2(g) + 2NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O$

Question 18

First white precipitate will be observed due to formation of insoluble $CaCO_3$ which dissolves into clear solution due to formation of soluble $Ca(HCO_3)_2$ (calcium bicarbonate) when carbon dioxide is added in excess.

i.e. $Ca(OH)_2 + CO_2 \rightarrow \underset{\text{(white precipitate)}}{CaCO_3} + H_2O$

Then: $CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$

(Or $Ca(OH)_2 + 2CO_2 \rightarrow Ca(HCO_3)_2$

Question 19

(i) $2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$
(ii) $Co + H_2O(g) \rightarrow CoO + H_2$
(iii) $Na_2O + H_2O \rightarrow 2NaOH$
(iv) $Rb_2O_2 + 2H_2O \rightarrow 2RbOH + H_2O_2$

Question 20

Mg^{2+} being smaller in size than Ba^{2+} is capable of holding lone pair from water which is to be removed by heating, thus $MgCl_2$ undergoes partial hydrolysis while $BaCl_2$ cannot.

i.e. $BaCl_2.2H_2O \underset{\Delta}{\rightarrow} BaCl_2(g) + 2H_2O(g)$

While: $MgCl_2.6H_2O \underset{\Delta}{\rightarrow} MgCl_2(g) + 6H_2O(g)$

Then $MgCl_2 + H_2O(g) \underset{\Delta}{\rightarrow} Mg(OH)Cl + HCl$

And the overall reaction becomes: $MgCl_2.6H_2O \underset{\Delta}{\rightarrow} Mg(OH)Cl + HCl + 5H_2O$

Question 21

Firstly white precipitate of lead (II) chloride will be observed due to common ion effect brought about by hydrochloric acid which is a strong electrolyte containing Cl^- as that present in partial ionisation of slightly soluble substance (weak electrolyte), $PbCl_2$; and when the acid becomes in excess the precipitate dissolves into a clear solution due to formation of complex which is soluble.

i.e. $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$ and $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

Introduction of Cl- shifts the equilibrium of dissociation of lead (II) chloride to the left thus forming precipitate of $PbCl_2(s)$

But when HCl is added to excess the lead (II) chloride precipitate dissolves:

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

Question 22

(i) $\underset{\text{Increase in boiling point}}{\underrightarrow{\mathrm{HCl} < HBr < HI < HF}}$

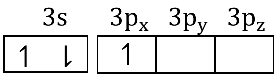
(ii) $\mathrm{HI, HBr, HCl, HF}$

Question 23

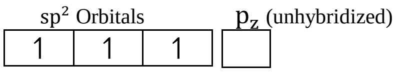
Al in $AlCl_3$ has an empty orbital in its electronic structure accompanied with its small atomic size thus making possible for $AlCl_3$ to accept and hold lone pair (electrons) from Lewis bases.

Consider electronic structure of $AlCl_3$ as shown below:

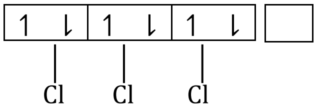
Outermost electronic configuration of Al at ground state;



After hybridization in sp² hybridization



In $AlCl_3$ $\quad$ p_z (empty orbital)



Question 24

Copper is not reactive (is not strong reducing agent) enough to react with (to displace hydrogen from) dilute acids like sulphuric and hydrochloric acid. But due to oxidising property of dilute nitric acid copper will be oxidised according to the following equation:

$$3Cu(s) + 8HNO_3(aq) \longrightarrow 3Cu(NO_3) + 4H_2O + 2NO$$

Question 25

(i) $Li_3N(s) + 3HCl(aq) \longrightarrow 3LiCl(s) + NH_3(g)$
(ii) $NaH(s) + H_2O(l) \longrightarrow NaOH + H_2$
(iii) $Rb_2O(s) + 2H_2O(l) \longrightarrow 2RbOH$
(iv) $Cs_2O_2 + 2H_2O(l) \longrightarrow 2CsOH + H_2O_2$

Question 26

Chlorine being an oxidising agent tends to oxidise iron which is reducing agent and has variable oxidation state to its higher oxidation state thus forming iron (III) chloride ($FeCl_3$) and not $FeCl_2$.

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

Question 27

Fluorine being stronger oxidising agent tends to combine with chromium to its highest oxidation state (Cr^{6+}) thus forming CrF_6 while chlorine being weaker oxidising agent (compared to fluorine) form $CrCl_3$

i.e. $2Cr + 3F_2 \longrightarrow CrF_6$ while $2Cr + 3Cl_2 \longrightarrow 2CrCl_3$

Question 28

In water (polar solvent) iodine is sparingly soluble due to its covalent characters and large atomic size which makes difficult for it to hold a lone pair of oxygen from water. With solution of KI, iodine forms the complex ion which is soluble.

i.e. $I^- + I_2 \longrightarrow [I_3]^-$

(from KI) (soluble)

Question 29

Alkali earth metals have greater ability to hold lone pair of ligands as:

- They have smaller cationic radii.
- They have high cationic charge (alkali earth metals have cationic charge of +2 while alkali metals have +1).

Question 30

Calcium being below Magnesium in the group has a larger atomic size (radius) accompanied with lower ionisation energy so that its valence electrons are weakly held by nuclear attractive forces such that normal radiant energy from the sun is enough to excite these valence electrons in Ca and on returning to ground state the electrons emit energy with wavelength in visible spectrum unlike in Mg where electrons are firmly (strongly) held by nuclear attractive force.

Question 31

There is a stronger metallic bond existing between atoms of alkali earth metals because:

- They have smaller metallic radii.
- They have a greater number of valence electrons (alkali earth metals have only one valence electron).

Stronger metallic bond for alkali earth metals account for their higher melting and boiling points.

Question 32

Hard water contains soluble Ca^{2+} and Mg^{2+}, so introducing washing soda in the water precipitates out insoluble $CaCO_3$ and $MgCO_3$ thus treating hard water.

i.e. $Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$ or $Mg^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow MgCO_3(s)$

Question 33

HgI_2 has a high degree of covalent character as a result of its high degree of polarisation caused by large polarising power of small Hg^{2+} and large polarisability of the large I^-, so cannot dissolve easily in water which is a polar solvent.

With KI solution, HgI_2 form complex ion which is soluble. i.e.:

$HgI_2 + 2I^- \longrightarrow [HgI_4]^{2-}$ Or $2KI + HgI_2 \longrightarrow K_2^+[HgI_4]^{2-}$

Question 34

With water, SO_2 form sulphurous acid (H_2SO_3) which is weaker reducing agent than H_2S, so the sulphurous acid oxidises the sulphide to sulphur which appears as a yellow solid.

i.e. $2H_2S(g) + SO_2(aq) \longrightarrow 2H_2O(l) + 3S(s)$

Note: $SO_2(\mathbf{aq}) = H_2SO_3$

Question 35

Under the presence of heat (warm sodium nitrite), ammonium nitrite which would be formed by double decomposition reaction between ammonium chloride and sodium nitrite, undergo thermal decomposition yielding nitrogen gas which appears as effervescence of colourless gas.

That is $NaNO_2\ (aq) + NH_4Cl(aq) \longrightarrow NaCl(aq) + NH_4NO_2(aq)$

Then $NH_4NO_2(aq) \longrightarrow 2H_2O(l) + N_2(g)$

Note: NH_4^+ is the radical with very high polarising power; when combine with anion, the resulting compound is either thermally unstable or has very high covalent character.

Question 36

Firstly ammonium chloride undergoes thermal decomposition yielding gaseous ammonia and hydrogen chloride, the mixture which appears as dense white fumes which in recombining the white sublimate of ammonium chloride is formed; i.e. $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

Question 37

Calcium carbonate has a high degree of covalent characters caused by its high degree of polarisation so cannot dissolve in water which is a polar solvent. In the presence of dissolved carbon dioxide, the carbonate form calcium bicarbonate which is capable of making hydrogen bonding with water molecules hence it becomes soluble. i.e.

$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$

Question 38

Effervescence of colourless gas which turns lime water milky i.e. CO_2 is observed.

i.e. $\underset{\text{Egg shell}}{CaCO_3(s)} + 2HCl(aq) \longrightarrow CaCl_2 + CO_2 + H_2O$

Question 39

Fluorine does not disproportionate in water like other halogens due to absence of empty d-orbitals so as to accommodate a lone pair of oxygen from water. But fluorine being on the top of halogen group, it has greatest oxidising power thus oxidising water to oxygen (and itself becoming reduced to HF).

That is $2F_2 + 2H_2O \longrightarrow 4HF + O_2$ while $X_2 + H_2O \longrightarrow HOX + HX$ where X is Cl or Br

Question 40

(i)$HIO_4.2H_2O$ (ii) HOBr (iii) $HBrO_4$

Question 41

(i) Both have oxidation state of -1.
(ii) Both have high affinity for metals and form salts e.g. KBr and KCN.
(iii) Both act as ligands in complex formation with transition elements e.g. $[Cu(CN)_4]^{2-}$ and $[CuBr_4]^{2-}$
(iv) Their hydrides are acidic i.e. both HCN and HBr are acidic.
(v) The CN^- forms precipitates with $Ag^+(aq)$ and $Pb^{2+}(aq)$ like bromide ions.

Other similarities include

(vi) CN^- undergo oxidation in a similar way to bromide ions.

$$2Br^- \longrightarrow Br_2 + 2e^-$$
$$2CN^- \longrightarrow (CN)_2 + 2e^-$$

(vii) CN^- forms $(CN)_2$ which undergoes disproportionation reaction in alkaline medium like Br_2 (formed after oxidation of Br^-).

i.e. $Br_2 + 2OH^- \longrightarrow Br^- + OBr^- + H_2O$ and $(CN)_2 + 2OH^- \longrightarrow CN^- + OCN^- + H_2O$

Question 42

Choking smell of ammonia is observed.

i.e. $Mg_3N_2(s) + 6H_2O(l) \longrightarrow 2NH_3(g) + 3Mg(OH)_2(s)$

Question 43

With cold water, Al is not strong reducing agent enough to react with the water.

i.e. $Al(s) + H_2O(l) \longrightarrow$ No reaction

With steam, the metal (Al) yields very thin but very strong impervious layer of Al_2O_3 which resists more reaction between steam and underlying aluminium i.e. $2Al(s) + 3H_2O(g \longrightarrow Al_2O_3(s) + 3H_2$

Question 44

Reddish grown colouration of bromine is observed i.e.

$Cl_2 + 2NaBr \longrightarrow 2NaCl + Br_2$ (Or ionically: $Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2$)

Question 45

Chlorine being a stronger oxidising agent than iodine as a result of its higher electronegativity oxidises iodide ions to iodine which appears in dark brown colouration and itself becoming reduced to Cl^- i.e.

$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$

Question 46

(i) Na (ii) Na (iii) Cl (iv) Na (v) Si

Question 47

Alkali metals have low atomisation energy (due to their weak metallic bond) accompanied with low ionisation energy. The two factors make the activation energy of oxidation reaction, $\mathbf{M(s) \rightarrow M^+(aq)}$**,** very low. In other words, alkali metals undergo oxidation readily and hence they become good reducing agent.

Question 48

(i) All group IA elements reacts with water (or steam) to liberate hydrogen gas

$2M + 2H_2O \rightarrow 2MOH + H_2$ where M is the group I element

(ii) With oxygen, all group IA elements form basic oxides which have no reaction with any other basic solution but they react with acidic solution

e.g. $M_2O + 2HCl(aq) \rightarrow 2MCl + H_2O$ but $M_2O + \text{basic solution e.g } Mg(OH)_2 \rightarrow \text{No reaction}$

(iii) All group IA elements liberate hydrogen gas from dilute acids like dilute HCl

$M + 2HCl\ (aq) \rightarrow MCl(aq) + H_2(g)$

(iv) All group IA elements react with hydrogen gas to give their corresponding hydrides

$2M + H_2 \underset{\Delta}{\rightarrow} 2MH$

Question 49

(i) Sodium hydride + water → sodium hydroxide + hydrogen gas

(ii) Phosphine + water → No reaction

(iii) Magnesium nitride + water → magnesium hydroxide + ammonia

Question50

(i) Oxidising agent gain electrons (get reduced), so it must have small atomic radius so that it can hold more added electrons and hence the atom with smaller atomic radius must be B.

(ii) Reducing agent donate electron (get oxidised). So it must have lower ability of holding or attracting electrons. In other words, it must have more positive electron affinity, i.e. electron add to it by difficult and hence **the element with higher reducing power is Q.**

Question 51

(i) Li^+ being very in size, exerts large attraction to N^{3-} making lattice energy of the nitride (Li_3N) large enough to compensate very large net energy absorbed in dissociating N_2 ($N \equiv N$) and electron affinity of N in forming N^{3-}

(ii) Due to its smallest ionic size in the group, Li^+ has greatest polarising power causing $LiNO_2$ (lithium nitrite) to have large degree of polarisation such that it undergo further decomposition to oxide while nitrite of other group IA elements are stable

$$4LiNO_3 \underset{\Delta}{\rightarrow} 2Li_2O + 4NO_2 + O_2$$

$$\text{While } 2MNO_3 \underset{\Delta}{\rightarrow} 2MNO_2 + O_2$$

(iii) Being smallest in size of all other alkali metals Li+ has greatest polarising power in the group so that it distort complex oxide ions (peroxide ion,O_2^{2-}, and super oxide ion, O_2^-) to normal oxide ion and hence lithium forms normal oxide only.

Question 52

(i) Sulphur exists in molecular state as S_8 which has greater molecular weight than that of phosphorous which exist as P_4 and hence there is stronger Van der Waals dispersion forces in sulphur.

(ii) Phosphorous exist in molecular state as P_4 which has greater molecular weight than that of chlorine which exist as Cl_2 and hence there is stronger Van der Waals dispersion forces in phosphorous.

(iii) F being on the top halogen group has highest electronegativity thus there is strong hydrogen bonding existing between HF molecules which is stronger intermolecular force of attraction than Van der Waals dispersion forces existing between molecules of other hydrogen halides and hence HF has higher boiling point.

(iv) Molecular weight of given elements increase regularly from F_2 to I_2, (F_2 having lowest molecular weight) thus making strength of Van der Waals dispersion forces to increase in the same trend and hence their melting and boiling point increase in the same order.

PART FOUR

Question 1

In solid form aluminium carbonate is thermally unstable caused by its high degree of polarisation brought about by a small sized and highly charged, Al^{3+} which has large polarising power accompanied with large polarisability of large anion, CO_3^{2-}, such that room temperature is enough to decompose the carbonate.

i.e. $Al_2(CO_3)_3(s) \xrightarrow{\text{Room temperature}} Al_2O_3(s) + 3CO_2(g)$

In aqueous solution the carbonate having significant degree of covalent characters undergo salt hydrolysis yielding $Al(OH)_3$ and H_2CO_3 (carbonic acid).

i.e. $Al_2(CO_3)_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2CO_3$

Question 2

(i) $Ba(OH)_2(aq) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + 2H_2O(l)$

(ii) Electrical conductivity decreases due to presence of extremely low concentration of free ions because $BaSO_4$ is insoluble and therefore does not ionise in water as a result of its ($BaSO_4$) low hydration energy brought about large size of Ba^{2+}.

Question 3

This is due to the formation of carbon dioxide gas which is obtained after decomposition of Copper (II) hydrogen carbonate which would be formed after double decomposition reaction as a result of its ($Cu(HCO_3)_2$) high degree of polarisation. i.e.:

$CuSO_4 + 2NaHCO_3 \rightarrow Na_2SO_4 + Cu(HCO_3)_2$

Then: $Cu(HCO_3)_2 \rightarrow CuCO_3 + CO_2 + H_2O$

Hence the overall reaction is :

$CuSO_4 + 2NaHCO_3 \rightarrow Na_2SO_4 + CuCO_3 3 + H_2O + CO_2$

Question 4

(i) White precipitate of insoluble $CaCO_3$ is formed which dissolves in excess of CO_2 to give clear solution due to formation of soluble $Ca(HCO_3)_2$.

That is $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3(s) + H_2O$
Then $CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2(aq)$

(ii) A gas with chocking smell. i.e. NH_3 is formed i.e.

$Ca(OH)_2 + 2NH_4^+ \longrightarrow Ca^{2+} + 2H_2O + 2NH_3$

(iii) White precipitate of insoluble $CaCO_3$ is formed

$Ca(HCO_3)_2(aq) + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O$

Question 5

(i) $CO_2(g) + NaOH(aq) \longrightarrow NaHCO_3(aq)$
(ii) $Na_2SO_4(aq) + H_2SO_4(aq) \longrightarrow 2NaHSO_4(aq)$
(iii) $Na_2SO_4(aq) + BaCl_2(aq) \xrightarrow{HCl(aq)} BaSO_4(s) + 2NaCl(aq)$

Question 6

Al^{3+} ion in $AlCl_3$ is smaller sized and higher charged than Na^+ in NaCl. This makes Al^{3+} to have greater polarising power making $AlCl_3$ to have greater degree of polarisation and hence $AlCl_3$ is highly covalent while NaCl is strongly ionic. As result:

(i) NaCl exists as giant ionic crystalline structure with very high melting and boiling point while $AlCl_3$ has simple covalent molecular structure which dimerize in vapour state. $AlCl_3$ has low melting and boiling point
(ii) $AlCl_3$ sublimes on heating while NaCl does not
(iii) $AlCl_3$ hydrolyse in water while NaCl does not
(iv) Molten NaCl conducts electricity while $AlCl_3$ does not

Question 7

(i) $Cu(s) + H_2SO_4(conc) \xrightarrow[\Delta]{} CuSO_4 + SO_2 + H_2O.$

(ii) $S(s) + HNO_3(aq) \longrightarrow$ no reaction

Note: Dilute HNO_3 has no action on sulphur unless it is concentrated where the reaction is:

$S(s) + 6HNO_3(aq) \xrightarrow{Br_2\ \text{catalyst}} H_2SO_4(aq) + 6NO_2(g) + 2H_2O(l)$

(iii) $Cu(s) + 4HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2H_2O(l) + 2NO_2(g)$

Question 8

(i) As result of double decomposition reaction, the insoluble lead(II) dichromate is formed which appears as yellow precipitate.

$$Pb(NO_3)_2(aq) + K_2CrO_4(aq) \longrightarrow PbCrO_4(s) + 2KNO_3(aq)$$

(ii) In strong alkaline solution like $NaOH, Zn^{2+,}$ is capable of making soluble complex, $[Zn(OH)_4]^{2-}$. So with solution of NaOH; initially the white precipitate, $Zn(OH)_2$ will be formed but the precipitate will dissolve when NaOH(aq) present in excess due to formation of the complex.

Initially: $Zn2 + (aq) + 2OH^- \rightarrow Zn(OH)_2(s)$

In excess NaOH: $Zn(OH)_2 + 2OH^- \rightarrow [Zn(OH)_4]^{2-}$

(i) With solution of $BaCl_2$, $AgNO_3$ give white precipitate of insoluble silver chloride

$2AgNO_3(aq) + BaCl_2(aq) \rightarrow Ba(NO_3)_2(aq) + 2AgCl(s)$

The precipitate dissolves in excess of aqueous ammonia due to formation of soluble complex

That is $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ … … … … … … … … … … … … … … … … … … (i)

And $Ag^+(aq) + 2NH_3(aq) \longrightarrow [Ag(NH_3)_2]^+$ … … … … … … … … … … … … … … … . (ii)

The reaction (ii) decreases concentration of Ag+ shifting the position of equilibrium in reaction (i) to right hand side by dissolving the precipitate.

Question 9

(i) Brown fumes of nitrogen dioxide (NO_2) is observed; $4Ag\,NO_3(s) \underset{\Delta}{\rightarrow} 2Ag_2O + 4NO_2 + O_2$

(ii) Yellow precipitate (sulphur) accompanied with evolvement of a gas with smell of burnt match (SO_2) will be observed.

$$2HNO_3(aq) + Na_2S_2O_3(aq) \longrightarrow S(s) + 2NaNO_3(aq) + SO_2(g) + H_2O(l)$$

(iii) Firstly white precipitate (BiOCl) will be observed and the precipitate dissolve to give clear solution (BCl_3) again after addition of the hydrochloric acid.

$BCl_3(aq) + H_2O(l) \rightleftharpoons BOCl(s) + 2HCl(aq)$ (Addition of the hydrochloric acid shift the position of equilibrium to the left)

Question 10

LiOH reacts with CO_2 (g) according to the following equation:

$$2LiOH + CO_2 \rightarrow Li_2CO_3 + H_2O$$

From which; mole ratio of LiOH to CO_2 is 2:1

Molar mass of LiOH is 24g/mol

Number of moles of LiOH $= \frac{1000}{24} = \frac{125}{3}$mol

Then from the mole ratio; number of moles of CO_2 absorbed $= \frac{125}{3\times2} = \frac{125}{6}$mol

And mass of CO_2 absorbed $\frac{125}{6} \times 44g = 917g$ or 0.917kg

Hence mass of CO_2 absorbed was 0.917kg

Question 11

Equation for the reaction:

$Al_2(SO_4)_3(aq) + 3BaCl_2(aq) \rightarrow 2AlCl_3(aq) + 3BaSO_4(s)$

Where mole ratio of $Al_2(SO_4)_3$ to $BaSO_4$ is 1:3

Molar mass of $BaSO_4 = 137 + 32 + (16 \times 4) = 233g/mol$

Number of moles of $BaSO_4$ produced $= \frac{2.047}{233} = 8.7854 \times 10^{-3}$mol

Then number of moles of $Al_2(SO_4)_3$ in a spray sample $= \frac{8.7854\times10^{-3}}{3}$mol (mole ratio of $Al_2(SO_4)_3$ to $BaSO_4$ is 1:3)

Molar mass of $Al_2(SO_4)_3$ is 342g/mol

Thus mass of $Al_2(SO_4)_3$ in 5g of spray sample $\frac{8.7854\times10^{-3}}{3} \times 342g = 1g$

Thus percentage of $Al_2(SO_4)_3$ in the spray sample $\frac{1}{5} \times 100g = 20\%$

Hence the percentage of $Al_2(SO_4)_3$ is 20%

Question 12

Since the metal is divalent, the formula of its oxide will be XO

The oxide reacts with HCl according to the following equation

$XO + 2HCl \rightarrow XCl_2 + H_2O$ … … … … … … … … … … … … … … … … … (i)

Since the acid (dil HCl) was only little excess, we may neglect the reaction between the unreacted acid and Na_2CO_3

Then only XCl_2 (from reaction (i) above) reacts with Na_2CO_3 according to the following equation:

$XCl_2 + Na_2CO_3 \rightarrow \underset{\text{Insoluble}}{XCO_3} + 2NaCl$……………………………………………………….(ii)

Let the relative atomic mass of X be y

Then molar mass of XO is $16 + y$

And molar mass of XCO_3 is $60 + y$

Number of moles of XO was $\frac{2.1}{16+y}$

From (i); the mole ratio of XO to XCl_2 is 1:1

Then number of moles of XCl_2 produced in (i) was also $\frac{2.1}{16+y}$

From (ii); mole ratio of XCl_2 to XCO_3 is 1:1

Then number of moles of insoluble XCO3 produced was also $\frac{2.1}{16+y}$

But mass of XCO_3 produced was 3.75g

Then number of moles of XCO_3 (in another way) is $\frac{3.75}{60+y}$

It follows that: $\frac{2.1}{16+y} = \frac{3.75}{60+y}$ or $1.65y = 66$ or $y = 40$

(i) The relative atomic mass of X is 40
(ii) The divalent element with atom of relative atomic mass of 40 is calcium. i.e. X is calcium

PART FIVE

Question 1

(b) $(n-1)\ d^{1-10}ns^{1-2}$ where n is the outermost energy level.

(c)With electronic configuration of $[Ar]3d^94s^0$, copper (II) ion (Cu^{2+}) has an incomplete 3d-orbital in its electronic configuration.

(d)Zinc atom and its ion (Zn^{2+}) have all of its d–orbitals completely filled with electrons ($3d^{10}$) in their electronic configuration.

Question 2

This is due to:

- Their ability to form variable (multiple) oxidation states.
- Their ability to adsorb reactants on their surfaces as they have a large surface area.

Question 3

(i) This is due to the fact that:
  - They have empty orbitals
  - They have small cationic radii.
  - Some of their ions have high cationic charge.

(ii) Transition metal ion has incomplete d-orbitals so as to enable d-d transition of electrons whereby energy required for this electron transition (d-d transition) has wavelength within visible range of light.

(iii) Because the small sized cations are hydrated by water to greater extent.

(iv) Transition metal atoms have similar atomic and ionic radii, form the metallic bonds and have interstices in their crystals.

Question 4

The outer electronic configuration of copper is $3d^{10}4s^1$. The removal of one electron results in Cu^+ with a configuration of $3d^{10}4s^0$. The removal of one electron from alkali metals (ns^1) is relatively easier because of their large atomic sizes than copper; because of which the attractive forces on the outer electrons become less and less. But the second electron from Cu^+ ($3d^{10}4s^0$) can be removed easily because 3d and 4s orbitals have almost the same energy. In case of alkali metals, the second electron is to be removed from a completely filled shell belonging to lower principal quantum number for which the energy difference is too much. The same reasoning applies to third ionisation energies.

Question 5

The outer- electronic configuration of Zinc is $3d^{10}4s^2$. Since 3d- orbitals are completely filled up, the 3d- electrons are not available for chemical bond formation due to extra stability of fully paired electronic structure. With addition of the fact that zinc has high nuclear charge, it shows $+2$ oxidation state only by losing two 4s electrons.

Question 6

(a) $[Cu(H_2O)_4]^{2+}$ (blue) (water molecules are from the solution)

(b) When $C_2O_4^{2-}(aq)$ is added, the insoluble normal salt, $CuC_2O_4^{2-}(s)$ (copper (II) oxalate) is formed which dissolves in excess of $C_2O_4^{2-}(aq)$ due to formation of $[Cu(C_2O_4^{2-})_2]^{2-}$ (bis(oxalato)cuprate (II) ion) which is soluble .i.e $Cu^{2+}(aq) + C_2O_4^{2-}(aq) \longrightarrow CuC_2O_4^{2-}(s)$ (white precipitate)

With excess $C_2O_4^{2-}(aq)$, the precipitate dissolves.
$Cu^{2+}(aq) + C_2O_4^{2-}(aq) \longrightarrow [Cu(C_2O_4^{2-})_2]^{2-}(aq)(soluble)$
or $CuC_2O_4^{2-}(s) + C_2O_4^{2-}(aq) \longrightarrow [Cu(C_2O_4^{2-})_2]^{2-}(aq)$
Note: $Cu^{2+}(aq) = [Cu(H_2O)_4]^{2+}$ and so the reaction : $Cu^{2+}(aq) + C_2O_4^{2-}(aq) \longrightarrow [Cu(C_2O_4^{2-})_2]^{2-}(aq)$

Is the same as writing as: $[Cu(H_2O)_4]^{2+}(aq) + 2C_2O_4^{2-}(aq) \longrightarrow [Cu(C_2O_4^{2-})_2]^{2-} + 4H_2O$

This is an example of a ligand substitution reaction.

Question 7

Because they contain aldehyde group in their either common form or after tautomerism, the group which was capable of reducing Cu^{2+} (from Fehling's or Benedict's solution) to Cu^+

$RCHO + Cu^{2+}(aq) \longrightarrow RCOO^- + Cu_2O$; where R is the group of carbons.

Question 8

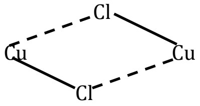
Copper is not reactive (is not strong reducing agent) enough to react with (to displace hydrogen from) dilute acids like sulphuric and hydrochloric acid. But due to oxidising property of dilute nitric acid copper will be oxidised according to the following equation:

$$3Cu(s) + 8HNO_3(aq) \longrightarrow 3Cu(NO_3) + 4H_2O + 2NO$$

Question 9

Copper (I) chloride is insoluble in water due to its high degree of covalent characters brought about by its high degree of polarisation caused by large polarising power of small sized, Cu^+, so water being polar solvent cannot dissolve covalent compounds.

In vapour state two molecules of copper (I) chloride associate to form a dimer corresponding to molecular formula of Cu_2Cl_2 thus doubling its molar mass.



Dimerisation in copper (I) chloride

Question 10

In sodium hydroxide solution, $Cu(OH)_2$ is insoluble due to common ion effect brought about by $NaOH(aq)$ which is a strong electrolyte containing the same ion (OH^-) as that present in $Cu(OH)_2$which is a weak electrolyte(slightly soluble substance).

i.e. $Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$

So the complete ionisation, $NaOH(aq) \longrightarrow Na^+ + OH^-(aq)$ shifts the position of the above equilibrium to the left thus precipitating $Cu(OH)_2(s)$

But in aqueous ammonia it is soluble due to the formation of ionic complex.

i.e. $Cu(OH)_2(s) + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}(aq) + 2OH^-$

Question 11

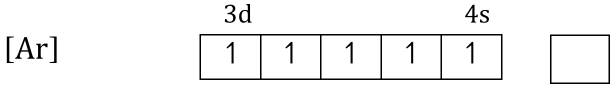
Cu^{2+} having electronic configuration of $[Ar]3d^94s^0$ and has one unpaired electron in 3d orbitals thus enabling its compounds to manifest transition metal characteristics, while Cu^+ having electronic configuration of $[Ar]3d^{10}4s^0$ has all of its 3d-electrons paired and hence its compounds do not manifest transition metal characteristics. e.g. copper (II) compounds exhibit paramagnetism while copper (I) compounds do not.

Question 12

In the absence of ligands (water molecules) there is no splitting of the five d-orbitals (which are degenerated) into treble and double degenerates so as to enable d-d transition of electrons which is important in colour formation in the compound. So after the addition of water molecules there is the formation of complex and the sulphate exist as $[Cu(OH)_4]^{2+}SO_4^{2-}$ the process which allows the d-d transition for colour formation.

Question 13

Both Fe^{3+} and Mn^{2+} have the same electronic configuration of $[Ar]3d^54s^0$ which has extra stability of exactly half filled electronic structures.



So with electronic configuration of $[Ar]3d^6$, Fe^{2+} is oxidised easily to Fe^{3+} so attain the stable electronic structure of Fe^{3+} while Mn^{2+} having the stable electronic structure it is hardly oxidised to Mn^{3+} to attain less stable electronic structure which is $[Ar]3d^4$.

Question 14

(i) Compound is $KMnO_4$ (or MnO_4^- for ion).

(ii)With electronic configuration of $[Ar]3d^54s^2$, manganese form oxidation state of +7 when all seven electrons from 3d and 4s orbitals are removed (ionised) so as to attain the stable electronic configuration of Argon. This occurs when manganese is bonded to very strong electronegative atom (mainly oxygen and fluorine) and is possible due to presence of outer seven electrons accompanied with its small nuclear charge (compared to other transition metals which have greater than 7 valence electrons but greater nuclear charge).

Question 15

(i) Firstly $Al^{3+} + 6H_2O \longrightarrow [Al(H_2O)_6]^{3+}$
Then $[Al(H_2O\ )_6]^{3+} + 6NH_3 \longrightarrow [Al(NH_3)_6]^{3+} + H_2O$
Hence the overall reaction is: $Al^{3+} + 6NH_3(aq) \longrightarrow [Al(NH_3)_6]^{3+}$
(ii) $Fe_2O_3(s) + 2Al(s) \underset{\Delta}{\rightarrow} Al_2O_3(s) + 2Fe(s)$

Question 16

Being sparingly soluble substance, copper (II) sulphide ionises in aqueous solution according to the following equation:

$CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)$

Thus introducing hydrochloric acid which ionises completely yielding H^+ which combines with S^{2-}(from above equilibrium) thus forming H_2S while Cl^- ions from the acid combine with Cu^{2+} to form soluble complex $[CuCl_4]^{2-}$, shifts the position of equilibrium to the right hand side i.e. more precipitate of $CuS(s)$ dissolves and ionises to compensate the S^{2-} and Cu^{2+}removed.

i.e. $HCl(aq) \longrightarrow H+ + Cl^-$

Then $2H + \ + S^{2-} \quad \longrightarrow \quad H_2S$

And $Cu^{2+} + 4Cl^- \longrightarrow [CuCl_4]^{2-}$, (The last two actions shifts the position of the above equilibrium to the right)

Question 17

(i) +3

(ii) Compounds of Fe have unpaired electrons in d orbitals(have incomplete d-orbitals) so as to enable d-d transition of electrons.

Question 18

AgCl is highly covalent in character due to its high degree of polarisation so the compound cannot dissolve in water which is polar solvent. In aqueous ammonia, the chloride forms the complex compound which is ionic and hence becomes soluble.

i.e. $AgCl(s) \ + \ 2NH_3(aq) \quad \longrightarrow \quad [Ag(NH_3)_2]^+Cl^-$

Question 19

AgI is more covalent in character as a result of its higher degree of polarisation brought about by greater polarisability of a larger I^- (than Cl^- in AgCl), so it does not give Ag^+ to form complex with ammonia while AgCl reacts with ammonia yielding complex ionic compound which is soluble.

i.e. $AgCl \ + \ 2NH_3 \ \longrightarrow \ [Ag(NH_3)2] + Cl^-$ while $AgI \ + \ NH_3 \ \longrightarrow$ No reaction

Question 20

Sodium peroxide being an oxidising agent, oxidises $Cr(OH)_3$ to chromate ions which appear in a yellow colouration (and itself becomes reduced to its normal oxide, Na_2O) i.e.

$$2Na_2O_2 \ + \ 2Cr(OH)_3 \ \longrightarrow \ \underset{\textbf{Yellow}}{2CrO_4^{2-}} \ + \ 3Na_2O \ + \ H_2O \ + \ 4H^+$$

Question 21

In aqueous solution, its hydration energy is not large enough to compensate ionisation energy of Cu in forming Cu^+ thus becoming unstable. Being unstable it disproportionates to copper atom and copper (II) ions.

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

Don't forget: In the solid compound talk about lattice energy instead of hydration energy.

Question 22

(a)(i) Deep blue solution of tetraamminecopper (II) ion, $[Cu(NH_3)_4]^{2+}$ is observed.

(ii) Copper (I) iodide, Cu_2I_2 and dark brown colouration of iodine, I_2 is observed.

(b)The nature of reaction is **redox**

Oxidation half reaction: $2I^- \longrightarrow I_2 + 2e$ … . . … (i)

Overall reaction equation: $2Cu^{2+} + 2I^- + 2e \longrightarrow Cu_2I_2$ … … … … … … … … … … … … … … … … … . . (ii)

Overall reaction equation: Taking (i) + (ii)

$$2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$$

Question 23

(i) $[Co(CN)_6]^{3-}$ is **inner orbital complex** while $[CoF_6]^{3-}$ is **outer orbital complex**

(ii) $[Co(CN)_6]^{3-}$ is the **low spin (unreactive)** complex while $[CoF_6]^{3-}$ is the **high spin (reactive)** complex

(iii) $[Co(CN)_6]^{3-}$ is **diamagnetic** while $[CoF_6]^{3-}$ is **paramagnetic**

Question 24

Prussian blue of $K[Fe(Fe(CN)_6)]$ is observed

$$Fe^{3+} + [Fe(CN)_6]^{4-} \longrightarrow \underset{\textbf{Prussian blue}}{[Fe(Fe(CN)_6)]^-}$$

The reaction is used as a chemical test of Fe^{3+}.

Question 25

Firstly the precipitate forms due to formation of insoluble HgI_2

$$HgCl_2 + \ 2KI \ \longrightarrow \ HgI_2 \ + \ 2KCl$$

Thereafter the precipitate dissolve because in presence of large concentration of iodide, I^- ions (from excess KI) due to formation of soluble complex, $[HgI_4]^{2-}$.

$HgI_2(s) + 2I^-(s) \longrightarrow [HgI_4]^{2-}$

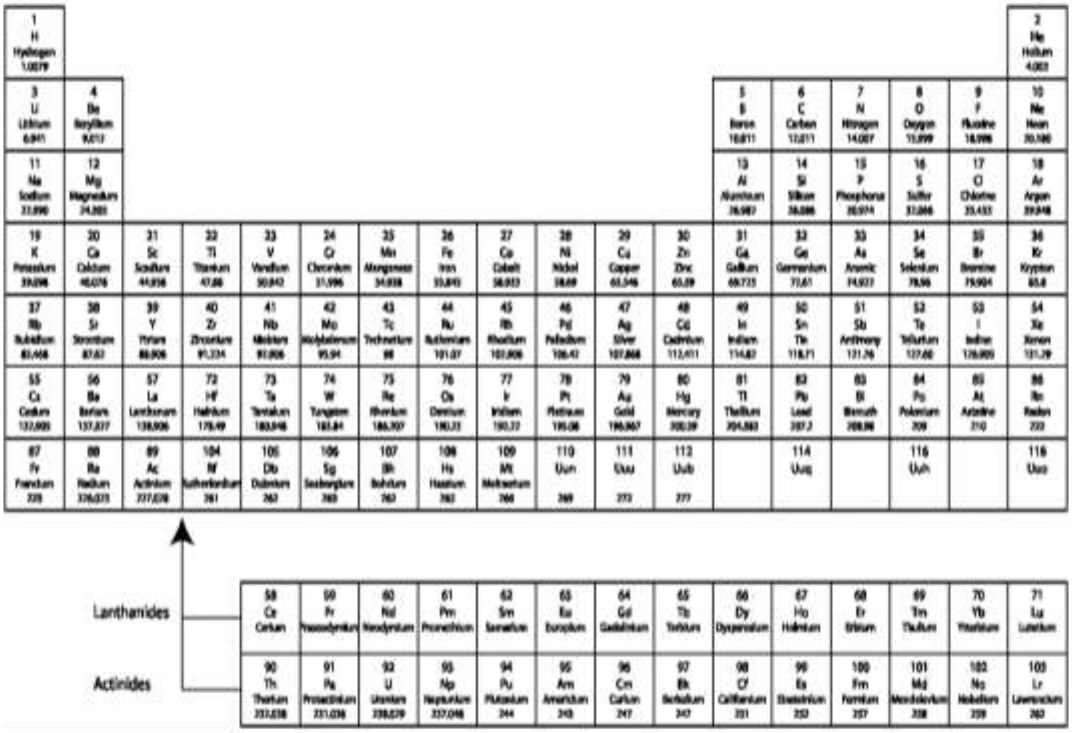
Question 26

In aqueous solution, Fe^{3+} tends to form acidic hexaaqua complex, $[Fe(H_2O)_6]^{3+}$. The acidity of the solution is responsible for liberating carbon dioxide (which appears as colourless gas) from the carbonate.

gm+H_3O^+

Then $2H_3O^+ + CO_3^{2-} \longrightarrow CO_2 + H_2O$

PERIODIC TABLE OF ELEMENTS



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