



# FUNDAMENTAL CONCEPTS OF INORGANIC CHEMISTRY

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**FUNDAMENTAL CONCEPTS OF**  
**INORGANIC CHEMISTRY**

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***DEDICATED***  
***TO***



***DEPARTMENT OF CHEMISTRY,***  
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## ***Preface.***

### ***To the E-book.***

There are already several textbooks of General Chemistry that treat the subjects in considerably less space than our comprehensive text. Moreover, most of them include a great deal of introductory theory, which was omitted from larger books because of space considerations. The net result is that these books contain very little of the real content of general chemistry –namely, the actual facts about the properties and behaviour of General Chemistry concepts.

The success of this e-book has been gratifying, for it tells us that teachers have found it effective and that students have been found it useful and informative. This e-book continues to be written for the first year chemistry course for sciences majors.

In this e-book we have two goals; to make the text more useful, readable, and interesting for the students and to ensure that the text continues to cover topics that teachers wish to present to their classes. In satisfying the first goal, we examined in this e-book line by line with an eye toward improving the readability and clarity of presentations. At the same time more examples of common chemicals and applications of chemistry have been woven into discussions. The visual appearance of this e-book has been enhanced and large number of photographs have been added to make chemistry seem more alive to students.

It now begins with general discussion of Fundamental laws of Chemistry, Atomic Structure, Acid and Base theories, Chemical Bonding, Chemistry of transition elements and Chemistry of S-block elements.

Chemistry of S-block elements and Transition elements is formerly presented in chapter -6 and chapter-7

### ***Chapter 1***

This chapter describes the importance of the different fundamental chemical laws.

### ***Chapter 2***

This chapter includes detailed Solid state.

### ***Chapter-3***

Acids and basetheoriesare incorporated in this chapter.

### ***Chapter 4***

Atomic Structure deals with the structure of atom and chapter-4 Atomic Structure incorporated in this chapter.

### ***Chapter 5***

This chapter includes the Chemical Bonding and Structures are incorporated.



## **Chapter 6**

This chapter includes the discussion on Chemistry Of Main Group Elements.

## **Chapter 7**

This chapter includes the Chemistry of Transition Elements

Our purpose of this General chemistry is to meet the needs of teachers who presents these subjects, who do not have the time or perhaps the inclination to pursue it in depth, but who may also require explicit coverage of basic concepts such as fundamental laws of chemistry, chemical bonding, acids and bases theories, Chemical Bonding and structure, Chemistry Of Main Group Elements and Chemistry of Transition Elements.

The point however is that this e-book does present the facts in a very systematic way. We have a vividly baconian philosophy about Chemistry, but particularly in General chemistry concepts. We are convinced that inorganic chemistry sans facts as presented in others e-books.

We believe that a student who has read a book on General chemistry that consists almost entirely of theory and so called principles with, but sporadic mention of the hard facts has not infact actually had a course on General chemistry. This e-book is written to encourage the teaching of General chemistry in a baconain manner. At the end of the each chapter there is a study guide. At the end of all chapters exercises have been revised and organised into three groups. Revision questions are straight forward and requires only, that the student must recall the material in chapters. Additional excerices generally requires applications of important principles or additional thoughts by the student. The study guide at the end of certain chapters give some idea , to the student and the instructor of the goals, and pre requisites are given for all chapters.

Chapter **1** covers the Fundamantal laws of Chemistry, Chapters **2 - 7** will be helpful towards the discussion of the fundamental topics in General chemistry. Ocasionally, this includes a few remarks on the scope and purpose of the chapters to help the student place it in the context of the entire e-book. A supplementary reading list is included in all chapters. However, the student and the instructor will find more detailed version in this e-book.

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**Ethiopia.**

## *To The Teacher*

Since visual material is especially important for learning General chemistry, which typically presents a pictorial view of chemical concepts, the illustrations representing the microscopic world of chemistry have been redone. Special illustrations and color photographs integrate descriptive chemistry with chemical principles and many new chemical features emphasize practical applications of newly learned concepts.

This edition of chemistry contains numerous discussions, illustrations and aimed to overcome common misconceptions. It has become increasingly clear from our own teaching experiences that students often struggle with chemistry because they misunderstand many of the fundamental concepts. In this text, we have gone to great lengths to provide illustrations and explanations aimed at giving students more accurate picture of the fundamental ideas of chemistry. In particular, we have attempted to represent the microscopic world of chemistry so that students have a picture in their minds of what the atoms and molecules are doing. Also we have made large emphasis on the quantitative understanding of the concepts before quantitative problems are considered. We have included a number of conceptual questions at the end of each chapter that are intended for group discussion. It is with our experience that students often learn the most when they teach each other. Students are focused to recognize their own lack of conceptual understanding, when they try and fail to explain a concept to a colleague.

We have presented a thorough treatment of reactions that occurs in solution, including acid – base reactions. This material appears in chapter-3 directly after the chapter on chemical stoichiometry, to emphasize the concentration between the solutions, reactions and chemical reactions in general.

Throughout the book a strong emphasis on models prevails. Coverage includes how they are constructed, how they are tested and what we learn when they inevitably fail. Models are developed naturally with pertinent observations and always presented first to show why a particular model was invented.

## ***To The Student***

The major purpose of this e-book, of course is to help you learn chemistry fundamentals. However, the main thrust is closely linked to two other goals; to show how important and how interesting the subject is, and to show how to think like a chemist. To solve complicated problems the chemist uses logic, trial and error, intuitions and above all patience. A chemist is used to doing wrong. The important thing is to learn from a mistake, recheck assumptions and try again.

Many of you using this text do not plan to be practising chemists. However the non-chemists can benefit from the chemists attitude. Problem solving is important in all professions and in all walks of life. The techniques you will learn from this e-book will serve you well in any career you choose. Thus we believe that the study of chemistry has much to offer for the majors, including an understanding of many fascinating and important phenomena and a chance to win problem solving skills.

This e-book attempts to present chemistry in manner that is sensible to the notice. Chemistry is not the result of inspired vision. It is the product of countless observations and many attempts, using logic and trial and error methods, to account for the observations. In this book the concepts are developed in a natural way. The observations come first and then models are constructed to explain the observation behaviour.

Models are a major focus in this e-book. The use and limitations of models are emphasized and science is treated as human activity, subject to all the normal human foibles.

A central theme of this book is a thoughtful, systematic approach to problems solving. Learning encompasses much more than simply memorizing facts. Truly educated people use their factual knowledge as a starting point, a base for creative approaches to solving problems.

Be patient and thoughtful and work hard towards understanding rather than simply memorizing. We wish you an interesting and successful year ahead.

## ***Acknowledgements***

This e-book represents the efforts of many talented and dedicated people. we particularly wish to thank Professor **Dr.N.DEVANNA** for his vision and oversight of this project. Professor **Dr.N.DEVANNA's** knowledge, judgement and enthusiasm have contributed immeasurably to the success of this e- text.

We also appreciate the excellent work of professor.**Dr.M. RAJASEKHAR** Assistant professor, Department of Chemistry, Arba Minch University, Ethiopia, who managed the revision process at the end of chapters, His extensive teaching experience in General chemistry and his high standard of accuracy and clarity have contributed in great improvements in the quality of the problems and the solutions in this e-book.

I express my deep sense of gratitude to my beloved parents **C.NAGALIAH AND C.RUKHMINAMMA** for their affectionate love and blessings towards me and whose co-operation, constant encouragement and support throughout my education gave me enthusiasm to carry out my research work.

I express my thanks to my brothers **C.MALLIKARJUNA AND C.MAHESH** for their moral support, and constant encouragement helped me through the hard times of the programme. My deepest appreciation is expressed to them for their understanding and inspiration. Without their encouragement, I would not have been able to finish this work.

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Last but not least my heartfelt thanks to **LORD VENKATESHWARA SWAMY** for his blessings to complete this work successfully.

**CHAPTER-1**  
***Fundamental Laws of Chemistry***

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## **Chapter-1.**

### **Fundamental Laws of Chemistry**

When does one start learning chemistry? Clearly we must consider some essential vocabulary and something about the origin of the fundamental sciences, before we can proceed very far. Thus chapter 1 provides background on the Fundamental Laws and systematic procedure of sciences in general.

#### **1.1.The Early History of Chemistry**

Chemistry has been important since ancient times. The processing of natural ores to produce metals for ornaments and weapons and the use of embalming fluids are two applications of chemical phenomenon that were utilized prior to 1000.B.C.

The Greeks were the first to try to explain why chemical changes occur. By about 400 B.C. They had proposed that all matter was composed of four fundamental substances; earth, fire, air and water. The Greeks also considered the question of whether matter is continuous and thus infinitely divisible into smaller particles or composed of small and indivisible particles. Supporters of the latter positions were Democritus and Leucippus, who used the term atoms (which later became atoms) to describe these ultimate particles. However, because the Greeks had no experiments to test their ideas and no definite conclusion could be reached about the divisibility of matter.

The next 2000 years of chemical history were dominated by pseudosciences called Alchemy. Some alchemists were mystics and fakes who were obsessed with the idea of turning cheap metals into gold. However, many alchemists were serious scientists and this period saw important advances. The alchemists discovered several elements and learned to prepare the mineral acids.

The first Chemists to perform truly quantitative experiments was Robert Boyle (1627-1691), who carefully measured the relationship between the pressure and volume of air. When Boyle published his book the Sceptical Chemist in 1661, on the quantitative behaviour of gases. Other major contribution to chemistry consisted of his ideas about the chemical elements. Boyle held no preconceived notion about the number of elements. In his view substances were elements unless it could be broken down into two or more simpler substances. As Boyle's experimental definition of an element became generally accepted, the list of known elements began to grow and the Greek system of four elements finally died. Although Boyle was an excellent scientist he was not always right. For example, he clung to the alchemists' views that metals were not true elements and that a way would eventually be found to change one metal into another.

## 1.2: Atomic Theory (Dalton's Atomic Theory)

The father of Modern chemistry is the English man John Dalton(1766-1844), who proposed his atomic theory of matter in 1803. The concept of the atom did not originate with Dalton's theory. In Greek language atoms meaning was 'indivisible'. The Greek philosopher Democritus suggested as early as 400 to 500 BC., that matter cannot be further divided into smaller and smaller parts and that ultimately particles would be indivisible. These early proposals, however were not based on the experimental results. Dalton's theory was different because, it was based on the laws of conservation of mass and definite proportions, However these laws have been derived from experimental results. He regarded that atom is the ultimate particle of matter.

**The theory proposed by Dalton can be expressed by the following postulates:**

Matter is composed of indivisible particles called 'atoms'. All the atoms of the given element have the same properties (e.g. size, shape and mass) which differ from the properties of all other elements. A chemical reaction simply consists of a reshuffling of atoms from one set of combinations to another. The Dalton's theory proved successful on both the laws of conservation of mass and definite proportions. The first law of conservation of mass says, A chemical reaction does nothing more than redistribute atoms and no atoms are lost from the system or reactions. This law finally concluded that the total mass must remain constant when the reaction occurs.

**Example :**  $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$ .

The second law explains the law of definite proportions. A substance is formed from two elements say A and B. This law simply explains molecules are collection of atoms. But this type of A and B atoms finally forms one molecule, However these molecule is formed from natural or synthetic sources but these compounds have same compositions.

**Examples:** Calcium carbonate( $\text{CaCO}_3$ )

**Draw backs: Dalton's Atomic Theory:**

An atom is the smallest indivisible particle of an element. However, it is now known that atoms can further be subdivided into elementary particles like electrons, protons, and neutrons.

Atoms of the same element are identical in all respects, having the same size, shape and structure, and especially mass. Today, we know that atoms of the same element can have slightly different masses. Such atoms are called *isotopes*.

Atoms of different elements have different properties and different masses. However, different elements do exist whose atoms have the same mass. Such atoms are called *isobars*.

### 1.3: Laws of Chemical Combination:

Compounds are formed by chemical combination of reactants (atoms or molecules) which may be solid, liquid or gases. Chemical combination occurs in definite proportion by weight or by volume. Based on various experiments performed by different scientists, the laws of chemical combinations were formulated.

These laws laid the foundation of stoichiometry, a branch of chemistry in which quantitative relationship between masses of reactants and products is established. The study of these laws led to the development of a theory concerning the nature of matter.

Dalton's theory could explain the laws of chemical combination.

There are three laws of chemical combinations: These laws deal with combination of substances by weight and the combination of gases by volume.

They are: 1) The law of conservation of mass  
2) The law of definite proportions and  
3) The law of multiple proportions.

#### 1.3.1: Law of Conservation of Mass:

This law was discovered by Antoine Lavoisier in 1789. In the scientific method, Lavoisier had always assumed this law was true and sought out experiments which would verify his assumptions.

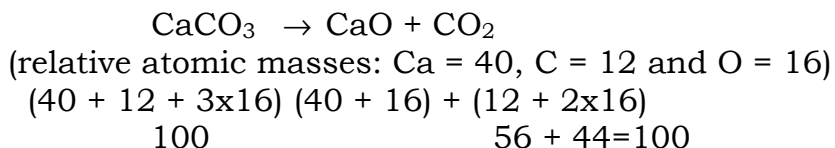
This law states that **"Matter can neither be created nor destroyed"**. (OR ) The total mass of material present after a chemical reaction is the same as before the reaction.

If a chemical reaction does nothing more than redistribute atoms and no atoms are lost from the system, it follows that the total mass must remain constant when the reaction occurs.

Dalton performed careful experimental studies for combustion. In fact, this was the result of exact measurement of masses of reactants and products.

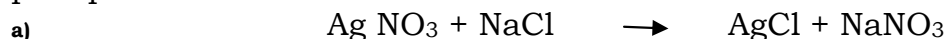
**Example 1:** Law of conservation of mass calculation:

When limestone (calcium carbonate) is strongly heated, it undergoes thermal decomposition to form lime (calcium oxide) and carbon dioxide gas.



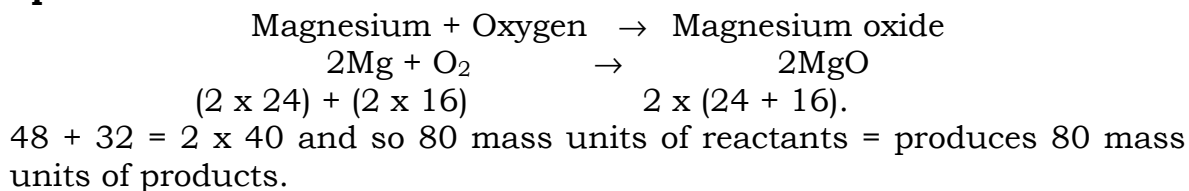
**Example 2:**

The conservation of mass can easily be verified by the study of the following reaction. When a solution of silver nitrate (AgNO<sub>3</sub>) is treated with a solution of sodium chloride, a white precipitate of silver chloride (AgCl) is obtained along with a solution of sodium nitrate (NaNO<sub>3</sub>). If the law is true, the total mass of AgNO<sub>3</sub> and NaCl should be the same as the total mass of AgCl precipitate and NaNO<sub>3</sub> solution.

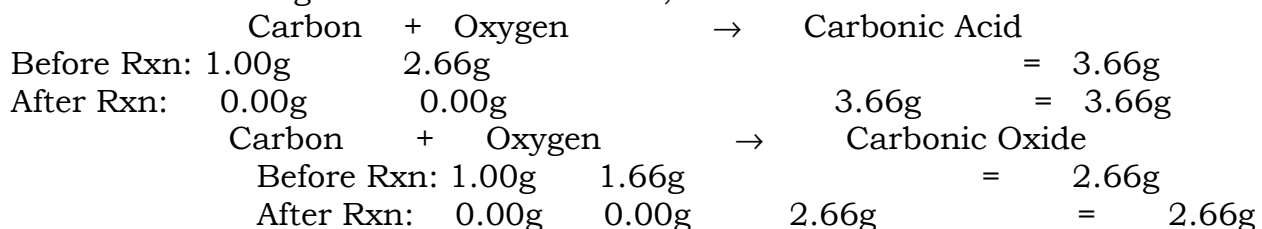




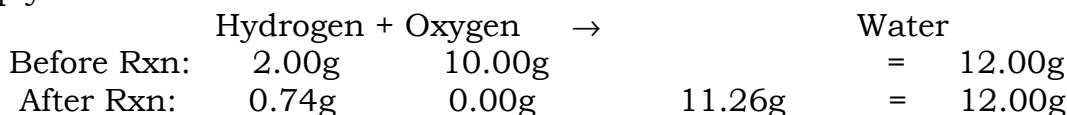
**Example 3:**



**Example 4:** consider combustion reactions of elemental carbon with oxygen . If the mass of the gases are accounted for, it is found.



From the above, each reactant is present in perfectly balanced amounts, such that the full quantity of each is consumed completely during the reaction. If this is not the case, some of the reagent in excess will remain at the conclusion of the reaction. However, the law of conservation of mass will still apply.



Finally, it must be noted that the law of Conservation of Mass, though a fundamental law of chemistry, is not a fundamental law of nature. When an energy difference occurs during a reaction, minute amounts of mass are either gained or lost. Mass is either converted to energy or Energy is converted to mass. The energy-mass equivalence was first postulated by Einstein in his famous formula;  $E = mc^2$ . While these mass differences are not detectable by the chemist, they are important in nuclear reactions.

**1.3.2: Law of Definite Proportions:**

This law was given by a French Chemist, Joseph Proust. This law is also called as proust law. He states that “a given compound always contains exactly the same proportion of elements by weight”. (OR) A compound by definition is a substance made up of two or more elements combined in a fixed proportion by weight.

In lab, two methods are used in determining the composition of a pure compound.

**a) Analysis 2) Synthesis.**

In analysis the compound is broken down into its component elements. Whereas, in synthesis, the pure elements are chemically combined to produce the compound.

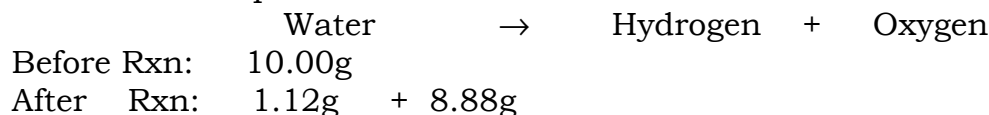
In lab, synthesis will be used to determine the amounts of the different elements which make up a compound.

For example Proust worked out with two samples of calcium carbonate – one of which was of natural origin and the other was synthetic one. He found that the composition of elements present in it was same for both the samples as shown below.

| <b>Typ of sample</b> | <b>% of copper</b> | <b>% of oxygen</b> | <b>% of carbon</b> |
|----------------------|--------------------|--------------------|--------------------|
| Natural Sample       | 51.35              | 9.74               | 38.91              |
| Synthetic Sample     | 51.35              | 9.74               | 38.91              |

Thus, irrespective of the source, a given compound always contains same elements in the same proportion. The validity of this law has been confirmed by various experiments. It is sometimes also referred to as law of Definite Proportions.

So, for example, if we decompose water by electrolysis and we recover the elemental gases hydrogen and oxygen (not a difficult task experimentally), and subsequently measure the masses of each gas respectively, we can determine the composition of this compound.



This data yields an elemental composition of:

$$\% \text{ oxygen} = \frac{\text{mass of oxygen}}{\text{mass compound}} \times 100 = \frac{8.88 \text{ g}}{10.00 \text{ g}} \times 100 = 88\%$$

$$\frac{\text{mass of hydrogen}}{\text{mass compound}} \times 100 = \frac{1.12 \text{ g}}{10.00 \text{ g}} \times 100 = 11.2\%$$

% hydrogen =

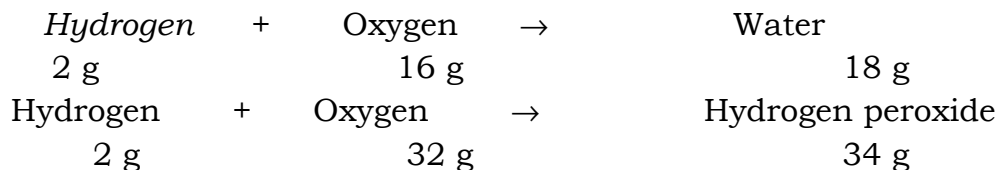
In a similar manner, from the data presented above, we can determine the elemental composition of the two Oxides of Carbon:

|          | Carbonic Acid | Carbonic Oxide |
|----------|---------------|----------------|
| % Carbon | 27.32 %       | 37.59 %        |
| % Oxygen | 72.67 %       | 62.40 %        |

### 1.3.3: Law of Multiple Proportions:

This law was proposed by Dalton in 1803. According to this law “ If two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in the ratio of small whole numbers”.

For example, hydrogen combines with oxygen to form two compounds, namely, water and hydrogen peroxide.



Here, the masses of oxygen (i.e. 16 g and 32 g) which combine with a fixed mass of hydrogen (2g) bear a simple ratio, i.e. 16:32 or 1:2.

This law deals with the relationship between two compounds composed of the same elements. carbonic acid - carbonic oxide example is a case in point. Both are composed of the same two elements; carbon and oxygen. Recall, the above data showed that 1.00g of carbon will combine with 2.66g of oxygen, in the case of carbonic Acid, and 1.33g of oxygen in the case of carbonic oxide. Thus, the amount of carbon, in each case, is fixed at 1.00g. We can, in turn, use this data to illustrate the application of the law of Multiple Proportions:

$$\frac{\text{mass of oxygen in carbonic acid}}{\text{mass of carbon}} = 1.66/1.00 = 1.66$$

$$\frac{\text{mass of oxygen in carbonic oxide}}{\text{mass of carbon}} = \frac{1.33}{1.00} = 1.33$$

**Fixed masses:**

Another example, it is found that elemental iron combines with elemental chlorine to form two different compounds; ferric chloride and ferrous chloride. The definite composition of these two compounds is:

|            | <b>Ferrous Chloride</b> | <b>Ferric Chloride</b> |
|------------|-------------------------|------------------------|
| % Iron     | 44.05 %                 | 34.48 %                |
| % Chlorine | 55.94 %                 | 65.51 %                |

This data can be used to determine the mass of chlorine per 1.00g of iron needed to produce these compounds. The results are:

|                  | <b>Ferrous Chloride</b> | <b>Ferric Chloride</b> |
|------------------|-------------------------|------------------------|
| mass of iron     | 1.00g                   | 1.00g                  |
| mass of chlorine | 1.27g                   | 1.90g                  |

Applying the law of multiple proportions to these results, we obtain:

$$\frac{\text{mass of chlorine in ferric Chloride}}{\text{mass of Iron}} = \frac{1.90 \text{ g}}{1.00 \text{ g}}$$

$$= 1.90 = 3/2$$

$$\frac{\text{mass Chlorine in ferrous Chloride}}{\text{mass of Iron}} = \frac{1.27 \text{ g}}{1.00 \text{ g}}$$

It must be kept in mind; these results are purely experimental in nature. The Law of Multiple Proportions, in conjunction with the other fundamental laws of chemistry, led directly to the postulates of the Atomic theory of Matter.

### Revision Questions:

1. Matter is composed of what?
2. Robert Boyle quantitative experiment measured the relation between\_\_\_\_\_
3. Who is The Father of Modern Chemistry
4. In Greek language what is meant by atom?
5. A chemical reaction simply consists of a ----- from one set of combinations to another.
6. Which theory proved successful on both the laws of Conservation of Mass and Definite Proportions.
7. What is first law of Conservation of Mass?
8. The atoms can further be subdivided into elementary particles like -----
9. Define Isotopes?
10. Define Isobars?
11. What are the laws of Chemical Combinations?
12. What is Law of Conservation of Mass?
13. Give an example for Law of conservation of mass calculation?
14. Einstein introduced the famous formula -----
15. What is Law of Definite Proportions?
16. What are the methods used in lab to determining the composition of a pure compound?
17. What is Law of Multiple Proportions?
18. Give an example for Law of Multiple Proportions?

## **Chapter-2**

### **SOLID STATE**

#### **Contents**

|     |  |
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| 2.0 | Introduction                               |
| 2.1 | Classification of Solids                   |
| 2.2 | The structures of Ionic Solids             |
| 2.3 | The radius ratio rules for ionic compounds |
| 2.4 | Close packing                              |
| 2.5 | Classification of Ionic Structures:        |

## 2.0. Introduction:

Matter is defined as anything which has mass and occupies space. Example: NaCl, H<sub>2</sub>O, CO<sub>2</sub>, All living beings are composed of matter . usually Matter can exist in three types.

a) They are:

1. Solid. Examples: NaCl, AgCl, etc.,
2. Liquid. Examples: H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>OH.,etc
3. Gas. Examples: CO, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, etc.,

In Solids, these particles are held very close to each other in an orderly fashion and there is no freedom of movement. These three states of matter are inter-convertible by changing the conditions of temperature and pressure.

**Solid → Liquid → Gas**

On heating, a solid usually changes to a liquid and the liquid on further heating changes to the gaseous (or vapor) state. In the reverse process gas on cooling liquefies to the liquid and the liquid on further cooling freezes to the solid. A solid is a material that has definite volume and definite shape. If a solid possesses long range, regularly repeating units, it is describes as a **crystalline material**. If there is no long-range structural order throughout the solid, the material is described as a as **amorphous substance**.

All ionic salts possess crystalline structures, The melting points of these solids are extremely high, Becase of very strong electrostatic attractions between ions. For example, the extremely high melting points of salts are directly associated with the strength of the ionic bonds between adjacent ions. Single crystals contains an infinite patterns of ions, atoms, or molecules, known as a **crystal lattice**.

Crystalline solids are arranged in fixed geometric patterns or lattices. Examples of crystalline solids are ice and sodium chloride. Depending on the kind of bonding in a pure substance is primarily ionic, covalent or metallic in character, a substance may be described as ionic, molecular, macromolecular or metallic.

### 2.1. Classification of Solids:

Usually, solids are classified into four types:

They are

- a) Molecular Solids
- b) Ionic Solids
- c) Covalent network orMacromolecular Solids
- d) Metallic Solids.

#### a).Molecular substances:

Molecular solids are formed from atoms. **Example** : The structure of Ice is a molecular solid All gases such as H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and F<sub>2</sub> forms molecular crystals with low melting points. and almost all liquids at room temperature are molecular in nature. In addition, many solids, especially organic solids are molecular in nature. The melting points of molecular solids are usually below

300°C. Molecular substances do not conduct electricity in either solid or liquid state.

### **b) Properties of Ionic Solids:**

Ionic solids are formed from ions. Ionic solids are arranged in fixed geometric patterns or lattices **Examples:** NaCl, KCl, etc., Ionic substances are all solids at room temperature. Ionic crystals are hard and brittle. They are typically crystalline, but may exist as fine powders as well as clearly defined crystals. Ionic substances have high melting points, usually above 300°C but below 1000°C.

Ionic solutions conduct electric current because the ions can move freely, but in the solid state, they do not conduct electricity due to the rigid structure and strong bonding in the crystal lattice. Ionic substances are frequently (but not always) soluble in water.

### **c). Macromolecular Solids (Network covalent solids)**

Macro molecular substances are all solids at room temperature.

**Example :** Diamond and graphite.

They have very high melting points, usually above 1000°C and low volatility. They are typically very resistant to thermal decomposition. They do not conduct electric current and are often good insulators.. They are not soluble in any solvent.

### **d). Metallic Solids:**

Metalic solids are formed from metals. They are very hard.

**Examples :** Fe, Ni, V, W, Mo and Cu., etc

Most metallic solids are solids at room temperature. Most have high melting points. Metallic solids are very good conductors in the solid and molten state. They are not soluble in any solvent. Many metals will chemically react with polar solvents like water to form solutions

## **2.2: The Structures of Ionic Solids:**

Ionic crystals consist of two or more different kinds of ions, usually having different sizes. Most monoatomic ions behave as charged spheres; their attraction for ions of opposite charge is the same in every direction.

### **Stable structures:**

Usually in stable structures, ions (cations) of one charge are surrounded by as many ions (anions) as possible of the opposite charge (OR) the cation is in contact with many anions of each other.

### **Structures:**

The structure is determined by **two factors;**

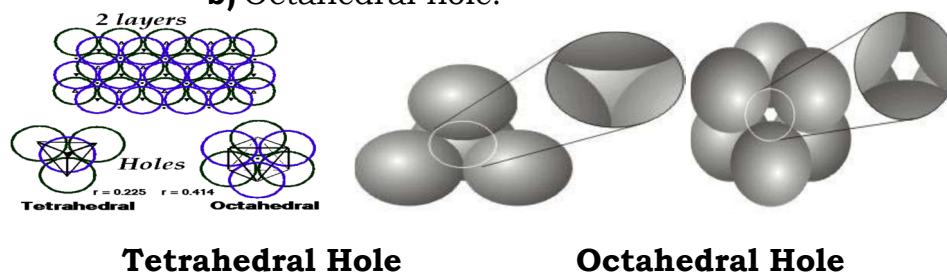
- a) the relative sizes of the ions** and
- b) The relative numbers of positive and negative ions** required to maintain the electrical neutrality of the crystals as a whole.

### **Simple ionic structure:**

In simple ionic structures the anions are normally larger than the cations and these ions are usually arranged in a **closed packed pattern (or) array**. The spaces remaining between the anions called **holes or interstices** are occupied by the smaller **cations**.

**Holes:** Two most common types of holes observed in solids are:

- a) Tetrahedral hole.
- b) Octahedral hole.



The smaller of these is found between three spheres that bound this hole and are arranged at the corners of a tetrahedron (fig .2).The four spheres that bound this hole are arranged at the corners of a tetrahedron (fig.3); the hole is called as Tetrahedral hole.The larger type of hole is found at the center of six spheres ( three in one layer and three in an adjacent layer) located at the corners of an octahedron(fig.4) Such a hole is called an Octahedral hole. Depending on the relative sizes of the cations and anions, the cations of an ionic compound can occupy tetrahedral or octahedral holes. As will be discussed in radius rules relatively small cations occupy tetrahedral holes and larger cations occupy octahedral holes.

If the cations are too large to fit into the octahedral holes, the packing of the anions may change to give more open structures such as a simple cubic array ( fig.11.29)The larger cations then occupy the larger cubic holes made possible by the more open spacing (fig.11.30).In either a hexagonal close packed or a cubic close packed patterns or array of anions, there are two tetrahedral closed packed holes for each anion in the array.Examples: The amorphous compounds  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{Li}_2\text{S}$ ,  $\text{Na}_2\text{S}$  and  $\text{Li}_2\text{Se}$  among others, crystallize with a cubic close packed array of anions with the relatively small cations in tetrahedral holes.

The ratio of tetrahedral holes to anions is 2 :1; thus all of these holes must be filled by cations, since the cation – to –anion ratio is 2 : 1 in the Se compounds. A compound that crystallizes in a close packed array of anions with cations in the tetrahedral holes can have a maximum cation –to–anion ratio of 2 to 1; all of the tetrahedral holes are filled at this ratio. Compounds with a ratio of less than 2 to 1 may also crystallize in a close packed array of anions with cations in the tetrahedral holes, if the ionic sizes fit.

In these compounds, however, some of the tetrahedral holes remain vacant.The ratio of octahedral holes to anions in either a hexagonal or a cubic close packed structure is 1 to 1. Thus compounds with cations in octahedral holes in a close packed array of anions can have a maximum cation –to– anion ratio of 1 to 1.Examples :  $\text{NiO}$ ,  $\text{MnS}$ ,  $\text{NaCl}$ , and  $\text{KH}$ ,where all the octahedral holes are filled.



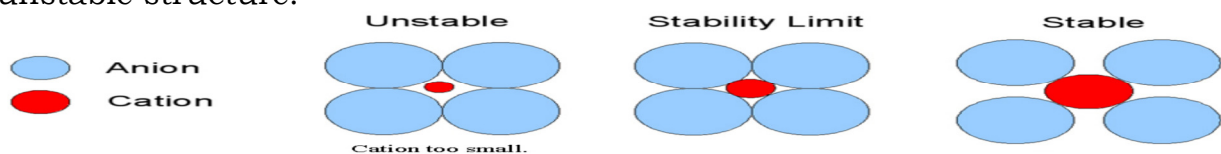
### 2.3: The radius ratio rules for ionic compounds:

The structure of ionic compounds is largely the result of stoichiometry, and of simple geometric and electrostatic relationships that depend on the **relative sizes of the cation and anion**. A relative large cation can touch a large number of anions and so occupies a **cubic** or an **octahedral hole**, where as a relatively small cation can touch only a few number of anions and so occupies **tetrahedral hole**. For example, a cation  $M^+$  with coordination number of 6.

The  $M^+$  ion touches four  $X^-$  ions in a plane. In addition, although they are not shown in figure, there is an  $X^-$  ion above the  $M^+$  ion and touching it and another below and touching it. **Note:** that the  $M^+$  ion is large enough to expand the array of  $X^-$  ions so that the  $X^-$  ions are not in contact with one another.

(Fig.3) As long as the expansion is not great enough to allow still another anion to touch the cation, this is a stable situation. The cation – anion contacts are mentioned (figure. no.2) This figure no.2) indicates the size of  $M^+$  cation is decreased.

Here the  $X^-$  ions touch each other, as do the  $M^+$  and  $X^-$  ions The figure no.1 indicates that the size of  $M^+$  is further decreased, it becomes impossible to get a structure with a coordination number of 6. The anions touch, but there is no contact between the  $M^+$  ion and  $X^-$  ions – this is an unstable structure.



Packing of anions (big spheres) around cations of (small spheres) increasing size of cations is illustrated successively in 1, 2 and 3. In this case a more stable structure (fig no.3) would be formed with only four anions about the cation. The limiting condition for the formation of a structure with a coordination number of 6 presented in figures. The  $X^-$  ions touch one another, and the  $M^+$  and  $X^-$  ions touch. This occurs when the sizes of the ions are such that the radius ratio (these radius of the positive ion  $r_+$  divided by the radius of the negative ion  $r_-$ ) is equal to 0.414.

$$\text{Radius ratio} = \frac{\text{radius of the positive ion}}{\text{radius of the negative ion}} = \frac{r_+}{r_-}$$

There is a minimum radius ratio ( $r_+$  and  $r_-$ ) for each coordination number. Below this value an ionic structures having that coordination number is generally not stable. The approximate limiting values for the radius ratios for ionic compounds are given in the table. The radius ratio rule is only a guide to the type of structure that may form. It applies strictly only to ionic crystals and in some cases fails with them. In compounds in which the bonds are covalent, these rules may not hold good.

| <b>Limiting values for the radius ratio for ionic compounds</b><br>( $r^+$ is radius of cation and $r^-$ radius of anion) |                              |  |
|---|------------------------------|--|
| <b>Coordination number</b>  | <b>Type of hole occupied</b> | <b>Approximate limiting values of <math>r^+ / r^-</math></b> |
| 8   | Cubic                        | Above 0.732  |
| 6   | Octahedral                   | 0.414 to 0.732   |
| 4   | Tetrahedral                  | 0.225 to 0.414   |

In spite of its limitations, however, the radius ratio rule is a useful guide for predicting many structures. It also underlines one of the most significant features responsible for the structures of ionic solids, the relative sizes of the cations and anions.

#### 2.4: Close packing:

The crystalline solid in the constituent particles or atoms are packed **closely** together in a repeating array or pattern in a plane, such arrangement is called **close packing**, if spheres of equal size are packed together as closely as possible in a plane with space or holes. In solids the spheres are arranged as layers. In solids, the constituent particles are identical hard spheres and close-packed, leaving the minimum vacant space and builds up the three dimensional structure in three steps.

They are

- a) Close packing in one dimension
- b) Close packing in two dimension
- c) Close packing in three dimension

##### a) Close Packing in One Dimension:

In one dimension close packed structures, the spheres are arranged in only one way. In one dimensional close packed structures spheres are arranged in a row and touching each other. Fig No.1 shows one dimensional close packing arrangement.



**Fig No.1**

In this arrangement, each sphere is in contact with two of its neighbours. The number of nearest neighbours of a particle is called its **Coordination number**. Thus, in one dimensional close packed arrangement, the coordination number is 2.

##### b) Close packing in two dimensions:

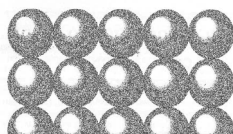
Two dimensional close packed structure can be generated by stacking (placing) the rows of close packed spheres. This can be done in **two different ways**.

They are

- a) Two dimensional square close packing
- b) Two dimensional hexagonal close packing

### (I) Two dimensional square close packing:

The second row may be placed in contact with the first one. The second row spheres are exactly above those of the first row. The spheres of the two rows are aligned horizontally as well as vertically. If we call the first row as 'A' type row, the second row being exactly the same as the first one, is also of 'A' type. Hence this arrangement is of AAA type. In this arrangement there is free space and this packing is more efficient. Fig No.2 shows AAA type arrangement.



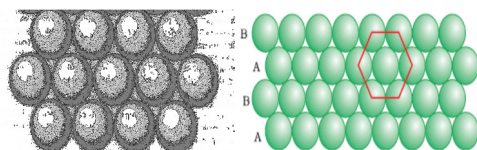
**Fig No.2**

Similarly, we may place more rows to obtain AAA type of arrangement. In this arrangement each sphere is in contact with four of its neighbour. Thus in the Two dimension square close packing coordination number is 4. And when four spheres are joined a square is formed. Hence this packing is called **two dimensional square close packing**.

#### a) Two dimensional hexagonal close packing

The second row may be placed above the first one in a staggered manner such that its spheres fit in the depressions of the first row. If the arrangement of spheres in the first row is called 'A' type, the one in the second row is different and may be called 'B' type.

When the third row is placed adjacent to the second in staggered manner, its spheres are aligned with those of the first layer. Hence this layer is also of 'A' type. The spheres of similarly placed fourth row will be aligned with those of the second row ('B' type). Hence this arrangement is of ABAB type. Fig No.3 shows ABAB type arrangement.



**Fig No.3**

In this arrangement there is less free space and this packing is more efficient than the square close packing. Each sphere is in contact with six of its neighbours and the two dimensional coordination number is 6.

The centres of these six spheres are at the corners of a regular hexagon. Hence this packing is called **two dimensional hexagonal closepacking**. In this layer there are some voids (empty spaces). These are triangular in shape and it is of two different types. In one row, the apex of the triangles are pointing upwards and in the next layer downwards.

#### b) Close Packing in Three Dimensions:

All real solid structures are three dimensional structures. They can be obtained by stacking two dimensional layers one above the other.

**They are:**

- a) Three dimensional close packing from two dimensional square close-packed layers
- b) Three dimensional close packing from two dimensional hexagonal close packed layers

**a) Three dimensional close packing from two dimensional square close-packed layers:**

The second layer is placed over the first layer such that the spheres of the upper layer are exactly above those of the first layer. In this arrangement spheres of both the layers are perfectly aligned horizontally as well as vertically as shown.

Similarly, we may place more layers one above the other. If the arrangement of spheres in the first layer is called 'A' type, all the layers have the same arrangement. Thus this lattice has AAA....type pattern. Fig no.4 shows AAA type square close packed layers.

**a) Three dimensional close packing from two dimensional hexagonal close packed layers**

Three dimensional close packed structure can be generated by placing layers one over the other. Two types.

**They are :**

- a) Placing second layer over the first layer.
- b) Placing third layer over the second layer.

**a) Placing second layer over the first layer:**

Two dimensional hexagonal close packed layer 'A' and place a similar layer above it such that the spheres of the second layer are placed in the depressions of the first layer. Since the spheres of the two layers are aligned differently, let us call the second layer as B. It can be observed from **Fig. 2.6** that not all the triangular voids of the first layer are covered by the spheres of the second layer. This gives rise to different arrangements.

Wherever a sphere of the second layer is above the void of the first layer (or vice versa) a tetrahedral void results. These voids are called **tetrahedral voids** because a tetrahedron is formed when the centres of these four spheres are joined. They have been marked as 'T' in Fig No. 5.0. Fig No 5.0 shows the placing second layer over the first layer.

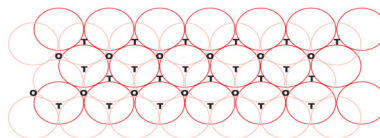


Fig No.5

At other places, the triangular voids in the second layer are above the triangular voids in the first layer, and the triangular shapes of these do not overlap. One of them has the apex of the triangle pointing upwards and the other downwards. These voids have been marked as 'O' in Fig. 2.6. Such voids are surrounded by six spheres and are called octahedral voids.

### (b) Placing third layer over the second layer

When third layer is placed over the second, there are two possibilities.

- a) Covering tetrahedral voids.
- b) Covering octahedral voids.

#### a) Covering tetrahedral voids.

Tetrahedral holes of the second layer may be covered by the spheres of the third layer. In this case, the spheres of the third layer are exactly aligned with those of the first layer. Thus, the pattern of spheres is repeated in alternate layers. This pattern is often written as ABAB ..... pattern. This structure is called **hexagonal close packed (hcp) structure**. This sort of arrangement of atoms is found in many metals like magnesium and zinc.

#### b) Covering octahedral voids.

The third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids. When placed in this manner, the spheres of the third layer are not aligned with those of either the first or the second layer. This arrangement is called 'C' type. Only when fourth layer is placed, its spheres are aligned with those of the first layer as shown in Figs. 2.8 and 2.9. This pattern of layers is often written as ABCABC ..... This structure is called cubic close packed (ccp) or face-centred cubic (fcc) structure. Example: Metals such as copper and silver crystallise in this structure. Both these types of close packing are highly efficient and 74% space in the crystal is filled. In either of them, each sphere is in contact with twelve spheres. Thus, the coordination number is 12 in either of these two structures.

### 2.5. Classification of Ionic Structures:

Usually solid ionic compounds consists of oppositely charged ions. In ionic compounds the larger ions occupies larger holes or octahedral holes and smaller ions occupies smaller holes or tetrahedral hole.

The larger ions are close packed, than the smaller ions. Usually in ionic compounds hole can be determined from the radius ratio. Usually if an ion occupying tetrahedral hole, its coordination number is 4. An ion occupying octahedral hole has coordination number 6. In some cases, ionic compounds have general formula AX type and AX<sub>2</sub> type. Examples NaCl and CaF<sub>2</sub>.

AX type solid consists of same kind of ions, the coordination number of both the ions is same. But, AX<sub>2</sub> type solids consists of different kind of ions and different ions have different coordination number. For example in CaCl<sub>2</sub>, chloride ions are twice as many as calcium ions. If two different substances have the same crystal structure, then the substances are said to be **isomorphous**. The phenomenon is called **isomorphism**. The phenomenon by which the same compound exists in more than one crystal structures it is called **polymorphism**.

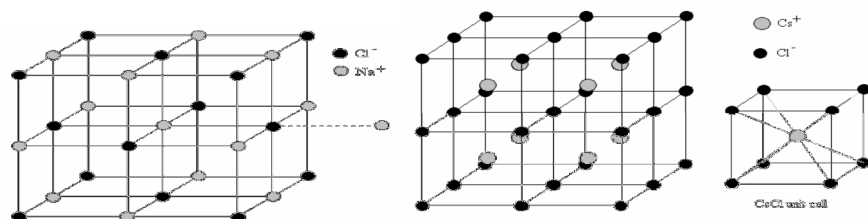
## STRUCTURES OF CRYSTALS OF TYPES AX:

### Example.1: Sodium chloride structure

Crystalline sodium chloride deposits are found in some places on land in the form of rocks. Hence the name is rock salt. A unit cell of NaCl **Fig No.1** is presented below. One can equally well imagine a face-centred cubic lattice (fcc) of sodium ions with  $\text{Cl}^-$  ions in all the octahedral voids.

But  $\text{Cl}^-$  ions are almost double the size of  $\text{Na}^+$  ions. The coordination numbers of both chloride ions and sodium ions is six (6:6 coordination). For precise fitting in an octahedral hole, the radius ratio must be 0.414, but the actual radius ratio of  $\text{Na}^+ / \text{Cl}^-$  is 0.525. Therefore the chloride ions in the lattice have to move apart slightly to accommodate the sodium ions. There are four sodium ions and four chloride ions (equal numbers) in a unit cell; therefore the ratio of cation to anion is 1:1, and the formula is NaCl.

**Examples:** Some other compounds having the rock salt structures are halides and hydrides of Li, Na, K, and Rb, cesium fluoride ( $\text{CsF}$ ),  $\text{AgCl}$ ,  $\text{AgBr}$  and  $\text{NH}_4\text{Cl}$ ; oxides of alkaline earth metals ( $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{SrO}$ ,  $\text{BaO}$ ) and  $\text{FeO}$ .



**Fig No.1**

**Fig No.2**

### Example.2: Cesium chloride structure:

In the cesium chloride unit cell, the chloride ions are at the corners of a cube and the cesium ions at the centre of the cube. A unit cell of  $\text{CsCl}$ . **Fig No.2** is presented above. Since the cesium ions are large, they occupy cubic holes in a 3D square close packing arrangement. There are 8 chloride ions around each cesium ion and 8 cesium ion surround each chloride ion.

Thus the coordination number of each ion is eight (8:8 coordination). There is one ( $8 \times 1/8 = 1$ ) chloride ion and one cesium ion (body centered) in a unit cell. The ratio of ions is thus 1:1; therefore formula is  $\text{CsCl}$ . The cesium chloride structure is also exhibited by  $\text{CsBr}$  and  $\text{CsI}$  ( $\text{CsF}$  has the rock salt structure). **Examples:** Thallium chloride and bromide also have this structure.  $\text{NH}_4\text{Cl}$  has this structure at low temperature.

### Example.3: The zinc blende structure:

The single compound (having same molecular formula) existing in different crystal forms are called **polymorphism**. The different varieties of the same compound are then known as polymorphs. Thus zinc sulphide exhibits polymorphism,

**They are:**

- a) Zinc blende structure
- b) Wurtzite structure.

### Example.3.1: Zinc blends structure(ZnS):

This structure is also known as the **sphalerite structure** or **cubic zinc sulphide structure**.

A unit cell of ZnS **Fig.No.3** is presented below. In this structure, the sulphide ions ( $S^{2-}$ ) are in a face-centered cubic close packing (ccp) with the  $Zn^{2+}$  ions but  $Zn^{2+}$  ions occupying only half of the available tetrahedral holes. For correct fit, the radius ratio of  $Zn^{2+}/S^{2-}$  should be 0.225, but the actual ratio is 0.4. Therefore the sulfide ions are forced apart and do not actually touch each other.

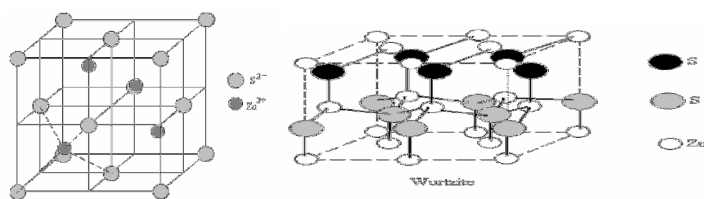
Each  $Zn^{2+}$  ion is tetrahedrally surrounded by four  $S^{2-}$  ions and each  $S^{2-}$  ion is tetrahedrally surrounded by four  $Zn^{2+}$  ions (4:4 coordination). There are four  $Zn^{2+}$  ions and four  $S^{2-}$  ions in a unit cell. The ratio of the ions is thus 1:1; therefore formula is ZnS. **Examples:** Cuprous chloride, bromide and iodide (CuCl, CuBr and CuI) also have this structure.

### Example.3.2: Wurtzite structure

This structure is also known as **hexagonal zinc sulphide structure**, or the **zinc oxide structure**. A unit cell of ZnS **Fig.No.4** is presented in below. While the sulphide ions are in ccp (...ABC...) arrangement in sphalerite, they are in hcp (...AB...) arrangement in wurtzite (hence the name "hexagonal" zinc sulphide structure).

In the figure.4, the grey layer represents the 'A' layer of sulphide ions and the black layer represents the 'B' layer of sulphide ions. In both cases, the zinc ions are occupying tetrahedral voids. Both  $Zn^{2+}$  and  $S^{2-}$  ions have tetrahedral (4:4) coordination. Since only half of all the tetrahedral voids are occupied, there are equal numbers of  $Zn^{2+}$  and  $S^{2-}$  ions.

The structure resembles the structure of diamond. Hexagonal rings in the chair form with alternate positions occupied by  $Zn^{2+}$  and  $S^{2-}$  ions can be easily found in the structure (very clear in the grey layer in the figure). In diamond, all the six positions in the ring are occupied by carbon atoms. In diamond, the atoms are covalently bonded, but in wurtzite, there are only ionic bonds. **Examples :** AgI, ZnO and aluminium nitride (AlN),  $NH_4F$ , SiC, BeS, MnS, CdS and HgS are some other compounds having the wurtzite type of crystal structure.



**FigNo.3**

**Fig No.4**

## THE 'AX<sub>2</sub>' TYPE CRYSTAL STRUCTURES

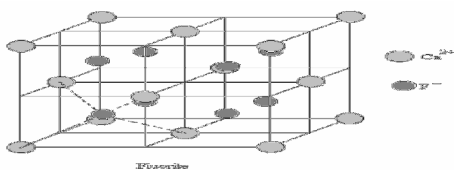
### Example.1: Fluorite (CaF<sub>2</sub>) structure:

In CaF<sub>2</sub>, the Ca<sup>2+</sup> ions have a face centered cubic struers (fcc) arrangement similar to that of S<sup>2-</sup> ions in zinc blende (sphalerite). A unit cell of CaF<sub>2</sub> **Fig No.5** is presented in below. All the eight tetrahedral holes are

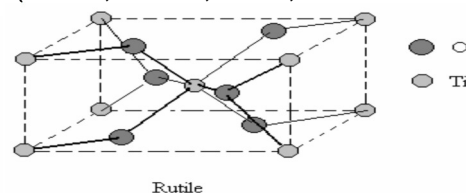
occupied by fluoride ions. The  $F^-$  ions are at the centers of each of the eight smaller cubes in the following figure, which represents a unit cell of fluorite. Each  $Ca^{2+}$  ion is surrounded by eight  $F^-$  ions and each  $F^-$  ion is surrounded by four  $Ca^{2+}$  ions.

The coordination is thus 8:4. The number of  $Ca^{2+}$  ions in the unit cell (fcc arrangement) = 4. Number of  $F^-$  ions in the unit cell (all within the cube) = 8. Thus cation and anion ratio = 4:8 or 1:2. The formula is thus  $CaF_2$ . There are four  $CaF_2$  units in the unit cell.

**Examples :** Other compounds which have the fluorite structure are alkaline earth metal fluorides ( $SrF_2$ ,  $BaF_2$ ),  $BaCl_2$ , fluorides of cadmium, mercury and lead ( $CdF_2$ ,  $HgF_2$  and  $PbF_2$ ) and dioxides of cerium thorium, uranium, zirconium and hafnium ( $CeO_2$ ,  $ThO_2$ ,  $UO_2$ ,  $ZrO_2$  and  $HfO_2$ ).



**Fig No.5**



**Fig No.6**

**Example.2: The rutile (titanium dioxide,  $TiO_2$ ) structure:**

Titanium dioxide ( $TiO_2$ ) solid has obtained in three different forms, A unit cell of  $TiO_2$  **Fig No.6** is presented in above

They are

1. Anatase,
2. Brookite
3. Rutile.

Rutile has the tetragonal symmetry ( $a = b \neq c$ ;  $\alpha = \beta = \gamma = 90^\circ$ ). The coordination number of  $Ti^{4+}$  is six (octahedral) and the coordination number of  $O^{2-}$  is three (equilateral triangle) i.e. 6:3. The number of  $Ti^{4+}$  ions in a unit cell is  $8 \times 1/8 + 1 = 2$  and that of  $O^{2-}$  is  $4 \times 1/2 + 2 = 4$ . Thus there are two  $TiO_2$  units per unit cell. **Examples :** This structure is also found in the dioxides of Cr, Mn, Ge, Ru, Rh, Sn, Os, Ir, Pt and Pb.

**Example.3: The (-cristobalite structure ( $SiO_2$  structure):**

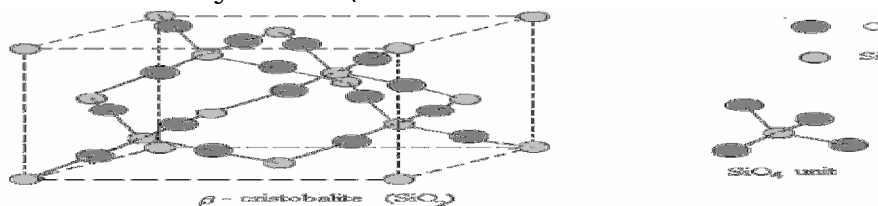
Silicon dioxide crystallizes in several forms, of which one is the (-cristobalite structure. One may think of this as the zinc blende structure in which all positions occupied by zinc and sulphur together are occupied by silicon atoms, with oxygen atoms between every two silicon atoms. A unit cell of  $SiO_2$  **Fig No.7** is presented in above

This structure has cubic symmetry for the unit cell. 14  $Si^{4+}$  ions (8 corners + 6 face centers) make a fcc lattice. Four tetrahedral  $SiO_2$  units are placed towards the alternate corners of this cube. One  $O^{2-}$  ion in each  $SiO_2$  unit points towards a  $Si^{4+}$  ion at the corner of the cube.

The remaining three  $O^{2-}$  ions point towards the nearest  $Si^{4+}$  ions at the face centers. The coordination number of each  $Si^{4+}$  ion is 4 ions). The coordination number of each  $O^{2-}$  ion is 2. The Si-O-Si bond angle is less than  $180^\circ$ . The total number of  $Si^{4+}$  ions is  $(8 \times 1/8 + 6 \times 1/2 + 4)$  eight. All the  $O^{2-}$



ions are fully with in the cube, thus 16. Therefore , there are eight  $\text{SiO}_2$  units in the unit cell. **Examples** :  $\text{BeF}_2$ ,  $\text{ZnCl}_2$ ,  $\text{Be}(\text{OH})_2$ ,  $\text{Zn}(\text{OH})_2$  and  $\text{GeO}_2$  also have the (- cristobalite structure. Another form of  $\text{SiO}_2$ , **tridymite**, is related to wurtzite in the same way as the (-cristobalite structure is related to sphalerite



**Fig No.7**

**Revision questions:**

1. The melting points of solids are extremely high. Give reason.
2. Give two examples of crystalline solids?
3. What is the classification of solids?
4. Molecular solids are formed from -----
5. Ionic solids are formed from -----
6. Examples for Molecular solids-----
7. Examples for Ionic solids-----
8. Examples for Macro molecular solids-----
9. Metallic solids are formed from-----
10. Examples for Metallic solids---
11. The structure of Ionic solids are determined on what factors?
12. Define simple ionic structure of ionic solids?
13. What is tetrahedral hole?
14. What is octahedral hole?
15. What is radius ratio of ionic compounds?
16. What are the coordination numbers of Tetrahedral, Octahedral and Cubic holes respectively?
17. What is the limiting value of Tetrahedral and Octahedral holes?
18. What is meant by coordination number of close packing?
19. Define close packing of crystal?
20. What is two dimensional square close packing?
21. What is two dimensional hexagonal close packing?
22. Define Isomorphism and Poly morphism?
23. What is Rock salt?
24. Which type of lattice is NaCl crystal?
25. What is the coordination number of NaCl crystal?
26. What is the coordination number of CsCl structure?
27. Give two examples for Zinc blende structure and Wurtzite structures?

## **Chapter-3**

### **ACIDS AND BASES.**

#### **Contents**

|       |   |
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| 3.2   | pH scale                                    |
| 3.3   | Overview of the Three Theories              |
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| 3.3.2 | Neutralization                              |
| 3.3.3 | Bronsted – Lowry concept of acids and bases |
| 3.3.4 | The Lewis concept of acids and bases        |
| 3.4   | Solvent –System concept                     |

### 3.0 Introduction:

The word Acid comes from the Latin **acidus**, meaning "sour" or "tart.".Davy proved that oxygen and hydrogen was the common constituent of acids. In our daily lives, many examples of acids and bases are used. In the home, vinegar (acetic acid), lemon juice (citric acid) and tartaric acid (the main acid found in wine) are common, while hydrochloric acid, sulfuric acid and nitric acid are examples of acids that are more likely to be found in laboratories and industries.

Hydrochloric acid is also found in the gastric juices in the stomach. Even fizzy drinks contain acid (carbonic acid). Bases that you may have heard of include sodium hydroxide (caustic soda), ammonium hydroxide and ammonia. Some of these are found in household cleaning products.

Acids and bases are also important commercial products in the fertilizer, plastics and petroleum refining industries. Some common acids and bases and their chemical formulae are presented in below table.

#### Acid Formula

|                   |                                |
|-------------------|--------------------------------|
| Hydrochloric acid | HCl                            |
| Sulfuric acid     | H <sub>2</sub> SO <sub>4</sub> |
| Nitric acid       | HNO <sub>3</sub>               |
| Acetic acid       | CH <sub>3</sub> COOH           |
| Carbonic acid     | H <sub>2</sub> CO <sub>3</sub> |
| Sulfurous acid    | H <sub>2</sub> SO <sub>3</sub> |
| Phosphoric acid   | H <sub>3</sub> PO <sub>4</sub> |

#### Base Formula

|                     |                                 |
|---------------------|---------------------------------|
| Sodium hydroxide    | NaOH                            |
| Potassium hydroxide | KOH                             |
| Sodium carbonate    | Na <sub>2</sub> CO <sub>3</sub> |
| Calcium hydroxide   | Ca(OH) <sub>2</sub>             |
| Magnesium hydroxide | Mg(OH) <sub>2</sub>             |
| Ammonia             | NH <sub>3</sub>                 |
| Sodium bicarbonate  | NaHCO <sub>3</sub>              |

### 3.1: Properties of Acids and Bases

#### Properties of Acids:

- ☞ Sour taste (like lemons)
- ☞ React with most metals to form hydrogen gas
- ☞ pH less than 7
- ☞ Frequently feels "sticky"
- ☞ Usually gases or liquids.
- ☞ Acids change the colors of indicators
  - Acids turn methyl orange to red.
  - Litmus turns from blue to red.
- ☞ Acids are electrolytes.
- ☞ Acids neutralize bases producing salt and water.

#### Properties of Bases:

- ☞ Feels "slippery". (The slippery feeling is caused because your skin dissolves a little when you touch them.)
- ☞ Bitter taste. (like baking soda)
- ☞ pH greater than 7
- ☞ React with oils and greases (that's why they're used as drain and window cleaners)
- ☞ Frequently solids (though ammonia is a gas that's usually dissolved in water).

- ☞ Bases change the colors of indicators
  - Litmus turns from red to blue
  - Bases turn methyl orange to yellow.
  - Bases turn phenolphthalein to purple.
- ☞ Bases are electrolytes
- ☞ Bases neutralize acids producing a salt and water

### 3.2: pH Scale:

#### Definitions of pH and pOH:

Negative logarithm of the Hydrogen ion concentration is pH.

$$\text{pH} = -\log [\text{H}^+].$$

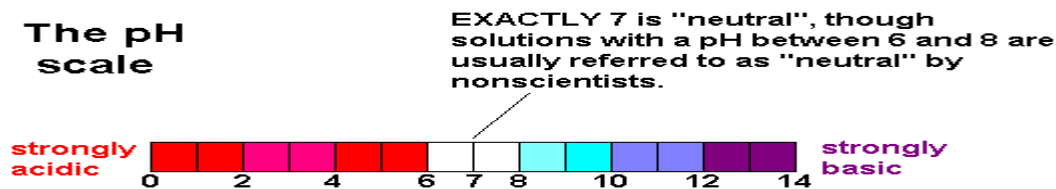
The common expression of hydroxide ion concentration is the pOH

$$\text{pOH} = -\log [\text{OH}^-].$$

pH values between 0 and 7 are acidic and pH values between 7 and 14 are basic. pH values of exactly seven are called "neutral" solutions - if the pH is 6.99 it's an acidic solution and if it is 7.01 it's basic. However, people usually refer to solutions with a pH between 6 and 8 as being "neutral" because they're mostly neutral. The pH of water is 7.

**Examples:** HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> (acids); NaOH, KOH, and Ba(OH)<sub>2</sub> (bases).

Most common acid-base reactions take place in water solutions (commonly referred to as **aqueous solutions**).



### 3.3: Overview of the Three Theories:

According to Arrhenius, probably the oldest, acids and bases are the sources of H<sup>+</sup> and OH<sup>-</sup> ions respectively. A somewhat broader but closely related definition (Bronsted – Lowry) is that an acid is a substance that supplies protons and a base is proton acceptor. According to Lewis acid is electron pair donor and base acts as electron pair acceptor.

| Theory         | Acid                    | Base                     |
|----------------|-------------------------|--------------------------|
| Arrhenius      | H <sup>+</sup> Producer | OH <sup>-</sup> producer |
| Bronsted-Lowry | H <sup>+</sup> donor    | H <sup>+</sup> acceptor  |
| Lewis          | Electron pair acceptor  | Electron pair donor      |

### 3.3.1: Arrhenius Concept of Acids and Bases:

The Swedish chemist Svante Arrhenius published his theory of acids and bases in 1887. It can be simply explained by these two points:

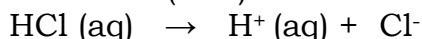
1. An acid is a substance which dissociates in water to produce one or more hydrogen ions (H<sup>+</sup>).
2. A base is a substance which dissociates in water to produce one or more hydroxide ions (OH<sup>-</sup>).

Based on this definition, you can see that Arrhenius acids must be soluble in water. Arrhenius acid-base reactions can be summarised with three generic equations:



(An acid will dissociate in water producing hydrogen ions)

Examples: 1. Hydrochloric acid (HCl), dissociates in water to yield the required hydrogen ions (H<sup>+</sup>) and also chloride ions (Cl<sup>-</sup>).



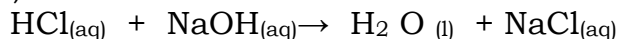
(A base (usually containing a metal) will dissociate in water to produce hydroxide ions).

Examples: 2. Sodium hydroxide dissociate in water to produce sodium ion (Na<sup>+</sup>) and hydroxide ion (OH<sup>-</sup>).



(Acids and bases will neutralize each other when mixed. They produce water and an ionic salt, neither of which are acidic or basic.).

Example.3: The Arrhenius theory simple explains many properties and reactions of acids and bases. For instance, mixing hydrochloric acid (HCl) with sodium hydroxide (NaOH) results in a neutral solution containing table salt (NaCl) and water.



However, the Arrhenius theory is not without flaws. There are many well known bases, such as ammonia (NH<sub>3</sub>) that do not contain the hydroxide ion. Further more, acid-base reactions are observed in solutions that do not contain water.

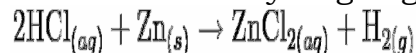
#### Limitations of the Arrhenius theory:

1. The theory defined an acid or a base in terms of hydrogen or hydroxyl compounds only.
2. It offered no satisfactory explanation for the acid property of various substances such as AlCl<sub>3</sub>, NH<sub>4</sub> NO<sub>3</sub> etc.
3. A bare proton cannot exist in solution.
4. The theory does not include non-aqueous solvents.
5. Arrhenius's ideas had to be extended as several substances are capable of releasing hydrogen ions by reacting with water, though they themselves do not contain hydrogen, e.g., SO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, Cl<sub>2</sub>O<sub>7</sub> etc. Similarly, there are compounds which may form OH<sup>-</sup> ions on their reaction with water. e.g. Na<sub>2</sub>O, K<sub>2</sub>O, etc.

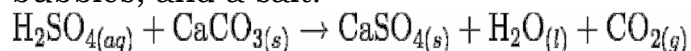
In spite of the objections, Arrhenius theory is still unrivalled in its simplicity and is found adequate for an elementary approach.

### 3.3.2: Neutralization:

Acids and bases react with one another to yield two products: water and an ionic compound known as a *salt*. This kind of reaction is called a *neutralization* reaction. For example 1: Acids react with metal to produce a metal salt and hydrogen gas bubbles.



For example: 2 Acids react with metal carbonates to produce water, CO<sub>2</sub> gas bubbles, and a salt.



This is a double displacement reaction. These reactions are both exothermic; although they involve different acids and bases. It has been determined experimentally that they all liberate the same amount of heat (57.7 kJ) per mole of H<sup>+</sup> neutralized. This implies that all neutralization reactions are really the one net reaction.

### Strong and Weak Acids/Bases

A **strong acid** is an acid which dissociates completely in water. That is, *all* the acid molecules break up into ions and solvate (attach) to water molecules. Therefore, the concentration of hydronium ions in a strong acid solution is equal to the concentration of the acid.

The majority of acids exist as **weak acids**, an acid which dissociates only partially. On average, only about 1% of a weak acid solution dissociates in water in a 0.1 mol/L solution. Therefore, the concentration of hydronium ions in a weak acid solution is always less than the concentration of the dissolved acid.

**Strong base** react with water to give 100% yield of hydroxides ions. **Weak base** gives only small yields of hydroxides ion..The strength of the binary acids increases from left to right across a period of the periodic table (Examples CH<sub>4</sub>, < NH<sub>3</sub><H<sub>2</sub>O) and they increase down a group of the table (Examples HF< HCl< HBr< HI).

This explains why, in all of the above example reactions, the reverse chemical reaction does not occur. The stronger acid/base will prevail, and the weaker one will not contribute to the overall acidity/basicity. For example, hydrochloric acid is strong, and upon dissociation chloride ions are formed. Chloride ions are a weak base, but the solution is not basic because the acidity of HCl is overwhelmingly stronger than basicity of Cl<sup>-</sup>. Although the other halogens make strong acids, **hydrofluoric acid** (HF) is a weak acid.

| Formula                        | Strong Acid      |
|--------------------------------|------------------|
| HClO <sub>4</sub>              | Perchloric acid  |
| HNO <sub>3</sub>               | Nitric acid      |
| H <sub>2</sub> SO <sub>4</sub> | Sulfuric acid    |
| HCl, HBr, HI                   | Hydrohalic acids |

Within a series of *oxyacids*, the ions with the greatest number of oxygen molecules are the strongest. For example, nitric acid (HNO<sub>3</sub>) is strong, but nitrous acid (HNO<sub>2</sub>) is weak. Perchloric acid (HClO<sub>4</sub>) is stronger than chloric acid (HClO<sub>3</sub>), which is stronger than the weak chlorous acid (HClO<sub>2</sub>). Hypochlorous acid (HClO) is the weakest of the four.

Common strong bases are the hydroxides of Group 1 and mostly Group 2 metals. For example, potassium hydroxide and calcium hydroxide are some of the strongest bases. You can assume that any other bases (including ammonia and ammonium hydroxide) are weak.

### 3.3.3: Bronsted – Lowry concept of Acids and Bases:

A general definition of acids and bases was given independently by Bronsted and Lowry in 1923. According to this concept an acid is defined as a compound or ion which gives a proton and a base is a compound or ion which accepts a proton from an acid. (Or) According to the Bronsted-Lowry theory of acids and bases, an acid is a substance that gives away protons (H<sup>+</sup>), and is therefore called a proton donor. A base is a substance that takes up protons, and is therefore called a proton acceptor. A proton may be donated by molecular acids Examples: HCl, H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>COOH, H<sub>2</sub>S and H<sub>2</sub>O. Potons also donated by either cations or anions.

**a)** Anions that exhibits acidic behavior.

Examples : HSO<sub>4</sub><sup>-</sup> H<sub>2</sub>PO<sub>4</sub><sup>-</sup> HPO<sub>4</sub><sup>2-</sup> and HS<sup>-</sup>

**b)** Cations also exhibit acidic behavior.

Examples : [Cu (H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> and [Fe(H<sub>2</sub>O)]<sup>3+</sup>

**c)** A proton may be accepted by molecular bases. Examples: H<sub>2</sub>O and NH<sub>3</sub>.

**d)** Anions that exhibits basic behavior.

Examples: OH<sup>-</sup> , HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, F<sup>-</sup> and NO<sub>3</sub><sup>-</sup>

**e)** Cations that exhibits basic behavior.

Examples: [Fe(H<sub>2</sub>O)<sub>5</sub> OH]<sup>2+</sup> and [Cu (H<sub>2</sub>O)<sub>3</sub> OH]<sup>+</sup>

**f)** The most familiar bases are ionic compounds.

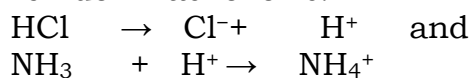
Examples: NaOH, KOH and Ca (OH)<sub>2</sub>.

### The Brownsted Lowry definition applies to protonic systems;

A general equation expressing proton transfer in aqueous solutions is:

**Examples: 1** HCl<sub>(g)</sub> + NH<sub>3(g)</sub> → NH<sub>4</sub><sup>+</sup> + Cl<sup>-</sup>

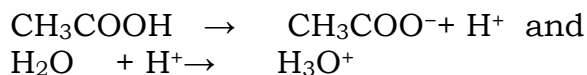
In order to decide which substance is a proton donor and which is a proton acceptor, we need to look at what happens to each reactant. The above reaction can be broken down as follows.



From the above reactions, it is clear that HCl is a proton donor and is therefore an acid, and that NH<sub>3</sub> is a proton acceptor and is therefore a base.

**Examples: 2** CH<sub>3</sub>COOH + H<sub>2</sub>O → H<sub>3</sub>O<sup>+</sup> + CH<sub>3</sub>COO<sup>-</sup>

The reaction can be broken down as follows:



Some substances act as acids or bases when they are dissolved in solvents other than water, such as liquid ammonia. In the Brønsted-Lowry theory, water H<sub>2</sub>O, can be considered an acid or a base since it can lose a proton to form a hydroxide ion, OH<sup>-</sup>, or accept a proton to form a hydronium ion, H<sub>3</sub>O<sup>+</sup> (see amphoterism).

When an acid loses a proton, the remaining species can be a proton acceptor and is called the **conjugate base** of the acid. The conjugate base is a base because it can pick up a proton (reform the acid).

| <b>Examples:Acid</b>           |   | <b>proton</b>  |   | <b>conjugate base</b>            |
|--------------------------------|---|----------------|---|----------------------------------|
| HCl                            | → | H <sup>+</sup> | + | Cl <sup>-</sup>                  |
| H <sub>2</sub> SO <sub>4</sub> | → | H <sup>+</sup> | + | HSO <sub>4</sub> <sup>-</sup>    |
| CH <sub>3</sub> COOH           | → | H <sup>+</sup> | + | CH <sub>3</sub> COO <sup>-</sup> |
| H <sub>2</sub> S               | → | H <sup>+</sup> | + | HS <sup>-</sup>                  |
| H <sub>2</sub> O               | → | H <sup>+</sup> | + | OH <sup>-</sup>                  |
| NH <sub>4</sub> <sup>+</sup>   | → | H <sup>+</sup> | + | NH <sub>3</sub>                  |

When a base accepts a proton, it forms conjugate **acid** of the base. The conjugate acid is an acid because it can give up a proton (reform the base).

| <b>Examples:Base</b>          |   | <b>proton</b>  |   | <b>conjugate acid</b>         |
|-------------------------------|---|----------------|---|-------------------------------|
| H <sub>2</sub> O              | + | H <sup>+</sup> | → | H <sub>3</sub> O <sup>+</sup> |
| NH <sub>3</sub>               | + | H <sup>+</sup> | → | NH <sub>4</sub> <sup>+</sup>  |
| OH <sup>-</sup>               | + | H <sup>+</sup> | → | H <sub>2</sub> O              |
| S <sub>2</sub> <sup>-</sup>   | + | H <sup>+</sup> | → | H <sub>2</sub> S,             |
| CO <sub>3</sub> <sup>2-</sup> | + | H <sup>+</sup> | → | HCO <sub>3</sub> <sup>-</sup> |
| F <sup>-</sup>                | + | H <sup>+</sup> | → | HF                            |

In all of these below acid base reactions the forward reaction is the transfer of a proton from acid<sub>1</sub> to base<sub>2</sub>. The reverse reaction is the transfer of a proton from acid<sub>2</sub> to base<sub>1</sub>. In these all reaction base<sub>1</sub> and base<sub>2</sub> are in competition for the proton. In all the examples given a table base<sub>2</sub> is the stronger base.

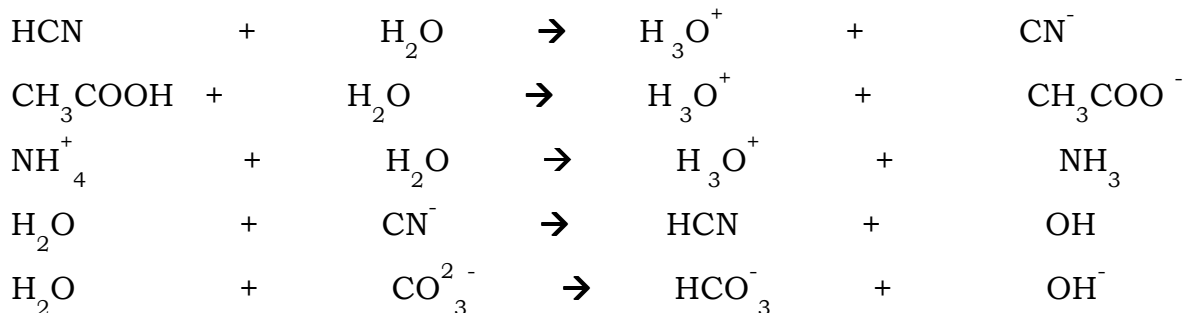
|                   |   |                   |   |                   |   |                   |
|-------------------|---|-------------------|---|-------------------|---|-------------------|
| HA                | + | B                 | → | BH <sup>+</sup>   | + | A <sup>-</sup>    |
| Conjugate         |   | Conjugate         |   | Conjugate         |   | Conjugate         |
| Acid <sub>1</sub> |   | Base <sub>2</sub> |   | Acid <sub>2</sub> |   | Base <sub>1</sub> |



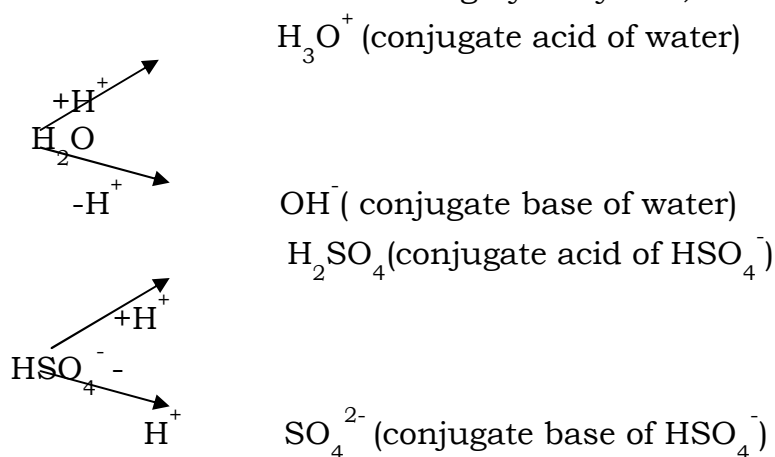
This concept is illustrated for a series of common acids and bases.

| <b>Acid<sub>1</sub></b>        |   | <b>Base<sub>2</sub></b> |   | <b>Acid<sub>2</sub></b>       |   | <b>Base<sub>1</sub></b>       |
|--------------------------------|---|-------------------------|---|-------------------------------|---|-------------------------------|
| HCl                            | + | H <sub>2</sub> O        | → | H <sub>3</sub> O <sup>+</sup> | + | Cl <sup>-</sup>               |
| HNO <sub>3</sub>               | + | H <sub>2</sub> O        | → | H <sub>3</sub> O <sup>+</sup> | + | NO <sub>3</sub> <sup>-</sup>  |
| HClO <sub>4</sub>              | + | H <sub>2</sub> O        | → | H <sub>3</sub> O <sup>+</sup> | + | ClO <sub>4</sub> <sup>-</sup> |
| H <sub>2</sub> SO <sub>4</sub> | + | H <sub>2</sub> O        | → | H <sub>3</sub> O <sup>+</sup> | + | HSO <sub>4</sub> <sup>-</sup> |
| H <sub>2</sub> S               | + | H <sub>2</sub> O        | → | H <sub>3</sub> O <sup>+</sup> | + | HS <sup>-</sup>               |





In general, stronger the acid, the weaker is its conjugate base; conversely stronger the base, the weaker is its conjugate acid. Actually no acid surrenders its proton unless it comes in contact with another substance (may be the solvent) of higher proton affinity acting as a base. Thus a base accepts a proton from a water molecule releasing hydroxyl ion,



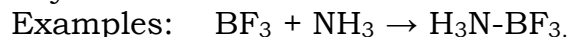
### 3.3.4: The Lewis Concept of Acids and Bases:

Another theory that provides a very broad definition of acids and bases has been put forth by the American chemist Gilbert Lewis.

The Lewis theory defines an acid as a compound that can accept a pair of electrons and a base as a compound that can donate a pair of electrons. (OR)

According to the Lewis theory definition a Lewis acid is an electron pair acceptor. Lewis base is an electron pair donor.

Examples: Boron tri fluoride ( $\text{BF}_3$ ) can be considered a Lewis acid and ethyl alcohol can be considered a Lewis base.



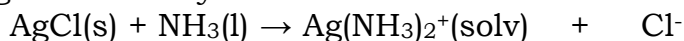
The above following reaction shows general application of the model. The boron atom in boron trifluoride ( $\text{BF}_3$ ) has only six electrons in its valence shell. Usually,  $\text{BF}_3$  is a very good Lewis acid and reacts with Lewis bases. Fluoride ion acts as the Lewis base in this reaction. In this reaction  $\text{NH}_3$  acts as Lewis acid and donating an electron pair to electron poor  $\text{BF}_3$ .  $\text{H}_3\text{N}-\text{BF}_3$  is a Lewis acid base complex, and the bond from N to B is called a coordinate covalent bond, but it really should not be distinguished from any covalent bond.

Lewis acids and bases react to create an **adduct**, a compound in which the acid and base have bonded by sharing the electron pair. Lewis acid or base reactions are different from redox reactions because there is no change in oxidation state.

Example 2: Two ammonia molecules (Lewis bases) each donate a pair of electrons to a silver ion, in this reaction ammonia molecules acts as Lewis bases and silver ion acts as the Lewis acid.

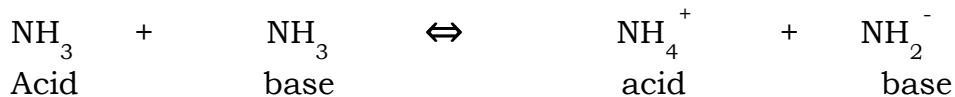


Metal cations (Lewis acids) can form complexes with Lewis bases called coordination complexes. For example silver ion  $\text{Ag}^+$  forms a complex in liquid ammonia.  $\text{AgCl}$  is actually soluble in ammonia.



### 3.4: Solvent –System concept

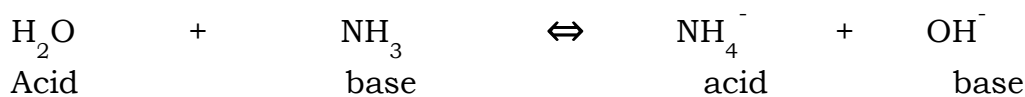
The Lowry-Bronsted concept of acid-base phenomenon is much broader than the one provided by Arrhenius. In this concept the acid-base behavior is neither restricted to nor dependent upon any particular solvent. In fact the Bronsted concept applies to many of the solvents that contain hydrogen. Liquid ammonia is another solvent most widely studied. Ammonia like water produces charges bearing particles as:



#### Compare



When water is added in liquid ammonia



Water becomes a weak acid. The acid properties of ammonia are much less known; when chlorine dissolves in ammonia



From the above reactions it is clear that when a substance acts as an acid or a base it acts in such a way as to furnish a particular type of ion characteristic of the solvent.

Earlier the solvent-system concept is proposed by Franklin in 1935. According to the Franklin definition of an acid:

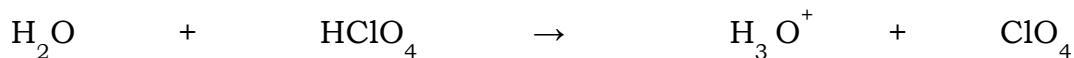
**Acid** : a *species* that increases the concentration of the characteristic cation of the solvent. **Base**: a species that increases the concentration of the characteristic anion. The usefulness of this concept is primarily in terms of convenience. One may treat nonaqueous solvents by analogy with each other. For example:

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = 10^{-14}$$

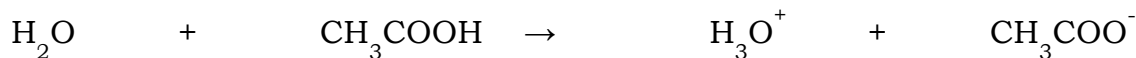
$$K_{AB} = \frac{[A^+][B^-]}{[AB]}$$

Where  $[A^+]$  and  $[B^-]$  are the concentrations of the cationic and anionic species characteristic of a particular solvent. Similarly, pH scale of water may be constructed with the neutral point equal to  $-1/2\log K_{AB}$ . The “levelling” effect follows quite naturally from this viewpoint. All acids and bases stronger than the characteristic cation and anion of the solvent respectively will be “levelled” to the latter; acids and bases weaker than those of the solvent system will remain in equilibrium with them. This solvent system has been used extensively as a method of classifying solvolysis reactions.

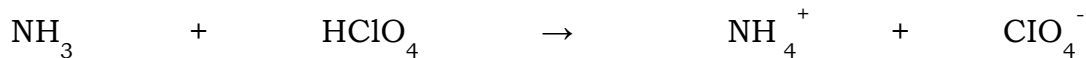
For example



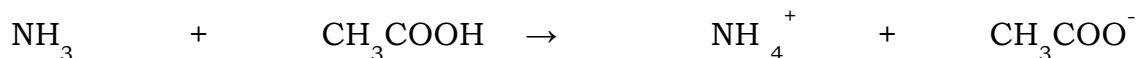
but



Similarly



And



but



### Revision Questions:

1. What is the taste of Acids?
2. What is the taste of Bases?
3. What is the pH range for acids and bases?
4. Define pH?
5. What is Arrhenius theory?
6. Give an example for strong acid and strong base according to Arrhenius theory?
7. Give an example for acid and base according to Bronsted lowry theory?
8. What is Bronsted-Lowry acid-base theory?
9. Give an example for conjugate acid and conjugate base according to Bronsted-lowry acid-base theory?
10. What is Lewis concept of acids and bases?
11. Give an example for acid and base according to Lewis concept of acids and bases?

**Chapter.4**  
**ATOMIC STRUCTURE.**

**Contents**

|     |                             |
|-----|-----------------------------|
| 4.0 | Atomic structure            |
| 4.1 | The Bohr's Model of an Atom |
| 4.2 | Quantum Numbers             |
| 4.3 | Atomic Spectrum of Hydrogen |

#### 4.1 The Bohr's Model of an Atom:

Danish scientist Neil Bohr proposed one new concept for behavior of matter in 1913. Bohr's theory explains the spectra of hydrogen atom and of hydrogen like ions led to its general concepts. Usually, the hydrogen or hydrogen like atoms contains only one electron moving about a nucleus.

According to this theory the energy of an electron in an atom cannot vary or move continuously, but it is quantized, that is restricted to distinct values. The Bohr's model of hydrogen atom or hydrogen like ion assumed that the single electron moved about the nucleus by an electrostatic attraction between the nucleus and the electron.

The energies of the electron were assumed to be restricted to certain values, each of which corresponds to an orbit with different radius. Each of these orbits could be characterised by an integer '**n**'. The integer n is called a quantum Number. Bohr suggested that the energy of an electron of these orbits is given by the equation.

$$E = \frac{-kZ^2}{n^2}$$

Where K is constant ( $2.179 \times 10^{-18}$  J)      Z= atomic number

n is integer characteristic of the orbit (n=1,2,3,...)

The distance of the electron from the nucleus is also related to the value of **n**.

$$\text{Radius of orbit} = \frac{n^2 a_0}{Z}$$

Where **a<sub>0</sub>** is the radius of the orbit in the hydrogen atom for which n=1 (0.529A<sup>0</sup>)

Where one A<sup>0</sup> =  $10^{-10}$ m or 100 pm.

According to this model, the closest electron in a hydrogen atom can get to the nucleus is 0.529 A<sup>0</sup> (in one orbit with n=1). Thus the electron cannot fall in to the nucleus. Because we must add energy to an electron to move it into an orbit with a large **n** value, as the electron moves away from the nucleus, its energy becomes higher. As the electron moves closer to the nucleus, it loses energy and its energy becomes lower. (more negative).

Thus the Bohr's model of the hydrogen atom (or hydrogen like ions postulates) A single electron that moves in circular orbits about the nucleus. When the electron is in this lowest energy orbit, the atom is said to be in **groundstate**. If the atom picks up energy from an outside source, it changes to an **excited state** as the electron moves to one of the higher energy orbits. Finally Bohr concluded that electron has discrete energies that are identified by n.

If we know the quantum number **n** of the electron in a hydrogen atom, we can easily evaluate the energy of the electron or the size of the orbit that it occupies. But some times letters (K, L, M, N, O, and P) are used to distinguish electrons. when we speak of K electron, we mean an electron with n=1. An L electron is an electron with n=2; an M electron with n=3;etc.

### Main Postulates of Bohr's Atomic Theory are:

Electrons move around the nucleus in circular path, which are known as **orbits** or **energy level**. (Fig no.1 shows the orbital's energy levels). If an electron jumps from lower energy level to a higher energy level, **it absorbs a definite amount of energy**. (Fig no.2 shows electron jumps lower to high).

If an electron jumps from higher energy level to a lower energy level, **it loses definite amount of energy**. (Fig no.3 shows electron jumps higher to lower). Energy released or absorbed by an electron is equal to the difference of energy of two energy levels. Let an electron jumps from a higher energy level  $E_2$  to a lower energy level  $E_1$ . The energy is emitted in the form of light. Amount of energy released is given by:

$$\Delta E = E_2 - E_1$$

$$E_2 - E_1 = h\nu$$

Where  $h$  = Planck's constant (  $6.6256 \times 10^{-34}$  j.s)

$\nu$  = Frequency of radiant light.

Spectrum of light emitted from an electron is a "**line spectrum**".

Angular momentum of an electron is given by:

$$m v r = nh / 2 \pi$$

Where  $n = 1, 2, 3, \dots$

$m$  = mass of electron

$v$  = velocity of electron

$r$  = radius of orbit

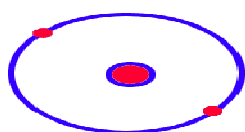


Fig No.1

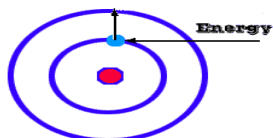


Fig No.2

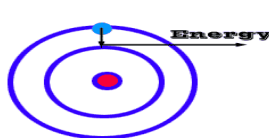


Fig No.3

### Limitations of Bohr's Model:

- Unable to explain the spectrum of atoms other than hydrogen, For example, helium atom which possesses only two electrons.
- Unable to explain multi-electron atoms.
- Unable to explain the splitting of spectral lines.
- It could not explain the ability of atoms to form molecules by chemical bonds. Does not predict fine structure of atomic spectral lines.
- Does not provide a method to calculate relative intensities of spectral lines. Predicts the wrong value of angular momentum for the electron in the atom

### 4.2: Quantum Numbers:

Each of the orbitals is characterized by a series of numbers called **quantum numbers**. The integer  $n$  is called a quantum number. Some times quantum number letters (K,L,M,N,O,P) are used to **distinguish electrons**. For example when we speak of a K electron, we mean an electron with  $n=1$ ; An L electron is a with  $n=2$ ; if an m electron with  $n=3$ ; etc. Quantum numbers are very important because of they can determine various properties Of the atoms.

They are

1. Electron properties of the atom
2. Shape of the orbitals
3. Size of the orbitals
4. Orientation of the orbital
5. Orbital's electronic configuration
6. Ionization energy
7. Atomic radius

Quantum numbers designate specific levels, sub shells, orbitals and spin of electrons. According to the previous theories suggested that four types of quantum numbers are very important.

**They are:**

- a) Principal quantum number (n).
- b) Angular momentum quantum numbers (l)
- c) Magnetic quantum number (m)
- d) Electron spin quantum number (ms)

**a).Principal quantum Number:**

The principal quantum number determines the size **and energy of the orbital**. The energy levels in an atom are arranged roughly into **main levels or shells**. The principal quantum numbers is **denoted by (n)** and Orbitals are characterised by n such as n=1, n=2, n=3...etc.,

Shells may be identified by either the values of Quantum number **(n) or letters of K, L, M, N, O, and P...respectively**. Some times the shell with n=1 is referred to as the K shell. The principal quantum numbers (n) has **integral values** like 1, 2, 3, 4...etc If n increases the orbital becomes larger and the electron spend more time further from the nucleus. If increase n also means higher energy, because the electron is less tightly bound to the nucleus and the energy is less negative.

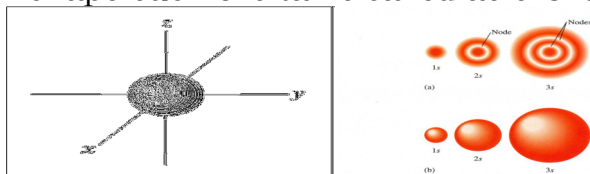
|              |   |   |   |   |   |   |   |
|--------------|---|---|---|---|---|---|---|
| <b>Shell</b> | K | L | M | N | O | P | Q |
| <b>n</b>     | 1 | 2 | 3 | 4 | 5 | 6 | 7 |

**a) Angular Momentum Quantum Number.**

According to the wave mechanics each main shell is composed of one or more **sub shells or sub levels**. Azimuthal quantum number (l) also called as angular momentum quantum number. The azimuthal quantum number or angular momentum quantum number is denoted by **(l)**. The azimuthal quantum number determines the **shape of an orbital and angular distribution to certain degree and its energy**.

Angular momentum quantum number( l) has integral values from 0,1,2,3,4...etc

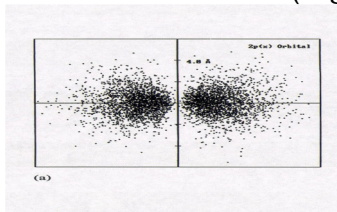
The different shapes of orbitals have different **angular distribution to certain degree and its energy**. An electron  $l=0$  occupies a spherical orbital shape such orbital is called as **s-orbital**. (Fig no.1 shows spherical shape).



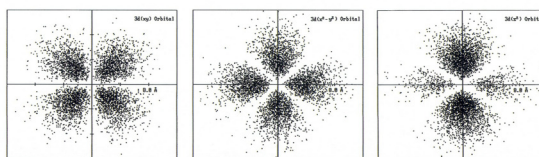
**Fig No.1**

If the electron  $l=1$  occupies a **dumbbell –shaped region of space**. Such orbital is called p **orbitals**. For example the dumbbell shape of a p orbital can be oriented in three ways along with the x,y and z axis of an xyz coordinates system (Fig no.2 shows dumbbell- shape of space.)

If the electron  $l=2$  occupies a volume of space usually has **clover leaf shape** with four lobes. (Fig no.3 shows clover leaf- shaped of space.)

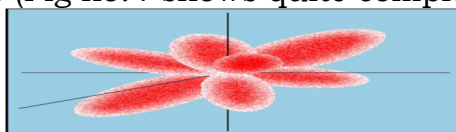


**Fig no.2**



**Fig no.3**

If the electron  $l=3$  occupies a rather complex – looking e a volume of space usually shown **eight lobes**. (Fig no.4 shows quite complex shaped of space.)



**Fig No.4**

The quantum number is related to the shape of orbitals. The value of  $l$  is assigned for particular letters like  $l=0$  is called as **S orbital**. If  $l=1$  is called as **P orbital**; If  $l= 2$  is called as **d orbital**. If  $l=3$  is called as **f orbital**.

#### **b) Magnetic Quantum Number:**

Each sub shell is composed of one or more orbitals. The magnetic quantum number ( $m$ ) determines the **number of orbitals and their orientation within a sub shell**. The magnetic quantum number is denoted by ( $|m|$ ). Magnetic quantum number has integral values between  $-l, 0$  and  $+l$  or  $-l, 0, +l$ . When  $l=0$  only one value of  $m$  is permitted  $m=0$ . (Fig no 1 shows one spherical shape) If  $l=1$  p sub shells contains three orbitals such as  $-1, 0, +1$ . (Fig no 2 shows three) orbitals.



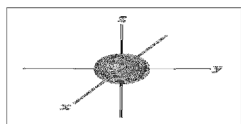


Fig no.1

If  $l=2$  d subshells contains five orbitals orientations such as  $-2,-1,0,+1,+2$ . (Fig no 3 shows five orbitals).

Fig no.2

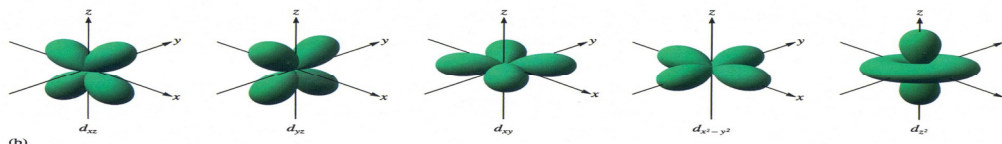


Fig no.3

If  $l=3$  f subshells contains seven orbitals orientations such as  $-3,-2,-1,0,+1,+2,+3$ . (Fig no 4 shows seven orbitals).

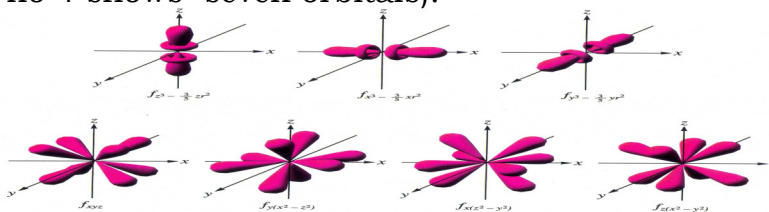


Fig no.4

### c) Spin Quantum Number:

This quantum number arises because the electron behaves as if it were spinning. The spin quantum number is denoted by **(ms)**. The electron has a magnetic moment with two possible orientations like when the atom placed in external magnetic field. In presence of magnetic field, the electron producing two oppositely charged orientations like clockwise or anti clockwise. and is designated arbitrarily by either . . (Fig no 1 and fig no.2 shows clockwise direction and anti clock wise direction). The spin quantum number specifies the direction of spin of an electron about its own axis. The spin can be either counter clockwise or clockwise Fig No.1 and Fig no.2



It designates the direction of the electron spin and may have a spin of  $+1/2$ , represented by  $\uparrow$ , or  $-1/2$ , represented by  $\downarrow$ . This means that when  $m_s$  is positive the electron has an upward spin direction, which can be referred to as "spin up." When it is negative, the electron has a downward spin direction, so it is "spin down."

### 4.3. Atomic Spectrum of Hydrogen:

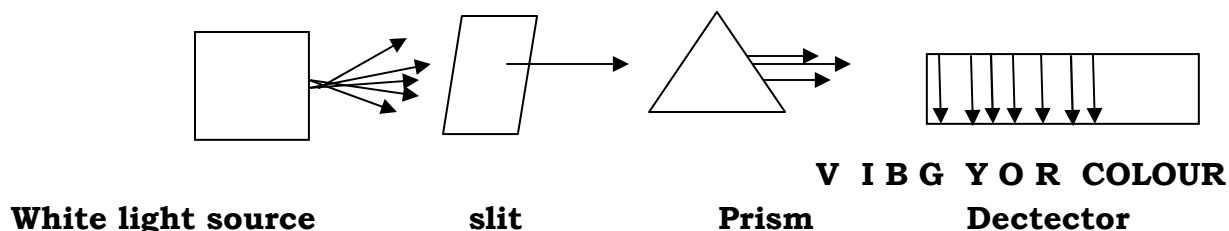
The structure of atom came from several experiments carried out in early twentieth century, in particular

1. Thomson's discovery of electrons
2. Rutherford's discovery of nucleus

Another important experiment was the study of **emission of light by excited hydrogen atoms**.

When a sample of hydrogen gas receives a high energy spark (or) radiation, the H<sub>2</sub> molecules **absorb** energy and some of the H---H bonds are **broken**. The resulting **hydrogen atoms are excited**; that is they contain excess of energy, which they release by **emitting light of various wavelengths**. That is also called the **emission spectrum of the hydrogen atom**.

When white light is passed through a prism. This spectrum like rainbow produced when sunlight is dispersed by raindrops, contains all the **wavelength of visible light** like **VIBGYOR** colour.



When the hydrogen emission spectrum in the visible region is passed through a prism, we see only few wavelenths (or) few lines. Each line contains particular wavelength. The hydrogen emission spectrum is called a **line spectrum**. Line spectrum table 1.0 indicates that only certain energies are allowed for the electron in the hydrogen atom. In other words the energy of the electron in the hydrogen atom is quantized. This observation ties in perfectly matches or ties with the postulates of max planck.

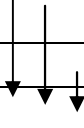
Where **h** is planks constant ( $6.626 \times 10^{-34}$ )  
 C = valocity,

$\lambda$  = wavelength,

$\nu$  = the frequency of the radiation.

However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state (E<sub>2</sub>) to lower stationary state (E<sub>1</sub>). The energy change does not take place in a continuous manner.

**Table.1:** The spectral lines for atomic hydrogen Various energy levels in the hydrogen atom

|                            |   |
|----------------------------|---|
| Infrared wavelength        | n=8   |
| Infrared wavelength        | n=7   |
| Infrared wavelength        | n=6   |
| Infrared wavelength        | n=5   |
| Infrared wavelength        | n=4   |
| Visiblewavelength(nm)      | n=3   |
|                            |  |
|                            |   |
| Ultraviolet wavelength(nm) | n=2   |

n=1

### Revision Questions:

1. According to the Bohr's concept what is the energy of Electron?
2. What is an Orbit or Energy level?
3. When does the Electron absorbs definite amount of Energy?
4. Write one limitation of Bohr's model?
5. What is the significance of Principal Quantum number?
6. What is the significance of Angular momentum Quantum number?
7. What is the significance of Magnetic Quantum number?
8. What is the significance of Spin Quantum number?
9. Who discovered the Electron and Nucleus?
10. What are the colors present in the Rainbow?
11. What is Line spectrum of Hydrogen atom?

## **Chapter.5**

### **CHEMICAL BONDING**

#### **Contents**

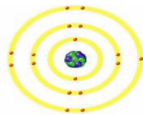
|       |  |
|-------|--|
| 5.0   | Introduction to Bonding:                               |
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## 5.0: Introduction to Bonding:

The forces that hold atoms together in compounds are called chemical bonds. Chemical bonding is one of the most basic fundamentals of chemistry that explains other concepts such as molecules and reactions. Without it, scientists wouldn't be able to explain why atoms are attracted to each other or how products are formed after a chemical reaction has taken place. In common atom contains electrons and nucleus is composed of protons and neutrons, in this Chapter, the main focus will be on electrons.

Elements are distinguished from each other due to their "electron cloud," or the area where electrons move around the nucleus of an atom. Because each element has a distinct electron cloud, this determines their chemical properties as well as the extent of their reactivity (i.e. noble gases are inert/not reactive while alkaline metals are highly reactive).

In chemical bonding, only valence electrons, electrons located in the orbitals of the outermost energy level (valence shell) of an element, are involved. A bond is the interaction between two or more atoms that allows them to form a substance different from the independent atoms. This interaction involves the outer electrons of the atoms. These electrons are transferred from one atom to another or shared between them. Bonds may be between atoms of different elements to make a compound, like the two hydrogen atoms and one oxygen atom in a water molecule. But bonds can also be between atoms of a single element.



This model shows how a chlorine atom's 17 electrons are arranged in energy levels.

All known elements do not exist in free nature due to their reactivity with various reagents. Only few elements which are placed in last group of periodic table has completely filled octet configuration and also termed as noble gases.

All other elements have tendency to attain octet configuration by formation of compounds. Electrons, especially those of the outermost valence electronic shell, play a fundamental role in chemical Bonding. In some cases chemical bonds results from the transfer of one or more electrons from one atom to another. This leads to the formation of positive and negative ions. The transfer or sharing of electrons occurs to the extent that each atom involved acquires an especially stable electron configuration. Often this configuration is that of a noble gas ( $ns^2np^6$ ), that is, involving eight outer-shell electrons called an octet. However, bonds may hold hundreds or thousands of atoms together to form a large molecule like insulin or DNA.

### 5.1 : Types of Bonds:

When different elements (different types of atom) react and combine to form a compound (new substance) chemical bonds are formed to keep the atoms together. Once these atoms are joined together it's usually difficult to separate them. Bonding produces new substances and usually involves only the 'outer shell' or 'valence' electrons and atoms can bond in two ways.

- a) Electrons are transferred from one atom to another atom
- b) Mutual sharing of electrons between atoms.

There are many types of chemical bonds and forces acting together to bind molecules together. The three most basic types of bonds are characterized as either:

- a) Ionic bonds
- b) Covalent bonds
- c) Metallic bonds

#### a) Ionic bond:

Ionic bonds are formed when electrons are transferred from one atom to another atom. Ionic bonds require at least one electron donor and one electron acceptor. Positive ions and negative ions form when atoms lose or gain electrons. Or, they can **transfer or accept electrons** to form positive and negative ions and form an **ionic bond**.

#### b) Covalent Bond:

Covalent compounds are formed when atoms of elements share electrons. The atoms can join together by **sharing electrons** and is known as a **covalent bond**

#### c) Metallic bond:

Metals form another kind of bond by sharing electrons called a metallic bond. Metallic bonds form by the attraction of metal ions and the electrons around them. Atoms of metals are held together by metallic bonds.

Metals form another kind of bond in sharing electrons called a **metallic bond**. The transfer or sharing of electrons occurs to the extent that each atom involved acquires an especially stable electron configuration. Often this configuration is that of a noble gas ( $ns^2np^6$ ), that is, involving eight outer-shell electrons called an octet

#### 5.1.1 Ionic bond: (chemical bonding by electron transfer)

Ionic bonds form when electrons are transferred from one atom to another atom [one atom loses electrons and another atom gains them]. An ionic bond usually occurs between a metal and a non-metal

The atom that loses electrons becomes a positive ion (cation) while the atom that accepted electrons becomes negatively charged (anion). When metals combine with non metals electrons are transferred from the metals to non metals and ionic compounds are formed. The best known ionic compound common examples: NaCl, Ag Cl etc This table salt formed from when neutral chlorine and sodium react. An electron is transferred from a sodium atom to a chlorine atom. If one electron is lost neutral sodium atom has 10 electrons with +1 charge. It has become a positive ion. A positive ion is called cation. the process can be represented as:



If an electron is added to chlorine the 18 electrons produces a net 1- charge. The chlorine has become an ion with a negative charge – an anion. The chloride ion is written as  $\text{Cl}^-$  and the process is represented as





According to the shared pair of electrons, covalent bond is classified as:

- a) Single bond
- b) Double bond
- c) Triple bond
- d) Coordinate covalent bond

A single shared pair of electrons is called a **single bond**. Example:  $H_2$  and  $Cl_2$ . A pair of atoms may share more than one pair of electrons is called as **double bond**. For example two pairs of electrons are shared between the two  $O_2$  molecules and carbon dioxide  $CO_2$  ( $O=C=O$ ). Carbon and Oxygen atoms  $CH_2O$  (formaldehyde) and between the two carbon atoms in  $C_2H_4$  (ethylene) giving rise in both cases to a double bond.

Example:  $O=O$  “**Double bond**”

A pair of atoms may share three pair of electrons is called triple **bond**. Example:  $NN$  “**Triple bond**”. Examples as in  $CO$  (Carbon monoxide) and  $N_2$  (Nitrogen molecule) a triple bond is formed. Some times phosphours, selenium, sulfur forms double bonds with carbon, nitrogen and oxygen.

**Polyatomic Atoms:** Ions such as  $OH^-$  and  $H_3O^+$  that are composed of one or more than one atom are called **polyatomic ions**. The atoms in a polyatomic ion are held together by covalent bond. Thus compounds containg polyatomic ions are stabilized by both covalent and ionic bonds. For example. Potassium nitrate  $KNO_3$  contains the  $K^+$  and the polyatomic  $NO_3^-$  anion. It has the an ionic bond resulting from the electrostatic attraction between the ions  $K^+$  and  $NO_3^-$  and covalent bonds between the nitrogen and oxygen atoms in  $NO_3^-$

### 5.1.3: Coordinate Covalent or Dative bond.

An atom like the boron atom in  $BCl_3$  which does not have a filled valence shell, is very reactive. It readily combines with a molecule containing an atom with unshared pair of electrons. The unshared pair is shared by both atoms when the bond forms. For example  $NH_3$  reacts with  $BCl_3$  to form the compound  $BCl_3NH_3$ . Because the unshared pair on nitrogen can be shared with the born atom.

A bond like the one between the boron and nitrogen atoms formed when one of the atoms provides both bonding electrons is called coordinate covalent or dative bond. Coordinated bond can also occur with ions, when water molecules combine with a hydrogen ion to form a hydronium ion or when an ammonia molecule combines with a hydrogen ion to form an ammonium ion.

The formation of a coordinate covalent bond is only possible between an atom or ion with an unshared pair of electrons in its valence shell and an atom or ion that needs a pair of electrons to acquire a more stable configuration. The difference between the coordinate covalent bond and normal covalent bond in the mode of formation---- that as whether each atom contributes one electron or one atom contribute both. Once established, covalent bonds are indistinguishable from one other. For example. All the  $O---H$  bonds in  $H_3O^+$  are the same as are the  $N---H$  bonds in  $NH_4^+$



If the molecule has positive end and negative end it is said to be polar and to possess a dipole. Polar molecules contain polar covalent bonds, in a molecule of hydrogen chloride for example the hydrogen atom has positively charged end and chlorine has negatively charged end of the molecule.

Polar molecules are attracted towards electrically charged objects, non-polar molecules are not. Polar covalent bonds are sometimes found in non-polar molecules. Example  $\text{HgCl}_2$  is non-polar, but it contains polar covalent bonds.

Each chlorine atom is negative with respect to positively charged mercury atom. So each mercury-chlorine bond is polar. Polar covalent bonds have positively charged end and a negatively charged end. Such a bond results when a covalent bond is formed between atoms of different electronegativities, because the shared pair of electrons stays closer to the more electronegative atom. For example, chlorine atom in a hydrogen chloride molecule attracts the pair of electrons of the covalent bond more strongly than does the hydrogen atom. The hydrogen-chlorine bond is polar with the chlorine atom somewhat negative and the hydrogen atom somewhat positive.

### **5.2.: Valence Shell Electron Pair Repulsion (VSEPR) Theory:**

Valence shell electron pair repulsion theory normally abbreviated to VSEPR theory. The concept of VSEPR theory was developed by Sedgwick and Powell in 1940. The name VSEPR suggests only valence shell electrons (ns and np) are involved in determining the shape of a molecule. This VSEPR theory is based on the **atoms valence shell electron pairs repulsion**. The approximate shape of the covalent molecule is predicted by valence shell electron pair repulsion theory.

#### **The main postulates of VSEPR theory are as follows:**

The **shape of a molecule** depends upon the number of **valence shell electron pairs** (bond pairs and lone pairs or non-bonded) around the central atom. In molecules, the atoms are held together by pairs of electrons, these are called **bonding pairs**. Some times molecules may have electron pairs that are not involved in bonding. These are called **lone pairs**. The lone pairs are also called as non-bonded pairs. Usually, electron pairs are negatively charged, they repel each other. In molecules, electron pairs tend to occupy such positions in space that minimize repulsion and thus maximize distance between them or increase the bond angle.

According to this theory a multiple bond is treated as **single super pair**. If a molecule represents two or more structures the VSEPR model is successfully applicable.

#### **The repulsive interaction of electron pairs decrease in the order:**

Lone pair (lp) – Lone pair (lp) > Lone pair (lp) - Bond pair (bp) > Bond pair (bp) – Bond pair (bp)

Again the VSEPR model was developed by Nyholm and Gillespie in 1957. Nyholm and Gillespie VSEPR theory was explained one important **difference between the lone pairs and bonding pairs of electrons**. According to this theory **the lone pairs are localized** on the central atom and each bonded pair is shared **between two atoms**. In molecules, the lone pair


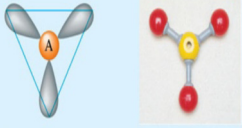

electrons occupy more space as compared to the bonding pairs of electrons. These results in greater repulsion between lone pairs of electrons as compared to the lone pair – bond pair and bond pair - bond pair repulsions. These repulsion effects result in **deviations from idealized shapes** and alterations in bond angles in molecules. For the prediction of geometrical shapes of molecules. With the help of VSEPR theory, it is convenient to divide molecules into two categories as

- a) Molecules in which the central atom has no lone pair and
- b) Molecules in which the central atom has one or more lone pairs.

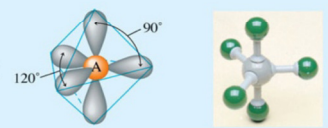
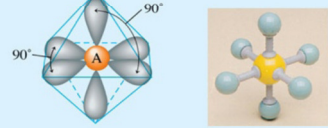
The table below 1.0 and 2.0 shows the arrangement of electron pairs about a central atom A (without any lone pairs) and geometries of some molecules/ions of the type AB.

**Table 1.0 Table 2.0**

**TABLE 13.8** Arrangements of Electron Pairs Around an Atom Yielding Minimum Repulsion

| Number of Electron Pairs | Arrangement of Electron Pairs | Example   |
|--------------------------|-------------------------------|---|
| 2                        | Linear                        |    |
| 3                        | Trigonal planar               |   |
| 4                        | Tetrahedral                   |  |

**TABLE 13.8** Arrangements of Electron Pairs Around an Atom Yielding Minimum Repulsion

| Number of Electron Pairs | Arrangement of Electron Pairs | Example  |
|--------------------------|-------------------------------|--|
| 5                        | Trigonal bipyramidal          |   |
| 6                        | Octahedral                    |  |

The above tables shows shapes of some simple molecules and ions in which the central atom has one or more lone pairs. Tables explains the reasons for the distortions in the geometry of the molecule. As depicted in Table 1.0, in the compounds of AB<sub>2</sub>, AB<sub>3</sub>, AB<sub>4</sub>, AB<sub>5</sub> and AB<sub>6</sub>, the arrangement of electron pairs and the B atoms around the central atom A are: **linear, trigonal planar, tetrahedral, trigonal bipyramidal and octahedral**, respectively. Such arrangement can be seen in the molecules like BF<sub>3</sub> (AB<sub>3</sub>), CH<sub>4</sub> (AB<sub>4</sub>) and PCl<sub>5</sub> (AB<sub>5</sub>) as depicted below by their ball and stick models.

The VSEPR Theory is able to predict geometry of a large number of molecules, especially the compounds of *p*-block elements accurately. It is also quite successful in determining the geometry quite-accurately even when the energy difference between possible structures is very small. The theoretical basis of the VSEPR theory regarding the effects of electron pair repulsions on molecular shapes is not clear and continues to be a subject of doubt and discussion.

### 5. 3: Valence Bond Theory

The concept of structure of the molecules proposed by Lewis approach fails to explain the formation of chemical bond. Lewis theory is unable to explain shapes of polyatomic molecules

Lewis theory is unable to explain shapes of formation of chemical bond. Lewis theory is unable to explain bond dissociation enthalpies and bond lengths. Simple molecules like  $H_2$  (435.8 kJ mol<sup>-1</sup>, 74 pm) and  $F_2$  (155 kJ mol<sup>-1</sup>, 144 pm), although in both the cases a single covalent bond is formed by the sharing of an electron pair between the respective atoms. Similarly the VSEPR theory gives the geometry of simple molecules but theoretically, it does not explain them and also it has limited applications. To overcome these limitations the two important theories based on quantum mechanical principles were introduced.

These are

1. Valence bond (VB) Theory
2. Molecular orbital (MO) Theory.

The concept of valence bond theory was introduced by **Heitler and London** in 1927 and developed further by Pauling and others. The valence bond theory is based on the knowledge of following postulates

They are

- a) Atomic orbitals
- b) Electronic configurations of elements
- c) The overlap criteria of atomic orbitals
- d) The hybridization of atomic orbitals and the principles of variation and superimposition.

Valence bond theory has been discussed in terms of qualitative and non-mathematical treatment only.

#### **For example: Hydrogen ( $H_2$ ) molecule:**

The formation of hydrogen molecule which is the simplest of all molecules. Consider two hydrogen atoms A and B approaching each other having nuclei  $N_A$  and  $N_B$  and electrons present in them are represented by  $e_A$  and  $e_B$ . When the two atoms are at large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate.

#### **Attractive forces arise between:**

1. Nucleus of one atom and its own electron that is  $N_A - e_A$  and  $N_B - e_B$ .
2. Nucleus of one atom and electron of other atom i.e.,  $N_A - e_B$ ,  $N_B - e_A$ .

#### **Similarly repulsive forces arise between**

- a) Electrons of two atoms like  $e_A - e_B$ ,
- b) Nuclei of two atoms  $N_A - N_B$ .

Attractive forces (fig 2.0) tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart.

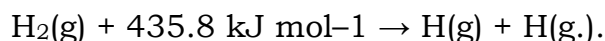
Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms approach each other and potential energy decreases.

Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy.

At this stage two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm.

Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as **bond enthalpy**, which is corresponding to minimum in the curve depicted in Fig. 4.8.

Conversely, 435.8 kJ of energy is required to dissociate one mole of H<sub>2</sub> molecule.



### Orbital Overlap Concept:

In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called **overlapping of atomic orbitals** which results in the pairing of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed between two atoms. Therefore, according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present in the valence shell having opposite spins.

The covalent bond is formed by overlapping of atomic orbitals. The molecule of hydrogen is formed due to the overlap of 1s-orbitals of two H atoms. In case of polyatomic molecules like CH<sub>4</sub>, NH<sub>3</sub> and H<sub>2</sub>O, the geometry of the molecules is also important in addition to the bond formation. The valence bond theory explains the shape, the formation and directional properties of bonds in polyatomic molecules like CH<sub>4</sub>, NH<sub>3</sub> and H<sub>2</sub>O, etc. in terms of overlap and hybridisation of atomic orbitals.

### Overlapping of Atomic Orbitals

When orbitals of two atoms come close to form bond, their overlap may be positive, negative or zero depending upon **the sign (phase) and direction of orientation of amplitude of orbital wave function in space**.

Orbitals forming bond should have same sign (phase) and orientation in space. This is called **positive overlap**. Various overlaps of s and p orbitals are depicted in below.

The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the **homonuclear or heteronuclear diatomic molecules and polyatomic molecules**.

### Types of Overlapping and Nature of Covalent Bonds

The covalent bond may be classified into two types depending upon the types of overlapping:

**They are**

- (i) Sigma( $\sigma$ ) bond
- (ii) Pi ( $\pi$ ) bond.

### **Sigma ( $\sigma$ ) bond:**

This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis. This is called as **head on overlap or axial overlap**. This can be formed by any one of the following types of combinations of atomic orbitals.

#### **s-s overlapping :**

In this case, there is overlap of two half filled s-orbitals along the internuclear axis as shown below



#### **s-p overlapping:**

This type of overlap occurs between half filled s-orbitals of one atom and half filled p-orbitals of another atom.



#### **p-p overlapping:**

This type of overlap takes place between half filled p-orbitals of the two approaching atoms.



### **Pi ( $\pi$ ) bond:**

In the formation of  $\pi$  bond the atomic orbitals overlap in such a way that their axes remain **parallel to each other and perpendicular to the internuclear axis**. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.

#### **Strength of Sigma and pi Bonds**

Basically the strength of a bond depends upon the extent of overlapping. In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that in the formation of multiple bonds between two atoms of a molecule, pi bond(s) is formed in addition to a sigma bond.

#### **Hybridisation:**

The concept of the hybridisation is proposed by **Pauling**. In order to explain the characteristic geometrical shapes of polyatomic molecules like  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$  etc., According to him the atomic orbitals combine to form new set of equivalent orbitals and shapes known as **Hybrid orbitals**.

Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as **Hybridisation** which can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape. For example when one 2s and three 2p-orbitals of carbon hybridise, there is the formation of four new  $sp^3$  hybrid orbitals.

#### **Salient Features of Hybridisation:**

The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised. The hybridised orbitals are always equivalent in energy and shape. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

#### **Important Conditions for Hybridisation**

- a) The orbitals present in the valence shell of the atom are hybridised
- b) The orbitals undergoing hybridisation should have almost equal energy
- c) Promotion of electron is not essential condition prior to hybridisation
- d) It is not necessary that only half filled orbitals participate in hybridisation
- e) In some cases, even filled orbitals of valence shell take part in hybridisation

#### **Types of Hybridisation:**

Depending on the involvement of atomic orbitals like s, p, d, f, the hybridisation is classified as various types

They are :

1.  $sp$ - hybridisation
2.  $sp^2$  hybridisation
3.  $sp^3$  hybridisation

#### **a) SP hybridisation:**

This type of hybridisation involves the mixing of one s and one p orbital resulting in the formation of two equivalent sp hybrid orbitals. Each sp hybrid orbital has 50% s-character and 50% p-character. Such a molecule in which the central atom is sp-hybridised and linked directly to two other central atoms possesses linear geometry.

This type of hybridisation is also known as **diagonal hybridisation**. The two sp hybrids point in the opposite direction along the z-axis with projecting positive lobes and very small negative lobes, which provides more effective overlapping resulting in the formation of stronger bonds.

Example of molecule having sp hybridisation **BeCl<sub>2</sub>**: The ground state electronic configuration of Be is  $1s^2 2s^2$ . In the excited state one of the 2s-electrons is promoted to vacant 2p orbital to account for its bivalency. One 2s and one 2p-orbital gets hybridised to form two sp hybridised orbitals. These two sp hybrid orbitals are oriented in opposite direction forming an angle of

180°. Each of the sp hybridised orbital overlaps with the 2p-orbital of chlorine axially and form two Be-Cl sigma bonds. This is shown in Fig. 4.0.

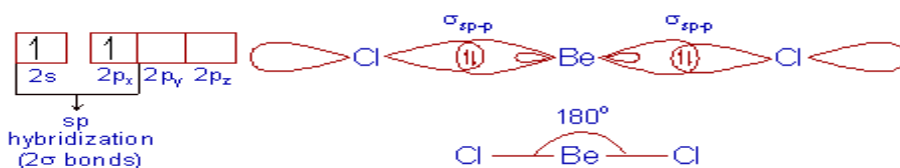


Fig.4.0 (a) Formation of sp hybrid orbitals from s and p orbitals;  
 (b) Formation of the linear BeCl<sub>2</sub> molecule

**(b). sp<sup>2</sup> hybridisation :**

In this hybridisation there is involvement of one s and two p-orbitals in order to form three equivalent sp<sup>2</sup> hybridised orbitals.

For example, in BCl<sub>3</sub> molecule, the ground state electronic configuration of central boron atom is 1s<sup>2</sup>2s<sup>2</sup>2p<sup>1</sup>. In the excited state, one of the 2s electrons is promoted to vacant 2p orbital as a result boron has three unpaired electrons.

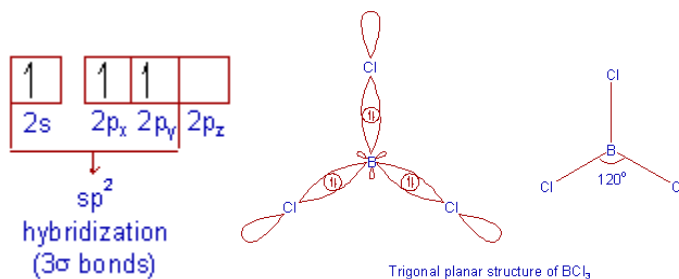
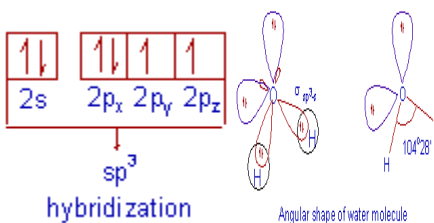


Fig.5.0: Formation of sp<sup>2</sup> hybrids and the BCl<sub>3</sub> molecule

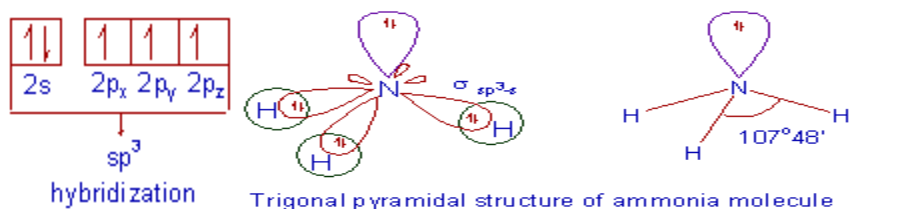
These three orbitals (one 2s and two 2p) hybridise to form three sp<sup>2</sup> hybrid orbitals. The three hybrid orbitals so formed are oriented in a trigonal planar arrangement and overlap with 2p orbitals of chlorine to form three B-Cl bonds. Therefore, in BCl<sub>3</sub> (Fig. 5.0), the geometry is trigonal planar with Cl-B-Cl bond angle of 120°.

**sp<sup>3</sup> hybridisation:**

This type of hybridisation involves the mixing of one s and three p orbitals resulting in the formation of four equivalent sp<sup>3</sup> hybrid orbitals. This type of hybridization can be explained by taking the example of CH<sub>4</sub> molecule in which there is mixing of one s-orbital and three p-orbitals of the valence shell to form four sp<sup>3</sup> hybrid orbitals of equivalent energies and shape. There is 25% s-character and 75% p-character in each sp<sup>3</sup> hybrid orbital. The four sp<sup>3</sup> hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between sp<sup>3</sup> hybrid orbitals is 109.5° as shown in Fig. 6.0.



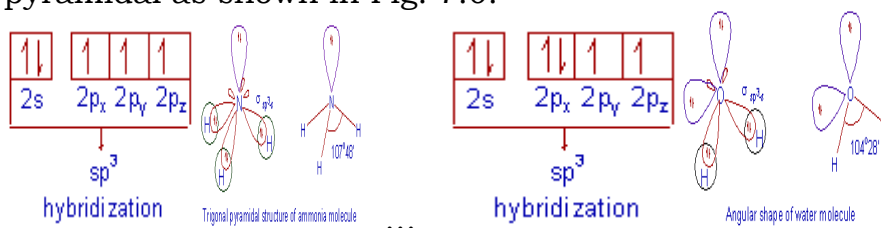
**Fig No.6**



**Fig No 7.0.**

Formation of  $sp^3$  hybrids by the combination of s,  $p_x$ ,  $p_y$  and  $p_z$  atomic orbitals of carbon and the formation of  $CH_4$  molecule. The structure of  $NH_3$  and  $H_2O$  molecules can also be explained with the help of  $sp^3$  hybridisation. In  $NH_3$ , the valence shell (outer) electronic configuration of nitrogen in the ground state is  $2s^2 2p^3$  having three unpaired electrons in the  $sp^3$  hybrid orbitals and a lone pair of electrons is present in the fourth one.

These three hybrid orbitals overlap with  $1s$  orbitals of hydrogen atoms to form three N–H sigma bonds. We know that the force of repulsion between a lone pair and a bond pair is more than the force of repulsion between two bond pairs of electrons. The molecule thus gets distorted and the bond angle is reduced to  $107^\circ$  from  $109.5^\circ$ . The geometry of such a molecule will be pyramidal as shown in Fig. 7.0.



**Fig. 7.0 Formation of  $NH_3$  molecule      Fig.8.0 Formation of  $H_2O$  molecule.**

In case of  $H_2O$  molecule, the four oxygen orbitals (one  $2s$  and three  $2p$ ) undergo  $sp^3$  hybridisation forming four  $sp^3$  hybrid orbitals out of which two contain one electron each and the other two contain a pair of electrons. These four  $sp^3$  hybrid orbitals acquire a tetrahedral geometry, with two corners occupied by hydrogen atoms while the other two by the lone pairs. The bond angle in this case is reduced to  $104.5^\circ$  from  $109.5^\circ$  (Fig. 4.14) and the molecule thus acquires a V-shape or angular geometry.

**Limitations of Valence Bond Theory:**

Valence Bond theory predicts bond strengths, bond lengths, and bond rigidity better than Lewis theory. Other properties, such as the magnetic



behavior of O<sub>2</sub> molecule are not predicted well. VB theory views electrons as localized in overlapping atomic orbitals and it doesn't account for delocalisation.

#### 5. 4: Molecular Orbital Theory

Molecular orbital (MO) theory was developed by F. Hund and R.S. Mulliken in 1932.

##### The salient features of this theory are:

**Molecules:** In molecules the electrons are presented in the various molecular orbitals. **Atoms:** In atoms the electrons are presented in the various atomic orbitals. The atomic orbital's of comparable energies and proper symmetry combine to form molecular orbitals.

**Atoms:** While an electron in an atomic orbital is influenced by one nucleus, **Molecules:** in a molecular orbital electrons influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus, an atomic orbital is monocentric while a molecular orbital is polycentric. The number of molecular orbital formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed.

##### They are

1. Bonding molecular orbital
2. Anti bonding molecular orbital

The bonding molecular orbital has lower energy and hence greater stability. The anti bonding molecular orbital has higher energy and hence lower stability. Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital. The molecular orbitals like atomic orbitals are filled in accordance with the Aufbau principle obeying the Pauli's exclusion principle and the Hund's rule.

##### 5. 4.1: Linear combination of Atomic Orbitals (LCAO)

According to wave mechanics, the atomic orbitals can be expressed by wave **function ( $\psi$ )**, which represent the amplitude of the **electron waves**. These are obtained from the solution of Schrödinger wave equation. However, since it cannot be solved for any system containing more than one electron, molecular orbitals which one electron wave functions are for molecules are difficult to obtain directly from the solution of Schrödinger wave equation. To overcome this problem, an approximate method known as **linear combination of atomic orbitals (LCAO) has been adopted**.

Let us apply this method to the homo **nuclear diatomic hydrogen molecule**. Consider the hydrogen molecule consisting of two atoms A and B. Each hydrogen atom in the ground state has one electron in 1s orbital. The atomic orbitals of these atoms may be represented by the wave functions  $\psi_A$  and  $\psi_B$ . **Mathematically**, the formation of molecular orbitals may be described by the linear combination of atomic orbitals that can take place **by addition and by subtraction** of wave functions of individual atomic orbitals as shown below:

$$\psi_{MO} = \psi_A + \psi_B$$

Therefore, the two molecular orbitals  $\sigma$  and  $\sigma^*$  are formed as:

$$\begin{aligned}\sigma &= \psi_A + \psi_B \\ \sigma^* &= \psi_A - \psi_B\end{aligned}$$

The molecular orbital  $\sigma$  formed by the addition of atomic orbitals is called the **bonding molecular orbital** while the molecular orbital  $\sigma^*$  formed by the subtraction of atomic orbital is called **antibonding molecular orbital**

**Qualitatively**, the formation of molecular orbitals can be understood in terms of the **constructive or destructive interference** of the electron waves of the combining atoms.

In the formation of bonding molecular orbital, the two electron waves of the bonding atoms reinforce each other due to constructive interference while in the formation of antibonding molecular orbital, the electron waves cancel each other due to destructive interference.

As a result, the electron density in a bonding molecular orbital is located between the nuclei of the bonded atoms because of which the repulsion between the nuclei is very less while in case of an antibonding molecular orbital, most of the electron density is located away from the space between the nuclei. Infact, there is a nodal plane (on which the electron density is zero) between the nuclei and hence the repulsion between the nuclei is high.

Electrons placed in a bonding molecular orbital tend to hold the nuclei together and stabilize a molecule. Therefore, a bonding molecular orbital always possesses lower energy than either of the atomic orbitals that have combined to form it.

In contrast, the electrons placed in the antibonding molecular orbital destabilize the molecule. This is because the mutual repulsion of the electrons in this orbital is more than the attraction between the electrons and the nuclei, which causes a net increase in energy.

#### **5.2.4.2: Rules for linear combination of atomic orbitals (LCAO)**

The linear combination of atomic orbitals to form molecular orbitals takes place only if the following conditions are satisfied:

**They are :**

- 1. The combining atomic orbitals must have the same or nearly the same energy.**

This means that 1s orbital can combine with another 1s orbital but not with 2s orbital because the energy of 2s orbital is appreciably higher than that of 1s orbital. This is not true if the atoms are very different.

- 2. The combining atomic orbitals must have the same symmetry about the molecular axis.**

It is important to note that atomic orbitals having same or nearly the same energy will not combine if they do not have the same symmetry. By convention z-axis is taken as the molecular axis. For example, 2p zorbital of one atom can combine with 2p zorbital of the other atom but not with the 2px or 2py orbitals because of their different symmetries.

**3. The combining atomic orbitals must overlap to the maximum extent.**

Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.

**Revision Questions:**

1. What is a Chemical bond?
2. What is Ionic bond ?Give an example
3. What is Covalent bond? Give an example
4. What is Metallic bond? Give an example
5. What is Coordinate covalent bond? Give an example
6. Who developed VSEPER theory?
7. What is the basic principle in VSEPER theory?
8. The VSEPR theory predicts the accurate geometry of which block elements?
9. What is Valence bond theory?
10. What is Sigma bond?
11. What is Pi bond?
12. Who proposed the concept of Hybridization?
13. What is the significance of Hybridization?
14. What is sp hybridization?
15. What is  $sp^2$  Hybridization?
16. What is  $sp^3$  Hybridization?
17. What is Molecular Orbital Theory?
18. What is LCAO?
19. What is positive overlap?

**CHAPTER.6**  
**Chemistry of Main Group Elements**

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## 6.0: Introduction

### Structural features of the periodic table.

On the basis of the modern periodic law, it consists of 18 vertical columns called **Groups** and 7 horizontal rows called **Periods**. Elements of groups 1, 2, 13 – 17 are called **Normal** or **Representative elements**. Elements of groups 3 – 11 are called **Transition elements**. The 14 elements with atomic numbers (Z) = 58 – 71 (occurring after lanthanum 57 La in the periodic table) are called **Lanthanides** or **rare earth elements** and are placed at the bottom of the periodic table.

The 14 elements with atomic numbers (Z) = 90 – 103 (occurring after actinium 89Ac in the periodic table) are called **Actinides** and are placed at the bottom of the periodic table. The Eleven elements with Z = 93 – 103 (93Np – 103Lr) which occur in the periodic table after uranium and have been prepared from it by artificial means are called **trans uranic elements**. These are all **radioactive elements**.

The elements belonging to a particular group are said to constitute a chemical family which is usually named after the name of the first element. For example, Boron family (group 13), carbon family (group 14), nitrogen family (group 15), and oxygen family (group 16).

In addition to this, some groups have typical names.

#### They are:

- a) Elements of group 1 are called **Alkali metals**
- b) Elements of group 2 are called **Alkaline earth metals**
- c) Elements of group 16 are called **Chalcogens**
- d) Elements of group 17 are called **Halogens**
- e) Elements of group 18 are called **Zero group or Noble gases**.

The long form of the periodic table contains seven periods.

#### They are :

- a) 1<sup>st</sup> period (1H, 2He) contains only two elements. This is the **shortest period**.
- b) 2<sup>nd</sup> period (3Li – 10Ne) and third period (11Na – 18Ar) contain **8 elements** each and are called **short periods**.
- c) 4<sup>th</sup> period (19K – 36Kr) and 5<sup>th</sup> period (37Rb – 54Xe) contain **18 elements** each and are called **long periods**.
- d) 6<sup>th</sup> period (55Cs – 86Rn) contains **32 elements** and is the longest period.
- e) 7<sup>th</sup> period (87Li –) is however incomplete and contains at present only **24 elements**.
- f) In yet another classification, the long form of the periodic table has been divided into four **blocks (i.e., s, p, d and f)**, depending upon the subshell to which the last electron enters.

### 6.1: Chemistry of Hydrogen:

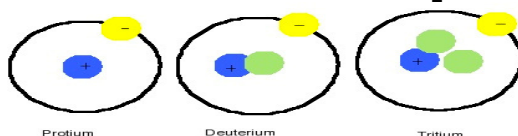
Hydrogen was first recognised as an element by the English chemist Henry Cavendish (1731-1810). In its elemental state hydrogen exists in diatomic molecules of H<sub>2</sub>.

### Physical properties of Hydrogen:

- g) Hydrogen atomic number is 1
- h) Hydrogen atomic symbol is H
- i) Hydrogen atomic weight is 1.0079
- j) Hydrogen electronic configuration:  $1s^1$
- k) Hydrogen exists two oxidation States: 1 and -1
- l) Hydrogen melting point is  $259.34^\circ\text{C}$  and its boiling point is  $252.87^\circ\text{C}$ .
- m) At room temperature: Hydrogen gas is colorless, no smell, non poisonous and tasteless
- n) Liquid hydrogen is colorless, very mobile liquid with low viscosity and surface tension.
- o) Solid hydrogen is a colorless, and crystallizes in the hexagonal close packed structure.
- p) It is insoluble in water, acids and most of the organic solvents.
- q) It enters into chemical combination with most of the elements and **hydrogen forms more compounds than** any other element like carbon nitrogen oxygen..etc.,

### Solubility of hydrogen in liquids:

Hydrogen is only **slightly soluble in liquids**, however the solubility generally increases with increasing temperature. **Protium ( $^1\text{H}$ )** is the most common isotope, consisting of 99.98% of naturally occurring hydrogen. It is a nucleus containing a single proton. **Deuterium ( $^2\text{H}$ )** is another an isotope containing a proton and neutron Commonly indicated with symbol D.  $\text{D}_2\text{O}$  is called **heavy water**, which has a higher density, melting point, and boiling point than regular water. **Tritium ( $^3\text{H}$ )** is a **radioactive isotope**. Tritium is also used in **nuclear chemical reactions** For examples: Hydrogen bombs.



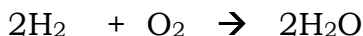
### Chemical properties

The first electron shell can be filled with maximum of two electrons. Therefore the chemistry of hydrogen depends mainly on three processes

1. Loss of the valence electron to yield the hydrogen ion  $\text{H}^+$
2. Gain of an electron to form the hydride ion  $\text{H}^-$
3. Formation of an electron pair bond

a) The most stable covalent bond are those formed between two hydrogen atoms, or with hydrogen, oxygen, carbon and nitrogen.

**Combustion:** Hydrogen is combustible and burns in air with pale blue flame.

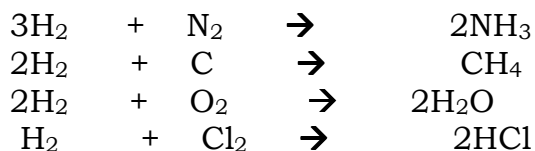


**Reducing property:** Hydrogen reduces heated metal oxides to metals.



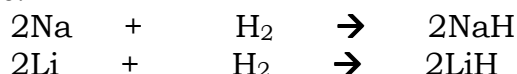
### Reaction with non-metals:

Hydrogen combines with nitrogen, carbon, oxygen and chlorine under appropriate conditions to form ammonia, methane, water and hydrogen chloride, respectively.



### Reaction with metals:

Hydrogen reacts with highly electropositive metals to form the corresponding hydrides.



### Uses

Hydrogen is used:

- For conversion of coal into synthetic petroleum.
- In the manufacture of bulk organic chemicals, particularly methanol.
- In the hydrogenation of oils. conversion of vegetable oils to vegetable ghee
- In the manufacture of ammonia, which is used in the production of fertilizers.
- As primary fuel for rockets.
- For filling balloons.

### Different process in which Hydrogen is used are: -

- ☞ Methanol synthesis.
- ☞ Water treatment.
- ☞ Methane synthesis
- ☞ Hydrogen plasma as heating agent.
- ☞ Hydro formulation of olefins
- ☞ Hydrogen in organic synthesis.
- ☞ Hydrogen in inorganic synthesis
- ☞ Hydrogen in metallurgy

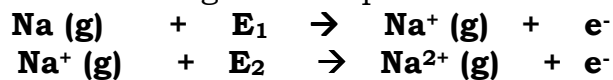
## 6.2: General properties of the elements:

### 6.2.1: Ionization Energy(IE):

**Ionization Energy** is also called as **ionization potential**. Ionization energy is denoted by **IE**. Ionisation energy is measured in  $\text{KJ mol}^{-1}$  or in kilocalories  $\text{mol}^{-1}$  or in electron volts,  $\text{eV /atom}$ . ( $1 \text{ eV /atom} = 23.06 \text{ Kcal/mol} = 96.45 \text{ KJ/mol} = 1.602 \times 10^{-19} \text{ J/atom}$ ) The amount of energy(work) required to remove an electron from the last orbit of a neutral atom or isolated (free atom) in its gaseous state is known as **ionization potential** or energy or **First ionization energy**. Second ionization energy is the amount of energy(work) required to remove an electron from the uni-positive ion is known as **Second ionization energy**.

Similarly third and fourth ionisation energies are as follows.

**For examples:** Ionisation energies are represented in following manner:



The ionization energy follows the order :

$$IE_4 > IE_3 > IE_2 > IE_1$$

### Factors affecting the values of ionization Energy:

#### Size of the atom (atomic radius):

As the size of the atom increases the outer electrons lie farther away from the nucleus and less attraction between the nucleus and the last electron, there fore, **ionisation energy decreases**.

#### Number of electrons in the inner shell (Screening effect):

The larger the number of electrons in the inner shell, the greater is the screening effect. As we move down the group, ionisation energy decreases. Increase in the **positive charge, increases ionisation energy** and increase in the negative charge decreases the ionisation energy.

#### Removal of s, p, d, and f electrons from the same shell:

Since s-orbital is more close to the nucleus its electron removal is high when compared with p, d, f, electrons. Therefore, ionization energy increases in the order  $s > p > d > f$ .

**Table 6.1:** The ionisation energy increases across the period and decreases down the group table 6.3.

| Period | Group       |             |             |             |             |             |              |              |
|--------|-------------|-------------|-------------|-------------|-------------|-------------|--------------|--------------|
|        | 1           | 2           | 13          | 14          | 15          | 16          | 17           | 18           |
| 1      | H<br>(1312) |             |             |             |             |             |              | He<br>(2372) |
| 2      | Li<br>(520) | Be<br>(900) | B<br>(800)  | C<br>(1086) | N<br>(1402) | O<br>(1314) | F<br>(1681)  | Ne<br>(2080) |
| 3      | Na<br>(496) | Mg<br>(738) | Al<br>(578) | Si<br>(787) | P<br>(1012) | S<br>(1000) | Cl<br>(1251) | Ar<br>(1521) |
| 4      | K<br>(419)  | Ca<br>(590) | Ga<br>(579) | Ge<br>(762) | As<br>(944) | Se<br>(941) | Br<br>(1140) | Kr<br>(1351) |
| 5      | Rb<br>(403) | Sr<br>(550) | In<br>(558) | Sn<br>(709) | Sb<br>(832) | Te<br>(869) | I<br>(1008)  | Xe<br>(1170) |

IONIZATION ENERGY DECREASES ↑  
 ↓ IONIZATION ENERGY INCREASES  
 ← IONIZATION ENERGY INCREASES →

### 6.2. 2: Electron Affinity:

The energy released when an extra electron is taken up by a neutral gaseous atom to form anion is called its **electron affinity**.



Electron affinity is expressed in eV/atom or KJ/mole or Kcal/mol. Electron affinity is influenced by four factors.

They are:

1. Size of an atom
2. Atomic number
3. Screening effect
4. Electronic configuration.



**a) Across a period:**

Due to the **increase in the charge the electron affinity increases across a period**. Halogens are having high electron affinity than alkali metals given in table 6.2

**b) Down the group:**

As the electrons are added up, down the group they are away from the nucleus, so electron affinity decreases in a group.

**c) Electron affinity follows the order:**

Halogens > Oxygen family > Nitrogen family > Group 1 and 13 metals > Group 14 non-metals > group 2 metals.

**Table 6.2**

| PERIOD<br>↓ | GROUP         |           |               |              |              |              |              |           |
|-------------|---------------|-----------|---------------|--------------|--------------|--------------|--------------|-----------|
| ↓           | 1             | 2         | 13            | 14           | 15           | 16           | 17           | 18        |
| 1           | H<br>(-73)    |           |               |              |              |              |              | He<br>(0) |
| 2           | Li<br>(-59.6) | Be<br>(0) | B<br>(-26.7)  | C<br>(-154)  | N<br>(-7)    | O<br>(-141)  | F<br>(-328)  | Ne<br>(0) |
| 3           | Na<br>(-53)   | Mg<br>(0) | Al<br>(-42.5) | Si<br>(-134) | P<br>(-72)   | S<br>(-200)  | Cl<br>(-349) | Ar<br>(0) |
| 4           | K<br>(-48)    | Ca<br>(0) | Ga<br>(-29)   | Ge<br>(-119) | As<br>(-78)  | Se<br>(-195) | Br<br>(-325) | Kr<br>(0) |
| 5           | Rb<br>(-47)   | Sr<br>(0) | In<br>(-28.9) | Sn<br>(-107) | Sb<br>(-103) | Te<br>(-190) | I<br>(-295)  | Xe<br>(0) |

**6.2. 3: Electro negativity:**

The tendency of an atom in a compound to attract a pair of bonded electrons towards itself is known as **electronegativity** of the atom. The electro negativity values depends on the two factors

They are :

- a) Size of the atom
- b) Electronic configuration.

Small atoms attract more electrons than the larger atoms so they are **more electronegative**. Secondly, atoms with nearly filled shells of electrons will tend to **have higher electronegativity** than those sparsely filled. Electronegativity of the main group elements are given in table 6.3.

**Across a Period:**

**Electronegativity increases** due to the increased **nuclear charge and decrease in size**. Alkali metals possess **lowest electronegativity** values. The halogens have **higher electronegativity**. The Inert gases have zero electronegativity values.

**Down the group:**

Electronegativity **decreases from top to bottom**, due to the **increase in atomic size**.

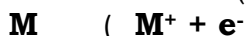
**Table 6.3**

| Period | Group     |           |           |           |           |           |           |           |
|--------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
|        | 1         | 2         | 13        | 14        | 15        | 16        | 17        | 18        |
| 1      | H<br>2.2  |           |           |           |           |           |           | He<br>—   |
| 2      | Li<br>1.0 | Be<br>1.5 | B<br>2.0  | C<br>2.5  | N<br>3.1  | O<br>3.5  | F<br>4.1  | Ne<br>—   |
| 3      | Na<br>1.0 | Mg<br>1.2 | Al<br>1.3 | Si<br>1.7 | P<br>2.1  | S<br>2.4  | Cl<br>2.8 | Ar<br>—   |
| 4      | K<br>0.9  | Ca<br>1.0 | Ga<br>1.8 | Ge<br>2.0 | As<br>2.2 | Se<br>2.5 | Br<br>2.7 | Kr<br>3.1 |
| 5      | Rb<br>0.9 | Sr<br>1.0 | In<br>1.5 | Sn<br>1.7 | Sb<br>1.8 | Te<br>2.0 | I<br>2.2  | Xe<br>2.4 |

Electronegativity Increases →

#### 6.2.4: Metallic Character:

Elements are broadly classified into metals and non metals. This classification is based on certain physical properties which are characteristics of each type. Metals are electropositive in character and have a ready tendency to lose electrons (which make them good conductors):



This reaction is closely related to the ionization energy of an element, therefore, we say that these two properties are inter-linked.

The lower the value of ionization energy of an element, the greater will be its tendency to undergo this reaction and therefore more electropositive and metallic the element is:

#### Two prominent observations are:

1. Metals exist on the left hand side and exhibit **low ionization energies**.
2. Metallic character **increases** as we go down a group.
3. Thus Cs is the most **electropositive metallic element**.
4. Elements on the right-hand side are called **non-metals**.
5. They **show ionization energies and large electron affinities** given in table 6.4.

But, these two extremes i.e., metallic and non-metallic behaviour, there are some elements which show properties that are intermediate between those metals and non-metals. They are generally called as 'Metalloids'. Ex, silicon, Arsenic.

**Table 6.4**

| Period | Group |    |    |    |    |    |    |    |
|--------|-------|----|----|----|----|----|----|----|
|        | 1     | 2  | 13 | 14 | 15 | 16 | 17 | 18 |
| 1      |       |    |    |    |    |    |    | He |
| 2      | Li    | Be | B  | C  | N  | O  | F  | Ne |
| 3      | Na    | Mg | Al | Si | P  | S  | Cl | Ar |
| 4      | K     | Ca | Ga | Ge | As | Se | Br | Kr |
| 5      | Rb    | Sr | In | Sn | Sb | Te | I  | Xe |
| 6      | Cs    | Ba | Tl | Pb | Bi | Po | At | Rn |

Metal ←
Metalloids

Non - metals

**Classification of main group elements into metal, non-metals and metalloids.**

**6.2.5 Polarizing Power and Polarizability-Fajans Rule:**

Consider making a bond theoretically by bringing two ions  $A^+$  and  $B^-$  together to their equilibrium distance. Will the bond be ionic or covalent? Ionic and covalent bonding are two extreme types of bonding, and almost always the bonds formed are intermediate in type and this is explained in terms of polarizing (that is deforming) the shape of the ions. The type of bond between  $A^+$  and  $B^-$  depends on the effect of one ion has on the other. The positive ion attracts the electrons on the negative ion and at the same time it repels the nucleus, thus distorting the polarizing power of the negative ion.

The negative ion will also distort the polarizing power of the positive ion, but since the anions are usually large, and cations small, the effect of a large ion will be much less pronounced. If the degree of polarization is large resulting in high concentration of electrons between the nuclei, a large degree of covalent character results. Generally the polarizing power increases as ions becomes smaller and more highly charged. The polarizability of a negative ion is greater than that of positive ion since the electrons are less firmly bound because of the difference in effective nuclear charge. Large negative ions are more polarizable than small ones.

**Fajan put forward the four rules**, which summarize the factors forming polarization and hence covalency.

**A small positive ion favours covalency:**

In small ions the positive charge is concentrated over a small area. This makes the ion highly polarizing and very good at distorting the negative ion.

**A large negative ion favours covalency:**

Large negative ions are highly polarizable, that is easily distorted by the positive ion, because the outermost electrons are shielded from the charge on the nucleus by filled shells of covalency.

### Large charges on either ion, or both ions favours covalency:

This is because the high charge increases the amount of polarization.

### Polarization and hence covalency is formed if the positive ion does not have a noble gas configuration:

Example of ion which does not have a noble gas configuration include a few main group elements such as  $Ti^{3+}$ ,  $Pb^{2+}$  and  $Bi^{3+}$  Many transition metal ions such as  $Ce^{3+}$ ,  $V^{3+}$ ,  $Mn^{2+}$  and  $Cu^{+}$ , and some lanthanide metal ions such as  $Ce^{3+}$  and  $Eu^{2+}$ . Noble gas configuration is the most effective at shielding the nuclear charge, so ions without the noble gas configuration will have charges at their surfaces and thus be highly polarizing.

### 6.2.6: Variable Valency:

Atoms try to achieve a stable state similar to that of the noble gases or the inert elements in their outermost orbit by accepting or donating electrons. This property is called the atom **valency**. Some elements differ in their capacity to combine with other elements depending on the **nature of the reaction** this property is called **variable valency**.

Certain elements combine with other atoms by donating, accepting or sharing electrons in different proportions depending on the **nature of the reaction**. For example, Iron combines with oxygen to form **ferrous oxide** as well as **ferric oxide**. In the formation of ferrous oxide, Iron exhibits a valency of +2 (nonmagnetic), where as in ferric oxide (magnetic), it has a valency of +3 with different properties.

This is termed **variable valency**.

**Examples:** a) Transition metals nickel, copper, tin and iron.

b) Non metals such as nitrogen and oxygen.

### 6.2.3: Diagonal relationship in the periodic table:

Elements of second period are known as bridge elements. Properties of the bridge elements resemble with the properties of the diagonal elements of the third period. The radius of  $Li^{+}$  is  $0.60A^{\circ}$  and is closer to that of  $Mg^{2+}$   $0.65A^{\circ}$ . Both  $Be^{2+}$  and  $Al^{3+}$  are small ions with radii of 0.31 and 0.35. The charge density of  $Be^{2+}$  is 6.5 is closer to that of  $Al^{3+}$  6.0 than that of  $Mg^{2+}$  3.1

|                        |    |    |    |    |   |
|------------------------|----|----|----|----|---|
| 2 <sup>nd</sup> period | Li | Be | B  | C  | N |
| 3 <sup>rd</sup> period | Na | Mg | Al | Si | P |

### Diagonal relationship between Li and Mg

- Li resembles Mg mainly due to similarity in sizes of their atoms and ions.
- The main points of similarity are:
- Both are quite hard.
- The melting points and Boiling points of lithium are comparatively high.
- Unlike Lithium, Magnesium is not affected by air.
- Both Li and Mg has great polarising power due to the reason that both has small size

- Both LiOH and Mg(OH)<sub>2</sub> are weak bases.
- Carbonates of both on heating decompose to produce oxides and carbondioxide.
- Both react with nitrogen to give ionic nitrides.
- Nitrates of both decompose on heating to give oxides.
- Both Li and Mg do not form solid bicarbonates.
- Because of covalent character LiCl and MgCl<sub>2</sub> are soluble in ethanol.
- Most of the salts, example hydroxides, bicarbonates and fluorides of both Li and Mg are sparingly soluble in water.

### Diagonal relationship between Be and Al

**Be resembles Al mainly due to similarity in sizes of their atoms and ions.**

The main points of similarity are:

- Both Be and Al has great polarising power due to the reason that both has small size
- Unlike Be, Al is not affected by air.
- Both Be and Al have same value of electronegativity 1.5
- The standard oxidation potential of Be is 1.69 V and Al is 1.7 V are of the same order.
- Both Be and Al forms strong covalent compounds. because of small size.
- Both Be and Al have low melting points, because of small size.
- Both Be and Al covalents compounds are soluble in organic solvents.
- Both Be and Al covalents compounds react slowly with dilute mineral acids.
- Both anhydrous beryllium chlorides and anhydrous aluminium chlorides covalent compounds are soluble in organic solvents.
- Both Be and Al is not easily affected by dry air.

### 6.4:The S- block elements.

#### Important points

Groups (1 & 2) belong to the **S-block** of the periodic table.

**Group 1 consists of:** Lithium, Sodium, Potassium, Rubidium, Cesium and Francium and collectively known as the **alkali metals**.

**Group 2 consists of:** Beryllium, Magnesium, Calcium, Strontium, Barium and Radium. **Except** Beryllium they are known as **alkaline** earth metals.

#### Physical properties-

##### Large atomic radii:

The atomic radii of alkali metals are the **largest** in their respective periods. These increases as we move down the group.

### Large ionic radii:

The ionic radii increases as we move down the group due to the addition of a new energy shell with each succeeding element.

### Low ionization enthalpy:

The ionization enthalpies decreases as we move down the group. The ionization enthalpies of the alkali metals are the lowest due to loosely held s-electron.

### Hydration enthalpy:

It decreases with the increase in ionic radii. The hydration enthalpy of Li ion is the maximum and the hydration enthalpy of Cs ion is the minimum.

### Oxidation state:

The alkali metals exhibit oxidation state of +1 in their compounds and are strongly electropositive in character. The electropositive character increases from Li to Cs.

### Metallic character:

The metallic character increases down the group.

### Melting point and boiling point:

The melting points(M.P) and boiling point(B.P) of **alkali metals are very low** and decrease with increase in **atomic number**.

### Nature of bonds formed:

These metals form ionic bonds. The ionic character increases as we down the group.

### Flame colouration:

All the alkali metals impart a characteristic colour to the flame.

### Photoelectric effect:

Alkali metals (except Li) exhibit photoelectric effect.

### Chemical features of alkali metals:

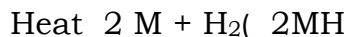
#### Reducing character:

As **the ionization enthalpies** of the alkali metals **decrease down the group** their reducing character or reactivity in the gaseous **state increases down the group**. i.e.,



#### Reaction with dry hydrogen:

Alkali metals react with dry hydrogen at about 673 K to form crystalline hydrides which are ionic in nature and have high melting points.



#### Oxides and hydroxides:

Alkali metals when burnt in air form different compounds,

**For example:** The alkali metals on reaction with limited quantity of oxygen form normal oxides ( $M_2O$ ).

M= Li, Na, K, Rb, Cs.

### Reaction with halogens:

The members of the family combine with **halogen to form** corresponding **halides** which are ionic crystalline solids. Reactivity of alkali metals with particular halogen increases from Li to Cs.

### Reaction with water:

Alkali metals react with water and other compounds containing acidic hydrogen atoms. **such as** hydrogen halides, acetylene etc. to liberate hydrogen gas.

### Solubility in liquid ammonia:

All alkali metals dissolve in **liquid ammonia giving deep blue solutions** which are conducting in nature.

### Reaction with sulphur and phosphorus:

Alkali metals react with **sulphur and phosphorus** on heating to form **sulphides and phosphides respectively**.

### Diagonal relationship between Li and Al

Li resembles Mg mainly due to similarity in sizes of their atoms and ions.

#### The main points of similarity are:

- Both are quite hard.
- Both LiOH and  $Mg(OH)_2$  are weak bases.
- Carbonates of both on heating decompose to produce oxides and carbondioxide.
- Both react with nitrogen to give ionic nitrides.
- Nitrates of both decompose on heating to give oxides.
- Both Li and Mg do not form solid bicarbonates.
- Because of covalent character LiCl and  $MgCl_2$  are soluble in ethanol.
- The hydroxides, bicarbonates and fluorides of both Li and Mg are sparingly soluble in water.

### Biological importance of Na and K

- Sodium ions participate in the transmission of nerve signals.
- Sodium ions also regulate flow of water across the cell membranes and in transport of sugars and amino acids into the cells.
- Potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in oxidation of glucose to produce ATP.
- Potassium ions in combination with sodium ions are responsible for transmission of nerve signals.

- The functional features of nerve cells depend upon the sodium potassium ion gradient that is established in the cell.

## Group 2 elements: Alkaline earth metals

### Atomic radii:

The atomic radii of **alkaline earth metals** are fairly large though smaller than the corresponding alkali metals and **increase down the group**. This is because on moving down the group, **atomic radii increase** primarily due to the addition of an extra shell of electrons in each succeeding element.

### Ionic radii:

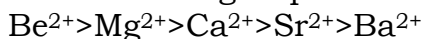
The atoms of these elements form divalent ions which show the same trend **of increase in their size down the group**.

### Ionization enthalpy:

The alkaline earth metals have fairly low **ionizations enthalpies though greater than** those of the corresponding elements of group one (1) and this value **decreases down the group**.

### Hydration enthalpy:

The hydration enthalpies of alkaline earth metal ions decreases as the size of the metal ion increases down the group.



### Oxidation State:

All the members of the family exhibit +2 oxidation state in their compound and they form divalent cations ( $\text{M}^{2+}$ )

### Electro negativity:

The electro negativity values of alkaline earth metals are quite close to those of alkali metals, though slightly more.

### Metallic Character:

Alkaline earth metals have stronger metallic bonds as compared to the alkali metals present in the same period.

### Melting and boiling point :

The Melting and Boiling points of these metals are **higher than those of alkali metals** present in the same period.

### Colouration to the flame:

With the exception of beryllium and magnesium, the rest of the elements impart characteristic colour to the flame.

### For example

| Metal ion   | Be    | Mg  | Ca      | Sr     | Ba    | Ra      |
|-------------|-------|-----|---------|--------|-------|---------|
| Flame color | Brick | Red | Crimson | Grassy | Green | Crimson |

### Complex formation:

Generally the members do not form complexes. However, smaller ions (Be & Mg ions) form complexes with the electron donor species

### Formation of organo-metallic compounds:

Both beryllium and magnesium form a number of organo-metallic compounds containing M-C bond with certain organic compounds. For



example, magnesium reacts with alkyl halide in the presence of dry ether to give Grignard reagent.

**Reducing character:**

Alkaline earth metals are weak **reducing agents** than the corresponding alkali metals which have **lower ionization enthalpies** and comparatively bigger atomic sizes.

**Reaction with oxygen:**

With the exception of Ba and Ra which form peroxides ( $\text{MO}_2$ ) rest of the metals form normal oxides (MO) on heating with excess of oxygen.

**Reaction with halogens:**

The members of the family combine directly with halogen at appropriate temperature to form corresponding halides.

**Reaction with water:**

The members of this group are less reactive towards water as compared to the corresponding alkali metals because these are less electropositive in nature.

**Reaction with hydrogen:**

The members except Be, combine with hydrogen directly upon heating to form metal hydrides.

**Uses of some important compounds:-**

**Caustic soda:**

It is used in soap, paper, textile, petroleum industry

**Sodium carbonate It is used:**

- ☞ in glass and soap industry
- ☞ in paper making and textile manufacturing
- ☞ in paint and dye stuffs
- ☞ in metal refining
- ☞ in production of sodium compounds such as borax, caustic soda, sodium phosphate etc.

**Quick lime: It is used:**

- ☞ in the preparation of cement, glass and calcium carbide.
- ☞ In the purification of sugar
- ☞ In softening of hard water
- ☞ As a flux in the extraction of metal

**Lime stone:It is used**

- ☞ as building material
- ☞ in the manufacture of quick lime
- ☞ in Solvay process to prepare  $\text{Na}_2\text{CO}_3$  as it is a source of  $\text{CO}_2$
- ☞ in metallurgy for the extraction of iron
- ☞ in toothpaste and certain cosmetics

**Cement:**

- ☞ It is an important building material.
- ☞ It is used in concrete and reinforced concrete, in plastering and in the construction of bridges, dams and buildings.

**Plaster of paris: It is used**

- ☞ in making moulds for pottery and ceramics etc.

- ☞ in surgical bandages for setting broken bones of the body
- ☞ for making statues, models, decorative materials and black board chalk.

### Biological importance of Ca and Mg

- ☞ Magnesium ions are concentrated in animal cells and Calcium ions are concentrated in body fluids, outside the cell.
- ☞ All enzymes that utilize ATP in phosphate transfer require magnesium ion as cofactor.
- ☞ In green plants magnesium is present in chlorophyll.
- ☞ Calcium and magnesium ions are also essential for the transmission of impulses along nerve fibres.
- ☞ Calcium ions are important in blood clotting and are required to trigger the contraction of muscles.
- ☞ Calcium ions also regulate the beating of the heart.

### Revision Questions:

1. According to Modern periodic table how many groups and periods are present in table?
2. What are normal or representative elements?
3. What are Transition elements?
4. What are Lanthanides?
5. What are Actinides?
6. Elements of Group 1 are called-----
7. Elements of Group 2 are called-----
8. Elements of Group 16 are called-----
9. Elements of Group 17 are called-----
10. Elements of Group 18 are called-----
11. How many elements are present in 6th period?
12. How many elements are present in 7th period?
13. Who invented Hydrogen?
14. Write the electronic configuration of Hydrogen atom
15. What are the Isotopes of Hydrogen atom?
16. What is the Radioactive Isotope of Hydrogen atom?
17. Write any two uses of Hydrogen?
18. Define Ionization potential?
19. What is the order of Ionization potential?
20. Define Electron Affinity? Mention the factors influencing the Electron Affinity?
21. Define Electro negativity?
22. Mention the factors influencing the electro negativity?
23. Why Electro negativity value decreases from top to bottom in a period?
24. What are Fajan's rules?
25. Give one example for diagonal relationship in periodic table?
26. Name the 1<sup>st</sup> Group elements
27. Name the 2<sup>nd</sup> Group elements

## **CHAPTER. 7**

### **Chemistry of Transition Elements**

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## 7.0: Introduction

All the transition elements are metals, Nowadays many of the d block metals are used as construction materials. Nine of the elements are essential for life and compounds of the d-block elements are used as catalysts, pigments and medicines. The d-block consists of the elements in group 3-12 of the periodic table. These elements are also known as the **transition metals**. f-block elements are called as **inner transition metals**. Here only the d-block elements will be considered for discussion Generally, the d-block elements become more electronegative from left to right across a period.

### **Definition of transition element:**

According to the IUPAC, whose atom has partially filled d orbitals is said to be transition element. d- block elements are classified into **four transition series**.

### **They are**

The **first transition** series: Scandium to Zinc.

The **second transition** series: Yttrium to Cadmium.

The **third transition** series: Lanthanum and Hafnium to Gold.

The **fourth transition** series: Actinium to leutacium, which is incomplete at present.

The elements in the periodic table are arranged together in blocks according to **their outer electronic configurations**.

The elements with a half-filled or fully-filled outer s orbital comprise the **s-block elements**.

Similarly, the elements with a partly filled or fully filled outer p orbitals comprise the **p-block elements**. The elements between these two blocks that is, between the groups 3 and 12 in the periodic table have at most two electrons in the outermost s orbital, and incompletely filled d-orbitals next to outermost orbital. These elements in which successive addition of electrons takes place progressively in the inner d-orbitals are called as **d- block elements**.

Similarly, the elements in which filling up of electrons takes place in inner to inner f-orbitals are known as **f-block elements**.

## **7.1: Generalphysical and chemical properties:**

### **Physical properties of transition metals:**

Transition metals have a **metallic appearance** (with the exception of copper and gold) Transition metals are **hard and have high melting points and boiling points**. (with the exception of mercury, a liquid at room temperature).

Transition metals are **highly conductors of heat and electricity**. Transition metals are **ductile** (able to be drawn into a wire) and **malleable** (able to be hammered into thin sheets). All are metals with **high tensile strength** and they **evaporate at high temperatures**. Although they are used widely as **simple substances and alloys**, All form **alloys with one another**, and with metallic main group elements. Transition metals form **paramagnetic species because** of partially filled shells.

Transition metals **form coordination compounds** or complexes and **organo metallic compounds with Lewis bases**, because of their small size, high charge and availability of low energy orbitals. Many Transition metals form **highly colored coordination** compounds. Transition metals are easily **oxidized**. Transition metals readily form ionic complexes. **For examples.1:**  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ , **Examples.2:**  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ .

Most of them show **more than one oxidation state** (variable valencies). Because of partly filled d orbitals. The Transition metals have various important properties like redox behavior, magnetic and optical properties.

### **Chemical properties of transition metals:**

Transition elements generally:

- React with **non oxidising acids to give salts** (usually metals in +2 oxidation state) and  **$\text{H}_2$  (g)**. (Fore examples: dil  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ )
- React with **oxidising acids**(conc.  $\text{H}_2\text{SO}_4$   $\text{HNO}_3$ ) **to give salts**( some times higher oxidation state) and a **gaseous reduction product of the acid**( $\text{SO}_2$  or a mixture of oxides of nitrogen).
- React with oxygen and halogens and sulphur to give a variety of oxides halides and sulphides.
- They are **not attacked by water**, but react **at higher temperature with steam** to give an oxide and  $\text{H}_2$ (g).

### **7.2.1:Melting point and boiling points**

#### **Melting point:**

The melting points of transition metals are generally high(> 1500o C) except for zinc. The melting points of s-block are generally low, especially for Group1.

All, except mercury (which is liquid at room temperature), appear as high melting point and boiling point lustrous solids. Melting point is an approximate **indication of the strength of the bonding** between particles. Strong bonding occurs in the transition metals where the **atomic radius is small and the atomic structures are closely packed**.

In the s- block metals **metallic bonding is weaker** because the atomic radius is larger. The differences is again most marked when comparing transition metals with group 1 metals which have the largest atomic radii and do not have closed packed structures.

#### **Boiling points:**

Boiling point of transition metals are generally high( 2000oC ) except for zinc again, compared to the s-block metals, which are generally low. This is for the same reason as for melting point, except boiling point is a better indication of bonding strength between particles because vapourisation separate the particles completely.

## 7.2.2: Catalytic properties:

### Definition of Catalyst.

A **catalyst** is a substance that speeds up a **chemical** reaction, but is not consumed by the reaction; hence a **catalyst** can be recovered chemically unchanged at the end of the reaction it has been used to speed up, or catalyze. Transition metals have high catalytic activity both as metals in heterogenous catalysis and as ions in homogenous catalysts in solutions. It is likely that the 3 d electrons enable the transition metal catalysts to form temporary bonds with the reaction molecules in heterogenous catalysis.

In homogenous catalysis the existence of a variety of oxidation states for each element explains how the transition metals is able to take part in a sequence of reaction stages and emerge un changed at the end. This activity is described to their ability to exhibit multiple oxidation states and to form complexes, alloys and forms transition compounds. One of the most popular example these days is the heterogeneous catalyst used in **car exhausts**. The transition metals and their compounds show catalytic activity in a variety of chemical processes.

### Some examples of catalysis in industry

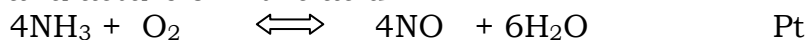
1. Haber process: Manufacture of ammonia



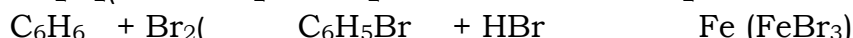
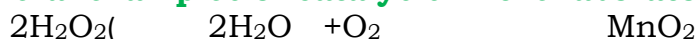
2. Contact process: Manufacture of sulphuric acid



3. Manufacture of nitric acid



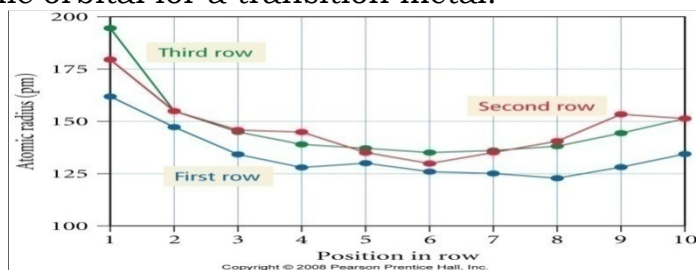
### General examples of catalysis in the laboratory



### 7.2.3: Atomic Size

In general, in a given period the atomic size of the transition metals decreases from left to right, but the change is not as significant as observed for the main-group elements.

Atomic size decreases from Sc to Mn but then levels out. In groups, the period 5 transition metals are larger than the period 4 transition metals but are the same size or only slightly smaller than the period 6 transition metals. The size of a transition metal is determined by the size of the *ns* orbital, the highest energy filled atomic orbital for a transition metal.



At the end of the transition metal group, atomic radius increases slightly due to one of the factors **electron–electron repulsion**. The general trend in size across a period is similar for all three groups of transition metals, but the trend in size moving down a group does not follow the trend of the main group elements. Although La is larger than Y, Hf and Zr are very similar in size, a trend that continues across the period. This phenomenon is called the **lanthanide contraction**, which is due to the inefficient shielding of nuclear charge by the 4f electrons.

Because the 4f electrons do not effectively shield outer (valence) electrons from the full nuclear charge, the valence electrons are more strongly attracted to the nucleus than predicted. As a result, the atomic radius for elements with a filled 4f subshell is smaller than we would predict based on periodic trends. The lanthanide contraction effectively offsets the increase in size expected when moving down a group in the periodic table.

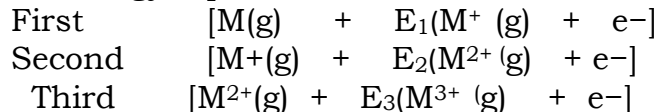
### 7.2.4: Ionization Energy

**Definition:** The amount of energy required to remove an electron from a neutral atom in the gas phase is said to be **Ionization Energy**

**Periods:** In a given period IE generally increases as we move from left to right across the periodic table, because of increasing effective nuclear charge

**Groups:** In a given group from top to down decreases, because of higher principal quantum number.

The ionization energy represents as:

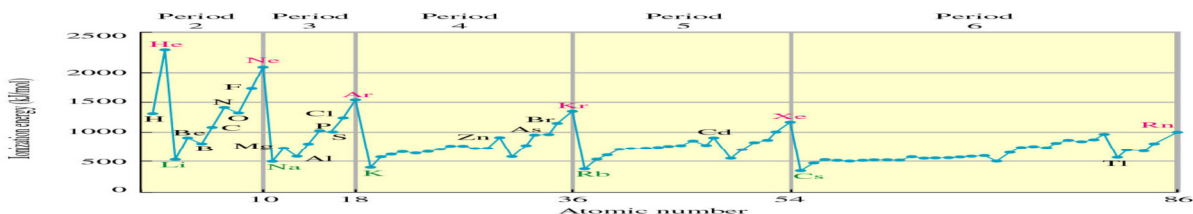


ionization energies order is

$$IE_3 > IE_2 > IE_1$$

Recall that each first-row transition metal has at least one 4s electron and one or more 3d electrons. When these elements form cations, 4s electrons are removed before 3d electrons, so the first ionization energy is the energy required to remove a 4s electron. As we described in our discussion of the trend in atomic radii, effective nuclear charge does not increase significantly from left to right in period in the transition metals, so the first ionization energies of these elements also does not increase very much.

The second ionization energy is greater than the first ionization energy, as expected, but the trend across the transition metals still shows only a slight increase.



### 7.2.5: Colour

Many transition metal ions are coloured due to the d-d transitions. The energy absorbed in excitation of an electron from a lower energy d orbital to a higher energy d orbital corresponds to the frequency which generally lies in the visible region. The colour observed corresponds to the complimentary colour of the light absorbed. The frequency of light absorbed is determined by the nature of ligand and nature of the metals.

### 7.2.6: Magnetic properties

Atoms ions and molecules with unpaired electrons are attracted to a magnet. This property is known as **Paramagnetism**. Many transition metal compounds are paramagnetic due to the presence of unpaired electrons. Any substance which is weakly attracted by a magnetic field is said to be paramagnetic while if it is repelled, is **Diamagnetic**.

A substance in which all the electrons are paired are repelled by a magnet and are said to exhibit **Ferromagnetism**. Transition elements and their ions are generally paramagnetic, whereas most others are diamagnetic. The greater the number of unpaired electrons the more paramagnetic is the ion. Paramagnetism in transition elements is associated with unpaired electrons found in their partially filled d-orbitals because there is a magnetic moment associated with the spinning electron. The magnetic moment arises with the number of unpaired electrons- and this gives a good indication of the number of unpaired electrons present in the atom or ion.

Magnetic moment of each such electron is associated with its spin angular momentum and orbital angular momentum. For these the magnetic moment is determined by the number of electrons and is calculated by using 'spin-only' formula, i.e.,

$$\mu_s = \sqrt{n(n+2)}$$

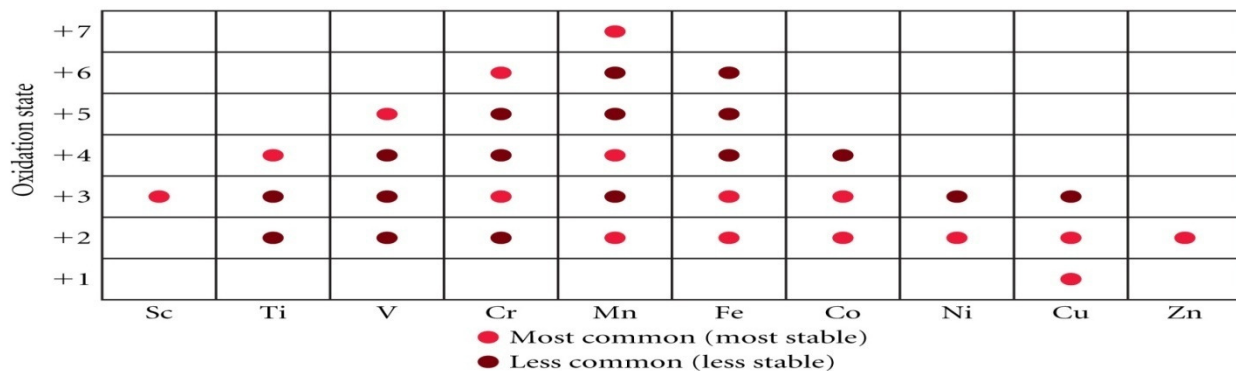
where n is the number of unpaired electrons and  $\mu_s$  is the magnetic moment in Bohr magneton (BM).

A single 1s electron has a magnetic moment of 1.73 BM (1 BM =  $9.2732 \times 10^{-24}$  A m<sup>2</sup>). The magnetic moment increases with increasing number of unpaired electrons. Thus, the observed magnetic moment value gives us useful information about the number of unpaired electrons present in the species.

### 7.2.7: Oxidation States

Most transition metals have at least two stable oxidation states. Below table shows most common and less common oxidation states.





For the Group 3B–7B elements, the maximum oxidation state is equal to the group number. In general, the maximum oxidation state for a transition metal is observed only when the metal is combined with the highly electronegative elements oxygen and fluorine. For example, manganese has an oxidation state of +7 in the permanganate ion ( $\text{MnO}_4^-$ ) and chromium has a +6 oxidation state in the chromate ion ( $\text{CrO}_4^{2-}$ ).

The high oxidation state on the metal means these ions are strong oxidizing agents. +1 up to +7 are observed, with +2 and +3 most common. As the oxidation state is increased, the *d* orbitals are stabilized, and the metals get harder to oxidize further. Ionization energies go up from left to right, following the trend in effective nuclear charge. It is obvious that the transition metals exhibit a great variety of oxidation states. The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7. Ruthenium and Osmium commonly form compounds in +8 oxidation state, which is among the highest for isolable compounds. At the other end, the only oxidation state of zinc is +2 (no *d* electrons are involved).

### Compound formation in maximum oxidation states

The highest oxidation state of an element is exhibited in its compounds with the two most electronegative and powerful oxidising elements – fluorine and oxygen. The less electronegative element, chlorine is expected to show slightly different range of oxidation states. It reveals that the transition elements towards the left can attain maximum possible oxidation states, while at the right of the series oxidation state +2 becomes dominant.

#### 7.3.1: Crystal field theory:

Valence bond theory is able to explain the bonding in complexes but this theory is unable to explain their color. This theory is unable to explain why some complexes are high-spin whereas others are low-spin. These properties are explained by crystal field theory. This model was first applied to transition metal ions in ionic crystals – hence the name crystal field theory – but it also

applies to metal complexes where the crystal field is the electric field due to the charges of the ligands.

Note the difference between crystal field theory and valence bond theory. Valence bond theory depends on various factors like covalent bonds, shared electrons, hybrid orbitals. In crystal field theory, there are no covalent bonds, no shared electrons, and no hybrid orbitals. But crystal field theory depends on just electrostatic interactions of metals of d-orbitals and ligands.

**In crystal field approach the following assumptions are made.**

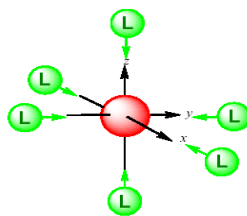
Ligands are treated as point charges. There is no interaction between metal orbitals and ligand orbitals. The d orbitals on the metal atom which were of same energy (degenerate) in an isolated atom, have their degeneracy removed by the ligands when a complex is formed. It results in splitting of d orbitals. The pattern of splitting depends on the nature of the crystal fields induced by ligands.

### **7.3.2: Octahedral complexes:**

According to the crystal field theory, the bonding is ionic and involves electrostatic attraction between the positively charged ion and negatively charged ligands. Of course the ligands repel one another, which is why they adopt the geometry (octahedral) that locates them as far apart from one another as possible. Because the metal – ligand attractions are greater than the ligand –ligand repulsions the complex is more stable than the separated ions, thus accounting for the bonding. In an isolated metal atom the five d orbitals have identical energies and are said to be **degenerate**.

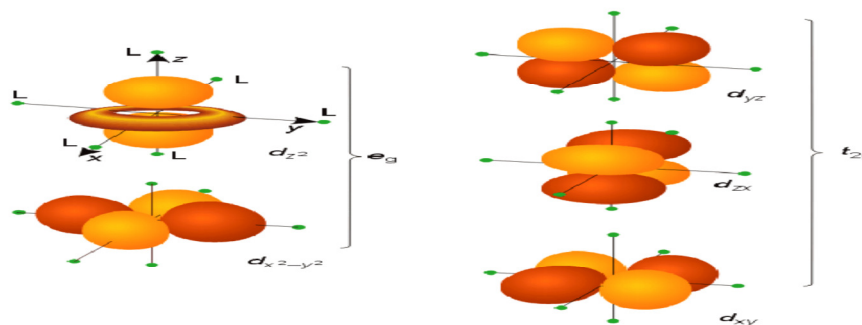
If the metal atom were surrounded by a spherical shell of negative charge, called a **spherical field**, their electrostatic interaction between this field and the d electrons electrostatic repulsion leads to all the d-orbitals increase in energy.

When spherical field is rearranged into octahedral field, none of the d-orbitals is directed exactly towards the point charges along the x-, y- z- axes at the vertices of an octahedron as shown below figure.1



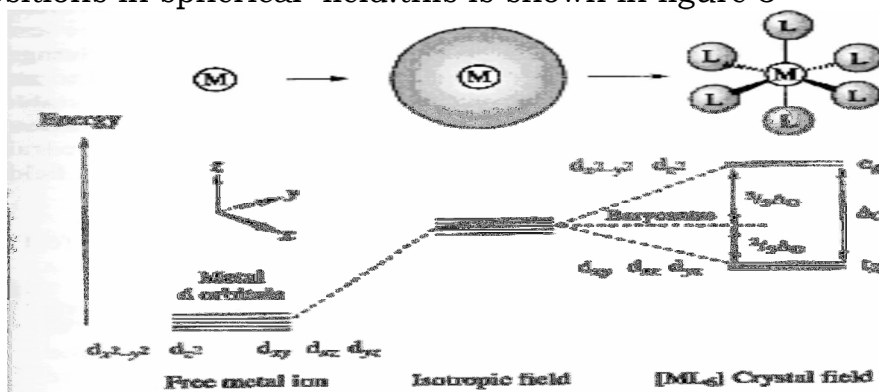
**Fig no.1 An octahedral field**

This is called octahedral field, since the total amount of charge has not altered, the average energy of the five d-orbitals is the same in the octahedral field as it was in the spherical field. The five orbitals are however, no longer of identical energy. figure 2 explains the direction of the different d orbitals.



**Fig no.2: The shapes of the five 3d-orbitals.**

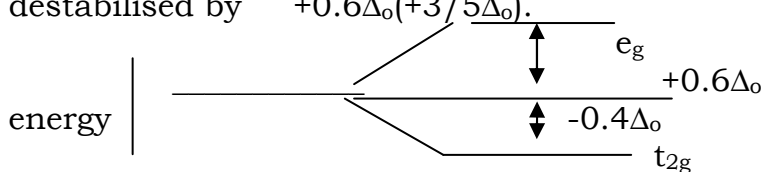
Two of the orbitals the  $d_{x^2-y^2}$  and  $d_{z^2}$ , point directly along the axes towards the negative charges. These orbitals will be at a higher energy than the  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals, all of which point between the axes and so are less influenced by the negative charge. This leads to the splitting of the d-orbitals into two sets, with three orbitals stabilized and two orbitals destabilized relative to their positions in spherical field. This is shown in figure 3



**Fig no.3. The octahedral field, the d-orbitals are split into two sets.**

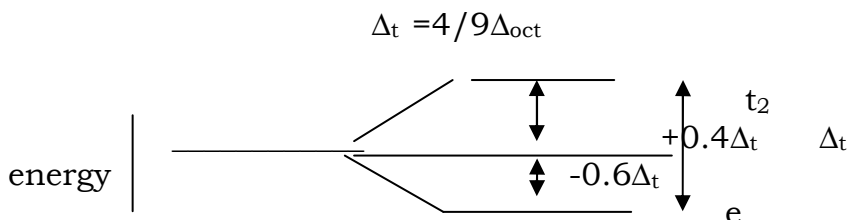
This is how the d-orbitals are split in an octahedral complex. In crystal field theory, degenerate orbitals are given group labels. In octahedral complex, the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals, are collectively called the  $t_{2g}$  orbitals, and the  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals are collectively called  $e_g$  orbitals. The g explains the orbital symmetry in respect to inversion.

The energy gap between the two sets of orbitals is known as the crystal field splitting energy. and it is given the symbol  $\Delta$ . The magnitude of  $\Delta$  depends on the metal ion and the ligands. For an octahedral complex, the splitting is  $\Delta_o$  (sometimes written  $\Delta_{oct}$ ). since the average energy of the five d-orbitals is unchanged on going from the spherical to the octahedral field, the three  $t_{2g}$  orbitals are stabilised by the same amount as the two  $e_g$  orbitals are destabilised. Each  $t_{2g}$  orbital is stabilised by  $-0.4\Delta_o$  ( $-2/5\Delta_o$ ), and each  $e_g$  orbital is destabilised by  $+0.6\Delta_o$  ( $+3/5\Delta_o$ ).



### 7.3.3: Tetrahedral complexes:

When the spherical field is rearranged into a tetrahedral field, none of the d-orbitals is directed exactly towards the point charges. Figure no.4 is explained. The  $d_{x^2-y^2}$  and  $d_{z^2}$ , orbitals are directed halfway between the points charges, where as the  $d_{xy}$   $d_{xz}$  and  $d_{yz}$ , orbitals point more towards the charges. There fore the  $d_{x^2-y^2}$  and  $d_{z^2}$ , orbitals are more influenced by the charges than the  $d_{xy}$   $d_{xz}$  and  $d_{yz}$  orbitals , so they are destabilized relative to them. This leads to the splitting pattern shown i figure.4 The sets of orbitals in tetrahedral complex are labelled e and  $t_2$  orbitals, The splitting between the e and  $t_2$  orbitals,  $\Delta_t$  ( $\Delta_{tet}$ ) is smaller than  $\Delta_{oct}$ . For the small metal ion and ligands  $\Delta_t$  ( $\Delta_{tet}$ ) and  $\Delta_{oct}$  are related by equation.



**Fig no.4 the tetrahedral field the d-orbitals are split into two sets.**

### 7.3.4: Color of transition metal complexes:

Most transition metal complexes have **beautiful colors** that depends on the metal and ligands. The colour of an aqua complex for example depends on the metal;

**Example.1:**  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is **pink**, **Example.3:**  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  is **green**

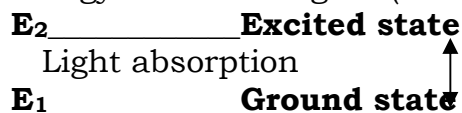
**Example.2:**  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  is **blue** **Example.4:**  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$  is colorless.

If we keep the metal constant but vary the ligand, the color also changes.

For examples:  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  is **green** and  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  is **blue**  
 $[\text{Ni}(\text{en})_3]^{2+}$  is **violet**.

How can we account for the color of transition metal complexes? Let's begin by recalling that white light consists of a continuous spectrum of wavelengths corresponding to different colors. When white light strikes a colored substance some wavelengths are transmitted while others are absorbed.

If atoms absorb light by undergoing electronic transition between atomic energy levels there by giving rise to atomic spectra, so metal complexes can absorb light by undergoing an electronic transition from its lowest (ground) energy state to a higher (excited) energy state.



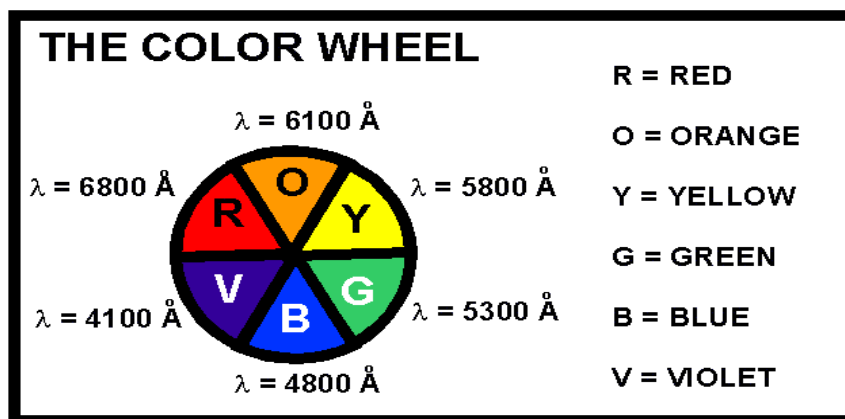
The wavelength  $\lambda$  of the light absorbed by a metal complex depends on the energy separation  $\Delta E = E_2 - E_1$  between the two states as given by the planck equation  $\Delta E = h\nu = hc / \lambda$ .

Where  $h$  is planck constant ,  
 $\nu$  is frequency of the light and  
 $C$  is the speed of light.

$$\Delta E = E_2 - E_1 = h\nu = hc / \lambda.$$

$$\text{Where } \lambda = hc / \Delta E$$

The measure of the amount of light absorbed by a substance is called the absorbance and a plot of absorbance versus wavelength is called an absorption spectrum. For example, the absorption spectrum of the red-violet  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ions has a broad absorption band at about 500nm, a wavelength in the blue-green part of the visible spectrum. Because the absorbance is smaller in the red and violet regions of the spectrum these colors are largely transmitted and we perceive the color of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  to be red-violet.



### 7.3.5: Nomenclature of Coordination Compounds

The nomenclature system as recommended by the IUPAC (International Union of Pure and Applied Chemistry). The names of coordination compounds are derived by following the principles of additive nomenclature. The groups that surround the central atom or structure must be identified in the name.

#### Rule.1. Order of naming ions

In ionic complexes, the cation is named first and then the anion irrespective, whether the cation or the anion is the complex species (which is enclosed in square brackets). No spaces are left between parts of the name that refer to the same coordination entity. For example:  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is named as potassium hexacyanoferrate(II).  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$  is named as hexaamminenickel(II) chloride.  $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{Cl}$  is named as penta aminocarbonatocobalt(III) chloride.

Non-ionic complexes are given a one word name, e.g.  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$  is named as diamine tetrachloroplatinum(IV).

#### Rule.2. Names of ligands

In the complex ion, the name of the ligand(s) precedes that of the central metal atom. (This procedure is reversed from writing formulas). Neutral ligands are named as the molecules. However, water molecule is named as 'aqua', ammonia as 'ammine', carbon monoxide as 'carbonyl' and nitric oxide as 'nitrosyl'.

Negative ligands generally end in “o” as illustrated below with a few examples : Cl- - chloro, CN- - cyano, H- - hydrido (Note that the 2004 draft on naming coordination compounds has recommended that the anionic ligands ending in ‘ide’, ‘ite’ or ‘ate’, the final ‘e’ is replaced by ‘ido’, ‘ito’ and ‘ato’, respectively; thus, Cl- - chlorido, CN- - cyanido, H- - hydrido, CH<sub>3</sub>COO- - acetato or ethanoato).

### Rule.3. Order of naming ligands

If more than one ligand is present in the complex species, then the ligands are named in alphabetical order without any separation by hyphens.

For example, [Pt(NH<sub>3</sub>)<sub>4</sub>(Cl)(NO<sub>2</sub>)]SO<sub>4</sub> is named as tetramine chloronitro platinum(IV) sulphate;

[Cu(CH<sub>3</sub>NH<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>] is named as dichloro-bis(methylamine)copper(II).

### Rule.4. Numerical prefixes to indicate number of ligands

Two kinds of numerical prefix are used for indicating the number of each type of ligand within the name of the coordination entity.

If ligands have simple names such as chloro, iodo, nitro etc., their number is indicated by prefixes such as di, tri, tetra, penta etc. If the ligands have complex names, their number is given by prefixes such as bis, tris, tetrakis etc.

**Ex.1:** [Co(CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>SO<sub>4</sub> is named as dichloro bis (ethylenediamine) cobalt(III) sulphate.

**Ex.2:** [Cr{(CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>;<sub>3</sub>}Cl<sub>3</sub>] is named as *d* or *l* tris(ethylenediamine)chromium(III)

### Rule.5. Ending of names

The name of an anionic complex which ends in ‘ate’, For example. K<sub>3</sub>[Al(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>] is named as potassium trioxalatoaluminate(III).

In case of cationic and neutral complexes, the name of the metal is written without any characteristic ending. For example, [Fe(H<sub>2</sub>O)<sub>6</sub>]SO<sub>4</sub>, which contains the cationic complex [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>, is named as hexaaquoiron(II)sulphate. Coordination compound K[Pt(NH<sub>3</sub>)Cl<sub>5</sub>] having the anionic complex [Pt(NH<sub>3</sub>)Cl<sub>5</sub>]<sup>-</sup> is named as potassium amminepentachloroplatinate(IV).

### Rule.6. Oxidation states of the central ion

The oxidation state of the central ion is designated by a roman numeral i.e., I, II, III, IV etc. in paranthesis at the end of the name of the central metal atom. For zero oxidation state, the letter 0 is written in paranthesis. A number of examples have already been given to illustrate this rule.

### Rule.7. Bridging groups in bidentate ligands.

Ligands which link two central metal atoms are usually separated from the rest of the complex by a hyphen and is/are denoted by the Greek letter  $\mu$ .

This is repeated before the name of each bridging group in the complex. For example: This coordination compound is named as octaquo- $\mu$ -dihydroxodiiron(III) sulphate and written as [(H<sub>2</sub>O)<sub>4</sub>Fe( $\mu$ -OH)<sub>2</sub>Fe(H<sub>2</sub>O)<sub>4</sub>](SO<sub>4</sub>)<sub>2</sub>.

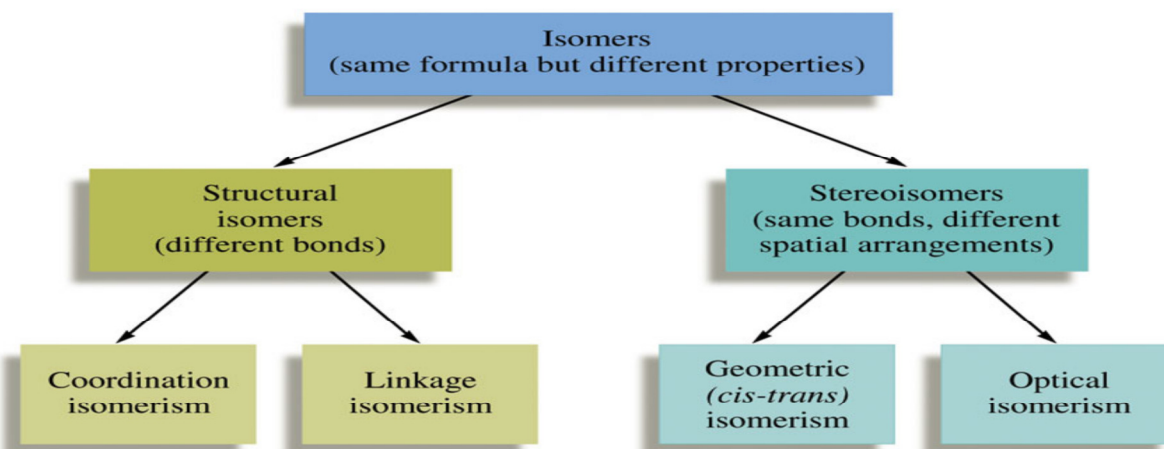
### Rule.8. Abbreviations for complicated molecules

While writing the structure of complex for complicated molecules, generally abbreviations are used. For example, en for ethylenediamine, py for pyridine.

#### 7.4:Isomerism

When two or more substances or species have the same molecular formula but their physical and chemical properties are different, these structures are said to be **isomers**. (Or) Compounds having same chemical formula but different structures are called **isomers**.

Although isomers contain exactly the same types and numbers of atoms, the arrangements of the atoms is different, and this leads to different properties. Below scheme represents classification of Isomers.



Depending on the given substances bonding and arrangements of the atoms, isomerism is classified into two types:

**They are**

1. Structural isomerism:
2. Stereoisomerism

#### Type 1. Structural isomerism:

When the isomers contain the same atoms but one or more bonds are different.

##### Example: 1:

$[\text{Cr}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  and  $[\text{Cr}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  are coordination isomers.

**Case:1**  $\text{SO}_4^{2-}$  is coordinated to  $\text{Cr}^{3+}$  and  $\text{Br}^-$  is the counter ion.

**Case:2**  $\text{Br}^-$  is coordinated to  $\text{Cr}^{3+}$  and  $\text{Br}^- \text{SO}_4^{2-}$  is the counter ion.

#### Each of the classes also has sub class

Depending on the bonding Structural isomerism is again classified as two types.

**They are:**

1. Coordination isomerism
2. Linkage isomerism

#### Coordination isomerism:

The composition of the complex ion is different. **Example:1:**  $[\text{Cr}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  and  $[\text{Cr}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  are coordination isomers.

**Case:1**  $\text{SO}_4^{2-}$  is coordinated to  $\text{Cr}^{3+}$  and  $\text{Br}^-$  is the counter ion.

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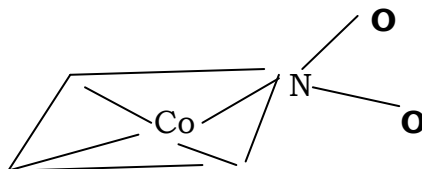
**Linkage isomerism:**

The composition of the complex ion is the same, but the point of attachment of at least one of the ligands is different.

Two ligands that can attach to metal ions in different ways.

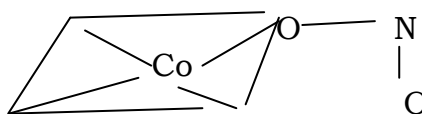
**Example** the following two compounds are linkage isomers.

**Case.1:**  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]\text{Cl}$  is called as tetraamminechloronitrocobalt(III) chloride(Yellow)



Tetraamminechlorocobalt (III) chloride (Yellow Colour)

**Case.2:**  $[\text{Co}(\text{NH}_3)_4(\text{ONO})\text{Cl}]\text{Cl}$  is called as tetraamminechloronitrocobalt(III) chloride(Yellow).



Tetraamminechlorocobalt(III) chloride ( Red Colour)

**Case:1.**

In the first case the  $\text{NO}_2$ -ligand is called nitro and is attached to  $\text{Co}^{3+}$  through the nitrogen atom;

**Case:2:**

In the second case the  $\text{NO}_2^-$ - ligand is called Nitrito. And it is attached to  $\text{Co}^{3+}$  through an oxygen atom.

**Type 2.Stereo isomerism:**

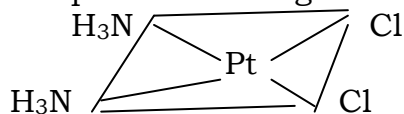
Stereo isomers have same bonds but the arrangements of the atoms is different. Each of the classes also has sub class. Stereo isomerism is again classified into two types.

**They are**

1. Geometrical isomerism or cis – trans isomerism
2. Optical isomerism

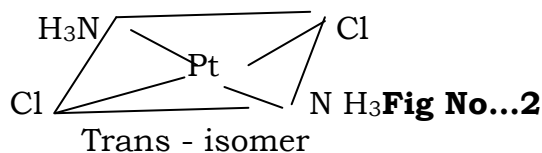
**Geometrical isomerism or cis–trans isomerism:**

When atoms or group of atoms can assume different positions around a rigid ring or bond. it is said to be cis-trans or geometrical isomerism. An important example is the  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  which has a square planar structure. The two possible arrangements of the ligands are shown in below figure



**Fig No...1**  
Cis-isomer





**Trans-isomers:**

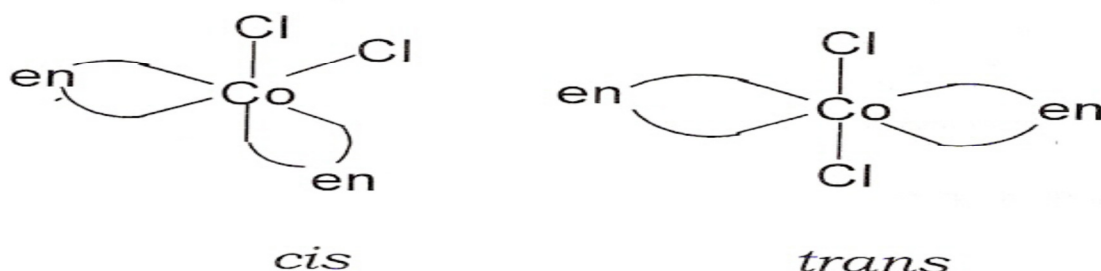
In the trans- isomers the ammonia molecules are across (trans) from each other.

**Cis-isomer:**

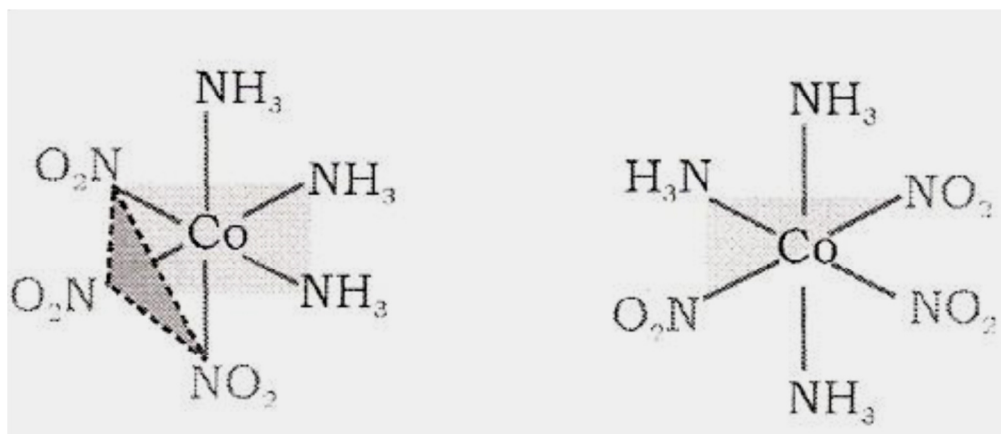
In cis-isomer, the ammonia molecules are cis to each other.

**Optical Isomerism:**

A second type of stereo isomerism is called as **optical isomerism** because the isomers have opposite effects on plane polarised light. Optical activity is exhibited by molecules that have non- super imposable mirror images. Your hands are non superimposable mirror images. The two hands are related like an object and its mirror image. One hand cannot be turned to make it identical to the other. Many molecules show this same features For example the complex ion  $[\text{Co}(\text{en})_3]^{3+}$  shown in fig...3 objects that have non superimposable mirror images are said to be chiral. The isomers of  $\text{Co}(\text{en})$



Among the complexes of the type  $\text{Ma}_3\text{b}_3$  in octahedral geometry, another type of isomerism is observed in which the isomers are known as **facial (fac)** and **meridional (mer) isomers**. If the three ligands 'a', or 'b', all are in the same plane it gives a **meridional (mer)** isomer. On the other hand, if they are adjacent forming a triangular face of the octahedron it gives a **facial (fac)** isomer.



*fac-isomer*

*mer-isomer*

In the case of coordination number 4, out of tetrahedral and square planar only square planar geometry exhibits geometrical isomerism. This type of isomerism is exhibited by complexes of type  $Ma_2b_2$ ,  $Ma_2bc$ ,  $Mabcd$ . In square planar  $Ma_2b_2$ , the two ligands 'a' may be arranged adjacent to each other, in a **cis** isomer, or opposite to each other, in a **trans** isomer as depicted below.

### Revision Questions

1. Define transition element?
2. What are the First Transition series elements?
3. Why Transition metals form paramagnetic species?
4. In s- block metals metallic bonding is weaker. Give reason
5. Define Catalyst?
6. Name the Catalyst used in Haber's process?
7. Name the Catalyst used in Contact process?
8. Name the Catalyst used in manufacture of Nitric acid?
9. Many transition metal ions are having color why?
10. What is the significance of Crystal field theory?
11. What is meant by Degenerate orbital?
12. What is the shape of d orbital?
13. What is the order of d orbitals according to the Energy?
14. Define crystal field splitting energy?
15. What is crystal field splitting energy of  $e_g$  orbital?
16. What is crystal field splitting energy of  $t_{2g}$  orbital?
17. What is the color of  $[Co(H_2O)_6]^{2+}$  ?
18. What is the color of  $[Ni(H_2O)_6]^{2+}$  ?
19. What is the color of  $[Ni(NH_3)_6]^{2+}$  ?
20. Define absorbance?

21. What is the IUPAC name of  $K_4[Fe(CN)_6]$  ?
22. What is the IUPAC name of  $[Co(NH_3)_5 CO_3] Cl$  ?
23. What is the name of  $Pt(NH_3)_4(Cl)(NO_2)]SO_4$ ?
24. Define Paramagnetism?
25. Define Diamagnetism?
26. Define Ferromagnetism?
27. Define isomers?
28. Give an example for coordination isomers?
29. Give an example for Linkage isomers?
30. Define Stereo isomerism?
31. Give an example of Geometrical and optical isomers?
32. What are facial (fac) and meridional (mer) isomers?



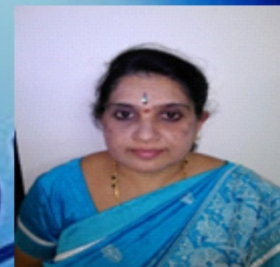
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