The Constitution of India

Preamble

WE, THE PEOPLE OF INDIA, having solemnly resolved to constitute India into a SOVEREIGN SOCIALIST SECULAR DEMOCRATIC REPUBLIC and to secure to all its citizens:

JUSTICE, social, economic and political;

LIBERTY of thought, expression, belief, faith and worship;

EQUALITY of status and of opportunity; and to promote among them all

FRATERNITY assuring the dignity of the individual and the unity and integrity of the Nation;

IN OUR CONSTITUENT ASSEMBLY this twenty-sixth day of November, 1949, do HEREBY ADOPT, ENACT AND GIVE TO OURSELVES THIS CONSTITUTION.

NATIONAL ANTHEM

Jana-gana-mana-adhināyaka jaya hē
Bhārata-bhāgya-vidhātā,

Panjāba-Sindhu-Gujarāta-Marāthā
Drāvida-Utkala-Banga

Vindhya-Himāchala-Yamunā-Gangā
uchchala-jaladhi-taranga

Tava subha nāmē jāgē, tava subha āsisa māgē,
gāhē tava jaya-gāthā,

Jana-gana-mangala-dāyaka jaya hē
Bhārata-bhāgya-vidhātā,

Jaya hē, Jaya hē, Jaya hē,
Jaya jaya jaya, jaya hē.

PLEDGE

India is my country. All Indians are my brothers and sisters.

I love my country, and I am proud of its rich and varied heritage. I shall always strive to be worthy of it.

I shall give my parents, teachers and all elders respect, and treat everyone with courtesy.

To my country and my people, I pledge my devotion. In their well-being and prosperity alone lies my happiness.

Preface

Dear Students,

We welcome you all to std. XI. For the first time, you are being introduced to the subject of chemistry discipline. You have already been acquainted with some of the concepts of chemistry from standard five onwards, especially in the subject of general science up to standard eight and science and technology for standard nine and ten.

Chemistry is very broad subject that covers many aspects of our everyday experience. This textbook aims to create awareness and to understand certain essential aspects by the national curriculum framework (NCF) which was formulated in 2005, followed by the state curriculum framework (SCF) in 2010. Based on these two framework, reconstruction of the curriculum and prepartion of a revised syllabus has been done and designed now.

The subject chemistry is the study of substances, their properties, structures and transformation. The world is full of chemical substances and we need chemicals for many useful purposes. Our body is a huge chemical factory. Keeping this in mind, the textbook is written in organized manner. You can learn a very basic principles, understand facts and put them into practice by learning in the classroom and laboratory. The textbook is presented in a simple language with relevant diagrams, graphs, tables, photographs. This will help you to understant various terminology, concepts with more clarity. All the illustrations are in color form. The new syllabus focuses on the basic principles, concepts, laws based on precise observations, their applications in everyday life and ability to solve different types of problems. The general teaching - learing objectives of the revised syllabus are further determined on the basis of the 'Principle of constructivism' i.e. self learning.

The curriculum and syllabus is designed to make the students to think independently. The student are encouraged to read, study more through the additional information given in the colored boxes. Activities have been introduced in each chapter. These activities will not only help to understand the content knowledge on your own efforts. QR code have been introduced for gaining the additional information, abstracts of chapters and practice questions/ activities.

The efforts taken to prepare the text book will help the students think about more than just the content of the chemical concepts. Teachers, parents as well as those aspiring condidates preparing for the competitive examinations will also be benefited.

We look forward to a positive response from the teachers and students.

Our best wishes to all !

(Dr. Sunil Magar)
Director
Maharashtra State Bureau of
Textbook Production and
Curriculum Research, Pune 4

Pune
Date : 20 June 2019
Bharatiya Saur : 30 Jyeshtha 1941

- For Teachers -

Dear Teachers,

We are happy to introduce the revised textbook of chemistry for std. XI. This book is a sincere attempt to follow the maxims of teaching as well as develop a 'constructivist' approach to enhance the quality of learning. The demand for more activity based, experiential and innovative learning opportunities is the need of the time. The present curriculum has been restructured so as to bridge the credibility gap that exists in the experience in the outside world. Guidelines provided below will help to enrich the teaching - lerning process and achieve the desired learning outcomes.

- To begin with, get familiar with the textbook yourself.
- The present book has been prepared for construtivism and activity based learning.
- Teachers must skillfully plan and organize the activities provided in each chapter to develop interest as well as to stimulate the thought process among the students.
- Always teach with proper planning.
- Use teaching aids as required for the proper understanding of the subject.
- Do not finish the chapter in short.
- Follow the order of the chapters strictly as listed in the contents because the units are introduced in a graded manner to facilitate knowledge building.
- Each unit is structured in a definite manner. It starts from the basic concepts of general chemistry required for each branch of chemistry. Application of this knowledge will help students to understand further chapters in each unit.
- Each chapter provides solved problems on each and every concept and various laws. The solved problems are put into boxes. Teachers should expalin each step of the problem and give them pratice.
- Ask the students about the related information, backgroud about the chapter. You are provided, for this with the different boxes like 'Can You Recall', 'Do you know?'
- Encourage the students to collect related information by providing them the websites.
- Teaching- learning interactions, processes and participation of all students are necessary and so is your active guidance.
- Do not use the content of the boxes titles 'Do you know'? for evaluation.
- Exercises include parameters such as co-relation, critical thinking, analytical reasoning etc. Evaluation pattern should be based on the given paramerters. Equal weightage should be assigned to all the topics. Use different combinations of questions.


Remember


Try this


Can you recall?


Can you tell?

Front Page : The photograph depicts transmission electron micrograph (TEM) of a few layer Graphene (left). The electron diffraction pattern (hexagonal arrangement of spots corresponds to the hexagonal symmetry of the structure of Graphene (Right).
Picture Credit : Prof. Dr. M. A. More, Department of Physics, Savitribai Phule Pune Universiy, Pune 411007.


Use your brain power


Just think


Activity :


Do you know ?


Exercises


Observe and Discuss


Find out


Internet my friend

Competency Statements - Standard XI	
Area/ Unit/ Lesson	**After studying the contents in Textbook students.....**
General chemistry	• Understand the SI unit of important fundamental scientific quantities. • Explain various fundamental laws of chemical combination, which are applied in day-to-day life. • Relate basic concepts of number of moles and molecules. • Differentiate between quantitative and qualitative analysis. • Develop accuracy, precision, concentration ability in taking accurate reading. • Calculate empirical formula and molecular formula of compounds. • Obtain information about different techniques to purify substance as well as separation of miscible solids and liquids. • Gain the information about various theories, principles, put up by eminent Scientists leading to atomic stucture. • Classify elements isotopes, isobars and isotones. • Understand the duel nature of electron. • Application of concept of quantum number in writing electronic configuration of various elements.
Inorganic chemistry	• Inculcate social and scientific awareness by gaining knowledge of oxidation-reduction concept. • Evaluate oxidation number of elements and balance the redox reaction by different methods. • Categorize oxidizing and reducing agents with their applications. • Classify elements based on electronic configuration. • Understand co-relation between the various properties like atomic size, valency, oxidation state, ionization enthalpy and electronegativity in a group and in a period. • Recognize isoelectronic species. • Compare the trends in physical and chemical properties in group I and group II. Understand the diagonal relationship. • Gain the knowledge of hydrogen from periodic table. • Develop interest in systematic study of elements present in Group 13, Group 14 and group15. • Learn anomalous behaviors of boron, carbon and nitrogen . • Draw the structures of some compounds of boron, carbon and nitrogen. • Elaborate information about various theories to explain nature of bonding in formation of molecules. • Inculcate skill to draw Lewis structure of molecules. • Assign the structures of various compounds with respect to geometry, bond angle and types of bond.

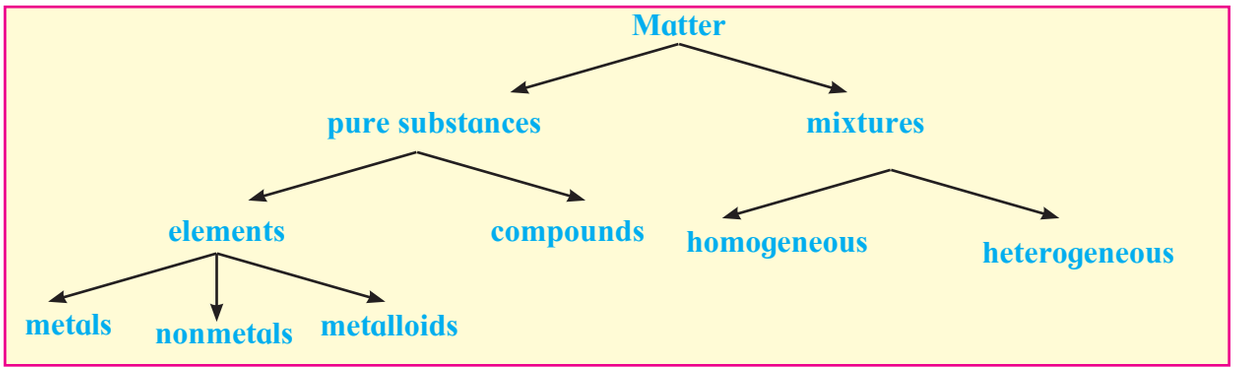
Physical chemistry	• Generate environmental awareness by compiling concepts of adsorption phenomenon. • Learn science behind the fact about colloids in day to day life. • Interpret nature, difference and relation of equilibrium constant. • Design the suitable conditions to get more yield of the desired product. • Differentiate nuclear reactions with ordinary chemical reaction. • Acquire knowledge of natural radioactivity and related terms like nuclear transmutation, nuclear fission, nuclear fusion. • Clarify the beneficial and harmful effects of radioactivity. • State the applications of radioactive elements like carbon dating, nuclear reactor, generation of electricity and medicinal uses. • Develop mathematical skills in finding radioactive decay constant, half life period and nuclear binding energy.
Organic chemistry	• Interpret the structure and functional group of organic compounds. • IUPAC nomenclature of organic compounds. • Understand the influence of electronic displacement and reactivity in organic molecules. • Draw the formulae of various isomers of organic compounds. • Illustrate different methods of preparation and chemical properties of hydrocarbons. • Infer importance of hydrocarbon. • Gain information of medicinal properties of some chemical compounds and chemistry behind food quality and cleasing action.

CONTENTS

1. Some Basic Concepts of Chemistry

1.1 Introduction : Chemistry is the study of matter, its physical and chemical properties and the physical and chemical changes it undergoes under different conditions.

1.2.1. Matter : You have learnt earlier that matter occupies space and has mass. **Matter** can be further **classified** into pure substances and mixtures **on the basis of chemical composition**.



Chemistry is a central science. Its knowledge is required in the studies of physics, biological sciences, applied sciences, and earth and space sciences. The scope of chemistry is in every aspect of life, for example, the air we breathe, the food we eat, the fluids we drink, our clothing, transportation and fuel supplies, and so on.

Though it is an ancient science, due to development and advancement in science and technology, chemistry has developed as modern science. Technological development in sophisticated instruments expanded our knowledge of chemistry which, now, has been used in applied sciences such as medicine, dentistry, engineering, agriculture and in daily home use products.

1.2 Nature of Chemistry : Chemistry is traditionally classified further into five branches : organic, inorganic, physical, bio and analytical. Organic chemistry is the study of the properties and reactions of compounds of carbon. Inorganic chemistry is the study of all substances which are not organic. Physical chemistry is the study of principles underlying chemistry. It deals with the studies of properties of matter. It is study of atoms, molecules, and fundamental concepts related to electrons, energies and dynamics therein. It provides basic framework for all the other branches of chemistry.

Let us understand first what are pure substances and mixtures.

1.2.2 Pure substances versus mixtures :

Pure substances have a definite chemical composition. They always have the same properties regardless of their origin. Mixtures have no definite chemical composition and hence no definite properties.

Examples of pure substances : Pure metal, distilled water, etc.

Examples of mixtures : Paint (mixture of oils, pigment, additive), concrete (a mixture of sand, cement, water)

Can you tell?

Which are mixtures and pure substances from the following ?

i. sea water ii. gasoline iii. skin iv. a rusty nail v. a page of the textbook. vi. diamond

Pure substances are further divided into elements and compounds. **Elements are pure substances which can not be broken down into simpler substances by ordinary chemical changes.** Elements are further classified as metals, nonmetals and metalloids.

1. Metals :
i. have a lustre (a shiny appearance).
ii. conduct heat and electricity.
iii. can be drawn into wire (are ductile).
iv. can be hammered into thin sheets (are malleable).
Examples : gold, silver, copper, iron. Mercury is a liquid metal at room temperature.

2. Non-metals :
i. have no lustre. (exception : diamond, iodine)
ii. are poor conductors of heat and electricity. (exception : graphite)
iii. can not be hammered into sheets or drawn into wire, because they are brittle.
Examples : Iodine, nitrogen, carbon, etc.

3.Metalloids : Some elements have properties intermediate between metals and non-metals and are called metalloids or semi-metals. Examples include arsenic, silicon and germanium.

Compounds are the pure substances which can be broken down into simpler substances by ordinary chemical changes. In a compound, two or three elements are combined in a fixed proportion.

Mixture contains two or more substances in no fixed proportions and may be separated by physical methods. Mixtures are further divided into homogeneous and heterogeneous. Solutions are homogeneous mixtures, because the molecules of constituent solute and solvent are uniformly mixed throughout its bulk. In heterogeneous mixtures the molecules of the constituents are not uniformly mixed throughout the bulk. For example : Suspension of an insoluble solid in a liquid.

1.2.3 States of matter : You are also aware that matter exists in three different states namely gas, liquid and solid. You are going to learn about these states in unit 3 (chapter 10).

In solids, constituent atoms or molecules (particles) are tightly held in perfect order and therefore solids possess definite shape and volume. Liquids contain particles close to each other and they can move around within the liquid. While in gases, the particles are far apart as compared to those in liquid and solid state.

Three states of matter are interconvertible by changing the conditions of temperature and pressure.

Can you tell?

Classify the following as element and compound.
i. mercuric oxide ii. helium gas iii. water iv. table salt v. iodine vi. mercury vii. oxygen viii. nitrogen

1.3 Properties of matter and their measurement :

Fig : 1.1 Burning of magnesium wire

Different kinds of matter have characteristic properties, which can be classified into two categories as **physical properties** and **chemical properties**.

Physical properties are those which can be measured or observed without changing the chemical composition of the substance. Colour, odour, melting point, boiling point, density, etc. are physical properties. Chemical properties are the properties where substances undergo a chemical change and thereby exhibit change in chemical composition. For example, coal burns in air to produce carbon dioxide or magnesium wire burns in air in the presence of oxygen to form magnesium oxide. (Fig. 1.1)

1.3.1 Measurement of properties : Many properties of matter are quantitative in nature. When you measure something, you are comparing it with some standard. The standard quantity is reproducible and unchanging.

Many properties of matter such as mass, length, area, pressure, volume, time, etc. are quantitative in nature. Any quantitative measurement is expressed by a number followed by units in which it is measured. For example, length of class room can be represented as 10 m. Here 10 is the number and 'm' denotes metre-the unit in which the length is measured.

The standards are chosen orbitrarily with some universally acceped criteria. **"The arbitrarily decided and universally accepted standards are called units."**

There are several systems in which units are expressed such as CGS (centimetre for length, gram for mass and second for time), FPS (foot, pound, second) and MKS (metre, kilogram, second) systems, etc.

SI units :

In 1960, the general conference of weights and measure, proposed revised metric system, called **International System of units,** that is, **SI units**.

The metric system which originated in France in late eighteenth century, was more convenient as it was based on the decimal system. Later, based on a common standard system, the International System of Units (SI units) was established.

The SI system has seven base units as listed in Table 1.1. These are fundamental scientific quantities. Other units like speed, volume, density, etc. can be derived from these quantities.

Table 1.1 SI Fundamental units

Base Physical Quantity	Symbol for Quantity	Name of SI Unit	Symbol for SI Unit
Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Thermodynamic temperature	T	Kelvin	K
Amount of substance	n	mole	mol
Luminous intensity	I_v	candela	cd

1.3.2 Physical properties

i. Mass and weight : We know that matter has mass. So mass is an inherent property of matter. It is the measure of the quantity of matter a body contains. The mass of a body does not vary as its position changes. On the other hand, the weight of a body is result of the mass and gravitational attraction. The weight of a body varies because the gravitational attraction of the earth for a body varies with the distance from the centre of the earth.

Hence, **the mass of a body is more fundamental property than its weight**.

The basic unit of mass in the SI system is the kilogram as given in Table 1.1. However, a fractional quantity 'gram' is used for weighing small quantities of chemicals in the laboratories. Therefore, in terms of grams it is defined (1kg = 1000 g = 10^3 g)

ii. Length : In chemistry we come across 'length' while expressing properties such as the atomic radius, bond length, wavelenght of electromagnetic radiation, and so on. These quantities are very small therefore fractional units of the SI unit of length are used for example, nanometre (nm), picometre (pm). Here 1nm = 10^{-9} m, 1 pm = 10^{-12} m.

iii. Volume : It is the amount of space occupied by a three dimensional object. It does not depend on shape. For measurement of volume of liquids and gases, a common unit, litre (L) which is not an SI unit is used.

1 L = 1 dm^3 = 1000 mL = 1000 cm^3

1000 cm^3 = 10 cm × 10 cm × 10 cm of volume

SI unit of volume is expressed as $(metre)^3$ or m^3.

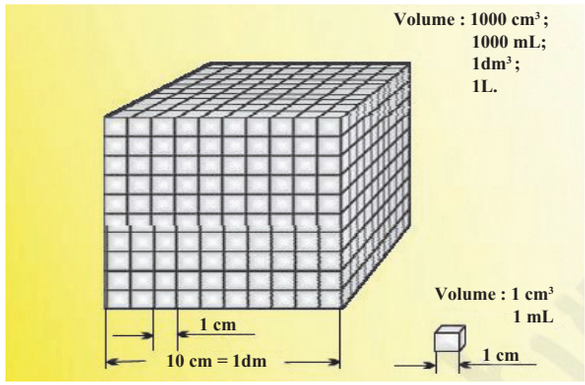


Fig. 1.2 : Litre and SI unit of volume

Different kinds of glassware are used to measure the volume of liquids and solutions. For example, graduated cylinder, burette, pipette, etc. A volumetric flask is used to prepare a known volume of a solution. Figure 1.3 shows the types of apparatus used in laboratory for measuring volume of liquids.

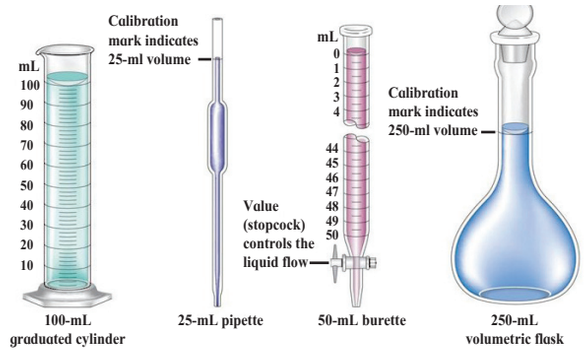


Fig. 1.3 : Volumetric glass apparatus

iv. Density : Density of a substance is its mass per unit volume. It is determined in the laboratory by measuring both the mass and the volume of a sample. The density is calculated by dividing mass by volume. It is the characteristic property of a substance.

So SI unit of density can be obtained as follows:

$$\text{SI unit of density} = \frac{\text{SI unit of mass}}{\text{SI unit of volume}}$$

$$= \frac{\text{kg}}{\text{m}^3} \text{ or kg m}^{-3}$$

CGS units it is $\frac{\text{g}}{\text{mL}}$ or g mL^{-1} or g cm^{-3}

v. Temperature : Temperature is a measure of the hotness or coldness of an object. There are three common scales to measure temperature, namely ^{0}C (degree Celsius), ^{0}F (degree Fahrenheit) and K (Kelvin). Here K is the SI unit. Figure 1.4 shows the thermometers based on these scales.

Generally, the thermometer with celsius scale are calibrated from 0 ^{0}C to 100 ^{0}C where these two temperatures are respectively the freezing point and the boiling point of water at atmospheric pressure. These are represented on fahrenheit scale as 32^0 F to 212^0 F.

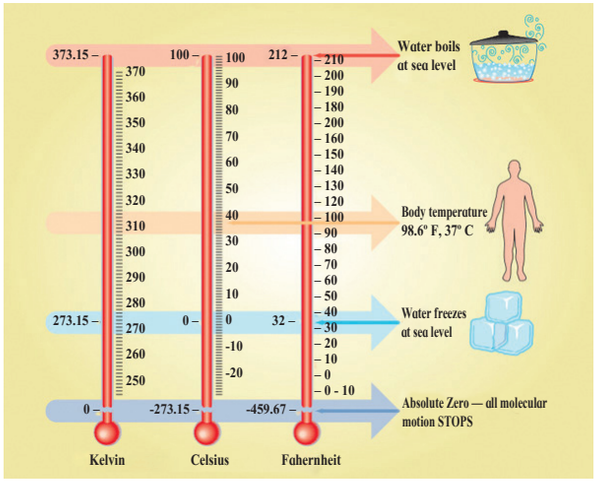


Fig 1.4 : Thermometers of different temperature scale

The temperatures on two scales are related to each other by the following relationship :

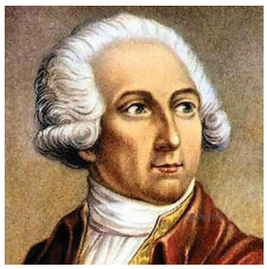
$$^0\text{F} = \frac{9}{5}(^0\text{C}) + 32$$

The Kelvin scale is related to Celsius scale as follows :

$$\text{K} = ^0\text{C} + 273.15$$

1.4 Laws of Chemical Combination : The elements combine with each other and form compounds. This process is governed by five basic laws discovered before the knowledge of molecular formulae.

1.4.1 Law of conservation of mass : Antoine



Lavoisier (1743-1794) a French scientist is often referred to as the father of modern chemistry. He carefully performed many combustion experiments, namely, burning of phosphorus and mercury, both in the presence of air. Both resulted in an increase in weight. After several experiments he found that the weight gained by the phosphorus was

exactly the same as the weight lost by the air. He observed that,

Total mass of reactants

= Total mass of products

When hydrogen gas burns and combines with oxygen to yield water, the mass of the water formed is equal to the mass of the hydrogen and oxygen consumed. Thus, the law of conservation of mass states that **'mass can neither be created nor destroyed.'**

1.4.2 Law of Definite Proportions :

French chemist, Joseph Proust performed experiments on two samples of cupric carbonate. One of the samples was natural in origin and the other was a synthetic one. He found that the composition of elements present in it was same for both the samples as shown below :

Cupric Carbonate	% of copper	% of oxygen	% of carbon
Natural sample	51.35	38.91	9.74
Synthetic sample	51.35	38.91	9.74

This led Joseph Proust to state the law of definite proportion as follows :

'A given compound always contains exactly the same proportion of elements by weight.' 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. This law is sometimes referred to as **Law of definite composition**.

1.4.3 Law of multiple proportions :

This law was proposed by John Dalton in 1803. It has been observed that two or more elements may form more than one compound. Law of multiple proportions summarizes many experiments on such compounds. **When two elements A and B form more than one compounds, the masses of element B that combine with a given mass of A are always in the ratio of small whole numbers.** For example, **i.** Hydrogen combines with oxygen to form two compounds, namely water and hydrogen peroxide.

Hydrogen + Oxygen ⟶ Water

2 g 16 g 18 g

Hydrogen + Oxygen ⟶ Hydrogen Peroxide

2 g 32 g 34 g

Here, it is found that, the two masses of oxygen i.e. 16 g and 32 g which combine with a fixed mass of hydrogen (2g) are in the ratio of small whole numbers, i. e. 16:32 or 1:2.

ii. Nitrogen and oxygen combine to form two compounds, nitric oxide and nitrogen dioxide.

Nitrogen + Oxygen ⟶ Nitric Oxide

14 g 16 g 30 g

Nitrogen + Oxygen ⟶ Nitrogen Dioxide

14 g 32 g 46 g

Here, you find that the two masses of oxygen i.e. 16 g and 32 g when combine with a fixed mass of Nitrogen (14 g) are in the ratio of small whole numbers i.e. 16:32 or 1:2.

(Similar examples such as CO and CO_2 (1:2 ratio), SO_2 and SO_3 (2:3 ratio), can be found.)

1.4.4 Gay Lussac Law of Gaseous Volume :

This law was put forth by Gay Lussac in 1808. The law states that **when gases combine or are produced in a chemical reaction they do so in a simple ratio by volume, provided all gases are at same temperature and pressure**.

Illustration : i. Under the same conditions of temperature and pressure, 100 mL of hydrogen combines with 50 mL of oxygen to give 100 mL of water vapour.

Hydrogen (g)	+ Oxygen (g)	⟶ Water(g)
100 mL	50 mL	100 mL
(2 vol)	(1 vol)	(2 vol)

Thus, the volumes of hydrogen gas and oxygen gas which combine together i.e. 100 mL and 50 mL producing two volumes of water vapour which amounts to 100 mL bear a simple ratio of 2:1:2

ii. Under the same condition of temperature and pressure,

1 L of nitrogen gas combines with 3 L of hydrogen gas to produce 2 L of ammonia gas.

Nitrogen (g) + Hydrogen (g) ⟶ Ammonia(g)

1 L 3 L 2 L

(1 vol) (3 vol) (2 vol)

Thus, the volume of nitrogen gas and hydrogen gas which combine together i.e. 1 L and 3 L and volume of ammonia gas produced i. e. 2 L bear a simple ratio of 1:3:2.

Remember

Gay Lussac's discovery of integer ratio in volume relationship is actually the law of definite proportion by gaseous volumes.

Can you tell?

If 10 volumes of dihydrogen gas react with 5 volumes of dioxygen gas, how many volumes of water vapour would be produced?

1.5 Avogadro Law : In 1811, Avogadro proposed that **equal volumes of all gases at the same temperature and pressure contain equal number of molecules**.

If we consider the reaction of hydrogen and oxygen to produce water vapour.

Hydrogen (g) + Oxygen (g) ⟶ Water (g)

100 mL 50 mL 100 mL

(2 vol) (1 vol) (2 vol)

(Gay Lussac Law)

2n molecules n molecules 2n molecules

(Avogadro law)

2 molecules 1 molecule 2 molecules

We see that 2 volumes of hydrogen combine with 1 volume of oxygen to give 2 volumes of water vapour, without leaving any unreacted oxygen. According to Avogadro law, if 1 volume contains n molecules, then 2n molecules of hydrogen combine with n molecules of oxygen to give 2n molecules of water.

Therefore, 2 molecules of hydrogen gas combine with 1 molecule of oxygen to give 2 molecules of water vapour. Avogadro could explain the above result by considering the molecules to be polyatomic. If hydrogen and oxygen were considered as diatomic, as recognized now, then the above results are easily understandable.

Remember

Avogadro made a distinction between atoms and molecules, which is quite understandable in the present time.

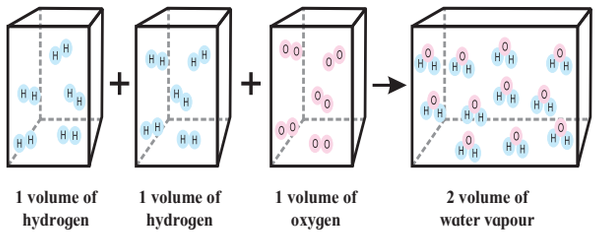


Fig. 1.5 : two volume of hydrogen react with one volume of oxygen to give two volumes of water vapour

1.6 Dalton's Atomic Theory : In 1808, Dalton published "A New System of chemical philosophy" in which he proposed the following features, which later became famous as Dalton's atomic theory.

1. Matter consists of **tiny, indivisible particles** called **atoms**.
2. All the atoms of a given elements have **identical** properties including **mass**. Atoms of different elements differ in mass.
3. **Compounds** are formed when atoms of different elements combine in a fixed ratio.
4. **Chemical reactions** involve only the **reorganization of atoms**. Atoms are neither created nor destroyed in a chemical reaction.

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

Can you recall?

What is an atom and a moleule ? What is the order of magnitude of mass of one atom ? What are isotopes?

1.7 Atomic and molecular masses : You know about the terms atoms and molecules. Thus it is appropriate here to understand what we mean by atomic and molecular masses.

1.7.1 Atomic Mass : Every element has a characteristic atomic mass. Atomic mass is the mass of an atom. It is actually very very small. For example, the mass of one hydrogen atom is 1.6736×10^{-24} g. This is very small quantity and not easy to measure.

In the present system, mass of an atom is determined relative to the mass of a carbon - 12 atom as the standard and this has been agreed upon in 1961 by IU PAC. In this system, an atom of carbon-12 is assigned a mass of exactly 12.00000 atomic mass unit **(amu)** and all other atoms of other elements are given a relative atomic mass, to that of carbon - 12. The atomic masses are expressed in **amu**. **One amu is defined** as a **mass exactly equal to one twelth of the mass of one carbon-12 atom**. Later on the exact value of atomic mass unit in grams was experimentally established.

$$1 \text{ amu} = \frac{1}{12} \times \text{mass of one C-12}$$

$$= \frac{1}{12} \times 1.992648 \times 10^{-23} \text{ g}$$

$$= 1.66056 \times 10^{-24} \text{ g}$$

Recently, amu has been replaced by **unified mass unit** called **dalton** (symbol '**u**' or '**Da**'), 'u' means unified mass.

Problem 1.1 : Mass of an atom of oxygen in gram is 26.56896×10^{-24} g. What is the atomic mass of oxygen in u ?

Solution : Mass of an atom of oxygen in gram is 26.56896×10^{-24} g, and

1.66056×10^{-24} g = 1 u

$\therefore$ 26.56896×10^{-24} g = ?

$$= \frac{26.56896 \times 10^{-24} \text{ g}}{1.66056 \times 10^{-24} \text{ g/u}} = 16.0 \text{ u}$$

Similarly mass of an atom of hydrogen = 1.0080 u

1.7.2 Average Atomic Mass : Many naturally occuring elements exist as mixture of more than one isotope. Isotopes have different atomic masses. The atomic mass of such an element is the weighted average of atomic masses of its isotopes (taking into account the atomic masses of isotopes and their relative abundance i.e. percent occurrance). This is called **average atomic mass** of an element. For example, carbon has the following three isotopes with relative abundances and atomic masses as shown against each of them.

Isotope	Atomic mass (u)	Relative Abundance (%)
^{12}C	12.00000	98.892
^{13}C	13.00335	1.108
^{14}C	14.00317	2×10^{-10}

From the above data, the average atomic mass of carbon

= (12 u) (98.892/100) + (13.00335 u) (1.108/100) + (14.00317) (2×10^{-10}/100)

= 12.011 u

Similary, average atomic masses for other elements can be calculated.

Remember

- In the periodic table of elements, the atomic masses mentioned for different elements are actually their average atomic masses.
- For practical purpose, the average atomic mass is rounded off to the nearest whole number when it differs from it by a very small fraction.

Element	Isotopes	Average atomic mass	Rounded off atomic mass
Carbon	^{12}C, ^{13}C, ^{14}C	12.011 u	12.0 u
Nitrogen	^{14}N, ^{15}N	14.007 u	14.0 u
Oxygen	^{16}O, ^{17}O, ^{18}O	15.999 u	16.0 u
Chlorine	^{35}Cl, ^{37}Cl	35.453 u	35.5 u
Bromine	^{79}Br, ^{81}Br	79.904 u	79.9 u

Problem 1.2 : Calculate the average atomic mass of neon using the following data :

Isotope	Atomic mass	Natural Abundance
^{20}Ne	19.9924 u	90.92%
^{21}Ne	20.9940 u	0.26 %
^{22}Ne	21.9914 u	8.82 %

Solution : Average atomic mass of Neon (Ne)

$$= \frac{\text{Atomic mass of } ^{20}Ne \times \% + \text{Atomic mass of } ^{21}Ne \times \% + \text{Atomic mass of } ^{22}Ne \times \%}{100}$$

$$= \frac{(19.9924u)(90.92) + (20.9940u)(0.26) + (21.9914u)(8.82)}{100} = 20.1707 \text{ u}$$

1.7.3 Molecular Mass : Molecular mass of a substance is the sum of average atomic masses of all the atoms of elements which constitute the molecule. Molecular mass of a substance is the mass of one molecule of that substance relative to the mass of one carbon-12 atom. It is obtained by multiplying average atomic mass of each element by the number of its atoms and adding them together.

For example, the molecular mass of carbon dioxide (CO_2) is

= 1(average atomic mass of C)
+ 2 (average atomic mass of O)
= 1 (12.0 u) + 2 (16.0 u) = 44.0 u

Some more examples of calculations of molecular mass.

i. $H_2O = 2 \times 1$ u + 16 u = 18 u

ii. $C_6H_5Cl = (6 \times 12 \text{ u}) + (5 \times 1 \text{ u}) + (35.5 \text{ u})$
= 112.5 u

iii. $H_2SO_4 = (2 \times 1 \text{ u}) + (32 \text{ u}) + (4 \times 16 \text{ u}) = 98$ u

Problem 1.3 : Find the mass of 1 molecule of oxygen (O_2) in amu (u) and in grams.

Solution : Molecular mass of $O_2 = 2 \times 16$ u

$\therefore$ mass of 1 molecule = 32 u

$\therefore$ mass of 1 molecule of O_2
$= 32.0 \times 1.66056 \times 10^{-24}$ g
$= 53.1379 \times 10^{-24}$ g

1.7.4 Formula Mass

Some substances such as sodium chloride do not contain discrete molecules as the constituent units. In such compounds, cationic (sodium) and anionic (chloride) entities are arranged in a three dimensional structure.

In sodium chloride crystal, one $Na^{\oplus}$ ion is surrounded by six $Cl^{\ominus}$ ions, all at the same distance from it and vice versa. Therefore, NaCl is the formula used to represent sodium chloride, though it is not a molecule. Similarly, a term 'formula mass' is used for such ionic compounds, instead of molecular mass. **The formula mass of a substance is the sum of atomic masses of the atoms present in the formula.**

Problem 1.4 : Find the formula mass of
i. NaCl ii. $Cu(NO_3)_2$

i. Formula mass of NaCl
= average atomic mass of Na
+ average atomic mass of Cl
= 23.0 u + 35.5u = 58.5 u

ii. Formula mass of $Cu(NO_3)_2$
= average atomic mass of Cu + 2 × (average atomic mass of nitrogen + average atomic mass of three oxygen)
= (63.5) + 2(14 + 3 x 16) = 187.5 u

Try this

Find the formula mass of $CaSO_4$
If atomic mass of Ca = 40.1 u,
S =32.1 u and O = 16.0 u

1.8 Mole concept and molar mass

Can you recall?

1. One dozen means how many items ?
2. One gross means how many items ?

Mole : Expressing large count of objects is made easy by using quantitative adjectives such as dozen, gross. You know that even a small amount of any substance contains very large number of atoms or molecules. We use a quantitative adjective 'mole' to express the large number of submicroscopic entities like atoms, ions, electrons, etc. present in a substance.

Definiton : One mole is the amount of a substance that contains as many entities or particles as there are atoms in exactly 12 g (or 0.012 kg) of the carbon -12 isotope.

Let us calculate the number of atoms in 12.0000 g of Carbon-12 isotopes. Mass of one carbon-12 atom (determined by mass spectrometer) = 1.992648×10^{-23} g,

Mass of one mole carbon atom = 12 g

$\therefore$ Number of atoms in 12 g of carbon -12

$$= \frac{12 \text{g/mol}}{1.992648 \times 10^{-23} \text{ g/atom}}$$

$$= 6.0221367 \times 10^{23} \text{ atom/mol}$$

Thus one mole is the amount of a substance that contains 6.0221367×10^{23} particles/ entities (such as atoms, molecules or ions).

Note that the name of the unit is **mole** and the symbol for the unit is **mol**.

Remember

The number 6.0221367×10^{23} is known as **Avogadro's Constant 'N_A'** in the honour of Amedo Avogadro.

In SI system, mole (Symbol mol) was introduced as seventh base quantity for the amount of a substance.

Example :

1 mole of oxygen atoms = 6.0221367×10^{23} atoms of oxygen

1 mole of water molecules = 6.0221367×10^{23} molecules of water

1 mole of sodium chloride = 6.0221367×10^{23} formula units of NaCl

Molar Mass : The mass of one mole of a substance (element/compound) in grams is called its molar mass. The molar mass of any element in grams is numerically equal to atomic mass of that element in u.

Element	Atomic mass (u)	Molar mass (g mol^{-1})
H	1.0 u	1.0 g mol^{-1}
C	12.0 u	12.0 g mol^{-1}
O	16.0 u	16.0 g mol^{-1}

Simillary molar mass of any substance, existing as polyatomic molecule, in grams is numerically equal to its molecular mass or formula mass in u.

Polyatomic substance	Molecular/ formula mass (u)	Molar mass (g mol^{-1})
O_2	32.0 u	32.0 g mol^{-1}
H_2O	18.0 u	18.0 g mol^{-1}
NaCl	58.5 u	58.5 g mol^{-1}

Molar mass of O atoms

$= 6.022 \times 10^{23}$atom/mol $\times$ 16 u/atom $\times$ 1.66056×10^{-24} g/u $= 16.0$ g/mol

Problem 1.5 : Calculate the number of moles and molecules of urea present in 5.6 g of urea.

Solution : Mass of urea = 5.6 g

Molecular mass of urea, NH_2CONH_2

= 2 (average atomic mass of N) + 4 (average atomic mass of H) + 1(average atomic mass of C) + 1(average atomic mass of O)

$= 2 \times 14$ u $+1 \times 12$ u $+4 \times 1$ u $+ 1 \times 16$ u

$= 60$ u

$\therefore$ molar mass of urea = 60 g mol^{-1}

Number of moles

$$= \frac{\text{mass of urea in g}}{\text{molar mass of urea in g mol}^{-1}}$$

$$= \frac{5.6 \text{ g}}{60 \text{ g mol}^{-1}} = 0.0933 \text{ mol}$$

Number of molecules = Number of moles $\times$ Avogadro's constant

Number of molecules of urea

$= 0.0933 \times 6.022 \times 10^{23}$ molecules/mol

$= 0.5618 \times 10^{23}$ molecules

$= 5.618 \times 10^{22}$ molecules

Ans : Number of moles = 0.0933 mol

Number of molecules of urea

$= 5.618 \times 10^{22}$ molecules

Problem 1.6 : Calculate the number of atoms in each of the following
i. 52 moles of Argon (Ar)
ii. 52 u of Helium (He)
iii. 52 g of Helium (He)

Solution :

i. 52 moles of Argon

1 mole Argon atoms = 6.022×10^{23} atoms of Ar

$\therefore$ 52 moles of Ar

$$= 52 \text{ moles} \times \frac{6.022 \times 10^{23}}{1 \text{mol}} \text{atoms}$$

$= 313.144 \times 10^{23}$ atoms of Argon

ii. 52 u of Helium

Atomic mass of He = mass of 1 atom of He = 4.0u

$\therefore$ 4.0 u = 1 He $\therefore$ 52 u = ?

$$= 52 \text{ u} \times \frac{1 \text{atom}}{4.0 \text{ u}} = 13$$ atoms of He

iii. 52 g of He

Mass of 1 mole of He = 4.0 g

Number of moles of He

$$= \frac{\text{mass of He}}{\text{mass of 1mole of He}}$$

$$= \frac{52 \text{ g}}{4.0 \text{ g mol}^{-1}} = 13 \text{ mol}$$

Number of atoms of He
= Number of moles $\times 6.022 \times 10^{23}$
= 13 mol $\times 6.022 \times 10^{23}$ atoms/mol
= 78.286×10^{23} atoms of He.

1.9 Moles and gases : Many substances exist as gases. If we want to find the number of moles of gas, we can do this more conveniently by measuring the volume rather than mass of the gas. Chemists have deduced from Avogardro law that "One mole of any gas occupies a volume of 22.4 dm^3 at **standard temperature (0^0C) and pressure (1 atm) (STP)**. The volume of 22.4 dm^3 at STP is known as molar volume of a gas.

Number of moles of a gas (n) =

$$\frac{\text{Volume of the gas at STP}}{\text{Molar volume of gas}}$$

Thus
Number of moles of a gas (n) =

$$\frac{\text{Volume of the gas at STP}}{22.4 \text{ dm}^3\text{mol}^{-1}}$$

Number of molecules = number of moles $\times$ 6.022×10^{23} molecules mol^{-1}
(Note : IUPAC has recently changed the standard pressure to 1 bar. Under these **new STP conditions** the molar volume of a gas is 22.71 L mol^{-1})

Problem 1.7 : Calculate the number of moles and molecules of ammonia (NH_3) gas in a volume 67.2 dm^3 of it measured at STP.

Solution :

Volume of NH_3 at STP = 67.2 dm^3
molar volume of a gas = 22.4 dm^3 mol^{-1}

Number of moles (n)

$$= \frac{\text{Volume of the gas at STP}}{\text{Molar volume of gas}}$$

$$\text{Number of moles of } NH_3 = \frac{67.2 \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}}$$

$= 3.0$ mol
Number of molecules = Number of moles $\times$ 6.022×10^{23} molecules mol^{-1}
Number of molecules of NH_3 = 3.0 mol $\times$ 6.022×10^{23} molecules mol^{-1}
$= 18.066 \times 10^{23}$ molecules

Try this

Calculate the volume in dm^3 occupied by 60.0 g of ethane at STP.

Exercises

1. Choose the most correct option.

A. A sample of pure water, whatever the source always contains ..... by mass of oxygen and 11.1 % by mass of hydrogen.
a. 88.9 b. 18 c. 80 d. 16

B. Which of the following compounds can NOT demonstrate the law of multiple proportions ?
a. NO, NO_2 b. CO, CO_2
c. H_2O, H_2O_2 d. Na_2S, NaF

C. Which of the following temperature will read the same value on Celsius and Fahrenheit scales.
a. -40^0 b. $+40^0$
c. -80^0 d. -20^0

D. SI unit of the quantity electric current is .....
a. Volt b. Ampere
c. Candela d. Newton

E. In the reaction $N_2 + 3H_2 \longrightarrow 2NH_3$, the ratio by volume of N_2, H_2 and NH_3 is 1 : 3 : 2 This illustrates the law of
a. definite proportion
b. reciprocal proportion
c. multiple proportion
d. gaseous volumes

F. Which of the following has maximum number of molecules ?
a. 7 g N_2 b. 2 g H_2
c. 8 g O_2 d. 20 g NO_2

G. How many g of H_2O are present in 0.25 mol of it ?
a. 4.5 b. 18
c. 0.25 d. 5.4

H. The number of molecules in 22.4 cm^3 of nitrogen gas at STP is
a. 6.022×10^{20}
b. 6.022×10^{23}
c. 22.4×10^{20}
d. 22.4×10^{23}

I. Which of the following has the largest number of atoms ?
a. 1g Au (s) b. 1g Na (s)
c. 1g Li (s) d. 1g Cl_2 (g)

2. Answer the following questions.

A. State and explain Avogadro's law.

B. Point out the difference between 12 g of carbon and 12 u of carbon

C How many grams does an atom of hydrogen weigh ?

D. Calculate the molecular mass of the following in u.
a. NH_3 b. CH_3COOH c. C_2H_5OH

E. How many particles are present in 1 mole of a substance ?

F. What is the SI unit of amount of a substance ?

G. What is meant by molar volume of a gas ?

H. State and explain the law of conservation of mass.

I. State the law of multiple proportions.

3. Give one example of each

A. homogeneous mixture
B. heterogeneous mixture
C. element D. compound

4. Solve problems :

A. What is the ratio of molecules in 1 mole of NH_3 and 1 mole of HNO_3.
(Ans. : 1:1)

B. Calculate number of moles of hydrogen in 0.448 litre of hydrogen gas at STP
(Ans. : 0.02 mol)

C. The mass of an atom of hydrogen is 1.008 u. What is the mass of 18 atoms of hydrogen. (18.144 u)

D. Calculate the number of atom in each of the following (Given : Atomic mass of I = 127 u).
a. 254 u of iodine (I)
b. 254 g of iodine (I)
(Ans. : 2 atoms, 1.2044×10^{24} atoms)

E. A student used a carbon pencil to write his homework. The mass of this was found to be 5 mg. With the help of this calculate.
a. The number of moles of carbon in his homework writing.
(Ans : 4.16×10^{-4})

b. The number of carbon atoms in 12 mg of his homework writting

(Ans : 6.022×10^{20})

F. Arjun purchased 250 g of glucose ($C_6H_{12}O_6$) for Rs 40. Find the cost of glucose per mole.

(Ans : Rs 28.8)

G. The natural isotopic abundance of ^{10}B is 19.60% and ^{11}B is 80.40 %. The exact isotopic masses are 10.13 and 11.009 respectively. Calculate the average atomic mass of boron

(Ans. :10.81)

H. Convert the following degree Celsius temperature to degree Fahrenheit.

a. 40 ^{0}C b. 30 ^{0}C

(Ans. : A. 104 ^{0}F, B. 86 ^{0}F)

I. Calculate the number of moles and molecules of acetic acid present in 22 g of it.

(Ans. : 0.3666 mol, 2.2076×10^{23} molecules)

J. 24 g of carbon reacts with some oxygen to make 88 grams of carbon dioxide. Find out how much oxygen must have been used.

(Ans. : 64.0)

K. Calculate number of atoms is each of the following. (Average atomic mass : N = 14 u, S = 32 u)

a. 0.4 mole of nitrogen

b. 1.6 g of sulfur

(Ans. : A. 2.4088×10^{23} , B. 3.011×10^{22} atom)

L. 2.0 g of a metal burnt in oxygen gave 3.2 g of its oxide. 1.42 g of the same metal heated in steam gave 2.27 of its oxide. Which law is verified by these data ?

M. In two moles of acetaldehyde (CH_3CHO) calculate the following

a. Number of moles of carbon

b. Number of moles of hydrogen

c. Number of moles of oxygen

d. Number of molecules of acetaldehyde

(Ans. : A. 4 mol, B. 8 mol, C. 2 mol, D. 12.044×10^{23} molecules)

N. Calculate the number of moles of magnesium oxide, MgO in i. 80 g and ii. 10 g of the compound. (Average atomic masses of Mg = 24 and O = 16)

(Ans. i. 2 mol ii. 0.25 mol)

O. What is volume of carbon dioxide, CO_2 occupying by i. 5 moles and ii. 0.5 mole of CO_2 gas measured at STP.

(Ans. i. 112 dm^3 ii. 11.2dm^3)

P. Calculate the mass of potassium chlorate required to liberate 6.72 dm^3 of oxygen at STP. Molar mass of $KClO_3$ is 122.5 g mol^{-1}.

(Ans. 24.5 g)

Q. Calculate the number of atoms of hydrogen present in 5.6 g of urea, $(NH_2)_2CO$. Also calculate the number of atoms of N, C and O.

(Ans. : No. of atoms of H = 2.24×10^{23}, N = 1.124×10^{23} and C = 0.562×10^{23}, O = 0.562×10^{23})

R. Calculate the mass of sulfur dioxide produced by burning 16 g of sulfur in excess of oxygen in contact process. (Average atomic mass : S = 32 u, O = 16 u)

(Ans. 32 g)

5. Explain

A. The need of the term average atomic mass.

B. Molar mass.

C. Mole concept.

D. Formula mass with an example.

E. Molar volume of gas.

F. Types of matter (on the basis of chemical composition).

Activity :

Collect information of various scientists and prepare charts of their contribution in chemistry.

2. Introduction to analytical chemistry

2.1 Introduction : Analytical chemistry facilitates investigation of chemical composition of substances. It uses the instruments and methods to separate, identify and quantify the matter under study. The analysis thus provides chemical or physical information about a sample. Analysis may be qualitative or quantitative. Qualitative analysis is concerned with the detection of the presence or absence of elements in compounds and mixture of compounds. Quantitative analysis deals with the determination of the relative proportions of elements in compounds and mixture compounds.

Remember

The branch of chemistry which deals with the study of seperation, identification, qualitative and quantitative determination of the compositions of different substances, is called analytical chemistry.

Importance of analytical chemistry :

The course of analytical chemistry extends the knowledge acquired by the students in studying general, inorganic and organic chemistry. Chemical analysis is one of the most important methods of monitoring the composition of raw materials, intermediates and finished products, and also the composition of air in streets and premises of industrial plants. In agriculture, chemical analysis is used to determine the composition of soils and fertilizers; in medicine, to determine the composition of medicinal preparations.Analytical chemistry has applications in forensic science, engineering and industry. Industrial process as a whole and the production of new kinds of materials are closely associated with analytical chemistry. Analytical chemistry consists of classical, wet chemical methods and modern instumental methods.

2.2 Analysis : Analysis is carried out on a small sample of the material to be tested, and not on the entire bulk. When the amount of a solid or liquid sample is a few grams, the analysis is called semi-microanalysis. It is of two types : **qualitative and quantitative**. Classical qualitative analysis methods include separations such as precipitation, extraction and distillation. Identification may be based on differences in colour, odour, melting point, boiling point, and reactivity. Classical quantitative methods consist of volumetric analysis, gravimetric analysis, etc.

2.2.1 Chemical methods of qualitative analysis : Chemical analysis of a sample is carried out mainly in two stages : by the dry method in which the sample under test is not dissolved and by the wet method in which the sample under test is first dissolved and then analyzed to determine its composition. The dry method is usually used as preliminary tests in the qualititative analysis.

The semi-micro qualitative analysis is carried out using apparatus such as : test tubes, beakers, evaporating dish, crucible, spot plate, watch glass, wire guaze, water bath, burner, blow pipe, pair of tongues, centrifuge, etc.

The qualitative analysis of **organic** and **inorganic** compounds involves **different** types of **tests**. The majority of organic compounds are composed of a relatively small number of elements. The most important ones are : carbon, hydrogen, oxygen, nitrogen, sulphur, halogen, phosphorous. Elementary qualitative analysis is concerned with the detection of the presence of these elements. The identification of an organic compound involves tests such as detection of functional group, determinition of melting/ boiling point, etc. The qualitative analysis of simple inorganic compounds involves detection and confirmation of cationic

and anionic species (basic and acidic radical) in them.

2.2.2 Chemical methods of quantitative analysis : Quantitative analysis of organic compounds involves methods such as (i) determination of percentage constituent element, (ii) concentrations of a known compound in the given sample, etc. Quantitative analysis of simple inorganic compounds involves methods based on (i) decomposition reaction (gravimetric analysis), and (ii) the progress of reaction between two solutions till its completion (titrametric or volumetric analysis), etc. The quantitative analytical methods involve measurement of quantities such as mass and volume, by means of some equipment/ apparatus such as weighing machine, burette.

2.3 Mathematical operation and error analysis : The accuracy of measurement is of a great concern in analytical chemistry. Also there can be intrinsic errors in the analytical measurement. The numerical data, obtained experimentally, are treated mathematically to reach some quantitative conclusion. Therefore, an anlytical chemist has to know how to report the quantitative analytical data, indicating the extent of the accuracy of measurement, perform the mathematical operation and properly express the quatitative error in the result. In the following subsection we will consider these aspects related to measurments and calculation.

2.3.2 Scientific notation (exponential notation) : A chemist has to deal with numbers as large as 602,200,000,000, 000, 000, 000, 000 for the molecules of 2 g of hydrogen gas or as small as 0.00000000000000000000000166g. that is, mass of a H atom. To avoid the writing of so many zeros in mathematical operations, scientific notations i.e. exponential notations are used. Here, any number can be represented into a form N x 10^n where 'n' is an exponent having positive or negative values and N can vary $1 \leqslant N < 10$. Thus, we can write the above values as 6.022 x 10^{23} and 1.66 x 10^{-24} g. The number 123.546 becomes 1.23546 x 10^2, in scientific notation. Note that while writing it, we have moved the decimal to the left by two places and same is the exponent (2) of 10 in the scientific notation. Similarly, 0.00015 can be written as 1.5 x 10^{-4}.

Problem 2.1 : For adding 5.55 x 10^4 and 6.95 x 10^3, first the exponent is made equal. Thus
5.55 x 10^4 + 0.695 x 10^4. Then these numbers can be added as follows :
(5.55 + 0.695) x 10^4 = 6.245 x 10^4

Problem 2.2 : The subtraction of two numbers can be done as shown below:
3.5 x 10^{-2} - 5.8 x 10^{-3}
= (3.5 x 10^{-2}) - (0.58 x 10^{-2})
= (3.5 - 0.58) x 10^{-2}
= 2.92 x 10^{-2}

Here the decimal has to be moved four places to the right and (-4) is the exponent in the scientific notation. Now let us perform mathematical operations on numbers expressed in scientific notation.

Problem 2.3 : (5.6 x 10^5) x (6.9 x 10^8)
= (5.6 x 6.9) (10^{5+8})
= (5.6 x 6.9) x 10^{13}
= 38.64 x 10^{13}
= 3.864 x 10^{14}

Problem 2.4 : (9.8 x 10^{-2}) x (2.5 x 10^{-6})
= (9.8 x 2.5) ($10^{-2 + (-6)}$)
= (9.8 x 2.5) x (10^{-2-6})
= 24.50 x 10^{-8}
= 2.45 x 10^{-7}

Addition and subtraction : To perform addition operation, first the numbers are written in such a way that they have the same exponent. The coefficients are then added. (Problems 2.1 and 2.2)

Multiplication : The rule for the multiplication of exponential numbers can be well explained from the solved problems 2.3 and 2.4.

2.3.2 Precision and accuracy of measurement

Aim of any measurement is to get the actual value called true value or accepted value of a quantity. Nearness of the measured value to the true value is called the accuracy of measurement. Larger the accuracy smaller the error. Accuracy depends upon the sensitivity or least count (the smallest quantity that can be measured) of the measuring quuipment. consider, for example, a burette reading of 10.2 mL. For all the three situations in the Fig. 2.1 the reading would be noted as 10.2 mL It means that there is an uncertainty about the digit appearing after the decimal point in the reading 10.2 mL. This is because the least count of the burette is 0.1 mL. The meaning of the reading 10.2 mL is that the true value of the reading lies between 10.1 mL and 10.3 mL. This is indicated by writing 10.2 ± 0.1 mL. Here, the burette reading has an error of ± 0.1mL (Fig. 2.1).

Errors may be expressed as **absolute** or **relative error**.

Absolute error = Observed value - True value

Relative error is generally a more useful quantity than absolute error. Relative error is the ratio of an absolute error to the true value. It is expressed as a percentage.

$$\text{Relative error} = \frac{\text{Absolute error}}{\text{True value}} \times 100\ \%$$

There can be error in a measurement due to a number of reasons including inefficiency of the person doing measurement.

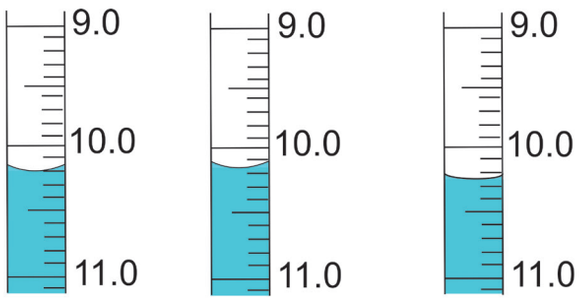


Fig. 2.1 : Three possibilities of a burette reading 10.2 mL

Multiple readings of the same quantity are noted to minimize the error. If the readings match closely, they are said to have high precision. High percision implies reproducibility of the readings. **High precision is a prerequisite for high accuracy**. Precision is expressed in terms of deviation. An absolute deviation is the modulus of the difference between an observed value and the arithmetic mean for the set of several measurements made in the same way. It is a measure of absolute error in the repeated observation.

Absolute deviation = | Observed value - Mean |

Arithmetic mean of all the absolute deviations is called the mean absolute deviation in the measurements. The ratio of mean absolute deviation to its arithmentic means is called relative deviation.

Relative deviation

$$= \frac{\text{Mean absolute deviation}}{\text{Mean}} \times 100\ \%$$

Problem 2.5 : In laboratory experiment, 10 g potassium chlorate sample on decomposition gives following data ; The sample contains 3.8 g of oxygen and the actual mass of oxygen in the quantity of potassium chlorate is 3.92 g. Calculate absolute error and relative error.

Solution : The observed is 3.8 g and accepted value is 3.92 g

Absolute error = Observed value - True value

$= 3.8 - 3.92 = -0.12$ g

The negative sign indicates that your experimental result is lower than the true value.

$$\text{The relative error} = \frac{\text{Absolute error}}{\text{True value}} \times 100\%$$

$$= \frac{-0.12}{3.92} \times 100\%$$

$$= -3.06\ \%$$

Problem 2.6 : The three identical samples of potassium chlorate are decomposed. The mass of oxygen is determined to be 3.87 g, 3.95 g and 3.89 g for the set. Calculate absolute deviation and relative deviation.

Solution :

$$\text{mean} = \frac{3.87 + 3.95 + 3.89}{3} = 3.90$$

Average deviation of a set of measurements		
Sample	**Mass of oxygen**	**Deviation**
1	3.87g	0.03g
2	3.95g	0.05g
3	3.89g	0.01g
Mean absolute deviation		0.03

Absolute deviation

$$= |\text{Observed value} - \text{Mean}|$$

$\therefore$ Mean absolute deviation = $\pm$ 0.03 g.

The relative deviation,

$$= \frac{\text{Mean absolute deviation}}{\text{Mean}} \times 100\ \%$$

$$= \frac{0.03}{3.9} \times 100\% = 0.8\%$$

2.3.3 Significant Figures : Uncertainty in measured value leads to uncertainty in calculated result. Uncertainty in a value is indicated by mentioning the number of significant figures in that value. Consider, the column reading 10.2 $\pm$ 0.1 mL recorded on a burette having the least count of 0.1 mL. Here it is said that the last digit '2' in the reading is uncertain, its uncertainty is $\pm$0.1 mL. On the other hand, the figure '10' is certain. The significant figures in a measurement or result are the number of digits known with certainty plus one uncertain digit. In a scientific experiment a result is obtained by doing calculation in which values of a number of quantities measured with equipment of different least counts are used.

Following rules are to be followed during such calculation.

2.3.4 Rules for deciding significant figures :

1. All non zero digits are significant; e. g. 127.34 g contains five significant figures which are 1, 2, 7, 3 and 4.
2. All zeros between two non zero digits are significant e. g. 120.007 m contains six significant figures.
3. Zeroes on the left of the first non zero digit are not significant. Such a zero indicates the position of the decimal point. For example, 0.025 has two significant figures, 0.005 has one significant figure.
4. Zeroes at the end of a number are significant if they are on the right side of the decimal point. Terminal zeros are not significant if there is no decimal point. (This is beacause the least count of an instrument contains decimal point) For example 0.400 g has three singnificant figures. The measurements here indicates that it is made on a weighing machine having least count of 0.001 g. Significant figures are also indicated in scientific notation by means of decimal point. For example, the measurment 400 g has one significant figure. The measurement 4.0×10^2 g has two significant figures, wheras the measurment 4.00×10^2 g has three significant figures. The zeros after the decimal points in these cases indicates that the least counts of the weighing machines are 1 g, 0.1 g and 0.01 g, respectively.
5. In numbers written is scientific notation, all digits are significant. For example, 2.035×10^2 has four significant figures, and 3.25×10^{-5} has three significant figures.

Problem 2.7 : How many significant figures are present in the following measurements ?

a. 4.065 m b. 0.32 g c. 57.98 cm^3
d. 0.02 s e. 4.0 x 10^{-4} km
f. 604.0820 kg g. 307.100 x 10^{-5} cm

Ans. : a. 4 b. 2 c. 4 d. 1
e. 2 f. 7 g. 6

In general, a quantity measured with an instrument of smaller least count will have more significant figures and will be more accurate than when measured with an instrument of larger least count.

2.3.5 Calculations with significant figures :

When performing calculations with measured quantities the rule is that the accuracy of the final result is limited to the accuracy of the least accurate measurement. In other words, the final result can not be more accurate than the least accurate number involved in the calculation.

Rounding off : The final result of a calculation often contains figures that are not significant. When this occurs the final result is rounded off. The following rules are used to round off a number to the required number of significant figures :

If the digit following the last digit to be kept is less than five, the last digit is left unchanged.

e.g. 46.32 rounded off to two significant figures is 46.

If the digit following the last digit to be kept is five or more, the last digit to be kept is increased by one. e.g. 52.87 rounded to three significant figures is 52.9.

Problem 2.8 : Round off each of the following to the number of significant digits indicated :
a. 1.223 to two digits b. 12.56 to three digits c. 122.17 to four digits d. 231.5 to three digits.
Ans. : i. 1. 2; the third digit is less than 5, so we drop it all the others to its right.
ii. 12.6 ; the fourth digit is greater than 5, so we drop it and add 1 to the third digit.
iii. 122.2 ; the fifth digit is greater than 5, so we do it and add 1 to the fourth digit.
iv. 232; the fourth digit is 5, so we drop it and add 1 to the third digit.

2.4 Determination of molecular formula :

Molecular formula of a compound is the formula which indicates the actual number of atoms of the constituent elements in a molecule. It can be obtained from the experimentally determined values of percent elemental composition and molar mass of that compound.

2.4.1 Percent composition and empirical formula : Compounds are formed by chemical combination of different elements. Quantitative determination of the constituent element by suitable methods provides the percent elemental composition of a compound. If the percent total is not 100, the difference is considered as percent oxygen. From the the per cent composition, the ratio of the atoms of the constituent elements in the molecule is calculated. **The simplest ratio of atoms of the constituent elements in a molecule is called the empirical formula of that compound**. Molecular formula can be obtained from the empirical formula if the molar mass is known. The molar mass of the substance under examination is determined by some convenient method. The following example illustrates this sequence.

Problem 2.9 : A compound contains 4.07 % hydrogen, 24.27% carbon and 71.65 % chlorine by mass. Its molar mass is 98.96 g. What is its empirical formula ? Atomic masses of hydrogen, carbon and chlorine are 1.008, 12.000 and 35.453 u, respectively
Solution :
Step I : Check whether the sum of all the percentages is 100.
$4.07 + 24.27 + 71.65 = 99.99 \approx 100$
Therefore no need to consider presence of oxygen atom in the molecule.
Step II : Conversion of mass percent to grams. Since we are having mass percent, it is convenient to use 100 g of the compound as the starting material. Thus in the 100 g sample of the above compound, 4.07 g hydrogen 24.27 g carbon and 71.65 g chlorine is present..... Contd on next page

Step III : Convert into number/of moles of each element. Divide the masses obtained above by respective atomic masses of various elements.

$$\text{Moles of hydrogen} = \frac{4.07\ g}{1.008\ g} = 4.04$$

$$\text{Moles of carbons} = \frac{24.27\ g}{12.01\ g} = 2.0225$$

$$\text{Moles of chlorine} = \frac{71.65\ g}{35.453\ g} = 2.021$$

Steps IV : Divide the mole values obtained above by the smallest value among them.
Since 2.021 is smallest value, division by it gives a ratio of 2:1:1 for H:C:Cl.
In case the ratio are not whole numbers, then they may be converted into whole number by multiplying by the suitable coefficient.
Step V : Write empirical formula by mentioning the numbers after writing the symbols of respective elements. CH_2Cl is thus, the empirical formula of the above compound.
Step VI : Writing molecular formula
a. Determine empirical formula mass : Add the atomic masses of various atoms present in the empirical formula.
For CH_2Cl, empirical formula mass is
$12.01 + 2 \times 1.008 + 35.453$
$= 49.48$ g
b. Divide molar mass by empirical formula mass

$$\therefore \frac{\text{Molar mass}}{\text{Empirical formula mass}} = \frac{98.96\ g}{49.48\ g}$$

$\therefore r = 2$
c. multiply empirical formula by r obtained above to get the molecular formula.
Molecular formula = r x empirical formula
molecular formula is 2 x CH_2Cl i.e. $C_2H_4Cl_2$.

Problem 2.10 : A compound with molar mass 159 was found to contain 39.62 % copper and 20.13 % sulfur. Suggest molecular formula for the compound (Atomic masses: Cu = 63, S = 32 and O = 16).
Solution :
% copper + % sulfur = 39.62 + 20.13
= 59.75
This is less than 100 % Hence compound contains adequate oxygen so that the total percentage of elements is 100%.
Hence % of oxygen = 100 - 59.75 = 40.25%

$$\text{Moles of Cu} = \frac{\%\ \text{of Cu}}{\text{Atomic mass of Cu}}$$

$$= \frac{39.62}{63} = 0.629$$

$$\text{Moles of S} = \frac{\%\ \text{of S}}{\text{Atomic mass of S}}$$

$$= \frac{20.13}{32} = 0.629$$

$$\text{Moles of O} = \frac{\%\ \text{of O}}{\text{Atomic mass of O}} = \frac{40.25}{16}$$
$= 2.516$
Hence the ratio of number of moles of Cu:S:O is

$$\frac{0.629}{0.629} = 1 \quad \frac{0.629}{0.629} = 1 \text{ and } \frac{2.516}{0.629} = 4$$

Hence empirical formula is $CuSO_4$
Empirical formula mass
$= 63 + 32 + 16 \times 4 = 159$
Molar mass = Empirical mass (Since Molar mass = Molecular mass)
$\therefore$ Molecular formula = Empirical formula
= $CuSO_4$

2.5 Chemical reactions and stoichiometric calculations

Calculation based on a balanced chemical equations are known as stoichiometric calculations.

Balanced chemical equation is symbolic representation of a chemical reaction. It supplies the following information which is useful in solving problems based on chemical equations

i. It indicates the number of moles of the reactants involved in a chemical reaction and the number of moles of the products formed.

ii. It indicates the relative masses of the reactants and products linked with a chemical change, and

iii. it indicates the relationship between the volume/s of the gaseous reactants and products, at STP.

2.5.1 Stoichiometric problems

Generally problems based on stoichiometry are of the following types :

a. Problems based on mass-mass relationship;

b. Problems based on mass-volume relationship and

c. Problems based on volume-volume relationship.

Steps involved in problems based on stoichiometric calculations :

1. Write down the balanced chemical equation representing the chemical reaction.
2. Write the number of moles and the relative masses or volumes of the reactants and products below the respective formulae.
3. Relative masses or volumes should be calculated from the respective formula mass referring to the condition of STP.
4. Apply the unitary method to calculate the unknown factor/s as required by the problem.

Problem 2.11 : Calculate the mass of carbon dioxide and water formed on complete combustion of 24 g of methane gas. (Atomic masses, C = 12 u, H = 1 u, O = 16 u)

Solution : The balanced chemical equation is,

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$

$(12 + 4)\quad 2 \times (16 \times 2)\quad 12 + (16 \times 2)\quad 2 \times (2 + 16)$

$= 16\ g \qquad = 64\ g \qquad = 44\ g \qquad = 36\ g$

Hence, 16 g of CH_4 on complete combustion will produce 44 g of CO_2

$\therefore$ 24 g of $CH_4 = \frac{24}{16} \times 44 = 66$ g of CO_2

Similarly, 16 g of CH_4 will produce 36 g of water.

24 g of $CH_4 \equiv \frac{24}{16} \times 36 = 54$ g water.

Problem 2.12 : How much CaO will be produced by decomposition of 5g $CaCO_3$?

Solution : Calcium carbonate decomposes according to the balanced equation,

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow$

$40 + 12 + 3 \times 16 \qquad 40 + 16 \qquad 12 + 2 \times 16$

$= 100$ parts $\qquad = 56$ parts $\qquad = 44$ parts

So, 100 g of $CaCO_3$ produces 56 g of CaO

$\therefore$ 5 g of $CaCO_3$ will produce

$= \frac{56\ \cancel{g}}{100\ \cancel{g}} \times 5g = 2.8$ g of $CaCO_3$

Problem 2.13 : How many litres of oxygen at STP are required to burn completely 2.2 g of propane, C_3H_8 ?

Solution : The balanced chemical equation for the combustion of propane is,

$C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$

$3 \times 12 + 8 \times 1 \qquad 5 \times 22.4$ L

(44 g) $\qquad$ (112 L)

(Where 1 mol of ideal gas occupies 22.4 L of volume)

Thus 44 g of propane requires 112 litres of oxygen for complete combustion

$\therefore$ 2.2 g of propane will require

$\frac{112}{44} \times 2.2 = 5.6$ litres of O_2 at STP for complete combustion.

Problem 2.14 : A piece of zinc weighing 0.635 g when treated with excess of dilute H_2SO_4 liberated 200 cm^3 of hydrogen at STP. Calculate the percentage purity of the zinc sample.

Solution : The relevant balanced chemical equation is,

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

It indicates that 22.4 L of hydrogen at STP = 65 g of Zn.

(where Atomic mass of Zn = 65 u)

$\therefore$ 0.200 L of hydrogen at STP

$= \frac{65g}{22.4\ L} \times 0.200\ L \qquad = 0.58$ g

$\therefore$ percentage purity of Zn $= \frac{0.58}{0.635} \times 100$

$= 91.33\ \%$

2.6 Limiting reagent

When a chemist carries out a reaction, the reactants are not usually present in exact stoichiometric amounts, that is, in the proportions indicated by the balanced equation. Because the goal of a reaction is to produce the maximum quantity of a useful compound from the starting materials, frequently, a large excess of one reactant is supplied to ensure that the more expensive reactant is completely converted into the desired product. The reactant which is present in lesser amount gets consumed after some time and subsequently, no further reaction takes place, whatever be the amount left of the other reactant present. Hence, the reactant which gets consumed, limits the amount of product formed and is therefore, called the **limiting reagent**.

Consider the formation of nitrogen dioxide (NO_2) from nitric axide (NO) and oxygen

$$2NO\,(g) + O_2\,(g) \longrightarrow 2NO_2\,(g)$$

Suppose initially we have 8 moles of NO and 7 moles of O_2. One way to determine which of the two reactants in the limiting reagent is to calculate the number of moles NO_2 obtainable from the given initial quantities of NO and O_2.

From the preceding definition, we see that the limiting reagent will yield the smaller amount of the product. Starting with 8 moles of NO, we find the number of NO_2 produced is

$$8 \text{ mol NO} \times \frac{2 \text{ mol } NO_2}{2 \text{ mol NO}} = 8 \text{ mol } NO_2$$

and starting with 7 moles of O_2, the number of moles NO_2 formed is

$$7 \text{ mol } O_2 \times \frac{2 \text{ mol } NO_2}{1 \text{ mol } O_2} = 14 \text{ mol } NO_2$$

Because 8 moles NO result in a smaller amount of NO_2, NO must be the limiting reagent, and O_2 is the excess reagent, before reaction has started.

Problem 2.15 : Urea [$(NH_2)_2CO$] is prepared by reacting ammonia with carbon dioxide.

$$2NH_3(g) + CO_2(g) \rightarrow (NH_2)_2CO\,(aq) + H_2O(l)$$

In one process, 637.2 g of NH_3 are treated with 1142 g of CO_2. (a) Which of the two reactants is the limiting reagent ? (b) Calculate the mass of $(NH_2)_2CO$ formed. (c) How much excess reagent (in grams) is left at the end of the reaction ?

Solution : (a) We carry out two separate calculations. First : If 637.2 g of NH_3 reacts completely, calculate the number of moles of $(NH_2)_2CO$, that could be produced, by the following relation.

mass of NH_3 → moles of NH_3 → moles of $(NH_2)_2CO$

$$\text{moles of } (NH_2)_2CO = 637.2 \text{ g } NH_3 \times \frac{1 \text{ mol } NH_3}{17.03 \text{ g } NH_3} \times \frac{1 \text{ mol } (NH_2)_2CO}{2 \text{ mol } NH_3}$$

$$= 18.71 \text{ moles } (NH_2)_2CO$$

Second : The relation from 1142 g of CO_2:

mass of CO_2 → moles of CO_2 → moles of $(NH_2)_2CO$

The number of moles of $(NH_2)_2CO$ that could be produced if all the CO_2 reacted :

$$\text{moles of } (NH_2)_2CO = 1142 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g } CO_2} \times \frac{1 \text{ mol } (NH_2)_2CO}{1 \text{ mol } CO_2}$$

$$= 25.95 \text{ mol } (NH_2)_2CO$$

It follows, therefore, that NH_3 must be the limiting reagent because it produces (a) smaller amount of $(NH_2)_2CO$) (b) The molar mass of $(NH_2)_2CO$ is 60.06 g. We use this as a conversion factor to convert from moles of $(NH_2)_2CO$ to grams of $(NH_2)_2CO$.

$$\text{mass of } (NH_2)_2CO = 18.71 \text{ mol } (NH_2)_2CO \times \frac{60.06 \text{ g } (NH_2)_2CO}{1 \text{ mol}}$$

$$\therefore \quad = 1124 \text{ g } (NH_2)_2CO$$

(c) Starting with 18.71 moles of $(NH_2)_2CO$, we can determine the mass of CO_2 that reacted using the mole ratio from the balanced equation and the molar mass of CO_2

.....Contd. on next page

The conversion steps are
moles of $(NH_2)_2CO$ ⟶ moles of CO_2 ⟶ grams of CO_2
So that,
mass of CO_2 reacted
$= 18.71 \text{ mol } (NH_2)_2CO \times \frac{1 \text{ mol } CO_2}{1 \text{ mol } (NH_2)_2CO} \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2}$

$= 823.4$ g
The amount of CO_2 remaining (in excess) is the difference between the initial amount (1142 g) and the amount reacted (823.4 g):
mass of CO_2 remaining = 1142 g - 823.4 g
= 318.6 g ≈ 319 g

2.7 Concentration of solution : A majority of reactions in the laboratory are carried out in solutions. Therefore, it is important to understand how the amount of substance is expressed when it is present in the form of a solution. The concerntration of a solution or the amount of substance present in given volume of a solution can be expressed in any of the following ways :

1. Mass percent or weight percent (w/w %)
2. Mole fraction
3. Molarity (M)
4. Molality (m)

2.7.1 Mass percent : It is obtained by using following relation:

$$\text{Mass percent} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100\ \%$$

Problem 2.16 : A solution is prepared by adding 2 g of a substance A to 18 g of water. Calculate the mass percent of the solute.

Solution : Mass percent of

$$A = \frac{\text{Mass of A}}{\text{Mass of solution}} \times 100$$

$$= \frac{2 \text{ g}}{2 \text{ g of A} + 18 \text{ g of water}} \times 100$$

$$= \frac{2 \text{ g}}{20 \text{ g}} \times 100 = 10\ \%$$

2.7.2 Mole fraction

It is the ratio of number of moles of a particular component of a solution to the total number of moles of the solution. If a substance 'A' dissolves in substance 'B' and their number of moles are n_A and n_B , repsectively, then the mole fraction of A and B are given as :

$$\text{Mole fraction of A} = \frac{\text{No. of moles of A}}{\text{No. of moles of solution}}$$

$$\therefore \text{ Mole fraction of A } = \frac{n_A}{n_A + n_B}$$

$$\text{Mole fraction of B} = \frac{\text{No. of moles of B}}{\text{No. of moles of solution}}$$

$$= \frac{n_B}{n_A + n_B}$$

2.7.3 Molarity

It is the most wideley used unit and is denoted by M. It is defined as the number of moles of the solute present in 1 litre of the solution . Thus,

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in litres}}$$

Problem 2.17 : Calculate the molarity of NaOH in the solution prepared by dissolving its 4 g in enough water to form 250 mL of the solution.

Solution :

Since molarity (M) = $\frac{\text{No. of moles of solute}}{\text{Volume of solution in litres}}$

$$\therefore \text{ M} = \frac{\text{Mass of NaOH / Molar mass of NaOH}}{0.250 \text{ L}}$$

$$\therefore \text{ M} = \frac{4 \text{ g} / 40 \text{ g}}{0.250 \text{ L}}$$

$$\therefore \text{ M} = \frac{0.1 \text{ mol}}{0.250 \text{ L}}$$

$$\therefore \text{ M} = 0.4 \text{ mol L}^{-1} = 0.4 \text{ M}$$

Note that molarity of a solution depends upon temperature because volume of a solution is temperature dependent.

2.7.4 Molality

It is defined as the number of moles of solute present in 1 kg of solvent. It is denoted by m.

$$\text{Molality (m)} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$$

Note that molality of a solution does not change with temperature since mass remains unaffected with temperature. Often in chemistry laboratory, a solution of desired concentration is prepared by diluting a solution of known higher concentration. The solution of higher concentration is also known as stock solution.

Problem 2.18 : The density of 3M solution of NaCl is 1.25 g mL^{-1} Calculate molality of the solution.

Solution : Molarity = 3 mol L^{-1}

Mass of NaCl in 1 L solution = 3×58.5

$\therefore$ = 175.5 g

Mass of 1L solution = $1000 \times 1.25 = 1250$ g

($\because$ density = 1.25 g mL^{-1})

Mass of water in solution = 1250 - 175.5

$\therefore$ = 1074.5 g

$$\text{Molality} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$$

$$= \frac{3 \text{ mol}}{1.0745 \text{ kg}} = 2.79 \text{ m}$$

2.8 Use of graph in analysis : Analytical chemistry also involves deducing some relation, if any, between two or more properties of matter under study. One of the classic example in the relation between temperature and volume of a given amount of gas. A set of experimentally measured values of volume and temperature of a definite mass of a gas upon plotting on a graph paper appeared as in the figure (Fig. 2.2 (a)). When the points are directly connected, a zig zag pattern results (Fig. 2.2 (b)). From this pattern no meaningful result can be deduced. A zig zag pattern results due to many types of errors that incur in many measurements involved an experiment. Figure 2.2 (c) shows a smooth curve which may be called an average curve passing through these points. In the above example it happens to be straight line and the inference is that $V \propto T$.

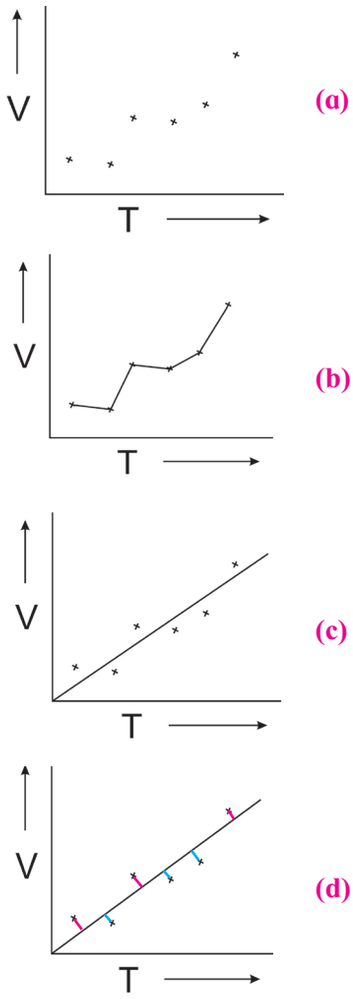


Fig. 2.2 : Drawing an average curve through the points on graph

While fitting it to a smooth curve, care is taken that the plotted points are evenly distributed about it. Mathematically 'even distribution' is understood as follows :

From each point draw a perpendicular to the curve. The perpendicular represents deviation of each point from the curve (Fig 2.2 (d)). The positive deviations are shown in red and negative deviations are shown in blue. Take sum of all the red perpendiculars and all the blue perpendiculars separately. If the two sums are equal (or nearly equal) the curve drawn shows the experimental points in the best possible representation.

Exercises

1. Choose correct option

A. The branch of chemistry which deals with study of separation, identification, and quantitaive determination of the composition of different substances is called as .....
   a. Physical chemistry
   b. Inorganic chemistry
   c. Organic chemistry
   d. Analytical chemistry

B. Which one of the following property of matter is Not quantitative in nature ?
   a. Mass b. Length
   c. Colour d. Volume

C. SI unit of mass is .....
   a. kg b. mol
   c. pound d. m^3

D. The number of significant figures in 1.50×10^4 g is .....
   a. 2 b. 3
   c. 4 d. 6

E. In Avogadro's constant 6.022×10^{23} mol^{-1}, the number of significant figures is .....
   a. 3 b. 4
   c. 5 d. 6

F. By decomposition of 25 g of $CaCO_3$, the amount of CaO produced will be .....
   a. 2.8 g b. 8.4 g
   c. 14.0 g d. 28.0 g

G. How many grams of water will be produced by complete combustion of 12 g of methane gas
   a. 16 b. 27 c. 36 d. 56

H. Two elements A (At. mass 75) and B (At. mass 16) combine to give a compound having 75.8 % of A. The formula of the compound is
   a. AB b. A_2B
   c. AB_2 d. A_2B_3

I. The hydrocarbon contains 79.87 % carbon and 20.13 % of hydrogen. What is its empirical formula ?
   a. CH b. CH_2
   c. CH_3 d. C_2H_5

J. How many grams of oxygen will be required to react completely with 27 g of Al? (Atomic mass : Al = 27, O = 16)
   a. 8 b. 16
   c. 24 d. 32

K. In $CuSO_4.5H_2O$ the percentage of water is .....
   (Cu = 63.5, S = 32, O = 16, H = 1)
   a. 10 % b. 36 %
   c. 60 % d. 72 %

L. When two properties of a system are mathematically related to each other, the relation can be deduced by
   a. Working out mean deviation
   b. Plotting a graph
   c. Calculating relative error
   d. all the above three

2. Answer the following questions

A. Define : Least count

B. What do you mean by significant figures? State the rules for deciding significant figures.

C. Distinguish between accuracy and precision.

D. Explain the terms percentage composition, empirical formula and molecular formula.

E. What is a limiting reagent ? Explain.

F. What do you mean by SI units ? What is the SI unit of mass ?

G. Explain the following terms
   (a) Mole fraction
   (b) Molarity
   (c) Molality

H. Define : Stoichiometry

I. Why there is a need of rounding off figures during calculation ?

J. Why does molarity of a solution depend upon temperature ?

M. Define Analytical chemistry. Why is accurate measurement crucial in science?

3. Solve the following questions

A. How many significant figures are in each of the following quantities ?
   a. 45.26 ft b. 0.109 in
   c. 0.00025 kg d. 2.3659×10^{-8} cm
   e. 52.0 cm^3 f. 0.00020 kg
   g. 8.50×10^4 mm h. 300.0 cg

B. Round off each of the following quantities to two significant figures :
   a. 25.55 mL b. 0.00254 m
   c. 1.491×10^5 mg d. 199 g

C. Round off each of the following quantities to three significant figures :
   a. 1.43 cm^3 b. 458×10^2 cm
   c. 643 cm^2 d. 0.039 m
   e. 6.398×10^{-3} km
   f. 0.0179 g g. 79,000 m
   h. 42,150 i. 649.85;
   j. 23,642,000 mm
   k. 0.0041962 kg

D. Express the following sum to appropriate number of significant figures :
   a. 2.3×10^3 mL + 4.22×10^4 mL + 9.04×10^3 mL + 8.71×10^5 mL;
   b. 319.5 g - 20460 g - 0.0639 g - 45.642 g - 4.173 g

4. Solve the following problems

A. Express the following quantities in exponential terms.
   a. 0.0003498 b. 235.4678
   c. 70000.0 d. 1569.00

B. Give the number of significant figures in each of the following
   a. 1.230×10^4 b. 0.002030
   c. 1.23×10^4 d. 1.89×10^{-4}

C. Express the quantities in above (B) with or without exponents as the case may be.

D. Find out the molar masses of the following compounds :
   a. Copper sulphate crystal ($CuSO_4.5H_2O$)
   (Ans.: 249.5 g/mol)
   b. Sodium carbonate, decahydrate ($Na_2CO_3.10H_2O$)
   (Ans.: 286 g/mol)
   c. Mohr's salt [$FeSO_4(NH_4)_2SO_4.6H_2O$]
   (Ans.: 392 g/mol)
   (At. mass : Cu = 63.5; S = 32; O = 16; H = 1; Na = 23; C = 12; Fe = 56; N = 14)

E. Work out the percentage composition of constituents elements in the following compounds :
   a. Lead phosphate [$Pb_3(PO_4)_2$],
   b. Potassium dichromate ($K_2Cr_2O_7$),
   c. Macrocosmic salt - Sodium ammonium hydrogen phosphate, tetrahydrate ($NaNH_4HPO_4.4H_2O$)
   (At. mass : Pb = 207; P = 31; O = 16; K = 39; Cr = 52; Na = 23; N = 14)

F. Find the percentage composition of constituent green vitriol crystals ($FeSO_4.7H_2O$). Also find out the mass of iron and the water of crystallisation in 4.54 kg of the crystals. (At. mass : Fe = 56; S = 32; O = 16)
   (Ans.: mass of Fe = 0.915 kg, mass of $7H_2O$ = 2.058 kg)

G. The red colour of blood is due to a compound called "haemoglobin". It contains 0.335 % of iron. Four atoms of iron are present in one molecule of haemoglobin. What is its molecular weight ? (At. mass : Fe 55.84)
   (Ans.: 66674.6 g/mol)

H. A substance, on analysis, gave the following percent composition: Na = 43.4 %, C = 11.3 % and O = 45.3 %. Calculate the empirical formula. (At. mass Na = 23 u, C = 12 u, O = 16 u).
   (Ans.: Na_2CO_3)

I. Assuming the atomic weight of a metal M to be 56, find the empirical formula of its oxide containing 70.0% of M.
   (Ans.: M_2O_3)

J. 1.00 g of a hydrated salt contains 0.2014 g of iron, 0.1153 g of sulfur, 0.2301 g of oxygen and

0.4532 g of water of crystallisation. Find the empirical formula. (At. wt. : Fe = 56; S = 32; O = 16)

(Ans.: $FeSO_4$)

K. An organic compound containing oxygen, carbon, hydrogen and nitrogen contains 20 % carbon, 6.7 % hydrogen and 46.67 % nitrogen. Its molecular mass was found to be 60. Find the molecular formula of the compound.

(Ans.: CH_4N_2O)

L. A compound on analysis gave the following percentage composition by mass : H = 9.09; O = 36.36; C = 54.55. Mol mass of compound is 88. Find its molecular formula.

M. Carbohydrates are compounds containing only carbon, hydrogen and oxygen. When heated in the absence of air, these compounds decompose to form carbon and water. If 310 g of a carbohydrate leave a residue of 124 g of carbon on heating in absence of air, what is the empirical formula of the carbohydrate ?

(Ans.: CH_2O)

N. Write each of the following in exponential notation :

a. 3,672,199 b. 0.000098

c. 0.00461 d. 198.75

O. Write each of the following numbers in ordinary decimal form :

a. 3.49×10^{-11} b. 3.75×10^{-1}

c. 5.16×10^{4} d. 43.71×10^{-4}

e. 0.011×10^{-3} f. 14.3×10^{-2}

g. 0.00477×10^{5} h. 5.00858585

P. Perform each of the following calculations. Round off your answers to two digits.

a. $\frac{1}{3.40 \times 10^{24}}$; b. $\frac{33}{9.00 \times 10^{-4}}$;

c. $\frac{1.4 \times 10^{9}}{(2.77 \times 10^{3})\,(3.76 \times 10^{5})}$;

d. $\frac{(4 \times 10^{-3})\,(9.9 \times 10^{-7)}}{(789)\,(1.002 \times 10^{-10})\,(0.3 \times 10^{2})}$

Q. Perform each of the following calculations. Round off your answers to three digits.

a. (3.26 104) (1.54 106)

b. (8.39 107) (4.53 109)

c. $\frac{8.94 \times 10^{6}}{4.35 \times 10^{4}}$

d. $\frac{(9.28 \times 10^{9})\,(9.9 \times 10^{-7})}{(511)\,(2.98 \times 10^{-6})}$

R. Perform the following operations :

a. $3.971 \times 10^{7} + 1.98 \times 10^{4}$;

b. $1.05 \times 10^{-4} - 9.7 \times 10^{-5}$;

c. $4.11 \times 10^{-3} + 8.1\ 10^{-4}$;

d. $2.12 \times 10^{6} - 3.5 \times 10^{5}$.

S. A 1.000 mL sample of acetone, a common solvent used as a paint remover, was placed in a small bottle whose mass was known to be 38.0015 g. The following values were obtained when the acetone - filled bottle was weighed : 38.7798 g, 38.7795 g and 38.7801 g. How would you characterise the precision and accuracy of these measurements if the actual mass of the acetone was 0.7791 g ?

(Ans.: ±0.07736% 0.1027%)

T. Your laboratory partner was given the task of measuring the length of a box (approx 5 in) as accurately as possible, using a metre stick graduated in milimeters. He supplied you with the following measurements:

12.65 cm, 12.6 cm, 12.65 cm, 12.655 cm, 126.55 mm, 12 cm.

a. State which of the measurements you would accept, giving the reason.

(Ans.: 12.6 cm)

b. Give your reason for rejecting each of the others.

U. What weight of calcium oxide will be formed on heating 19.3 g of calcium carbonate ?
(At. wt. : Ca = 40; C = 12; O = 16)
(Ans. : 10.8 g)

V. The hourly energy requirements of an astronaut can be satisfied by the energy released when 34 grams of sucrose are "burnt" in his body. How many grams of oxygen would be needed to be carried in space capsule to meet his requirement for one day ?
(Ans. : 916.21 g)

Activity :

Collect information about various apparatus/instruments used in chemistry laboratory and make presentation of it in science exhibition.

Internet my friend

1.Error in chemical analysis
https://chem.libretexts.org>...>chapters
2. Collect information about Analytical chemistry.

3. Some Analytical Techniques

3.1 Introduction

There has been a systematic development in the techniques used for analysis of chemical substances. In this chapter we are going to look into basic analytical techniques, namely, purification and separation techniques. Chemical substances occur in nature in impure stage. Also, when synthesized in the laboratory they are obtained in crude and impure form. Before investigating their composition and properties it is essential to obtain them in the pure form. Methods of purification and separation of compounds depend on the difference in their physical properties.

3.2 Purification of solids

A solid substance may contain two types of impurities, those (i) which are soluble in the same solvent as the main substance and (ii) which are not soluble in the same solvent as the substance. The second type of impurity can be separated easily using a suitable solvent to dissolve the main compound when the impurities remain undissolved and can be separated by a simple process called **filtration**. This process is similar to separating tea leaves from a decoction of tea, or sand from mixture of sand and water. Filtration is carried out with the help of a filter paper cone placed in a funnel as shown in the Fig. 3.1. A circular piece of filter paper is folded to form a cone and fitted in the funnel. The funnel is fixed on a stand and a beaker kept below it. The paper is made moist, the solution to be filtered is poured on the filter paper.

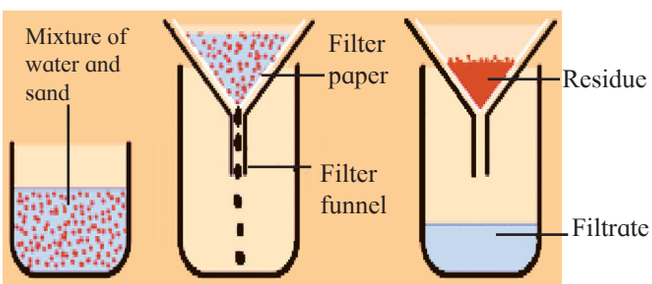


Fig. 3.1 : Separation of mixture of water and sand by simple filtration

The insoluble part remaining on the filter paper is called **residue** and the liquid collected in the beaker is called **filtrate**.

Filtration under suction : When filtration is carried out using a vacuum pump it is called filtration under suction. It is a faster and more efficient technique than simple filtration.

The assembly for filtration under suction consists of a thick wall conical flask with a side arm. The flask is connected to a safety bottle by rubber tube through the side arm. The safety bottle is used to prevent sucking of the filtrate into suction pump. A special porcelain funnel called Buchner funnel is fitted on the conical flask with the help of a rubber cork as shown in Fig. 3.2.

The Buchner funnel has a porous circular bottom. A circular filter paper of correct size is placed on the circular porous bottom of the Buchner funnel and the funnel is placed on the flask. It is moistened with a few drops of water or solvent. Suction is created by starting the pump and filtration is carried out. Crystals are collected on the filter paper and filtrate in the flask.

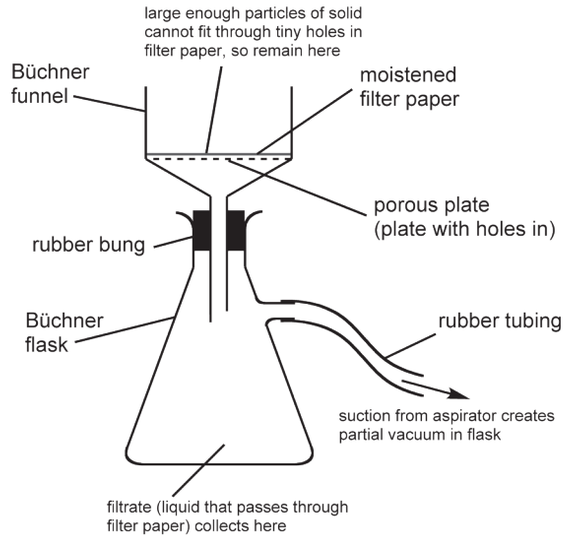


Fig. 3.2 : Setup for filtration under suction

3.2.1 Crystallization : When a crude solid is made of mainly one substance and has some impurities, it is purified by the process of crystallization. It is done in four steps:

(i) Preparation of saturated solution : A saturated solution is a solution which cannot dissolve addtional quantity of solute. A saturated solution of the crude solid is prepared by boiling it in a small but sufficient quantity of a suitable solvent. On doing so the main solute forms an almost saturated solution, but the solution is not saturated with respect to the soluble impurities, as they are in small proportion.

(ii) Hot filtration : The above solution is quickly filtered while hot. Filtration under suction allows rapid filtration. Undissolved impurities get removed in this process as residue.

(iii) Cooling of the filtrate : The hot filtrate is allowed to cool. Solubility of a substance decreases with lowering of temperature. As a result, the filtrate becomes supersaturated with respect to the main dissolved solute. The excess quantity of the dissolved solute comes out of the solution in the form of crystals. The dissolved impurities, however, do not supersaturate the solution, as their quantity is small. These continue to stay in the solution in dissolved state even on cooling. The separated crystals are, therefore, free from soluble impurities as well.

(iv) Filtration : The crystals of the pure substance are separated by filtration. The filtrate obtained is called **mother liquor**. The crystals so formed are free from soluble as well as insoluble impurities.

Choice of the solvent : The solvent to be used for crystallization must have following properties :

1. The compound to be crystallized should be least or sparingly soluble in the solvent at room temperature but highly soluble at high temperature.
2. Solvent should not react chemically with the compound to be purified.
3. Solvent should be volatile so that it can be removed easily.

Water, ethyl alcohol, methyl alcohol, acetone, ether or their combinations are generally used as solvent for crystallization. The choice is done by trial and error method.

Activity : Crystallization of common salt from impure sample.

Many times the common salt obtained from the market may contain some siliceous matter and other impurities. These can be removed and larger crystals of pure NaCl can be obtained.

Apparatus : Beaker, glass rod, funnel, filter paper and stand, evaporating dish, etc.

Materials : Impure market salt or a mixture of salt and fine sand, etc.

Procedure : Arrange apparatus as shown in Fig. 3.3. Take some water in a beaker. Add salt to the beaker and stir it with a glass rod. Add more salt and stir till no more salt dissolves. Heat the solution. Filter the hot solution, insoluble impurities will remain on the filter paper. Collect the filtrate in an evaporating dish and allow to cool. Crystals of pure salt NaCl will separate leaving soluble impurities in the mother liquor. Filter the solution and collect the crystals on the filter paper and dry them.

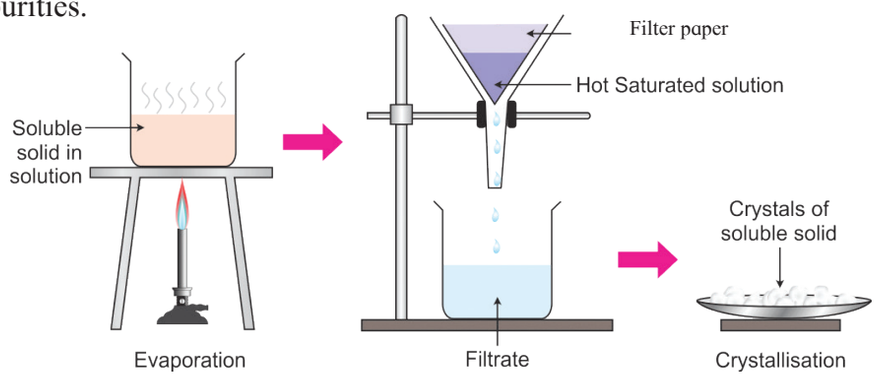


Fig. 3.3 : Process of crystallization

Impure copper sulphate can be purified by crystallization using water as solvent. Similarly, Benzoic acid can also be purified by crystallization using water as solvent.

3.2.2 Fractional crystallization :

Two or more substances in a mixture can be separated by fractional crystallisation process. Fractional crystallisation is a process wherein two or more soluble substances having widely different solubilities in the same solvent at room temperature are separated by crystallization.

Mixture of two solutes A and B are dissolved in a suitable hot solvent to prepare a saturated solution. The saturated solution is filtered to remove dust particles and then allowed to cool. As the solution cools, the solute which is less soluble crystallizes out first. The crystals are filtered, washed with solvent and dried. The mother liquor is concentrated by evaporating the solvent. The second solute crystallizes from the mother liquor. These crystals are filtered to obtain the separated and purified second component.

3.3 : Distillation : Distillation is an important method used to separate. **(i)** Volatile liquids from non-volatile impurities **(ii)** Liquids having sufficient difference in their boiling point.

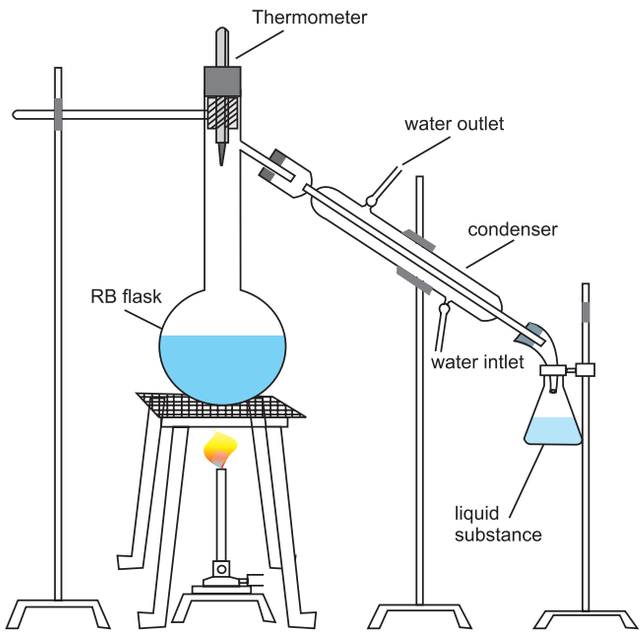


Fig. 3.4 : Simple distillation

3.3.1 Simple distillation :

Liquids which boil without decomposition at atmospheric pressure are purified by the process of **simple distillation**. In this process the liquid is first converted into its vapour by boiling and then the vapour is condensed back into liquid by cooling and the pure liquid trickles down in the reciver.

The apparatus used for simple distillation is shown in Fig. 3.4. It consists of round bottom flask fitted with a cork having a thermometer. The flask has a side arm through which it is connected to a condenser. The condenser has a jacket with two outlets through which water is circulated. The liquid to be distilled is taken in the round bottom flask fixed by clamp. The flask is placed in a water bath or oil bath or sometimes wire gauze is kept on a stand as shown in Fig 3.4.

The condenser is connected to receiver to collect the purified liquid. Care is taken that the bulb of the thermometer is just below the side arm of the round bottom flask.

The flask is heated. As the boiling point of the liquid is reached it starts boiling and the vapors rise to the neck of the flask and pass through the side arm into the cooler parts of the condenser, which is kept cool by circulating water through its jacket. The vapours condense and the liquid is collected in the receiver.

Activity : To separate the components of a liquid mixture containing acetone (b. p. 56 ^{0}C) and water (b. p. 100 ^{0}C)

Apparatus : Distillation flask with condenser, two receivers, thermometer, etc.

Chemicals : mixture of acetone and water.

Principle : Acetone and water are two miscible liquids having a wide difference in their boiling points. Acetone boils at 56 ^{0}C while boiling point of water is 100 ^{0}C. When the mixture of acetone and water is heated and temperature of the mixture reaches 56 ^{0}C acetone would distil off. When all acetone distils out and when the temperature rises to 100 ^{0}C water would to distil out.

Procedure : Take the mixture of water and acetone in the distillation flask and arrange the apparatus. Heat the flask on a water bath carefully. At 56 ^{0}C acetone will distil out, collect it in reciever number 1. After all acetone distilled, change the receiver. Discard a few ml of the liquid. As the temperature reaches 100 ^{0}C water will begin to distil. Collect this in reciever number 2.

3.3.2 Fractional Distillation :

If in a mixture the difference in boiling points of two liquids is not appreciable, they cannot be separated from each other using the simple distillation assembly.

To separate such liquids, the process called fractional distillation is employed in which a special assembly is used (see Fig. 2.5(a)). In this assembly the distillation flask is fitted with a fractionating column (Fig. 3.5 (b)). Hence, the vapours first pass through the fractionating column. Vapours of more volatile liquid with lower boiling point rise up more than the vapours of liquid having higher boiling point.

Suppose we have a mixture of two liquid (A) and (B) having boiling points 363 K and 373 K respectively. A is more volatile and B is less volatile. As the mixture is heated, vapors of (A) along with a little of (B) rise up and come in contact with the large surface of the fractionating column. Vapors of (B) condense rapidly into the distillation flask. While passing through the fractionating column there is an exchange between the ascending vapors and descending liquid. The vapors of B are scrubbed off by the descending liquid, this makes the vapors richer in (A). This process is repeated each time the vapors and liquid come in contact with the surface in the fractionating column. Rising vapors become richer in (A) and escape through the fractionating column and reach the condenser while the liquid in the distillation flask is richer in B. The separated components are further purified by repeating the process. Mixtures of acetone (b.p. 329 K) and methyl alcohol (b.p. 337.7 K); acetone and benzene (353 K) can be separated by fractional distillation.

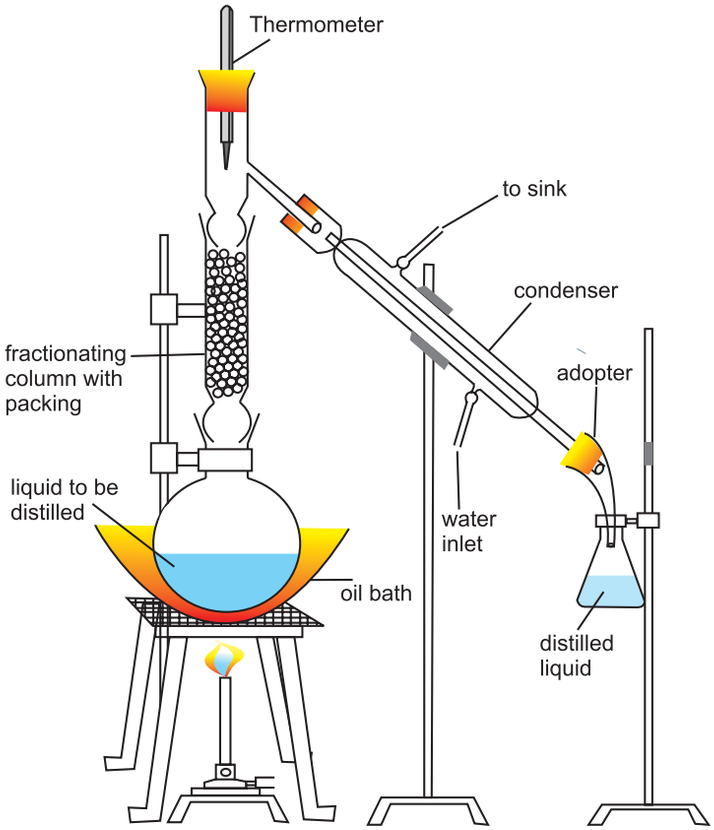


Fig. 3.5 (a) :Fractional distillation

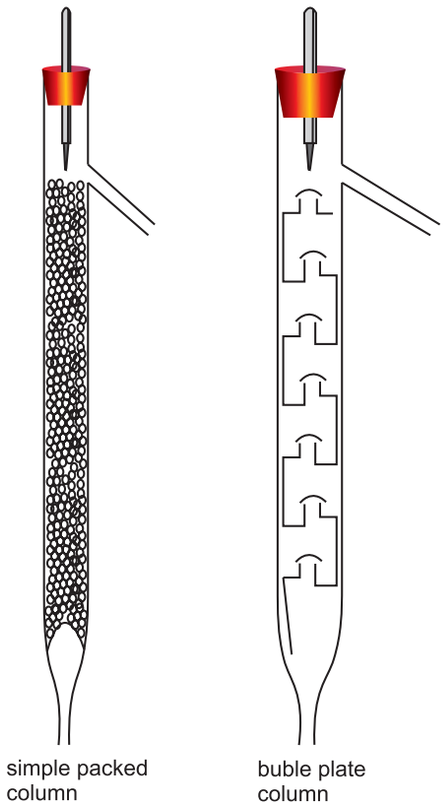


Fig 3.5 (b) : Fractionating Columns

This process is used in petroleum industry to separate different fractions of crude oil.

3.3.3 Distillation under Reduced Pressure :

Liquids having very high boiling point or those which decompose on heating are purified by carrying out distillation under reduced pressure. In this method the liquid is made to boil at a temperature which is below its normal boiling point by reducing the pressure on the surface of the liquid. Pressure is reduced using a water pump or vacuum pump. In soap industry glycerol is separated from soap by using this technique.

3.4 Solvent Extraction : When an organic substance is present in an aqueous solution, it can be extracted from that solution by shaking it with an organic solvent in which the substance is more soluble. The organic liquid should be immiscible with water and be able to form two layers. In this process the solute distributes itself between two immiscible liquids. From the aqueous phase the solute gets extracted in the organic phase. Extraction of compound takes place based on the difference in solubility of compound in two liquids (See Fig. 3.6). On shaking for a few times with small volumes of organic phase, most of the solute gets extracted into the organic phase. The organic solvent is, then, removed by distillation and the solute is collected.

The solvent extraction process is important as it helps clean separations in a short time span.

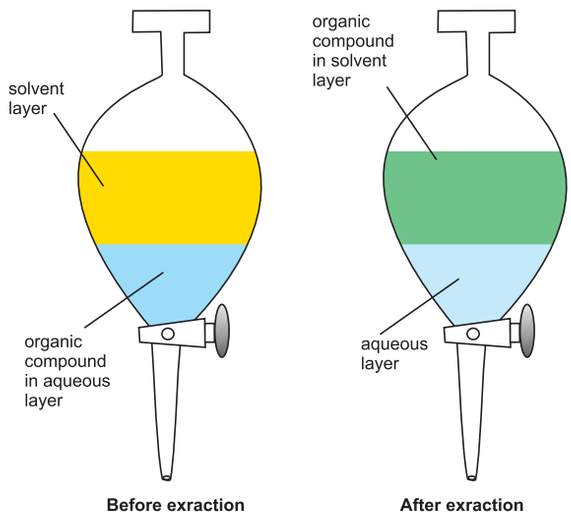


Fig. 3.6 : Solvent Extraction

If the solute is less soluble in organic phase then a technique called **continuous extraction** is used where the same amount of organic solvent is used repeatedly for extraction. This technique involves continuous distillation of the solvent within the same assembly. Thus use of large quantity of organic solvent is avoided.

Internet my friend

Get more information about continuous extraction/soxhlet extraction from YouTube.Royal Scociety of chemistry Soxhlet extraction.

3.5 Chromatographic techniques :

Chromatography is a technique used to separate components of a mixture, and also purify compounds. The name of the technique comes from the Greek word Chroma meaning Colour.

In 1903, Tswett discovered this technique for separating the coloured components found in plants. The principle of separation of substances in this technique is similar to solvent extraction i. e. distribution of the solutes in two phases. In chromatography we use two phases for separation. **(a)** Stationary phase and **(b)** Mobile phase. This technique is based on the difference in rates at which components in the mixture move through the stationary phase under the influence of the mobile phase. First the mixture of components is loaded at one end of the stationary phase and then the mobile phase, which is a pure solvent or a mixture of solvents, is allowed to move over the stationary phase. Depending on the relative affinity of the components toward the stationary phase and mobile phase they remain on the surface of the stationary phase or move along with the mobile phase, and gradually get separated.

The stationary phase can be a solid or a liquid. Depending on the stationary phase, chromatography is classified into Adsorption Chromatography and Partition Chromatography.

3.5.1 Adsorption Chromatography : This type of Chromatography is based on the principle of Differential Adsorption. Different solutes are adsorbed to different extent on the stationary phase. Adsorption Chromatography is of the following two types.

i. Column Chromatography : This type involves the separation of components over a column of stationary phase. The stationary phase material can be Alumina, Silica gel. A slurry of the stationary phase material is filled in a long glass tube provided with a stopcock at the bottom and a glass wool plug at the lower end. The mixture to be separated is dissolved in a small amount of appropriate solvent and is then loaded on top of the adsorbent column. A suitable mobile phase which could be a single solvent or a mixture of solvents is then poured over the adsorbent column. The mixture along with the mobile phase slowly moves down the column. The solutes get adsorbed on the stationary phase and depending on the degree to which they are adsorbed, the solutes get separated from each other. The most strongly adsorbed component is retained on the column and others move down the column to various distances forming bands as seen in Fig. 3.7. The component which is less strongly adsorbed is desorbed first and leaves the column first, while the strongly adsorbed component is eluted later. The solutions of these components are collected separately. On evaporating the solvent the solutes can be recovered.

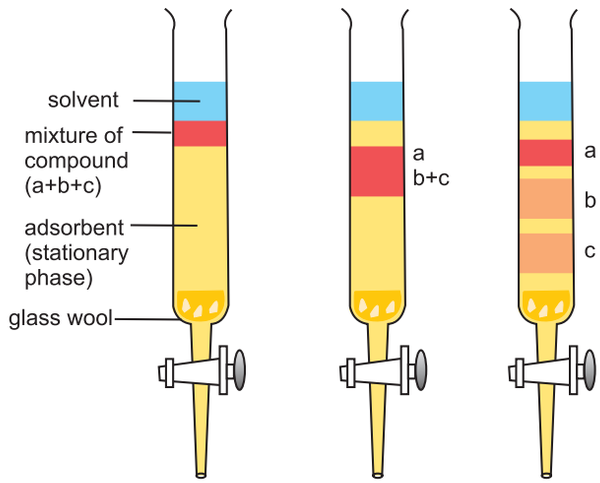


FIG 3.7 Column Chromatography. Different stages of separation.

ii. Thin Layer Chromatography : A thin layer (0.2 mm thick)of adsorbent silica gel or alumina spread over a glass plate acts as the stationary phase. The plate is called the TLC plate or chromplate. The mixture of solutes is applied on the Chromplate as a small spot about 2 cm from one end of the plate as shown in Fig. 3.8.

The plate is then placed in a closed jar containing the mobile phase such that the spot is well above the mobile phase. As the mobile phase rises up the components of the mixture move along with it. They move upto different distances depending upon their degree of adsorption and thus get separated. If the components are colored they appear as separated colored spots on the plate. If the components are not colored but have property of fluorescence they can be visualised under UV light, or the plate can be kept in a chamber containing a few iodine crystals. The Iodine vapors are adsorbed by the components and

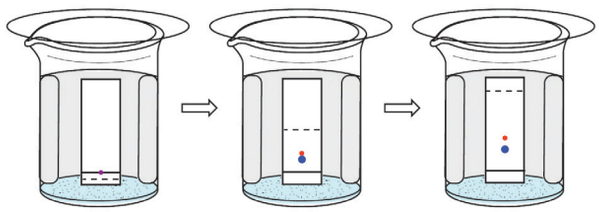


Fig. 3.8 (a)Stages in Thin Layer Chromatography

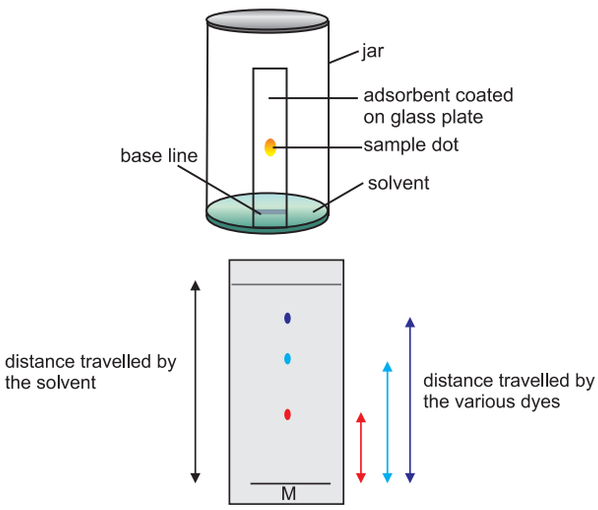


Fig. 3.8 (b) Developed chromatogram.

the spots appear brown. Amino acids are visualised by spraying the plate with a solution of ninhydrin. This is known as spraying agent.

3.5.2 Partition Chromatography : In this type of chromatography the stationary phase and mobile phase both are liquids. Separation of components takes place by continuous differential partitioning of the components between the stationary and mobile phases. For example, Paper Chromatography : In this technique a special quality paper, Whatmann paper number 1, is used. The water trapped in the fibres of the paper acts as the stationary phase. The solution of mixture is spotted on the strip of the Chromatography paper at the about 2 cm from one end of the paper using a glass capillary. The paper is then suspended in a chamber containing the mobile phase taking care that the spot does not dip in the mobile phase (Fig. 3.9).

The mobile phase rises up by capillary action and flows over the spot. Partitioning of the components takes place between stationary phase (water) and the mobile phase.

Different solutes are retained differently on the paper depending on their selective partitioning between the two phases. This developed paper strip is the chromatogram. Similar to TLC (Thin layer chromatography) the colored components are visible as colored spots and the colourless components are observed under UV light or using a spraying agent.

Retention factor (R_f) : Migration of the solute relative to the solvent front gives an idea about the relative retention of the solutes on the stationary phase. This is termed as the R_f of the solute.

$$R_f = \frac{\text{Distance travelled by the solute from the base line}}{\text{Distance travelled by the solvent from the base line}}$$

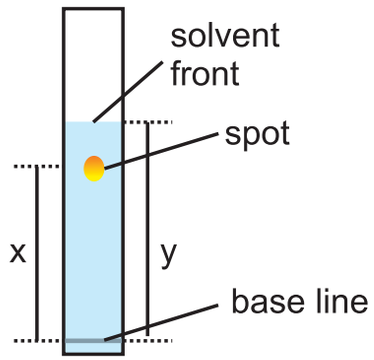


Fig. 3.10 : Retention factor

Internet my friend

Column chromatography
https ://youtube/KqQITxvFDLB8

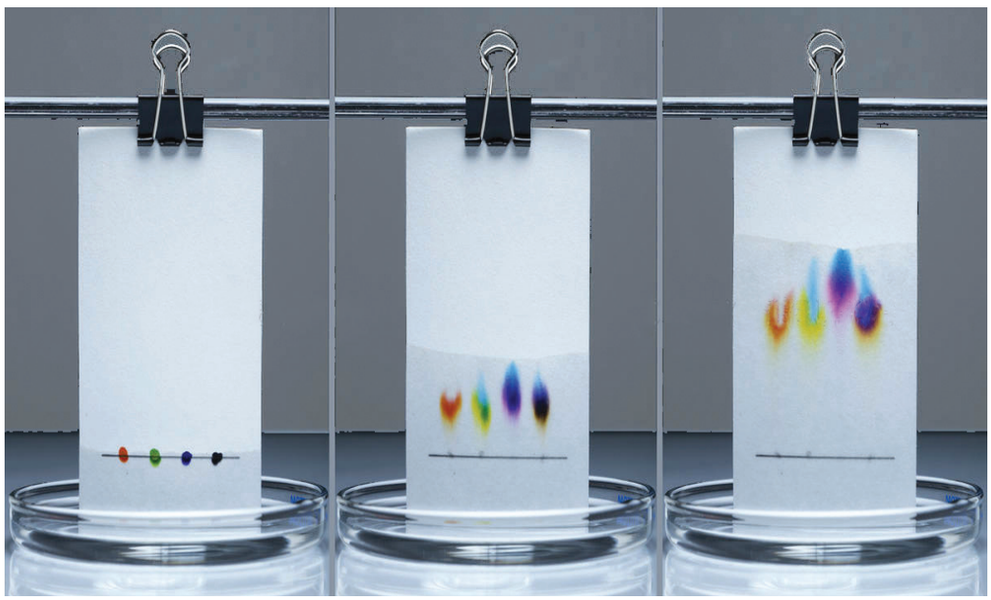


Fig. 3.9 : Stages in Paper chromatography

Exercises

1. Choose the correct option

A. Which of the following methods can be used to seperate two compounds with different solubilities in the same solvent?
   a. Fractional crystallization
   b. Crystallization
   c. Distillation
   d. Solvent extraction

B. Which of the following techniques is used for seperation of glycerol from soap in soap industry ?
   a. Distillation under reduced pressure
   b. Fractional distillation
   c. Filtration
   d. Crystallization

C. Which technique is widely used in industry to seperate components of mixture and also to purify them ?
   a. Steam distillation
   b. Chromatography
   c. Solvent extraction
   d. Filtration

D. A mixture of acetone and benzene can be seperated by the following method :
   a. Simple distillation
   b. Fractional distillation
   c. Distillation under reduced pressure
   d. Sublimation

E. Colourless components on chromatogram can not be observed by the following :
   a. Using UV light
   b. Using iodine chamber
   c. Using the spraying reagent
   d. Using infrared light

2. Answer the following

A. Which of the following techniques is used for purification of solid organic compounds?
   a. Crystallisation b. Distillation

B. What do you understand by the terms
   a. residue b. filtrate.

C. Why is a condenser used in distillation process?

D. Why is paper moistened before filtration?

E. What is the stationary phase in Paper Chromatography?

F. What will happen if the upper outlet of the condenser is connected to the tap instead of the lower outlet?

G. Give names of two materials used as stationary phase in chromatography.

H. Which properties of solvents are useful for solvent extraction?

I. Why should spotting of mixture be done above the level of mobile phase ?

J. Define : a. Stationary phase b. Saturated solution

K. What is the difference between simple distillation and fractional distillation?

L. Define a. Solvent extraction b. Distillation.

M. List the properties of solvents which make them suitable for crystallization.

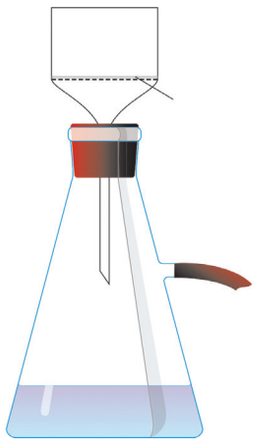
N. Name the different types of Chromatography and explain the principles underlying them.

O. Why do we see bands separating in column chromatography?

P. How do you visualize colourless compounds after separation in TLC and Paper Chromatography?

Q. Compare TLC and Paper Chromatography techniques.

3. Label the diagram and explain the process in your words.



Activity :

Use any one analytical technique in labroratory and discuss it in groups.

4. Structure of Atom

Can you recall?

- What is the smallest unit of matter ?
- What is the difference between molecules of an element and those of a compound ?
- Does an atom have any internal structure or is it indivisible ?
- Which particle was identified by J. J. Thomson in the cathode ray tube experiment ?
- Which part of an atom was discovered by Ernest Rutherford from the experiment of scattering of α-particles by gold foil ?

4.1 Subatomic particles : Dalton's atomic theory was able to explain the laws of chemical combination successfully. However, it failed to explain some properties of matter. For example, it could not explain why substances like glass or ebonite when rubbed with silk or fur, generate electricity. Discovery of subatomic particles in late nineteenth and early twentieth century set a blow to Dalton's atomic model of hard sphere. Three important subatomic particles, namely, proton, electron and neutron which are of concern to Chemistry were discovered. Proton and neutron are present in the atomic nucleus and together are called nucleons. Electrons are present in the extranuclear part of an atom.The properties of electron, proton and neutron are summarised in Table 4.1

Table 4.1 : Properties of subatomic particles

Name	Symbol	Absolute charge/C	Relative charge	Symbol for charge	Mass/kg	Mass/u	Approxinate mass/u
Electron	e^-	-1.6022×10^{-19}	-1	$-e$	9.10938×10^{-31}	0.00054	0 u
Proton	p	$+1.6022\times10^{-19}$	+1	$+e$	1.6726×10^{-27}	1.00727	1 u
Neutron	n	0	0		1.67493×10^{-27}	1.00867	1 u

4.1.1 Discovery of electron : In the year 1897, **J. J. Thomson** investigated the cathode rays and found that the cathode rays are a stream of very small, negatively charged particles which are 1837 times lighter than a hydrogen atom and are present in all atoms. Later these particles were named as electrons.

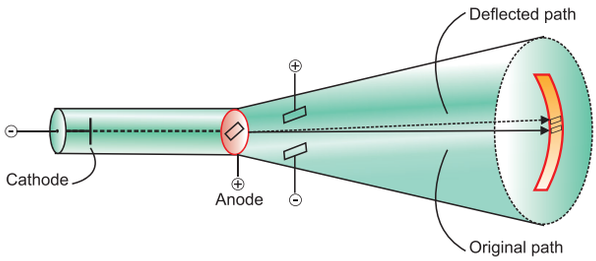


Fig. 4.1 : Cothode ray tube experiment

4.1.2 Discovery of proton : In the year 1911, **Ernest Rutherford** found in the experiment of scattering of α-particles by thin gold foil (see Fig. 4.2) that a few α-particles bounce back. From this he inferred the presence of massive and positively charged nucleus inside the atom. Following the discovery of nucleus in an atom, Rutherford found (1919) that fast moving α-particles transmuted nitrogen into oxygen with simultaneous liberation of hydrogen.

$$^{14}_{7}N + {}^{4}_{2}\alpha \longrightarrow {}^{17}_{8}O + {}^{1}_{1}H$$

He further showed that other elements could also be transmuted, but hydrogen was always emitted.

On this basis Rutherford proposed that the hydrogen nucleus must be contained inside nuclei of all the elements. Hence, the hydrogen nucleus was renamed as **proton**.

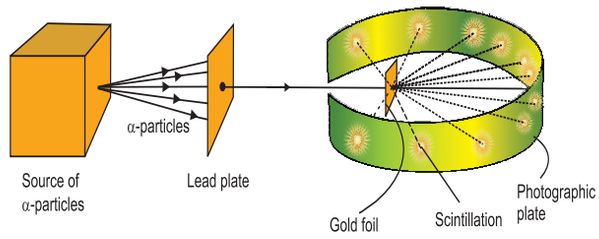


Fig. 4.2 : Rutherford's scattering experiment

4.1.3 Discovery of neutron : Existence of an electrically neutral and massive particle in the nucleus was predicted by Ernest Rutherford in 1920 to account for the disparity in atomic number and atomic mass of an element. In the year 1932, **James Chadwick** measured velocity of protons knocked out from paraffin by an unidentified radiation from beryllium (see Fig. 4.3). From that he determined the mass of the particles of the unidentified neutral radiation which came out to be almost the same as that of a proton. He named this particle as **'neutron'** which was predicted by Rutherford earlier.

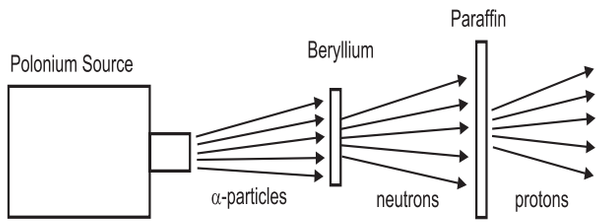


Fig. 4.3 : Discovery of neutron

4.2 Atomic number and atomic mass number

The number of protons in the nucleus is chemical identity of an element. This number is called atomic number (Z) of the element The positive charge on the nucleus is due to the protons present in it ($+Ze$). Atom being electrically neutral, it contains the same number of extranuclear electrons in it as its atomic number. Therefore the total electronic charge on an atom is $-Ze$. Thus in any atom,

Atomic number (Z) = Number of protons
= Number of electrons

As can be seen from Table 4.1, mass of an electron is negligibly small compared to that of the nucleons. As a result the mass of an atom can be considered to be concentrated in its nucleus. The approximate mass of one proton or one neutron is 1u. Therefore approximate atomic mass in daltons is numerically equal to the number of nucleons in the atom. The number of neutrons in the nucleus is designated by the symbol N; and the total number of protons and neutrons, that is nucleons, in an atom is called its atomic mass number (A).

Mass number (A) = Proton number (Z)
+ Neutron Number (N)

Therefore $A = Z + N, \quad N = A - Z$

The composition of any atom is represented by element symbol (X) with the atomic mass number (A) as superscript on left and atomic number (Z) as subscript on left :

$${}^{A}_{Z}\mathrm{X}$$

The atom or nucleus having a unique composition as specified by ${}^{A}_{Z}\mathrm{X}$ is called a **nuclide**.

Problem 4.1: Find out the number of protons, electrons and neutrons in the nuclide ${}^{40}_{18}\mathrm{Ar}$

Solution : In case of the nuclide ${}^{40}_{18}\mathrm{Ar}$,

$A = 40$ and $Z = 18$

Number of protons = number of electrons = $Z = 18$ and number of neutrons $N = A - Z$

$= 40 - 18 = 22$

4.3 Isotopes, isobars and isotones : Similarities in composition of nuclides results in three types of relationships.

i. Isotopes : Some elements exist as single natural nuclide. For example ${}^{19}_{9}\mathrm{F}$.

However, many elements exist naturally as mixture of two or more types of atoms or nuclides. These individual nuclides are called isotopes of that element.

All the isotopes of an element have the same number of protons but different number of neutrons in their nuclei. As the proton number is the atomic number, all the isotopes of an element have the same position in the modern periodic table and exhibit similar chemical properties. All the natural isotopes of an element coexist and have a definite natural abundance. Table 4.2 shows various features of the three common isotopes of carbon.

ii. Isobars : The atoms of different elements having the same mass number but different atomic numbers are called isobars. Isobars are different elements. They have different chemical properties and occupy different positions in modern periodic table. Table 4.3 shows an illustration of isobars.

Problem 4.2 : The two natural isotopes of chlorine, viz. $^{35}_{17}Cl$ and $^{37}_{17}Cl$ exist in relative abundance of 3:1. Find out the average atomic mass of chlorine.

Solution: From the relative abundance 3:1, it is understood that out of 4 chlorine atoms, 3 atoms have mass 35 and 1 has mass 37.

Therefore, the average atomic mass of chlorine

$$= \frac{3\times35 + 1\times37}{4} = 35.5$$

Table 4.2 : Isotopes of carbon

Symbol	Atomic number Z	Atomic mass number A	Neutron number $N = A - Z$	% Abundance	Stability
$^{12}_{6}C$ or C-12	6	12	6	98.9 %	Stable
$^{13}_{6}C$ or C-13	6	13	7	1.1 %	Stable
$^{14}_{6}C$ or C-14	6	14	8	< 0.00017 %	Radioactive

Table 4.3 : Isobars

Isobars	Atomic number Z	Mass number A	Number of protons Z	Number of neutrons N
$^{14}_{6}C$	6	14	6	8
$^{14}_{7}N$	7	14	7	7

Problem 4.3 : Three elements Q, R and T have mass number 40. Their atoms contain 22, 21 and 20 neutrons, respectively. Represent their atomic composition with appropriate symbol.

Solution : $A = Z + N \quad \therefore Z = A - N$

For the given three elements $A = 40$. Values of their atomic numbers Z, are obtained from the given values of neutron numbers, N, using the above expression.

for Q : $Z = A - N = 40 - 22 = 18$

for R : $Z = A - N = 40 - 21 = 19$

for T : $Z = A - N = 40 - 20 = 20$

$\therefore$ The atomic composition of the three elements is written as follows :

$$^{40}_{18}Q \;,\; ^{40}_{19}R \;,\; ^{40}_{20}T$$

iii. Isotones : The atoms of different elements having same number of neutrons in their nuclei are called isotones. Table 4.4 shows examples of isotones.

Table 4.4 : Isotones

Isotones	Atomic number Z	Mass number A	Number of Neutrons $N = A - Z$
$^{11}_{5}B$	5	11	6
$^{12}_{6}C$	6	12	6

We will consider some more aspects of nuclides in the Chapter 13.

4.4 Drawbacks of Rutherford atomic model

i. Let us now go back to the point of time when Rutherford put forth his nuclear model of atom. It is akin to a miniature of the solar system, the nucleus playing the role of the massive sun and the electrons are lighter planets. Electrons in this model could not be stationary as the electrostatic force of attraction exerted would pull them towards itself, and this would form a miniature version of Thomson's atomic model. However, the electrons revolving about the nucleus, as described by Rutherford, also pose a problem. Electrons in the Rutherford model are negatively charged particles in orbital motion. Such orbital motion is an acceleraled motion accompanied by a continuous change in the velocity of electron as noticed from the continuously changing direction. According to the electromagnetic theory of Maxwell, accelerated charged particles would emit electromagnetic radiation. An electron in an orbit would emit radiation, equivalent energy possessed by the radiation associated with the electronic motion. The orbit would, therefore, shrink continuously. **Thus, an electron orbiting about the nucleus would follow a spiral path to the nucleus.** It can be seen that the Rutherford atomic model has an intrinsic instability of atom. However, real atoms are stable.

ii. The second serious drawback of the Rutherford model is that it **does not describe the distribution of electrons** around the nucleus **and their energies**. The drawbacks of the Rutherford model were overcome in the Bohr atomic model.

4.5 Developments leading to the Bohr's atomic model :

At the time when different models of atomic structure were being put forth, some results obtained from the studies of **interactions of radiation with matter** required to be correlated to atomic structure. Niels Bohr utilized these results to get over the drawbacks of Rutherford atomic model. These results were : (1) wave particle duality of electromagnatic radiation and (2) line emission spectra of hydrogen.

4.5.1 Wave particle duality of electromagnetic radiation :

A dilemma was posed by electromagnetic radiation in the world of science. Phenomena such as **diffraction and interference of light** could be explained by treating light as electromagnetic wave. On the other hand, the **black-body radiation or photoelectric effect** could not be explained by wave nature of light, and could be accounted for by considering particle nature of light. The only way to resolve the dilemma was to accept that light has dual behaviour. When light interacts with matter it behaves as a stream of **particles** called **photons**, when light propagates, it behaves as an **electromagnetic wave**.

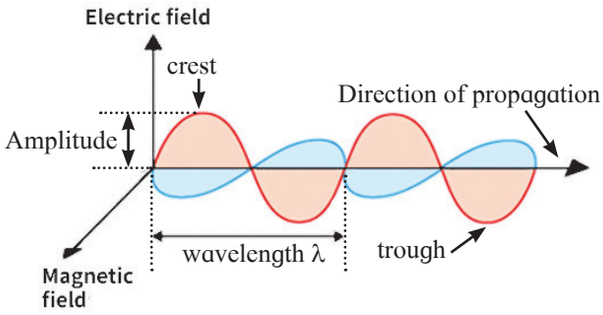


Fig 4.4 : Electromagnetic wave

a. Characteristics of electromagnetic wave

Figure 4.4 shows a schematic representation of an electromagnetic wave. Various parameters used to describe the different types of electromagnetic radiation are wavelength, frequency, wavenumber, amplitude, and velocity.

i. Wavelength (λ) : The distance between two consecutive crests or troughs is called wavelength. It is represented by the symbol λ which is a greek letter (lambda). The SI unit for wavelngth is metre (**m**).

ii. Frequency (ν) : The number of waves that pass a given point in one second is called frequency. It is represented by the greek letter nu, (ν). The SI unit of frequency is Hertz (Hz or s^{-1}).

iii. Wavenumber ($\bar{\nu}$) : Wavenumber is the number of wavelengths per unit length. Wavenumber is represented by the symbol (nu bar) ($\bar{\nu}$). The commonly used unit for wavenumber is reciprocal centimeter (cm^{-1}), while the SI unit is m^{-1}. Wavenumber is related to the wavelength by an expression $\bar{\nu} = \frac{1}{\lambda}$

iv. Amplitude (*A*): Amplitude of a wave is the height of the crest. Square of the amplitude denotes the intensity of the radiation.

Problem 4.4 : Visible light has wavelengths ranging from 400 nm (violet) to 750 nm (red). Express these wavelengths in terms of frequency (Hz).
(1 nm = 10^{-9} m)

Solution : $c = \nu\lambda \quad \therefore \nu = \frac{c}{\lambda}$

$\therefore$ frequency of violet light = $\frac{3\times10^{8}\,m\,s^{-1}}{400\times10^{-9}\,m} = 7.50 \times 10^{14}$ Hz

and frequency of red light = $\frac{3\times10^{8}\ m\ s^{-1}}{750 \times 10^{-9}\ m} = 4.00 \times 10^{14}$ Hz

Different regions of electromagnetic radiation have different values of frequency or wavelengths. Thus the radiofrequency region is around 10^{6} Hz, microwave region is around 10^{10} Hz, infrared region is around 10^{13} Hz, ultraviolet region is around 10^{16} Hz.

In vacuum, the speed of all the types of electromagnetic radiation is the same, which is 3.0×10^{8} m s^{-1} (2.997925×10^{8} m s^{-1} to be accurate). This is called speed of light, and is denoted by the symbol '*c*'.

The parameters wavelength (λ), frequency (ν) and the speed of light (c) are related by the expression : $c = \nu\,\lambda$

b. Particle nature of electromagnetic radiation : In the year 1900, **Max Plank** put forth his **quantum theory** to explain black-body radiation. According to this theory, the energy of electromagnetic radiation depends upon the frequency and not the amplitude. Plank gave the name **'quantum'** to the smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation. The energy (E) of one quantum of radiation is proportional to its frequency (ν) and given by

$$E = h\nu \qquad \text{.....(4.1)}$$

The proportionality constant **'*h*'** is called **Plank's Constant**. Later its value was found out to be 6.626×10^{-34} J s.

In the year 1905, Albert Einstein explained the photoelectric effect using Plank's quantum theory. In doing so he considered **electromagnetic radiation as a stream of photons of energy $h\nu$** . A photon has zero rest mass.

4.5.2 Line emission spectrum of hydrogen :

When a substance is irradiated with light it absorbs energy. Atoms, molecules or ions, which have absorbed radiation are said to be **'excited'**. Heating can also result in an excited state. When an excited species gives away the absorbed energy in the form of radiation, the process is called emission of radiation. The recorded spectrum of this emitted radiation is called **'emission spectrum'**.

Problem 4.5 : Parameters of blue and red light are 400 nm and 750 nm respectively. Which of the two is of higher energy ?

Solution : 400 nm and 750 nm are the wave lengths of blue and red light, respectively. Energy of radiation is given by the expression $E = h\nu$ and ν, the frequency, of radiation is related to the wavelength by the expression.

$$\nu = \frac{c}{\lambda}$$

Therefore, shorter the wavelength, λ, larger the frequency, ν, and higher the energy, E. Thus, blue light which has shorter λ (400 nm) than red light (750 nm) has higher energy.

Of all the elements, hydrogen has the simplest emission spectrum.

Do you know ?

Fluorescent tube, sodium vapor lamp, neon sign, halogen lamp are all examples of atomic emission.

When electric discharge is passed through gaseous hydrogen, it emits radiation. Hydrogen emission spectrum was studied by five scientists in late nineteenth century. They recorded the hydrogen emission spectra in different regions of electromagnetic radiation. The spectra were not continuous and comprised of a series of lines corressponding to different frequencies (see Fig. 4.5)

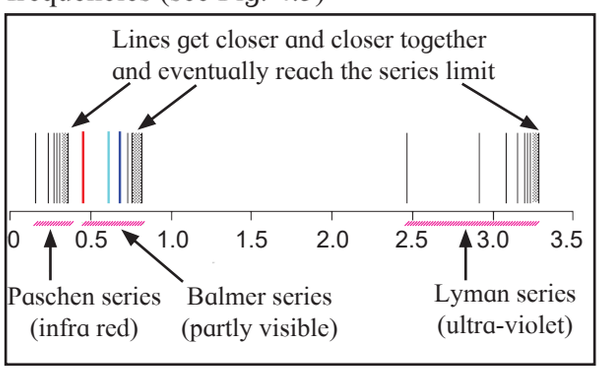


Fig. 4.5 : Emission line spectrum of hydrogen

In the year 1885 Balmer expressed the wavenumbers of the emission lines in the visible region of electromagnetic radiation by the formula

$$\bar{\nu} = 109677 \left[\frac{1}{2^2} - \frac{1}{n^2} \right] \text{cm}^{-1}, \qquad \text{.....(4.2)}$$

where n = 3,4,5.....

The lines described by this formula are called Balmer series. J. Rydberg found that all the five series of lines could be described by the following general expression.

$$\bar{\nu} = 109677 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{cm}^{-1}, \qquad \text{.....(4.3)}$$

where $n_1 = 1,2,3$ .....

$n_2 = [n_1+1], [n_1+2], [n_1+3],$.....

The value 109,677 cm^{-1} is called Rydberg constant for hydrogen 'R_H'. Table 4.5 shows the distinctive features of these five series.

Table 4.5 : Series of emission spectral lines for hydrogen

Series	n_1	n_2	Spectral region
Lyman	1	2,3,.....	Ultraviolet
Balmer	2	3,4,.....	Visible
Paschen	3	4,5,.....	Infrared
Bracket	4	5,6,.....	Infrared
Pfund	5	6,7,.....	Infrared

4.6 Bohr's model for hydrogen atom :

Niels Bohr (1913) put forth his postulates about the atomic model for hydrogen. While doing so he used the quantum theory, wave particle duality of electromagnetic radiation and the emission line spectra of hydrogen.

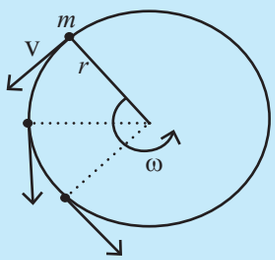
4.6.1 Postulates of Bohr atomic theory

Bohr's model of hydrogen atom is based on the following postulates.

1. The electron in the hydrogen atom can move around the nucleus in one of the many possible circular paths of fixed radius and energy. These paths are called orbits, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus in an increasing order of energy.

2. The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state if and when the required amount of energy is absorbed by the electron. Energy is emitted when electron moves from a higher stationary state to a lower one. The energy change does not take place in a continuous manner.

Angular Momentum :
Angular momentum is a product of moment of inertia (I) and angular velocity (ω) omega
Angular momentum = $I \times \omega$; but
$I = m\ r^2$ and $\omega = v/r$
$\therefore$ Angular momentum = $mr^2 \times v/r = mvr$



3. The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE is given by the following expression

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h} \quad \ldots\ldots (4.4)$$

Where E_1 and E_2 are the energies of the lower and higher allowed energy states respectively. This expression is commonly known as **Bohr's frequency rule**.

4. The angular momentum of an electron in a given stationary state can be expressed as

$$mvr = n \times \frac{h}{2\pi} \text{ where } n = 1, 2, 3 \quad \ldots\ldots (4.5)$$

Thus, an electron can move only in those orbits for which its angular momentum is integral multiple of $h/2\pi$. Thus only certain fixed orbits are allowed here.

4.6.2 Results of Bohr's theory : Bohr's theory is used to derive the energies of orbits, that is, the stationary states, in hydrogen atom. The results of Bohr's theory for hydrogen atom are summarized here.

a. The stationary states for electron are numbered n = 1, 2, 3..... .These integers are known as **principal quantum numbers**.

b. The radii of the stationary states are

$$r_n = n^2 a_0,$$

where a_o = 52.9 pm (picometer). Thus, the radius of the first stationary state, called the Bohr radius is 52.9 pm.

c. The most important property associated with the electron is the energy of its stationary state. It is given by the expression.

$E_1 = -R_H (1/n^2)$, where n = 1, 2, 3, ... (4.6)

R_H is the Rydberg constant for hydrogen and its value in joules is 2.18×10^{-18} J

The lowest energy state is called the **ground state**. Energy of the ground $1/1^2$ state is

$E_1 = -2.18 \times 10^{-18}\ 1/1^2 = -2.18 \times 10^{-18}$ J

Energy of the stationary state corresponding to n = 2 is

$E_2 = -2.18 \times 10^{-18}\ (1/(2)^2) = -0.545 \times 10^{-18}$ J

Just think

What does the negative sign of electron energy convey ?

A free electron at rest is an electron that is at infinity from the nucleus and does not experience any electrostatic force of attraction towards the nucleus and therefore, it is assigned the energy value of zero.

The negative sign means that the energy of the electron in the atom is lower than the energy of a free electron at rest. Mathematically this corresponds to setting 'n' equal to infinity in the equation so that $E_\infty = 0$. As the electron gets close to the nucleus,'n' decreases E_n becomes large in absolute value and more and more negative. Thus stationary states with smaller values of 'n' have large and negative energy. The negative sign corresponds to attractive force between the electron and nucleus.

Do you know ?

The Bohr's theory is applicable to hydrogen atom and hydrogen-like species which contain only one extranuclear electron.

Problem 4.6 :
How many electrons are present in $^{2}_{1}H$, $_{2}He$ and $He^{\oplus}$? Which of these are hydrogen like specis?
Solution : Hydrogen-like species contain only one electron.
$^{2}_{1}H$ number of protons = 1
= number of electrons
$_{2}He$: number of protons = 2
= number of electrons
$He^{\oplus}$: (number of electron in He)-1
= (number of electron in $He^{\oplus}$)
= (2 - 1) = 1
Thus $^{2}_{1}H$ and $He^{\oplus}$ are hydrogen-like species.

d. Bohr theory can be applied to hydrogen like species. For example $He^{\oplus}$, $Li^{2\oplus}$, $Be^{3\oplus}$ and so on. Energies of the stationary states associated with these species are given by :

$$E_n = -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2}\right) \text{ J} \qquad \ldots\ldots (4.7)$$

and radii by the expression

$$r_n = \frac{52.9(n^2)}{Z} \text{ pm}, \qquad \ldots\ldots (4.8)$$

where Z is the atomic number. From the above expression it can be seen that the energy decreases (becomes more negative) and radius becomes smaller as the value of Z increases.
e. Velocities of electrons can also be calculated from the Bohr theory. Qualitatively it is found that the magnitude of velocity of an electron increases with increase of Z and decreases with increase in the principal quantum number n.

Problem 4.7 :
Calculate the radius and energy associated with the first orbit of $He^{\oplus}$.
Solution : $He^{\oplus}$ is a hydrogen-like species having the nuclear charge $Z = 2$ and for the first orbit $n = 1$
radius of first orbit of $He^{\oplus}$

$$r_1 = \frac{52.9(n^2)}{Z} = \frac{52.9 \times 1^2}{2}$$

Energy of first orbit of $He^{\oplus}$

$$E_n = -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2}\right) \text{ J}$$

$$= -2.18 \times 10^{-18} \left(\frac{2^2}{1^2}\right)$$

$$= -8.72 \times 10^{-18} \text{ J}$$

4.6.3 Explanation of the line spectrum of hydrogen using Bohr theory : The line emission spectrum (Fig. 4.5) obtained from atomic hydrogen can be explained qnantitatively using Bohr theory. According to second postulate of Bohr theory, radiation is emitted when electron moves from an outer orbit of higher principal quantum number (n_i) to an inner orbit of lower principal quantum number (n_f). The energy difference (ΔE) between the initial and final orbit of the electronic transition corresponds to the energy of the emitted radiation. From the third postulate of Bohr theory ΔE can be expressed as

$$\Delta E = E_i - E_f \qquad \ldots\ldots (4.9)$$

According to the results derived from Bohr theory the energy E of an orbit is related to its principal quantum number 'n' by the Eq. (4.6).

$$E = -R_H \left(\frac{1}{n^2}\right) \qquad \ldots\ldots (4.6)$$

Combinig these two Eq. (4.9) and Eq. (4.6) we get:

$$\Delta E = \left[-\frac{R_H}{n_i^{\,2}}\right] - \left[-\frac{R_H}{n_f^{\,2}}\right] = R_H \left[\frac{1}{n_f^{\,2}} - \frac{1}{n_i^{\,2}}\right]$$

Substituting the value of R_H in joules we get

$$\Delta E = 2.18 \times 10^{-18} \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right] \text{J} \quad \text{.....(4.10)}$$

This expression can be rewritten in terms of wavenumber of the emitted radiation in the following steps.

We know: (ΔE) J = (h) J s × (ν) Hz ... (4.1)

and by definition

$$(\bar{\nu})\,\text{cm}^{-1} = \frac{(\nu)\,Hz}{(c)\,\text{cm s}^{-1}} \quad \text{..... (4.11)}$$

combining these Eq. (4.10), Eq. (4.1) and Eq. (4.11) we get

$$\therefore (\bar{\nu})\ \text{cm}^{-1} = \frac{(\Delta E)}{(h)\ \text{Js}} \times \frac{1}{(c)\ \text{cms}^{-1}}$$

$$= \frac{2.18 \times 10^{-18}}{6.626 \times 10^{-34} \times 3 \times 10^{10}} \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right] \text{cm}^{-1}$$

$$\therefore (\bar{\nu})\ \text{cm}^{-1} = 109677 \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right] \text{cm}^{-1}$$

This appears like the Rydberg Eq. (4.3), where $n_f = n_1$ and $n_i = n_2$.

In other words, Bohr theory successfully accounts for the empirical Rydberg equation for the line emission spectrum of hydrogen. In the Rydberg equation 'n_1' and 'n_f' are integers. Bohr's theory assigns physical meaning to them as principal quantum numbers corresponding to the concentric orbits. The integers in Rydberg equation, stand for the final orbit, n_f of electronic transition and n_1 for the initial orbit.

The emission lines comprising the five series thus, are result of electronic transitions from the excited hydrogen atoms. The Lyman series is the result of moving of electron excited to higher orbits of $n_2 = n_i = 2$, 3, 4,.....etc. to lower orbits of $n_1 = n_f = 1$; the Balmer series results from electron from $n_2 = n_i = 3$, 4,..... to the lower orbit of $n_1 = n_f = 2$, so on and so forth. The electronic transitions giving rise to different emmission line series of atomic hydrogen are shown in Fig. 4.6.

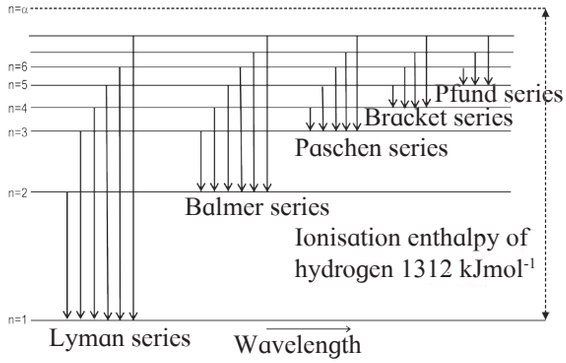


Fig. 4.6 : Electronic transition in the hydrogen spectrum

Problem 4.8 :
What is the wavelength of the photon emitted during the transition from the orbit of $n = 5$ to that of $n = 2$ in hydrogen atom?

Solution: The wavenumber of transition is given by Rydberg expression

$$(\bar{\nu}) = 109677 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{cm}^{-1}$$

Here $n_1 = 2$ and $n_2 = 5$

$$\therefore (\bar{\nu}) = 109677 \left[\frac{1}{2^2} - \frac{1}{5^2} \right]$$

$$= 109677 \left[\frac{1}{4} - \frac{1}{25} \right]$$

$$= 109677 \times \frac{21}{100} = 23032.17 \text{ cm}^{-1}$$

$$\lambda = \frac{1}{23032.17}$$

$$\lambda = \frac{1}{\bar{\nu}} = 4.34 \times 10^{-5} \text{ cm}$$

wavelength of photon

$\lambda = 4.34 \times 10^{-5}$ cm

$= 4.34 \times 10^{-5} \times 10^{7}$ nm $= 434$ nm

4.6.4 Limitations of Bohr model

1. Bohr's atomic model failed to account for finer details of the hydrogen atom spectrum observed in sophisticated spectroscop experiments.
2. Bohr model was unable to explain the spectrum of atoms other than hydrogen .
3. Bohr theory could not explain the splitting of spectral lines in the presence of a magnetic field (Zeeman effect) or electric field (Stark effect).

4. Bohr theory failed to explain the ability of atoms to form molecules by chemical bonds.

It was, therefore, thought that a better theory was needed to explain salient features of atomic structure.

4.6.5 Reasons for failure of the Bohr model

With the limitations of Bohr model for hydrogen atom becoming transparent, attempts were made to develop a better and general model for atom. This was possible because two important developments took place after the Bohr model was postulated. **These development were :**

1. de Broglie's proposal of dual behaviour of matter, and
2. Heisenberg uncertainty principle.

In Bohr model an electron is regarded as a charged particle moving in well defined circular orbits about the nucleus. In contrast to this **de Broglie** proposed in **1924** that matter should exhibit **a dual behaviour**, that is,both particle and wave like properties. This means that electron should have momentum, p, a property of particle as well as wavelength, λ, a property of wave. He gave the following relation between λ and p of a material particle.

$$\lambda = \frac{h}{m\mathrm{v}} = \frac{h}{p}$$

De Broglie's prediction was confirmed by diffraction experiments (a wave property).

Internet my friend

Collect information about Structure of Atom.

In the year **1927 Werner Heisenberg** stated the uncertainty principle : **"It is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron.** In other words the position and momentum of an electron can not be determined with the same certainty. If the certainty of determination of one property of the two is high, it means that the uncertainty of its determination is low. In that case the uncertainty of determination of the other property is very high.

Mathematically Heisenberg uncertainty principle is expressed as:

$$\Delta x \times \Delta p_x \geq \frac{\mathrm{h}}{4\pi}$$

$$\Delta x \times \Delta(m\mathrm{v}_x) \geq \frac{\mathrm{h}}{4\pi}$$

$$\Delta x \times \Delta \mathrm{v}_x \geq \frac{\mathrm{h}}{4\pi}$$

Here Δx is the uncertainty in position and Δp_x (or $\Delta \mathrm{v}_x$) is the uncertainty in momentum. A further implication of the uncertainty principle is that for an electron having certain energy one can only determine its probability at a particular point x around the nucleus. Bohr's model describes concentric orbits as well defined paths of the electron rotating about the nucleus and calculate energy of electron occupying these orbits. Bohr model assumes that both position and momentum, of the electron in hydrogen atom are known exactly at the same time, which is ruled out by the Heiesenberg uncertainty principle. Hence no attempt was made to extend the Bohr model to other atoms. A different approach to atomic model which would account for particle duality of matter and would be consistent with Heisenberg uncertainty principle was required. This became possible with the development of quantum mechanics.

4.7 Quantum mechanical model of atom :

A new branch of science, called **quantum machanics,** was developed in **1926** by **Werner Heisenberg** and **Erwin Schrodinger** based on uncertainty principle and wave motion, respectively. Quantum mechanics based on the ideas of wave motion will be discussed here. Schrodinger developed the fundamental equation of quantum mechanics which incorporates wave particle duality of matter. The **Schordinger equation** or **wave equation** is written as

$$\hat{\mathrm{H}}\psi = \mathrm{E}\psi \qquad \ldots\ldots (4.12)$$

Here $\hat{H}$ is a mathematical operator called Hamiltonian, ψ (psi) is the wave function and E the total energy of the system. Solving Schrodinger equation is beyond the scope of this book. It may, however, be noted that solution of Schrodinger equation gives E and ψ .

4.7.1 Schrodinger equation : When Schrodinger equation is solved for hydrogen atom, the possible values of energy (E) that the electron may have along with the corresponding wave function (ψ) are obtained. As a natural consequence of solving this equation, **a set of three quantum numbers** characteristic of the quantized energy levels and the corresponding wave functions are obtained. These are : **Principal quantum number (n), azimuthal quantum number (l) and magnetic quantum number (m_l).**

The solution of Schrodinger wave equation led to three quantum numbers and successfully predicted features of hydrogen atom emission spectrum. Splitting of spectral lines in multi-electron atomic emission spectra could not be explained through such model. These were explained by **George Uhlenbeck** and **Samuel Goudsmit (1925)** who proposed the presence of the **fourth quantum number** called **electron spin quantum number, m_s.**

Wave function, ψ, as such does not have any physical meaning. The probability of finding an electron at a point within an atom is proportional to ψ^2 in the neighbourhood of that point (within a tiny volume element) around it.

4.7.2 Atomic orbitals and quantum numbers

Many wave functions are possible for an electron, and therefore, many atomic orbitals are present in an atom. Thus the wave functions or atomic orbitals form the basis of the quantum mechanical electronic structure of an atom. Various orbitals in an atom differ in size, shape and orientation with respect to the nucleus depending upon the value of ψ^2. Each orbital is designated by three quantum numbers labelled as n, l and m_l, and each electron being assigned with four quantum numbers, viz, n, l, m_l and m_s.

The **principal quantum number *'n'*** is a positive integer with values of n being 1, 2, 3, 4, ... It identifies the shell. Atomic orbitals, having the same value 'n' belong to the same shell. With increase of 'n', the number of allowed orbitals in that shell increases and is given by 'n^2'. A set of orbitals with given value of 'n' constitutes a single shell. Shells are represented by symbols K, L, M, N,..... so on, (see Table 4.6).

Table 4.6 : Allowed orbitals in he first four shells

Principal quantum number n	Shell symbol	Allowed number of orbitals n^2	Size of shell
1	K	1	↓ increases
2	L	4	
3	M	9	
4	N	16	

With an increase of 'n', the distance from the nucleus and size of the shell increases and also the energy increases (becoming lesser and lesser negative). In hydrogen-like species the energy of orbital depends only on the value of 'n'. In the case of multi-electron atoms the energy of orbital depends on two quantum numbers 'n' and 'l' as well.

The **azimuthal quantum number**, l, is also called **subsidiary quantum mumber**. Atomic orbitals with the same value of 'n' but different values of 'l' constitute a subshell belonging to the shell for the given 'n'. The number of subshells in a shell is equal to 'n'. Thus, the third shell contains three subshells (with three different values of 'l'), the second shell contains two subshells and the first shell contains only one subshell. The values of 'l' range from 0 to (n - 1). Thus, the K shell (with n = 1) contains only one subshell having l = 0. The subshells or sub-levels having 'l' equal to 0, 1, 2, 3, ... are represented by the symbols s, p, d, f,....., respectively.

The magnetic orbital quantum number, m_l, gives information about the relative spatial orientation of the orbitals in a given subshell.

For any subshell (defined by 'l' value) $(2l + 1)$ values of m_l are possible which range through :

$m_l = -l, -(l-1), -(l-2)$.....,0,.....$(l-2), (l-1), l$.

Thus for the subshell 's' with $l = 0$, the only allowed value of $m_l = 0$. In other words, 's' subshells has only one orbital in it. For the subshell 'p' having $l = 1$, the allowed values of m_l are -1, 0, +1. Thus 'p' subshell contain three orbitals having distinct orientations, and so on.

The sum of orbitals in a constituent subshells gives the total number of orbitals in a concerned shell and is given by n^2 (see Table 4.7)

Electron spin quantum number, m_s, specifies the spin state of the electron in an orbital. An electron spins around its axis. This imparts spin angular momentum, to the electron.

The two orientations which the spin angular momentum of an electron can take up give rise to the spin states which can be distinguished from each other by the spin quantum number, m_s, which can be either **+ 1/2 or -1/2**. The two spin states are represented by two arrows, ↑ **(pointing up) and** ↓ **(pointing down)** and thus have opposite spins. **"An orbital can accomodate maximum two electrons and they must have opposite spins."**

This is known as **Pauli exclusion principle** which will be dealt with in section 4.7.5

4.7.3 Shapes of atomic orbitals : The probability of finding an electron at a given point in an atom is proportional to square of the wave function ψ^2 at that point. According to Max Born ψ^2 at a point in an atom is the probability density of electron at that point.

Figure 4.7 (a) shows the probability density diagrams of 1s and 2s atomic orbitals. These diagrams appear like a cloud. The electron cloud of 2s orbital shows one node, which is a region with nearly zero probability density and displays the change of sign for its corresponding wavefunction.

Table 4.7 : Distribution of orbitals in shells and subshells

Shell	Principal quantum number n	Total orbitals in the shell n^2	Total number of subshells in a shell n	Azimuthal quantum number l	Number of orbitals in the subshell $2l+1$	Sum of orbitals in all the subshells
K	$n = 1$	$1^2 = \mathbf{1}$	1	$l = 0$	$2 \times 0 + 1 = 1$	**1**
L	$n = 2$	$2^2 = \mathbf{4}$	2	$l = 0$ $l = 1$	$2 \times 0 + 1 = 1$ $2 \times 1 + 1 = 3$	$1 + 3 = \mathbf{4}$
M	$n = 3$	$3^2 = \mathbf{9}$	3	$l = 0$ $l = 1$ $l = 2$	$2 \times 0 + 1 = 1$ $2 \times 1 + 1 = 3$ $2 \times 2 + 1 = 5$	$1 + 3 + 5 = \mathbf{9}$

(a) Probability density plots

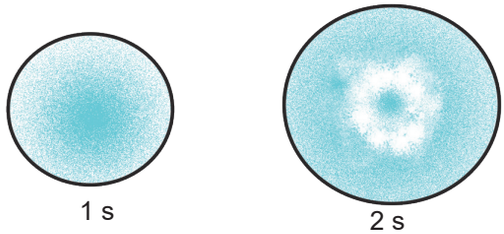


Fig. 4.7 : (a) Shapes of 1s and 2s orbitals

The Table 4.8 shows orbitals in the first four shells with the three quantum numbers for each orbital.

Table 4.8 : Orbital distribution in the first four shells

Symbol of Shell	Value of Principal quantum umber (n)	Number of subshells	Value of Azimuthal Quantum number l	Symbol of subshell	Total Number of orbitals in the subshell $= 2l + 1$	Values of the magnetic quantum number m_l for the subshell
K	$n = 1$	1	$l = 0$	1s	$2 \times 0 + 1 = 1$	$m_l = 0$
L	$n = 2$	2	$l = 0$	2s	$2 \times 0 + 1 = 1$	$m_l = 0$
			$l = 1$	2p	$2 \times 1 + 1 = 3$	$m_l = -1$ $m_l = 0$ $m_l = +1$
M	$n = 3$	3	$l = 0$	3s	$2 \times 0 + 1 = 1$	$m_l = 0$
			$l = 1$	3p	$2 \times 1 + 1 = 3$	$m_l = -1$ $m_l = 0$ $m_l = +1$
			$l = 2$	3d	$2 \times 2 + 1 = 5$	$m_l = -2$ $m_l = -1$ $m_l = 0$ $m_l = +1$ $m_l = +2$
N	$n = 4$	4	$l = 0$	4s	$2 \times 0 + 1 = 1$	$m_l = 0$
			$l = 1$	4p	$2 \times 1 + 1 = 3$	$m_l = -1$ $m_l = 0$ $m_l = +1$
			$l = 2$	4d	$2 \times 2 + 1 = 5$	$m_l = -2$ $m_l = -1$ $m_l = 0$ $m_l = +1$ $m_l = +2$
			$l = 3$	4f	$2 \times 3 + 1 = 7$	$m_l = -3$ $m_l = -2$ $m_l = -1$ $m_l = 0$ $m_l = +1$ $m_l = +2$ $m_l = +3$

Problem 4.9 How many orbitals make the N shell? What is the subshell wise distribution of orbitals in the N shell?

Solution: For N shell principal quantum number $n = 4$ $\therefore$ Total number of orbitals in N shell $= n^2 = 4^2 = 16$ The total number of subshells in N shell $= n = 4$. The four subshells with their azimuthal quantum numbers and the constituent orbital number are as shown below

Azimuthal quantum number l	Symbol of subshell	number of orbitals $2l + 1$
$l = 0$	s	$(2 \times 0) + 1 = 1$
$l = 1$	p	$(2 \times 1) + 1 = 3$
$l = 2$	d	$(2 \times 2) + 1 = 5$
$l = 3$	f	$(2 \times 3) + 1 = 7$

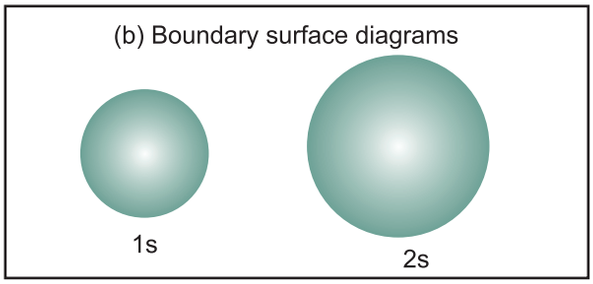


Fig 4.7 (b) : Shapes of 1s and 2s orbitals

Figure 4.7 (b) shows the boundary surface diagram of atomic orbitals 1s and 2s, which are spherical in shape. Here, a boundary surface is drawn in space for an orbital such that the value of probability density ψ^2 is constant and encloses a region where the probability of finding electron is typically more than 90%. Such a boundary surface diagram is a good representation of shape of an orbital.

Problem 4.10 : An atom has two electrons in its 4s orbital. Write the values of the four quantum numbers for each of them.

Solution: For the 4s orbital 4 stands for the principal quantum number n; s stands for the subshell s having the value of azimuthal quantum number $l = 0$. In the 's' subshell there is only one orbital and has magnetic quantum number $m_l = 0$. The two electrons in this orbital have opposite spins. Thus the four quantum numbers of two electrons in 4s orbital are :

	n	l	m_l	m_s
electron 1	4	0	0	+ 1/2
electron 2	4	0	0	- 1/2

Do you know ?

The value of ψ^2 at any finite distance from the nucleus is never zero. Therefore a boundary surface enclosing 100% probability density (which occurs only at the infinity) cannot be drawn.

The s orbitals are spherical in shape. Their size increases with increase of n. It means that the electron is located farther away from the nucleus as the principal quantum number n increases.

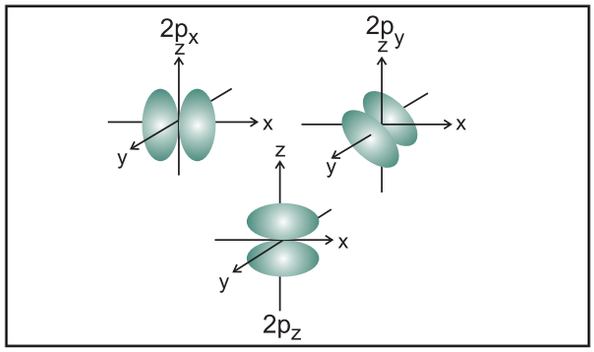


Fig. 4.8 : Shapes of 2p orbitals

Figure 4.8 displays the boundary surface diagram with the nucleus being at the origin, for the three 2p orbitals ($n = 2$ and $l = 1$). It can be seen that each p orbital has two lobes on the two sides of a nodal plane passing through the nucleus. (A nodal plane has ψ^2 very close to zero)

The size and energy of the dumbell shaped three 2p orbitals are the same. Their orientations in space are, however, different. The lobes of the three 2p orbitals are along the x, y and z axes. Accordingly the corresponding orbitals are designated as $2p_x$, $2p_y$ and $2p_z$. The size and energy of the orbitals in p subshell increase with the increase of principal quantum number.

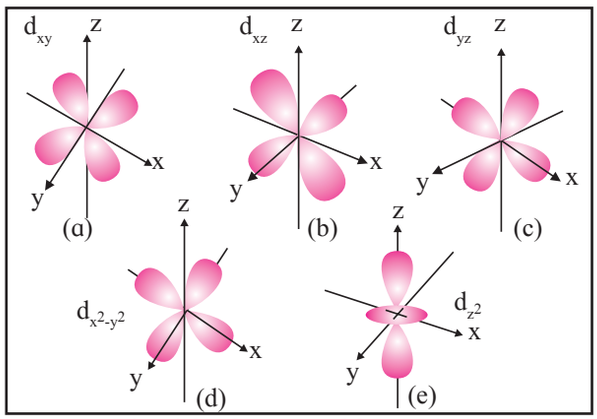


Fig. 4.9 : Shapes of 3d orbitals

There are five orbitals associated with d subshell. Designated by d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2}. The shapes of the five 3d orbitals are shown in Figure 4.9. In spite of difference in their shapes, the five d orbitals are equivalent in energy. The shapes of 4d, 5d, 6d..... orbitals are similar to those of 3d orbitals, but their respective size and energies are large or they are said to be more diffused.

4.7.4 Energies of orbitals : The energy of an electron in the hydrogen atom or hydrogen-like species is determined by the principal quantum number alone. This is because the only interaction in these species is attraction between the electron and nucleus. An increasing order of energies of orbitals in the hydrogen atom is given by

1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < .....

Of course the shapes of the concerned s, p, d, f orbitals are different, as described earlier. The orbitals with the same energy and the corresponding wave functions being different are called **degenerate orbitals**.

Thus, in hydrogen atom 2s amd 2p are degenerate orbitals. In multi-electron atoms there is mutual repulsion among the electrons. The energy of an electron in a multi-electron atom, therefore, depends both on the principal quantum number, n, and the azimuthal quantum number, l. The lower the sum ($n + l$) for an orbital, the lower is its energy. If two orbitals have the same ($n + l$) values then orbital with the lower value of n is of lower energy. This is called the **($n + l$) rule**.

From the ($n + l$) rule the increasing order of energy of orbitals in multi-electron atoms can be written as: 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s..... (See Table 4.9)

In a multi-electron atom, electrons occupy different orbitals. The lowest total electronic energy corresponds to the most stable, that is, the **ground state of an atom**. The orbital wise distribution of electrons in the ground state can be understood from what is called the **aufbau principle**.

4.7.5 Aufbau principle : 'Aufbau' is a German word meaning 'building up'. The building up of orbital means filling up of orbitals with electrons in the ground state of an atom. The aufbau principle is based on, (i) Increasing order of energies of orbitals, (ii) Pauli's exclusion principle, and (iii) Hund's rule of maximum multiplicity.

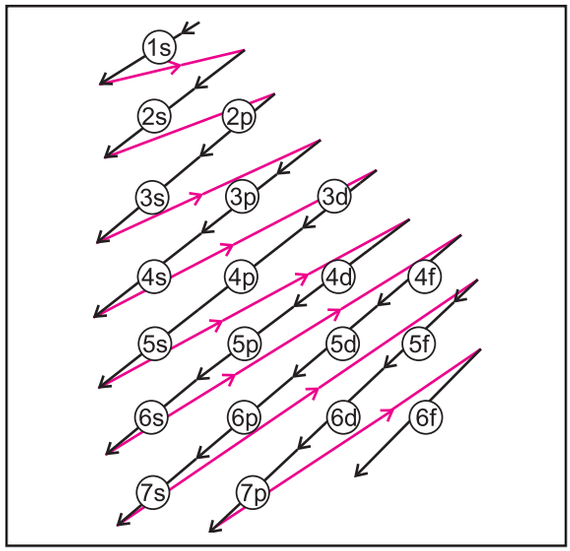


Fig. 4.10 : Increasing order of orbital energy

Table 4.9 : Dependance of orbital energy on (n + l) value

Orbital Energy	Principal quantum number n	Azimuthal quantum number l	($n + l$)
1s	n = 1	l = 0	1 + 0 = 1
2s	n = 2	l = 0	2 + 0 = 2
2p	n = 2	l = 1	2 + 1 = 3 (n = 2 (lower))
3s	n = 3	l = 0	3 + 0 = 3 (n = 3 (higher))
3p	n = 3	l = 1	3 + 1 = 4 (n = 3 (lower))
4s	n = 4	l = 0	4 + 0 = 4 (n = 4 (higher))
3d	n = 3	l = 2	3 + 2 = 5 (n = 3 (lower))
4p	n = 4	l = 1	4 + 1 = 5 (n = 4 (higher))

Energy increases

i. The increasing order of energies of orbitals

As seen in section 4.7.4, the increasing order of energies of obitals is decided by the $(n + l)$ value. Electrons in the ground state atom are filled in the orbitals in an increasing order of energy. Fig 4.10 shows a useful method to remember this increasing order of orbital energy.

ii. Pauli exclusion principle : The capacity of an orbital to accommodate electrons is decided by Pauli exclusion principle. **Wolfgang Pauli (1926)** recognized that **"No two electrons in an atom can have the same set of four quantum numbers."** Another way to state this Pauli exclusion principle is: **"Only two electrons can occpy the same orbital and they must have opposite spins."** Pauli exclusion principle implies that for an electron belonging to the same orbital, the spin quantum number 'm_s' must be different since the other three quantum numbers n, l and m_l are the same. There are only two values that 'm_s' can which are +1/2 and -1/2. An orbital thus can accommodate only two electrons with opposite spins, so that the fourth quantum number is different for two occupying electrons. These two electrons with opposite spins occupying the same orbital are called an **electron pair**.

This principle is illustrated with helium atom He (Z = 2). Its electronic configuration is $1s^2$ as  . And two electrons are in 1s orbital. The two non - identical combinations of the four quantum numbers of both electrons in helium are given in Table 4.10.

Table 4.10

Electron	Quantum number				Set of values of four quantum numbers
	n	l	m_l	m_s	
1st electron	1	0	0	+1/2	(1, 0, 0, +1/2)
2nd electron	1	0	0	-1/2	(1, 0, 0, -1/2)

It implies that two electrons in the same atom have always different set of quantum numbers that means, the set of (n, l, m_l) is the same and the m_s, is different.

Since an orbital can accommodate up to two electrons only, the capacity of a shell with the principal quantum number n, to accommolate electrons is given by $\mathbf{2n^2}$.

iii. Hund's rule of maximum multiplicity : Filling of electrons in the orbitals belonging to the same subshell (orbitals of equal energy or degenerate orbitals) follows the Hund's rule of maximum multiplicity. As per this rule **"Pairing of electrons in the orbitals belonging to the same subshell does not occur unless each orbital belonging to that subshell has got one electron each."**

Consider, for example, filling of p subshell. The p subshell has three degenerate orbitals. Here pairing of electrons starts when the fourth electron enters the p subshell. The electronic configuration of four electrons occupying p-orbital then will be  and not as  . It is observed that **half-filled and fully filled set of degenerate orbitals has extra stability.**

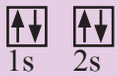
4.7.6 Electronic configuration of atoms and its representation : Electronic configuration of an atom is the distribution of its electrons in orbitals. The electronic configuration can be written by applying the aufbau principle. There are two methods of representing electronic configuration:

(i) Orbital notation: $ns^a np^b nd^c$.....

(ii) Orbital diagram: 

In the **orbital notation method,** a shells is represented by the principal quantum number followed by respective symbol of a subshell and number of electrons occupying that subshell being written as super script on right side of the symbol. In the **orbital diagram method** each orbital in a subshell is represented by a box and the electron represented by an arrow (↑ for up spin and ↓ for low spin) placed in the respective boxes. In this second method all the four quantum numbers of electron are accounted for. Electronic configuration of a few elements is illustrated in Table 4.11.

Table 4.11 : Representation of electronic configuration

Element symbol	Orbital notation	Orbital diagram
$_1H$	$1s^1$	
$_2He$	$1s^2$	
$_3Li$	$1s^2 2s^1$	
$_4Be$	$1s^2 2s^2$	
$_9F$	$1s^2 2s^2 2p^5$	

Condensed orbital notation of electronic configuration : The orbital notation of electronic configuration of an element with high atomic number comprises a long train of symbols of orbitals with an increasing order of energy. It can be condensed by dividing it into two parts. Electronic configuration of the preceding inert gas is a part of the electronic configuration of any element. In the condensed orbital notation it is implied by writing symbol of that inert gas in a square bracket. It is core part of the electronic configuration of that element. The outer configuration is specific to a particular element and written immediately after the bracket. For example, the orbital notation of potassium, K (Z = 19) is , $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$' Its core part is the electronic configuration of the preceding inert gas argon 'Ar : $1s^2 2s^2 2p^6 3s^2 3p^6$, while '$4s^1$' is an outer part. Therefore the condensed orbital notation of electronic configuration of potassium is 'K : [Ar] $4s^1$.' Table 4.12 displays detailed and condensed orbital notations of electronic configuration of various elements with atomic numbers from 1 to 30.

Electronic configurations of Cu and Cr

Chromium : Atomic number of chromium is 24. Expected electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$; In that case 3d is not half-filled. Hence, it has less stability.

Interelectronic repulsion makes one 4s electron enter into one of empty 3d orbitals, thereby both 4s and 3d orbitals become half-filled so that chromium atom acquires extra stability. Its electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$.

Copper : Atomic number of copper is 29. The expected electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$. Here 3d orbital is neither half-filled nor fully filled. Due to interelectronic repulsions forces one 4s electron to enter into 3d which makes it completely filled with 4s being half-filled. Hence copper atom accquires extra stability. Now electronic configuration of Cu is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$.

Isoelectronic species : Atoms and ions having the **same number of electrons** are **isoelectronic**. The electronic configuration of the isoelectronic species is the same. Consider $K^{\oplus}$ formed by removal of one electron from K atom.

Which has 19 electrons (Z = 19). Therefore $K^{\oplus}$ has 18 electrons

Number of electrons	$K\ (Z = 19)$	$\rightarrow$	$K^{\oplus} + e^{\ominus}$
	19		18

Species such as Ar, $Ca^{2\oplus}$ containing 18 electrons are isoelectronic with $K^{\oplus}$.

Electronic configuration of all these species with 18 electrons is $1s^2 2s^2 2p^6 3s^2 3p^6$.

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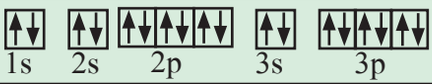
Table 4.12 Electronic configuration of the first thirty elments

Atomic Number	Element	K ($n = 1$)	L ($n = 2$)	M ($n = 3$)	N ($n = 4$)	Condensed notation of eletronic configuration
1	Hydrogen	$1s^1$				$1s^1$
2	Helium	$1s^2$				$1s^2$
3	Lithilum	$1s^2$	$2s^1$			[He] $2s^1$
4	Beryllium	$1s^2$	$2s^2$			[He]$2s^2$
5	Boron	$1s^2$	$2s^22p^1$			[He] $2s^22p^1$
6	Carbon	$1s^2$	$2s^22p^2$			[He] $2s^22p^2$
7	Nitrogen	$1s^2$	$2s^22p^3$			[He] $2s^22p^3$
8	Oxygen	$1s^2$	$2s^22p^4$			[He] $2s^22p^4$
9	Fluorine	$1s^2$	$2s^22p^5$			[He] $2s^22p^5$
10	Neon	$1s^2$	$2s^22p^6$			[He] $2s^22p^6$
11	Sodium	$1s^2$	$2s^22p^6$	$3s^1$		[Ne]$3s^1$
12	Magnesium	$1s^2$	$2s^22p^6$	$3s^2$		[Ne]$3s^2$
13	Aluminium	$1s^2$	$2s^22p^6$	$3s^2\,3p^1$		[Ne]$3s^23p^1$
14	Silicon	$1s^2$	$2s^22p^6$	$3s^2\,3p^2$		[Ne]$3s^23p^2$
15	Phospho-rous	$1s^2$	$2s^22p^6$	$3s^2\,3p^3$		[Ne]$3s^23p^3$
16	Sulfur	$1s^2$	$2s^22p^6$	$3s^2\,3p^4$		[Ne]$3s^23p^4$
17	Chlorine	$1s^2$	$2s^22p^6$	$3s^2\,3p^5$		[Ne]$3s^23p^5$
18	Argon	$1s^2$	$2s^22p^6$	$3s^2\,3p^6$		[Ne]$3s^23p^6$
19	Potassium	$1s^2$	$2s^22p^6$	$3s^2\,3p^6$	$4s^1$	[Ar] $4s^1$
20	Calcium	$1s^2$	$2s^22p^6$	$3s^2\,3p^6$	$4s^2$	[Ar] $4s^2$
21	Scandium	$1s^2$	$2s^22p^6$	$3s^2\,3p^63d^1$	$4s^2$	[Ar] $4s^23d^1$
22	Titanium	$1s^2$	$2s^22p^6$	$3s^2\,3p^63d^2$	$4s^2$	[Ar]$4s^23d^2$
23	Vanadium	$1s^2$	$2s^22p^6$	$3s^2\,3p^63d^3$	$4s^2$	[Ar] $4s^23d^3$
24	Chromium	$1s^2$	$2s^22p^6$	$3s^2\,3p^63d^5$	$4s^1$	[Ar] $4s^23d^5$
25	Manganese	$1s^2$	$2s^22p^6$	$3s^2\,3p^63d^5$	$4s^2$	[Ar] $4s^23d^5$
26	Iron	$1s^2$	$2s^22p^6$	$3s^2\,3p^63d^6$	$4s^2$	[Ar]$4s^23d^6$
27	Cobalt	$1s^2$	$2s^22p^6$	$3s^2\,3p^63d^7$	$4s^2$	[Ar] $4s^23d^7$
28	Nickel	$1s^2$	$2s^22p^6$	$3s^2\,3p^63d^8$	$4s^2$	[Ar] $4s^23d^8$
29	Copper	$1s^2$	$2s^22p^6$	$3s^2\,3p^63d^{10}$	$4s^1$	[Ar] $4s^13d^{10}$
30	Zinc	$1s^2$	$2s^22p^6$	$3s^2\,3p^63d^{10}$	$4s^2$	[Ar] $4s^23d^{10}$

Problem 4.11 : Write electronic configuration of $_{18}Ar$ and $_{19}K$ using orbital notation and orbital diagram method.

Solution : From the atomic numbers it is unterstood that 18 electron are to be filled in Ar atom and 19 electrons are to be filled in K atom. These are to be filled in the orbitals according to the aufbau principle. The electronic configuration of these atoms can be represented as.

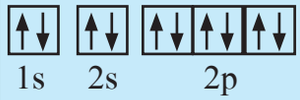
	Orbital notation	Orbital diagram
$_{18}Ar$	$1s^2 2s^2 2p^6 3s^2 3p^6$	
$_{19}K$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	

Problem 4.12

Find out one dinegative anion and one unipositive cation which are isoelectronic with Ne atom. Write their electronic configuration using orbital notations and orbital digram method.

Solution:

Ne has $Z = 10$. Therefore Ne and its isoelectronic species contain 10 electrons each. The dinegative anionic species isoelectronic with Ne is obtained by adding two electrons to the atom with $Z = 8$. This is $O^{2\ominus}$. The unipositive cationic species isoelectronic with Ne is obtained by removing one electron from an atom of $Z = 11$. It is $Na^{\oplus}$. These species and their electronic configuration are shown below :

	Number of electron	Orbital Notation	Orbital diagram
Ne	10	$1s^2 2s^2 2p^6$	
$O + 2e^{\ominus} \rightarrow O^{2\ominus}$	10		
$Na - e^{\ominus} \rightarrow Na^{\oplus}$	10		

Exercises

1. Choose correct option.

A. The energy difference between the shells goes on ..... when moved away from the nucleus.
   a. Increasing b. decreasing
   c. equalizing d. static

B. The value of Plank's constant is -
   a. 6.626×10^{-34}Js b. 6.023×10^{-24}Js
   c. 1.667×10^{-28}Js d. 6.626×10^{-28}Js

C. p-orbitals are..... in shape.
   a. spherical b. dumb bell
   c. double dumbell d. diagonal

D. "No two electrons in the same atoms can have identical set of four quantum numbers". This statement is known as -
   a. Pauli's exclusion principle
   b. Hund's rule
   c. Aufbau rule
   d. Heisenberg uncertainty principle

E. Principal Quantum number describes-
   a. shape of orbital
   b. size of the orbital
   c. spin of electron
   d. orientation of in the orbital electron cloud

2. Make the pairs:

'A'	'B'
a. Neutrons	i. six electrons
b. p-orbital	ii. -1.6×10^{-19} C
c. charge on electron	iii. Ultraviolet region
d. Lyman series	iv. Chadwick

3. Complete the following information about the isotopes in the chart given below :

Substance	Mass Number	Number of		
		Protons	Neutrons	Electrons
Carbon-14				
Lead-208				
Chlorine-35				
Uranium-238				
Oxygen-18				
Radium-223				

(Hint: Refer to Periodic Table if required)

4. Match the following :

Element	No. of Neutron
a. $^{40}_{18}Ar$	i. 7
b. $^{14}_{6}C$	ii.21
c. $^{40}_{19}K$	iii. 8
d. $^{14}_{7}N$	iv. 22

5. Answer in one sentence :

A. If an element 'X' has mass number 11 and it has 6 neutrons, then write its representation.

B. Name the element that shows simplest emission spectrum.

C. State Heisenberg uncertainty principle.

D. Give the names of quantum numbers.

E. Identify from the following the isoelectronic species:
Ne, O^{2-}, Na^{+} OR Ar, Cl^{2-}, $K^{\oplus}$

6. Answer the following questions.

A. Differentiate between Isotopes and Isobars.

B. Define the terms:
i. Isotones ii. Isoelectronic species
iii. Electronic configuration

C. State and explain Pauli's exclusion principle.

D. State Hund's rule of maximum multiplicity with suitable example.

E. Write the drawbacks of Rutherford's model of an atom.

F. Write postulates of Bohr's Theory of hydrogen atom.

G. Mention demerits of Bohr's Atomic model.

H. State the order of filling atomic orbitals following Aufbau principle.

I. Explain the anomalous behavior of copper and chromium.

J. Write orbital notations for electrons in orbitals with the following quantum numbrs.
a. n = 2, l =1 b. n =4, l = 2
c. n = 3, l = 2

K. Write electronic configurations of Fe, Fe^{2+}, Fe^{3+}

J. Write condensed orbital notation of electonic configuration of the following elements:
a. Lithium (Z=3) b. Carbon (Z=6)
c. Oxygen (Z=8) d. Silicon (Z=14)
e. Chlorine (Z=17) f. Calcium (Z=20)

M. Draw shapes of 2s and 2p orbitals.

N. Explain in brief, the significance of azimuthal quantum number.

O. If n=3, what are the quantum number *l* and *m*?

P. The electronic configuration of oxygen is written as $1s^2\,2s^2\,2p_x^{\,2}\,2p_y^{\,1}\,2p_z^{\,1}$ and not as $1s^2\,2s^2\,2p_x^{\,2}, 2p_y^{\,2}\,2p_z^{\,0}$, Explain.

Q. Write note on 'Principal Quantum number.

R. Using concept of quantum numbers, calculate the maximum numbers of electrons present in the 'M' shell. Give their distribution in shells, subshells and orbitals.

S. Indicate the number of unpaired electrons in :
a. Si (Z=14) b. Cr (Z=24)

T. An atom of an element contains 29 electrons and 35 neutrons. Deduce-
a. the number of protons
b. the electronic configuration of that element

Activity :

Collect information about discoveries of sub atomic particles and present in class by using power point presentation.

5. Chemical Bonding

5.1 Introduction : Why are atoms held together in chemical compounds ? There must be some force that holds them together. You have already learnt in lower classes that the forces holding atoms together in a compound are the chemical bonds.

How are chemical bonds formed between two atoms ? There are two ways of formation of chemcial bonds (i) by loss and gain of electrons (ii) by sharing a pair of electrons between the two atoms. In either process of formation of chemical bond each atom attains a stable noble gas electronic configuration.

Which electrons are involved in the formation of chemical bonds ? The electrons present in the outermost shell of an atom are involved in the formation of a chemical bond.

5.2 Kossel and Lewis approach to chemical bonding : Number of attempts were made to explain the formation of chemical bond in terms of electrons, but the first satisfactory explanation was given by W.Kossel and G.N. Lewis independently. They gave a logical explanation of valence which was based on the inertness of noble gases. On the basis of this they proposed a theory of valence known as Electronic theory of valence in 1916.

According to Lewis, the atom can be pictured in terms of a positively charged 'kernel' (the nucleus plus inner electrons) and outer shell that can accommodate a maximum of eight electrons. This octet of electrons represents a stable electronic arrangement.

Lewis stated that each atom achieves stable octet during the formation of a chemical bond. In case of sodium and chlorine this can be achieved by transfer of one electron from sodium to chlorine. Thus $Na^{\oplus}$ (2, 8) and $Cl^{\ominus}$ (2, 8, 8) ions are formed which held together. In case of other molecules like H_2, F_2, Cl_2, HCl etc. the bond is formed by the sharing of a pair of electrons between the atoms. In this process each atom attains a stable outer octet of electrons.

Octet rule : In 1916 Kossel and Lewis proposed an important theory for explaining the formation of chemical bond known as Electronic Theory of Valence. This theory is mainly based on octet rule developed by Lewis. Octet rule is based on stability of noble gases due to presence of eight electrons (ns^2np^6) in the valence shell.

This rule states that during the formation of chemical bond, atom loses, gains or shares electrons so that its outermost orbit (valence shell) contains eight electrons. Therefore the atom attains the nearest inert gas electronic configuration.

The octet rule is found to be very useful in explaining the normal valence of elements and in the study of the chemical combination of atoms leading to the formation of molecule. However it should be noted that octet rule is not valid for H and Li atoms. These atoms tend to have only two electrons in their valence shell similar to that of Helium ($1s^2$) which called duplet.

5.2.1 Ionic bond

I. Formation of sodium chloride (NaCl)

The electronic configurations of Sodium and Chlorine are :

Na (Z = 11) $1s^2 2s^2 2p^6 3s^1$ or 2, 8, 1

Cl (Z = 17) $1s^2 2s^2 2p^6 3s^2 3p^5$ or 2, 8, 7

Internet my friend

Search more atoms which complete their octet during chemical combinations.

Sodium has one electron in its valence shell. It has a tendency to lose one elctron to acquire the configuration of the nearest nobel gas Ne (2, 8). Chlorine has seven elctrons in its valence shell. It has a tendency to gain one electron and thereby acquire the configuration of the nearest nobel gas Ar (2, 8, 8). During the combination of sodium and chlorine atoms, the sodium atom transfers its valence electron

to the chlorine atom, sodium atom changes into $Na^{\oplus}$ ion while the chlorine atom changes into $Cl^{\ominus}$ ion. The two ions are held together by strong electrostatic force of attraction. The formation of ionic bond between Na and Cl can be shown as follows.

$$\underset{2,8,1}{Na} + \cdot\underset{2,8,7}{\ddot{Cl}}: \longrightarrow \underset{2,8}{Na^{\oplus}} + :\underset{2,8,8}{\ddot{Cl}}:^{\ominus}$$

$$Na^{\oplus} + Cl^{\ominus} \longrightarrow \underset{\text{Ionic bond}}{Na^{\oplus}Cl^{\ominus}} \text{ or } NaCl$$

II. Formation of calcium chloride ($CaCl_2$) : The following representation shows the formation of compound calcium chloride from the elements calcium and chlorine :

Electronic configuration of

Calcium : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Cl : $1s^2 2s^2 2p^6 3s^2 3p^5$

$$\underset{2,8,7}{:\ddot{Cl}\cdot} + \underset{2,8,8,2}{\ddot{Ca}} + \underset{2,8,7}{\cdot\ddot{Cl}:} \longrightarrow \underset{2,8,8}{:\ddot{Cl}:^{\ominus}} + \underset{2,8,8}{Ca^{2\oplus}} + \underset{2,8,8}{:\ddot{Cl}:^{\ominus}}$$

$$Cl^{\ominus} + Ca^{2\oplus} + Cl^{\ominus} \longrightarrow CaCl_2 \text{ or } Ca^{2\oplus}(Cl^{\ominus})_2$$

5.2.2 Ionic solids and Lattice Enthalpy :

Ionic solids are solids which contain cations and anions held together by ionic bonds. Kossel treatment helps us to understand the formation of ionic bonds between ions of different elements. Formation of ions depends on the ease with which an atom can lose or gain electrons.

$M(g) \longrightarrow M^{\oplus}(g) + e^{\ominus}$

$X(g) + e^{\ominus} \longrightarrow X^{-}(g)$ electron gain enthalpy

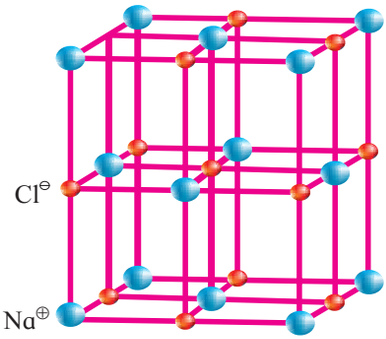
$M^{\oplus}(g) + X^{\ominus}(g) \longrightarrow MX(g) \longrightarrow MX(s)$

Do you know ?

CsF is the most ionic compound. Because Cs is the most electropositive while F is the most elctronegative element. The electronegativity difference between them is the largest. Hence ions are easily seperable, the bond is weakest and the compound is least stable ionic compound.

Ionization is always an endothermic process while electron gain process can be exothermic or endothermic. Based on the ionisation enthalpy ($\Delta_i H$) and electron gain enthalpy, we can predict which elements can form ionic compounds.

Elements having low ionization enthalpy can readily form ionic bond with elements having a high negative value of electron gain enthalpy. Both these processes take place in gaseous phase. All ionic compounds in the solid state have each cation surrounded by a specific number of anions and vice versa.



NaCl crystal lattice

The arrangements of cations and anions in a crystalline solid is ordered and they are held together by coulombic forces of attraction. During their formation, these compounds crystallize from the gaseous state (MX(g) $\longrightarrow$ MX(s)) to the solid state. The structure in which they crystallize depends upon the size of the ions, their packing arrangement and other factors. The overall stability of the ionic solid depends upon the interactions between all these ions and the energy released during the formation of the crystal lattice.

Let us consider the formation of NaCl ionic solid.

$Na(g) \longrightarrow Na^{\oplus}(g) + e^{\ominus}$ $\Delta_i H = 495.8$ kJmol^{-1}

$Cl(g) + e^{\ominus} \longrightarrow Cl^{\ominus}(g)$ $\Delta_{eg} H$ - 348.7 kJmol^{-1}

$Na^{\oplus}(g) + Cl^{\ominus}(s) \longrightarrow NaCl(g) + 147.7$ kJmol^{-1}

Conversion of NaCl(g) $\longrightarrow$ NaCl (s) is associated with release of energy which is -788 kJ mol^{-1}. This released energy is much more than the absorbed energy. Thus stability of an ionic compound can be estimated by knowing the amount of energy released during lattice formation and not just by energy associated with completion of octet around the ionic species in the gaseous state alone.

Lattice Enthalpy : Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of solid

ionic compound into the gaseous components. Lattice enthalpy of NaCl is -788 kJ mol^{-1} which means that 788 kJ of energy is required to separate 1 mole of NaCl into one mole of gasesous $Na^{\oplus}(g)$ and $Cl^{\ominus}(g)$ to an infinite distance.

Table 5.1 : Lattice Enthalpy values of some ionic Compounds

Compound	Lattice enthalpy $kJmol^{-1}$
LiCl	853
NaCl	788
BeF_2	3020
$CaCl_2$	2258
$AlCl_3$	5492

For same anion and different cations :

1. Cations having higher charge have large lattice energies than compounds having cations with lower charge. $AlCl_3 > CaCl_2 >$ NaCl
2. As size of cation decrease, lattice energy increases.
   LiF > NaF > KF.

5.2.3 Covalent bond : In 1919 Lewis suggested that there are atoms which attain inert gas configuration (i.e. $1s^2$ or ns^2np^6 configuration) by sharing one or more electron pairs with similar or dissimilar atoms. Each atom contributes one electron to the shared electron pair and has equal claim on the shared electron pair. Langmuir called the Lewis electron pair bond a covalent bond. Thus the concept of covalent bond is known as Lewis Langmuir concept. A shared pair of electron is represented as a dash (–) and is responsible for holding the two atoms together.

A covalent bond may be defined as follows :

The attractive force which exists due to the mutual sharing of electrons between the two atoms of similar electronegativity or having small difference in electronegativities is called a covalent bond.

I. Formation of H_2 molecule : The electronic configuration of H atom is $1s^1$. It needs one more electron to complete its valence shell. When two hydrogen atoms approach each other at a certain internuclear distance they share their valence electrons. The shared pair of electrons belongs equally to both the hydrogen atoms. The two atoms are said to be linked by a single covalent bond and a molecule H_2 is formed.

$H\cdot + \cdot H \longrightarrow$ H : H or H – H

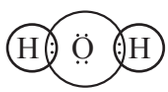
shared pair of electrons

II. Formation of Cl_2 : The Lewis-Langmuir theory can explain the formation of chlorine molecule, Cl_2. The Cl atom with electronic configuration $[Ne]3s^23p^5$ is one electron short of Argon configuration. The formation of Cl_2 molecule can be understood in terms of the sharing of a pair of electrons between two chlorine atoms. Each chlorine atom contributes one electron to the shared pair. In the process both the chlorine atoms attain the valence shell octet of the nearest noble gas (i.e. Argon)

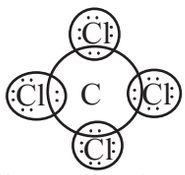
The dots represent the electrons. Such structures are referred to as Lewis structures. The Lewis dot structure can be written for other molecules also in which the combining atoms may be identical or different. Following are the important features of covalent bond.

- Each bond is formed as a result of sharing of electron pair between the two atoms.
- When a bond is formed, each combining atom contributes one electron to the shared pair.
- The combining atoms attain the outer shell nobel gas configuration as a result of the sharing of electrons.

Thus in H_2O and CCl_4 the formation of covalent bonds can be represented as,

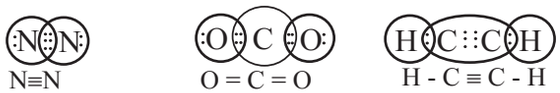


H acquires duplet
O acquires octet
H_2O



All atoms acquire octet
CCl_4

III. Formation of Multiple bond : When two atoms share one electron pair they are said to be joined by a single covalent bond. When two combining atoms share two pairs of electrons, the covalent bond between them is called a double bond. For example a double bond between two carbon atoms in ethylene molecule. When two combining atoms share three electron pairs a triple bond is formed as in the case of two nitrogen atoms in the N_2 molecule [Fig 5.1(a)]. Some other examples of multiple bonds are CO_2 and C_2H_2 [Fig 5.1]



(a) (b) (c)

Fig 5.1 Multiple bonding

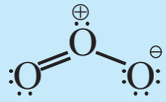
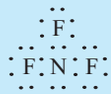
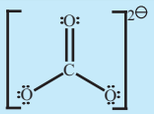
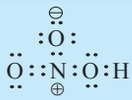
5.2.4 Lewis structures (Lewis representations of simple molecules) : Lewis dot structures show a picture of bonding in molecules and ions in terms of the shared pairs of electrons and the octet rule. Although such a picture does not explain completely the bonding and behaviour of a molecule, it helps to understand the formation and properties of molecule.

5.2.5 Steps to write Lewis dot structures

1. Add the total number of valence electrons of combining atoms in the molecule.
2. Write skeletal structure of the molecule to show the atoms and number of valence electrons forming the single bond between the atoms.
3. Add remaining electron pairs to complete the octet of each atom.
4. If octet is not complete form multiple bonds between the atoms such that octet of each atom is complete.
5. In anions add one electron for each negative charge.
6. In cations remove or subtract one electron from valence electrons for each positive charge.
7. In polyatomic atoms and ions, the least electronegative atom is the central atom for eg. 'S' is the central atom in $SO_4^{2\ominus}$, 'N' is the central atom in $NO_3^{\ominus}$.
8. After writing the number of electrons as shared pairs forming single bonds, the remaining electron pairs are used either for multiple bonds or remain as lone pairs.

Table 5.2 includes Lewis representation of some molecules.

Table 5.2 Lewis dot structures of some molecules/ions

Molecul/Ion	Lewis Representation
H_2	H:H, H-H
O_2	
O_3	
NF_3	
$CO_3^{2\ominus}$	
HNO_3	

Problem 5.1 : Write Lewis structure of nitrite ion $NO_2^{\ominus}$.

Solution

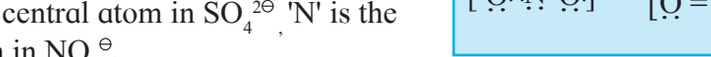
Step I : Count the total number of valence electrons of nitrogen atom, oxygen atom and one electron of additional negative charge.

$N(2s^2 2p^3)$, $O(2s^2 2p^4)$

$5 + (2\times6) + 1 = 18$ electrons

Step II : The skeletal structure of $NO_2^{\ominus}$ is written as O N O

Step III : Draw a single bond i.e. one shared electron pair between the nitrogen and each oxygen atoms completing the octet on oxygen atom. This does not complete the octet of nitrogen. Hence, there is a multiple bond between nitrogen and one of the oxygen atoms (a double bond). The remaining two electrons constitute a lone pair on nitrogen. Following are Lewis dot structures of $NO_2^{\ominus}$.



Problem 5.2 : Write the Lewis structure of CO molecule.

Solution :

Step - I . Count number of electrons of carbon and oxygen atoms. The valence shell configuration of carbon and oxygen atoms are : $2s^2 2p^2$ and $2s^2 2p^4$ respectively.

The valence electrons available are

$4 + 6 = 10$

Step - II : The skeletal structure of CO is written as

:C:⋮:O: or :C-⋮O:

Step - III : Draw a single bond (One shared electron pair) between C and O and complete the octet on O. The remaining two electrons is a lone pair on C.

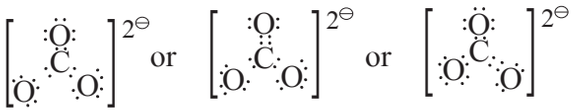
The octet on carbon is not complete hence there is a multiple bond between C and O (a triple bond between C and O atom). This satisfies the octet rule for carbon and oxygen atoms.

: C ≡ O : or

Each H atom attains the configuration of helium (a duplet of electons)

5.2.6 Formal charge

The Lewis dot diagrams help us to get a picture of bonding in molecules which obey the octet rule.In case of polyatomic molecules double bonds or some times triple bonds are present and can be represented by more than one Lewis structure. In the case of $CO_3^{2\ominus}$ we can have three dot diagrams.



Double bonds can be present between Carbon and any one of the three oxygen atoms. Formal charges can help us in assigning bonds when several structures are possible. Formal charge is the charge assigned to an atom in a molecule, assuming that all electrons are shared equally between atoms, regardless of their relative electronegativities. While determing the best Lewis structure per molecule the structure is chosen such that the formal charge is as close to zero as possible. Formal charge is assigned to an atom based on electron dot structures of the molecule/ion. e.g. O_3, $NH_4^{\oplus}$, $[N = C = O]^{\ominus}$, $[S = C = N]^{\ominus}$

Formal charge on an atom in a Lewis structure of a polyatomic species can be determined using the following expression.

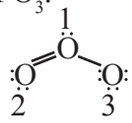
[Formal charge on an atom in a Lewis structure] = [Total no. of valence electrons in free atom] - [Total no. of non bonding or lone pairs of electrons] - 1/2 [Total no. of bonding or shared electrons]

or FC=VE – NE – (BE/2)

The structure having the lowest formal charge has the lowest energy.

1. Let us consider ozone molecule O_3

Lewis structure of O_3.



Here three oxygen atoms are numbered as 1, 2, 3. The formal charge on the central oxygen atom no.1 = 6-2 -1/2(6) = +1

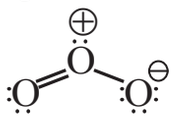
Formal charge on the end oxygen atoms is marked as 2

= 6 - 4 - 1/2(4) = 0

Formal charge on the end oxygen atoms marked as 3

= 6 - 6 - 1/2(2) = -1

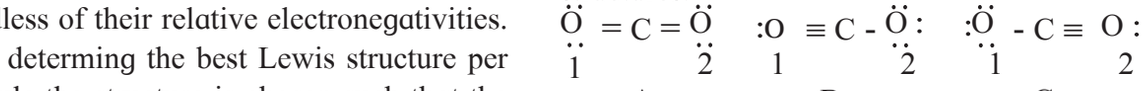
Hence, O_3 molecule can be represented along with formal charge as follows :



The lowest energy structure can be selected using formal charges from the number of possible Lewis stuctures, for a given species.

2. Let us take the example of CO_2.

CO_2 can be represented by the following structures.



Assigning the formal charges on the carbon atom and the two oxygen atoms numbered 1 and 2

Structure A

Number of electrons: 4 from carbon and 6 from each Oxygen

So total number of electrons=4+6+6=16

Formal charge on C =4-0-1/2(8)=0

Formal charge on O-1 and O-2 =6-4-1/2(4)=0

In this structure formal charge on all atoms is zero.

Structure B.

Formal charge on C =4-0-1/2(8)=0

Formal charge on O -1 = 6 - 2 - 6/2 = 4 - 3= +1

Formal charge on O - 2 = 6 - 6 -2/2 = -1

Structure C.

Formal charge on C =4-0-1/2(8)=0

Formal charge on 1st O = 6 - 6-2/2 = -1

Formal charge on 2nd O = 6-2-6/2=4-3=+1

We find that in structure A the formal charge on all atoms is 0 while in structures B and C formal charge on Carbon is 0 while Oxygens have formal charge -1 or +1. So the possible structure with the lowest energy will be Structure A.

Use your brain power

Which atom in $NH_4^{\oplus}$ will have formal charge +1?

Generally the lowest energy structure has the smallest formal charges on the atoms.

5.2.7 Limitation of octet rule :

1. Octet rule does not explain stability of some molecules.

The octet rule is based on the inert behaviour of noble gases which have their octet complete i.e. have eight electrons in their valence shell. It is very useful to explain the structures and stability of organic molecules. However there are many molecules whose existence cannot be explained by the octet theory. The central atoms in these molecules does not have eight electrons in their valence shell, and yet they are stable. eg. $BeCl_2$, PF_5 etc such molecules can be categorized as having

Problem 5.3 :

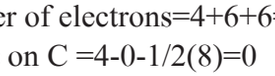
Find out the formal charges on S, C, N.

$(S = C = N)^{\ominus}$; $(S - C \equiv N)^{\ominus}$; $(S \equiv C\text{-}N)^{\ominus}$

Solution :

Step I

Write Lewis dot diagrams for the structure



A B C

Step II

Assign formal charges

FC = V.E - N.E - 1/2 B.E.

Structure A :

Formal charge on S = 6 - 4 - 1/2(4) =0

Formal charge on C = 4 - 0 - 1/2 (8) = 0

Formal charge on N = 5 - 4 - 1/2 (4) = -1

Structure B :

Formal charge on S = 6 - 6 - 1/2(2) = -1

Formal charge on C = 4 - 0 - 1/2 (8) = 0

Formal charge on N = 5 - 2 - 1/2 (6) = 0

Structure C :

Formal charge on S = 6 - 2 - 1/2(6) = +1

Formal charge on C = 4 - 0 - 1/2 (8) = 0

Formal charge on N = 5 - 6 - 1/2 (2) = -2

i. Incomplete octet

ii. Expanded octet

iii. Odd electrons

i. Molecules with incomplete octet :

eg. BF_3, $BeCl_2$, LiCl

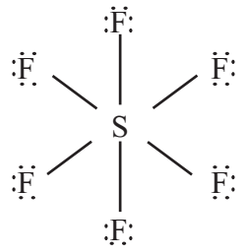
In these covalent molecules the central atoms B, Be and Li have less than eight electrons in their valence shell but are stable.

Li in LiCl has only two electrons

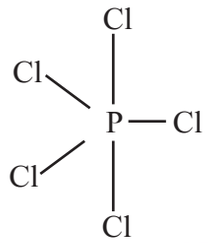
Be in $BeCl_2$ has four electrons while

B in BF_3 has six electrons in the valence shell.

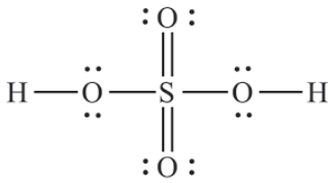
ii. Molecules with expanded octet : Some molecules like SF_6, PCl_5, H_2SO_4 have more than eight electrons around the central atom.



SF_6:12 electrons around sulfur



PCl_5;10 electrons around Phosphorus



H_2SO_4; 12 electrons around sulfur

It must be remembered that sulfur also forms many compounds in which octet rule is obeyed. For example, sulfur dichloride the sulfur atom has eight electrons around it.

SCl_2 8 electrons around sulfur

Use your brain power

How many electrons will be around I in the compound IF_7 ?

iii. Odd electron molecules

Some molecules like NO (nitric oxide) and NO_2 (nitrogen dioxide) do not obey the octet rule. Both N and O atoms, have odd number of electrons.

2. The observed shape and geometry of a molecule, cannot be explained, by the octet rule.

3. Octet rule fails to explain the difference in energies of molecules, though all the covalent bonds are formed in an identical manner that is by sharing a pair of electrons. The rule fails to explain the differene in reactivities of different molecules.

Use your brain power

Why is H_2 stable even though it never satisfies the octet rule ?

5.3 Valence Shell Electron Pair Repulsion Theory (VSEPR) : Properties of substances are dependent on the shape of the molecules. Lewis concept is unable to explain the shapes of molecules. Shapes of all molecules cannot be described completely by any single theory. One of the popular models used earlier to predict the shapes of covalent molecules is the valence shell electron pair repulsion theory proposed by Sidgwick and Powell. It is based on the basic idea that the electron pairs on the atoms shown in the Lewis diagram repel each other. In the real molecule they arrange themselves in such a way that there is minimum repulsion between them.

The arrangement of electrons is called as electron pair geometry. These pairs may be shared in a covalent bond or they may be lone pairs.

Rules of VSEPR :

1. Electron pairs arrange themselves in such a way that repulsion between them is minimum.
2. The molecule acquires minimum energy and maximum stability.
3. Lone pair of electrons also contribute in determining the shape of the molecule.
4. Repulsion of other electron pairs by the lone pair (L.P) stronger than that of bonding pair (B.P)

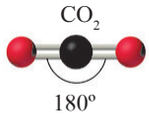
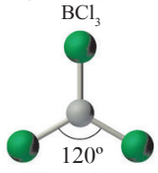
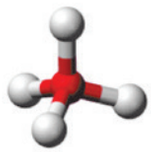
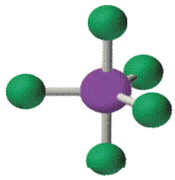
Trend for repulsion between electron pair is

L.P - L.P > L.P - B.P > B.P - B.P

Lone pair -Lone pair repulsion is maximum because this electron pair is under the influence of only one nucleus while the bonded pair is shared between two nuclei.

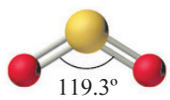
Thus the number of lone pair and bonded pair of electrons decide the shape of the molecules. Molecules having no lone pair of electrons have a regular geometry.

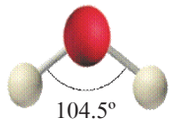
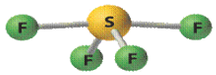
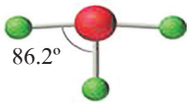
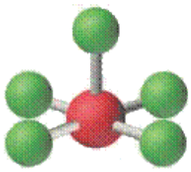
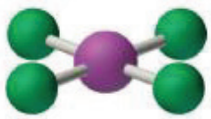
Table 5.3 : Geometry of molecules (having no lone pair of electrons)

Number of electron pairs	Arrangement of electron pairs	Molecular geomentry	Examples
2	Linear 	Linear	$BeBr_2$, CO_2,
3	Trigonal planar 	Trigonal planar	BF_3, BCl_3, BH_3
4	Tetrahedral 	Tetrahedral	CH_4, NH_4^+ $SiCl_4$
5	Trigonal bipyramidal 	Trigonal bipyramidal	PCl_5, SbF_5, A_5F_5
6	octahedral 	octahedral	SF_6, TeF_6, SeF_6,

Depending on the number of lone pair and bonded pairs of electrons the molecules can be represented as AB_2E, AB_3E, AB_2E_2, AB_4D, AB_3E_2, AB_5E, AB_4E_2 where A is the central atom, B - bonded atom E - lone pair of electrons. examples of the above type of molecules are given in table 5.7.

Table 5.4 : Geometry of some molecules (having one or more long pairs of electrons)

Molecule type	No. of lone pairs	No. of bonding pairs	Arrangement of bonded electron pairs	shape	examples
AB_2E	1	2	SO_2 	Bent	SO_2, O_3

AB_3E	1	3		Trigonal pyramidal	NH_3, PCl_3
AB_2E_2	2	2		Bent	H_2O, OF_2, H_2S, SCl_2, etc.
AB_4E	1	4		See saw	SF_4
AB_3E_2	2	3		T-shape	ClF_3, BrF_3,ICl_3, etc
AB_5E	1	5		square pyramid	BrF_5, IF_5
AB_4E_2	2	4		square planar	XeF_4

The VSEPR theory is therefore able to predict and also explain the geometry of large number of compounds, particularly of p-block elements.

Let us explain the bond angles in NH_3 and H_2O.

1. Ammonia NH_3 : Expected geometry is tetrahedral and bond angle 109^0 28'. Central nitrogen atom has in all 8 electrons in its valence shell, out of which 6 are involved in forming, three N-H covalent bonds the remaining pair forms the lone pair. There are two types of repulsions between the electron pairs.

i. Lone-pair-bond pair

ii. Bond pair - bond pair

The lone-pair-bond pair repulsions are stronger and the bonded pairs are pushed inside thus reducing the bond angle to $107^0$18'. and shape of the molecules becomes pyramidal.

2. Water molecule H_2O : The central atom oxygen has six electrons in its valence shell. On bond formation with two hydrogen atoms there are 8 electrons in the valence shell of oxygen. Out of these two pairs are bonded pairs and two are lone pairs.

Due to lone pair - lone pair repulsion the lone pairs are pushed towards the bond pairs and bond pair- Lone pair repulsions becomes stronger thereby reducing the HOH bond angle from the tetrahedral one to $104^0$35' and the geometry of the molecule is angular.

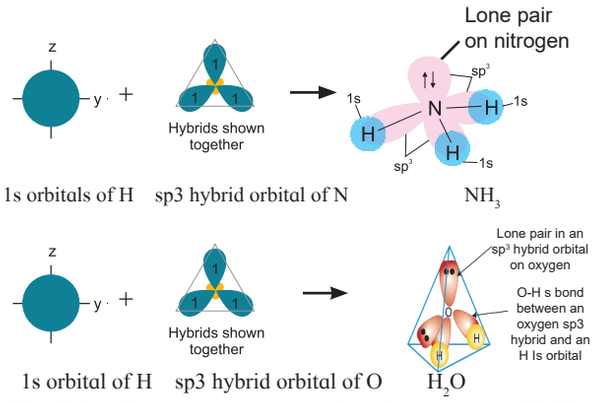


Fig 5.1 : Formation and orbital pictures of NH_3 and H_2O molecules

Advanced theories of Bonding :

The Kossel and Lewis approach to chemical bonding is the first step in understanding the nature of chemical bond. More advanced theories of bonding were put forth to account for the newly discovered properties of compounds in the light of quantum mechanical theory of atomic structures. Two important approaches regarding nature of chemical bond are **valence bond theory** and **molecular orbital theory**.

5.4 Valence Bond Theory :

In order to explain the covalent bonding, Heitler and London developed the valence bond theory on the basis of wave mechanics. This theory was further extended by Pauling and Slater.

5.4.1 Postulates of Valence Bond Theory :

i. A covalent bond is formed when the half-filled valence orbital of one atom overlaps with a half filled valence orbital of another atom.

ii. The electrons in the half-filled valence orbitals must have opposite spins.

iii. During bond formation the half-filled orbitals overlap and the opposite spins of the electrons get neutralized. The increased electron density decreases the nuclear repulsion and energy is released during overlapping of the orbitals.

iv. Greater the extent of overlap stronger is the bond formed, however complete overlap of orbitals does not take place due to internuclear repulsions.

v. If an atom possesses more than one unpaired electrons, then it can form more than one bond. So number of bonds formed will be equal to the number of half-filled orbitals in the valence shell i.e. number of unpaired electrons.

vi. The distance at which the attractive and repulsive forces balance each other is the equilibrium distance between the nuclei of the bonded atoms. At this distance the total energy of the bonded atoms is minimum and stability is maximum.

vii. Electrons which are paired in the valence shell cannot participate in bond formation. However in an atom if there is one or more vacant orbital present then these electrons can unpair and participate in bond formation provided the energies of the filled and vacant orbitals differ slightly from each other.

viii. During bond formation the 's' orbital which is spherical can overlap in any direction. The 'p' orbitals can overlap only in the x, y or z directions. [similarly 'd' and 'f' orbitals are oriented in certain directions in space and overlap only in these direction]. Thus the covalent bond is directional in nature.

5.4.2 Interacting forces during covalent bond formation :

By now we have understood that a covalent bond is formed by the overlap of two half filled atomic orbitals and the bonded atoms are stable than the free atoms and the energy of the bonded atoms is less than that of free atoms. So lowering of energy takes during bond formation. How does this happen ?

This happens due to interactive forces which develop between the nuclei of the two atoms and also their electrons. These forces may be attractive and repulsive between nuclei of A and electrons of B and those arising from attraction between nuclei of atom A and electrons of B and the repulsion between electrons.

The balance between attractive and repulsive forces decide whether the bond will be formed or not.

When the attractive forces are stronger than the repulsive forces overlap takes place between the two half filled orbitals a bond is formed and energy of the system is lowered.

This lowering of energy during bond formation is depicted in the potential energy diagram. To understand this let us consider the formation of H_2 molecule from atoms of hydrogen each containing one unpaired electrons. When the two atoms are for away from each other there are no interactions between them. The energy of the system is the sum of the potential energies of the two atoms which is arbitarily taken as zero.

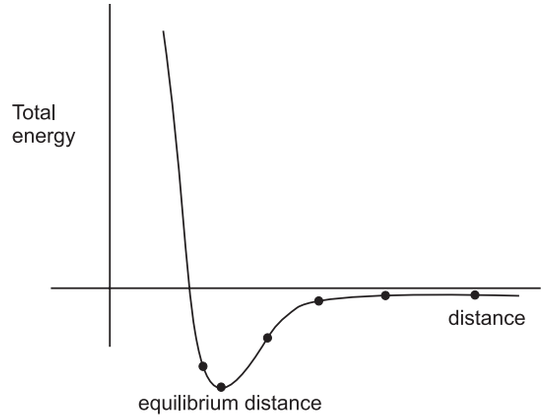


Fig. 5.2 : Potential energy diagram for formation hydrogen molecule

Repulsive forces be stabilize the system with increase energy of the system while attractive forces decrease the energy. Experimetally it has been found that during formation of hydrogen molecule the magnitude of the newly developed attractive forces contribute more than the newly developed repulsive forces. As a result the potential energy of the system begins to decrease.

As the atoms come closer to one another the energy of the system decreases. The overlap increases only upto a certain distance between the two nuclei, where the attractive and repulsive forces balance each other and the system attains minimum energy (see Fig 5.3). At this stage a bond is formed between the two atoms of hydrogen. If the two atoms are further pushed closer to each other the repulsive forces become more predominant and the energy of the system starts increasing and stability decreases. (See Fig. 5.2 potential energy diagram)

If atoms containing electrons with parallel spins are brought close to each other, the potential energy of the system increases and bond formation does not take place.

5.4.3 Overlap of atomic orbitals : Formation of a bond has been explained on the basis of overlap of atomic orbital having same energy and symetry. In the preceding section, we have seen that the strength of the bond depends on the extent of overlap of the orbitals. Greater the overlap stronger is the bond.

The orbitals holding the electrons vary in shape, energy and symetry. So the extent of overlap depends on the shape and size of the orbital

On the basis of the above considerations we have 2 types of bonds.

i. sigma bond (σ)
ii. pi bond (π)

i. Sigma Bond :

When the overlap of the bonding orbitals is along the internuclear axis it is called as sigma overlap or sigma bond.

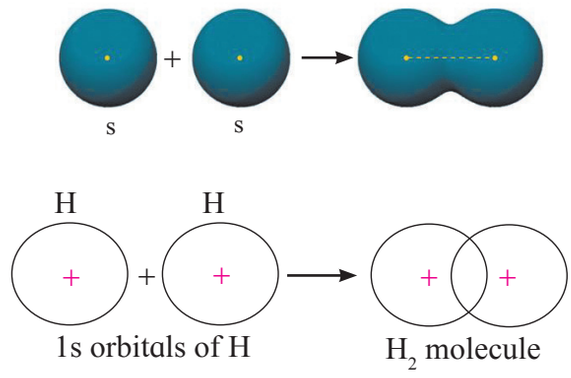
The σ bond is formed by the overlap of following orbitals.

a. Two 's' orbitals
b. One 's' and one p_z orbital
c. Two 'p' orbitals

a. s-s overlap : eg. H_2

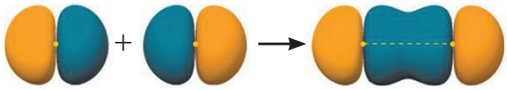
The $1s^1$ orbitals of two hydrogen atoms overlap along the internuclear axis to form a σ bond between the atoms in H_2 molecule.

electronic configuration of H : $1s^1$



b. p-p overlap

This type of overlap takes place when two p orbitals from different atoms overlap along the internuclear axis eg. F_2 molecule.



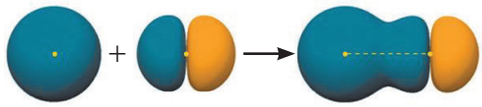
p p

Electronic configuration of fluorine $1s^2$, $2s^2$, $2p_x^2$, p_y^2, p_z^1, The $2p_z$ orbitals of the fluorine atoms overlaps along internuclear axis to form p-p σ overlap.

F_2 molecule :$1s^2$, $2s^2$, $2p_x^2$, p_y^2, p_z^1

c. s-p σ bond

In this type of overlap one half filled 's' orbital of one atom and one half filled 'p' orbital of another orbital overlap along the internuclear axis. eg. HF molecule



s p

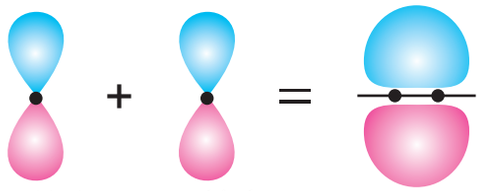
Electronic configuration :

H ⟶ $1s^1$; F : $1s^2$, $2s^2$, $2p_x^2$, p_y^2, p_z^1

$1s^1$ orbital of hydrogen and $2p_z^1$ of fluorine overlap to form s - p σ overlap.

ii. p-p overlap/ π overlap/π bond :

When two half filled orbitals of two atoms overlap side ways (laterally) it is called π overlap and it is perpendicular to the interuclear axis.



p- orbital p- orbital π - overlap

5.4.4 Hybridization : The valence bond theory explained well the formation of covalent bond by the overlap of orbitals in case of simple molecules like H_2, F_2, H-F etc. Accordingly the maximum number of covalent bonds which an atom can form equals the number of unpaired electrons present in its valence shell. But the theory does not explain how berylium forms two covalent bonds or how boron shows trivalency, carbon shows tetravalency in spite of their electronic configuration e.g. BeH_2, BF_3, CH_4, CCl_4 etc.

Be : $1s^2$, $2s^2$

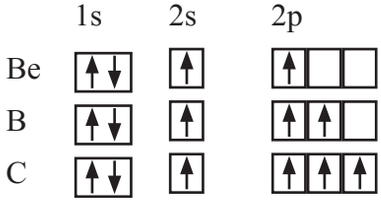
B : $1s^2$, $2s^2$, $2p^1$

C : $1s^2$, $2s^2$, $2p^1_x$, $2p^1$

In order to explain the observed valency in these and such other compounds a concept of hybridization was put forward.

It was suggested that one elctron in '2s' orbital is promoted to the empty '2p' orbital. Thus in the excited state Be, B and C have two, three and four half filled orbitals, respectively.

Electronic configurations in excited state :



In the excited state Be, B and C have 2, 3 and 4 half filled orbitals. So Be, B and C can form 2, 3 and 4 bonds respectively. This concept helps to understand how Be forms 2 bonds whereas B and C form 3 and 4 bonds, respectively but it cannot explain how all bonds have same bond length and bond strength.

For example, in BeF_2 berylium will use one s and one half-filled p orbitals to overlap with two half filled 'p' orbitals on fluorine, so in the molecule there will be one s-p bond and one p-p bond. which will not be of equal strength, but actually both Be-F bonds are of the same strength.Similar situation is seen in BF_3, BH_3, CH_4, CCl_4. In CH_4 all bonds are of equal strength although the overlaps are between s, p_x, p_y, p_z orbitals of carbon and 's' orbital of hydrogen, experimentally all C-H bond lengths bond strengths and bond angles are found to be identical.

This can be explained using another concept. "**Hybridiztion**" in the valence bond theory. This concept helps to explain the observed structural properties of many molecules.

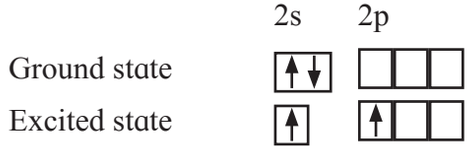
Hybridization refers to mixing of valence orbitals of same atom and recasting them into equal number of new equivalent orbitals- **Hybrid orbitals**.

Steps considered in Hybridization

i. Formation of excited state

ii. Mixing and Recasting of orbitals

i. Formation of the excited state : The paired electrons in the ground state are uncoupled and one electron is promoted to the a vacant orbial having slightly higher energy. Now total number of half filled orbitals is equal to the valency of the element in the stable compound. e.g. in BeF_2, valency of Be is two. In the excited state one electron from 2s orbital is uncoupled and promoted to 2p orbital.



ii. Mixing and Recasting : In this step the two 's' and 'p' orbitals having slightly different energies mix with each other. Redistribution of electron density and energy takes place and **two new orbitals having exactly same shape and energy are formed.**

These new orbitals arrange themselves in space in such a way that there is minimum repulsion and maximum sepration between them.

So during formation of sp hybrid orbitals as in Be the two sp hybrid orbitals are 180^0.

Conditions for hybridization :

1. Orbitals belonging to the same atom can participate in hybridization.
2. Orbitals having nearly same energy can undergo hybridization, so 2s and 2p orbitals undergo hybridization but 3s and 2p orbitals do not.

Characteristic features of hybrid orbitals :

i. Number of hybrid orbitals formed is exactly the same as the participating atomic orbitals.

ii. They have same energy and shape.

iii. Hybrid orbitals are oriented in space in such a way that there is minimum repulsion and thus are directional in nature.

iv. The hybrid orbitals are different in shape from the participating atomic orbitals, but they bear the characteristics of the atomic orbitals from which they are derived.

v. Each hybrid orbitals can hold two electrons with opposite spins.

vi. A hybrid orbital has two lobes on the two sides of the nucleous. One lobe is large and the other small.

vii. Covalent bonds formed by hybrid orbitals are stronger than those formed by pure orbitals, because the hybrid orbital has electron density concentrated on the side with a larger lobe and the other is small allowing greater overlap of the orbitals.

5.4.5 Types of Hybridization and Geometry of Molecules : Different types of hybrid orbitals are obtained from the atomic orbitals that participate in hybridization.

s and p orbitals can hybridize to form the following hybrid orbitals

i. sp^3

ii. sp^2

iii. sp

i. sp^3 Hybridization : In this type one 's' and three 'p' orbitals having comparable energy mix and recast to form four sp^3 hybrid orbitals. It should be remembered that 's' orbital is spherically symmetrical while the p_x, p_y, p_z, orbitals have two lobes and are directed along x, y and z axes, respectively.

The four sp^3 hybrid orbitals formed are equivalent in energy. and shape. They have one large lobe and one small lobe. They are at an angle of 109^028 with each other in space and point towards the corners of a tetrahedron CH_4, NH_3, H_2O are examples where the orbitals on central atom undergo sp^3 hybridization.

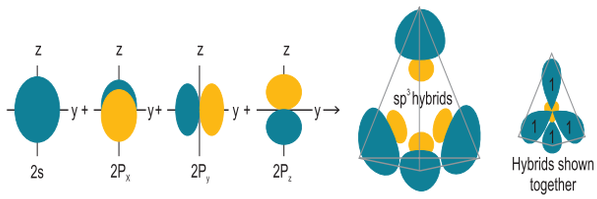


Fig 5.3 : Formation of sp^3 hybrid orbitals

Formation of methane (CH_4) molecule :

Ground state electronic configuration of Carbon is $1s^2$, $2s^2$, $2p_x^1$, p_y^1, p_z^0. In order to form four equivalent bonds with hydrogen the 2s and 2p orbitals undergo hybridization.

Electronic configuration of carbon 1s 2s 2p

Ground state

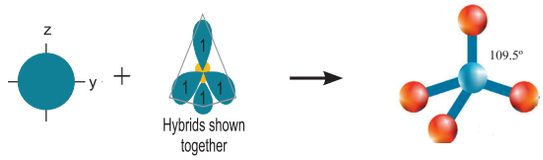
Excited state

sp^3 Hybrid orbitals

(four sp^3 hybrid orbitals.)

One electron from the 2s orbital of Carbon atom is excited to the $2p_z$ orbital. Then the four orbitals 2s, p_x, p_y, p_z mix and recast to form four new sp^3 hybrid orbitals having same shape and equal energy. They are maximum apart and have tetrahedral geometry. Each hybrid orbital contains one unpaired electron.

Each of these sp^3 hybrid orbitals with one electron overlap axially with the 1s orbital of hydrogen atom to form one C-H sigma bond. Thus in CH_4 molecule we have four C-H bonds formed by the sp^3-s overlap.



1s orbitals of H sp3 hybrid orbital of C CH_4

ii. sp^2 Hybridization : This hybridization involves the mixing of one s and two p orbitals to give three sp^2 hybrid orbitals of same energy and shape. The three orbitals are maximum apart and oriented at an angle of 120^0 and are in one plane. The third p orbital does not participate in hybridization and remains at right angles to the plane of the sp^2 hybrid orbitals. BF_3, C_2H_4 molecules are examples of sp^2 hybridization.

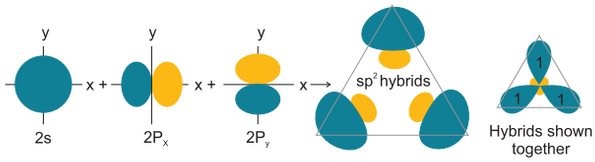


Fig 5.4 : Formation of sp^2 hybrid orbitals

Formation of C_2H_4 molecule : This molecule contains two carbon atoms each bound to two hydrogen. Each carbon atom undergoes sp^2 hybridization. One 's' orbital and two 'p' orbitals on carbon hybridize to form three sp^2 hybrid orbitals of equal energy and symetry.

Two sp^2 hybrid orbitals overlap axially two 's' orbitals of hydrogen to form sp^2-s σ bond. The unhydrized 'p' orbitals on the two carbon atoms overlap laterally to form a lateral π overlap. Thus the C_2H_4 molecule has four sp2-s σ bonds. One sp^2-sp^2 σ bond one p-p π bond.

Electronic configuration of carbon

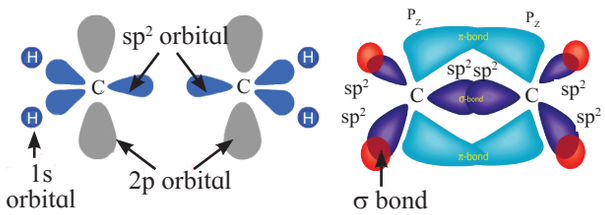
1s 2s 2p

Ground state

Excited state

sp^2 Hybridized

sp^2 hybrid orbitals pure 'p'orbital



Formation of Boron trifluoride (BF_3) molecule :

1. Need of hybridisation : Observed valency of boron in BF_3 is three and its geometry is triangular planar which can be explained on the basis of sp^2 hybridisation.
2. sp^2 hybridisation of Boron atom : In BF_3 molecule central boron atom undergoes sp^2 hybridisation. The ground state electronic configuration of Boron (z = 5) is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$

$1s^2$ $2s^2$ $2p_x^1 2p_y^0 2p_z^0$

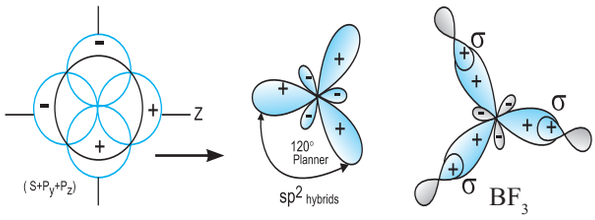
To explain valency of boron in BF_3 one electron from 2s orbital of boron atom is uncoupled and promoted to vacant $2p_y$ orbital. Thus excited state electronic configuration of boron becomes $s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$

$1s^2$ $2s$ $2p_x^1 2p_y^0 2p_z^0$

The three orbitals i.e. 2s, $2p_x$ of and $2p_y$ of boron undergoes sp^2 hybridisation to form three sp^2 hybrid orbitals of equivalent energy which are oriented along the three corners of an equilateral triangle making an angle of 120^0.

Thus boron in hybridised state has electronic following configuration.

3. orbital overlap : Each sp^2 hybrid orbital of boron atom having unpaired electron overlaps axially with half filled $2p_z$ orbital of fluorine atom containing electron with opposite spin to form three B-F sigma bond by sp^2-p type of overlap.
4. Bond angle : Each F-B-F bond angle in BF_3 molecule is 120^0.
5. Geometry : The geometry of BF_3 molecule is trigonal planar.



iii. sp hybridization : In this type one 's' and one 'p' orbital undergo mixing and recasting to form two sp hybrid orbitals of same energy and shape. The two hybrid orbitals are placed at an angle of 180^0. Other two p orbitals do not participate in hybridization and are at right angles to the hybrid orbitals. For example : $BeCl_2$ and acetylene molecule HC ≡ CH,

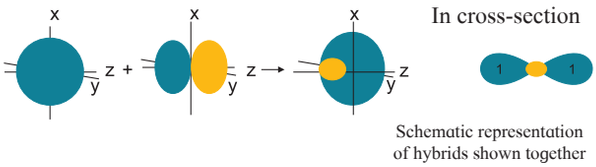


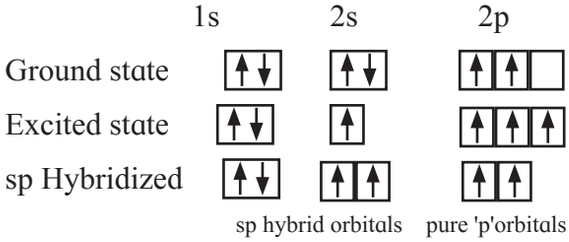
Fig 5.5 : formation of sp hybrid orbitals

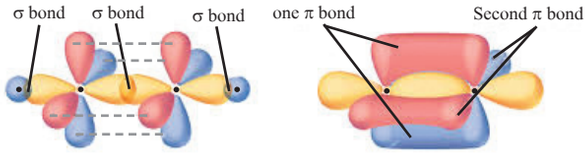
Formation of acetylene molecule : This molecule contains two carbon and two hydrogen atoms. Each carbon atom undergoes sp hybridization. One s and one p orbitals mix and recast to give two sp hybrid orbitals arranged at 180^0 to other.

Out of the two sp hybrid orbitals of carbon atom one overlaps axially with 's' orbital of hydrogen while the other sp hybrid orbital overlaps with sp hybrid orbital of other carbon atom to form the sp-sp σ bond. The C-H σ bond is formed by sp-s overlap.

The remaining two unhybridized p orbitals overlap laterally to form two p-p π bonds. So there are three bonds between the two carbon atoms : one C-C σ bond (sp-sp) overlap, two C-C π bonds (p-p) overlap and fourth sp-s σ bond between C and H satisfy the fourth valency of carbon.

Electronic configuration of carbon





5.4.6 Importance and limitation of valence bond theory

Importance of valence bond theory (V.B)

V.B. theory introduced five new concepts in chemical bonding.

i. Delocalization of electron over the two nuclei.

ii. shielding effect of electrons.

iii. covalent character of bond.

iv. partial ionic character of a covalent bond.

v.The concept of resonance and connection between resonance energy and molecular stability.

5.4.7 Limitations of valence bond theory

i. V.B. Theory explains only the formation of covalent bond in which a shared pair of electrons comes from two bonding atoms.

However, it offers no explanation for the formation of a co-ordinate covalent bond in which both the electrons are contributed by one of the bonded atoms.

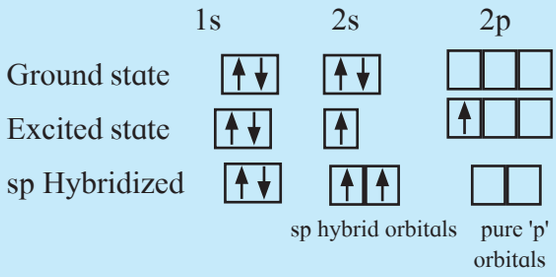
ii. Oxygen molecule is expected to be dimagnetic according to this theory. The two atoms in oxygen molecule should have completely filled electronic shells which give no unpaired electrons to the molecule making it diamagnetic. However, experimentally the molecule is found to be para-magnetic having

two unpaired electrons. Thus, this theory fails to explain paramagnetism of oxygen molecule.

Problem 5.4

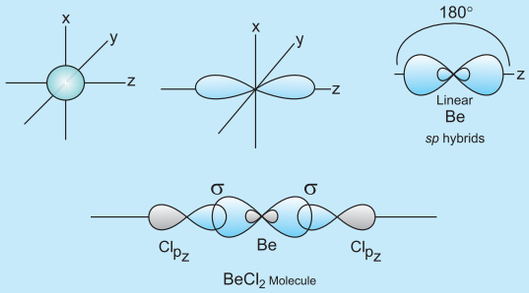
Explain the formation of $BeCl_2$

Electronic configuration of berylium



Formation of $BeCl_2$ molecule.

This molecule has one Be atom and two chlorine atoms. Electronic configuration of Be is $1s^2$, $2s^2$, $2p_z^0$. The 2s and $2p_z$ orbitals undergo sp hybridization to form two sp hybrid orbitals oriented at 180^0 with each other. $2p_z$ orbitals of two chlorine atoms overlap with the sp hybrid orbitals to form two sp-p σ bond.



iii. Valence bond theory does not explain the bonding in electron deficient molecules like B_2H_6 in which the central atom possesses less number of electrons than required for an octet of electron.

5.5 Molecular orbital theory : You are familiar with the valence bond theory which describes the formation of covalent bonds by overlap of half filled atomic orbitals. This theory is successful to give satisfactory electronic description for a large number of molecules. In some cases it gives to incorrect electronic description. Therefore another bonding description called Molecular Orbital Theory (MO) has been introduced.

It has been found that the MO theory gives more accurate description of electronic structure of molecules.

The concept of an orbital is introduced by quantum mechanics. The quantum mechanical wave equation is a differential equation and its solution is called wave function. The square of the wavefunction gives a measure of probability of finding an electron within a cetain region of space of an atom. It is nothing but an atomic orbital.

MO theory does not concentrate on individual atoms. It considers the molecule as a whole rather than an atom for the bonding. Accordingly a molecular orbital MOT is the property of a molecule similar to what an atomic orbital is to an atom. Hence, molecular orbital can be depicted through a square of wavefunction that gives the probability of finding an electron within a certain region of space in a molecule. Like atomic orbitals, molecular orbitals have energy levels and definite shapes. They also contain maximium two electrons with opposite spins.

5.5.1 Formation of molecular orbitals :

According to the MO theory the formation of molecular orbitals from atomic orbitals is expressed in terms of Linear Combination of Atomic Orbitals (LCAO). Formation of molecular orbitals can be understood by considering the interference of the electron waves of combining atoms. Interference of electron waves can be constructives or destructive i.e. the waves can reinforce each other or cancel each other. So we can say that. Two atomic orbitals combine in two ways to form molecular orbitals. 1. By addition of their wave functions. 2. By subtraction of their wave functions. Addition of the atomic orbtials wave functions results in formation of a molecular orbital which is lower in energy than atomic orbitals and is termed as Bonding Molecular Orbital (BMO). Subtraction of the atomic orbitals results in the formation of a molecular orbital which is higher in energy than the atomic orbitals and is termed as Antibonding Molecular Orbital (AMO).

In bonding molecular orbital the large electron density is observed between the nuclei of the bonding atoms than the individual atomic orbitals. On the other hand in the antibonding orbital the electron density is nearly zero between the nuclei.

So placing an electron in bonding orbital leads to formation of a covalent bond. While placing electron in antibonding orbital makes the bond unstable.

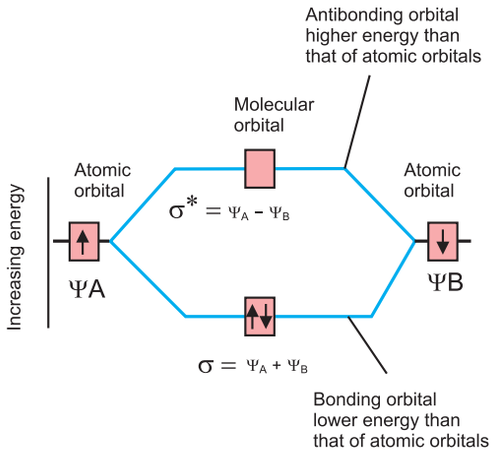


Fig. 5.5 : formation of MOs

5.5.2 Conditions for the combination of Atomic Orbitals : Atomic orbitals can be combined linearly which give molecular orbitals only if following conditions are fulfilled.

i. The combining atomic orbitals must have comparable energies.
So 1s orbitals of one atom can combine with 1s orbital of another atom but not with 2s orbital, because energy of 2s orbital is much higher than that of 1s orbital.

ii. The combining atomic orbitals must have the same symetry along the molecular axis. Conventially z axis is taken as the internuclear axis. So even if atomic orbitals have same energy but their symetry is not same they cannot combine. For example, 2s orbital of an atom can combine only with $2p_z$ orbital of another atom, and not with $2p_x$ or $2p_y$ orbital of that atom because the symmetries are not same. p_z is symetrical along z axis while p_x is symetrical along x axis.

iii. The combining atomic orbitals must overlap to the maximum extent. Greater the overlap, greater is the electron density between the nuclei and so stronger is the bond formed.

5.5.3 Types of molecular orbitals : In diatomic molecules, molecular orbitals formed by combination of atomic orbitals are of two types (i) σ (ii) π.

According to this nomenclature a σ designates a molecular orbital which is symetrical around the bond axis and π designates a molecular orbitals those are unsymetrical.

This is clear if we consider a linear combination of i. two 's' orbitals ii. two p orbitals.

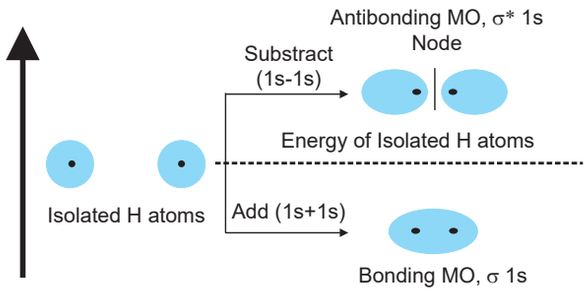


Fig 5.6 : Linear combination of two s orbitals

i. The s orbitals are spherically symmetric along x, y and z axes, combination of two '1s' orbitals centred on two nuclei of two atoms, led to two σ molecular orbitals which are symetrical along the bond axis. One of which is σ bonding and other σ* antibonding (Fig. 5.6)

ii. If we consider 'z' to be internuclear axis then linear combination of p_z orbitals from two atoms can form σ $2p_z$ bonding and antibonding σ*($2p_z$) molecular orbitals.

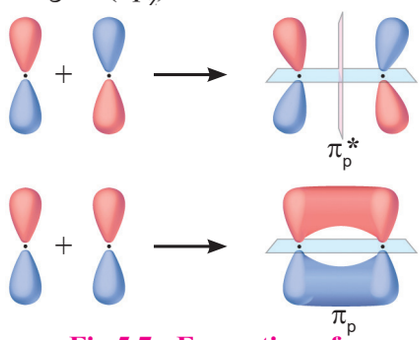


Fig 5.7 : Formation of π and π* molecular orbitals

The p_x, p_y orbitals are not symetrical along the bond axis, they have a positive lobe above the axis and negative lobe below the axis. Hence linear combination of such orbitals leads to the formation of molecular orbitals with positive and negative lobes above and below the bond axis. These are designed as π bonding and π antibonding orbitals. The electron density in such π orbitals is concentrated above and below the bond axis. The π molecular orbitals has a node between the nuclei (Fig. 5.7)

5.5.4 Energy levels and electronic configuration : We have seen earlier that on combination of two 1s orbitals; two molecular orbitals σ 1s and σ* 1s are formed. Similarly two 2s orbitals yield σ* 2s and σ 2s molecular orbitals.

The three 2p orbitals on one atom combine with three 2p orbitals on another atom forming six molecular orbitals, designated as σ $2p_z$, πp_x, πp_y and σ *$2p_z$, $\pi^* p_x$, $\pi^* p_y$

The molecular orbitals in homonuclear diatomic molecules have been determined experimentally.

For diatomic molecules of second row elements except O_2 and F_2 the rank order of energies is

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_x = \pi 2p_y > < \sigma 2p_z < (\pi^* 2p_y = \pi^* 2p_x) < \sigma^* 2p_z$

For O_2 and F_2 increasing order of energies was found to be :

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$

The sequence of filling the molecular orbitals give electronic configuration of molecules. The electronic configuration of molecules provides the following information.

a. Stability of molecules : If the number of electrons in bonding MOs is greater than the number in antibonding MOs the molecule is stable.

b. Magnetic nature of molecules : If all MOs in a molecule are completely filled with two electrons each, the molecule is diamagnetic (i.e. repelled by magnetic field).

However, if at least one MO is half filled (having one electron), the molecule is paramagnetic (i. e. attracted by magnetic field).

c. Bond order of molecule : The bond order of the molecule can be calculated from the number of electrons in bonding (N_b) and antibonding MOs (N_a).

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

5.5.5 Key ideas of MO theory :

i. MOs in molecules are similar to AOs of atoms. Molecular orbital describes region of space in the molecule representing the probability of an electron.

ii. MOs are formed by combining AOs of different atoms. The number of MOs formed is equal to the number of AOs combined.

iii. Atomic orbitals of comparable energies and proper symetry combine to form molecular orbitals.

iv MOs those are lower in energy than the starting AOs are bonding (σ) MOs and those higher in energy are antibonding (σ) MOs.

v. The electrons are filled in MOs begining with the lowest energy.

vi. Only two electrons occupy each molecular orbital and they have opposite spins that is, their spins are paired.

vii. The bond order of the molecule can be calculated from the number of bonding and antibonding electrons.

5.5.6 MO description of simple diatomic Molecules

1. Hydrogen molecule.-H_2

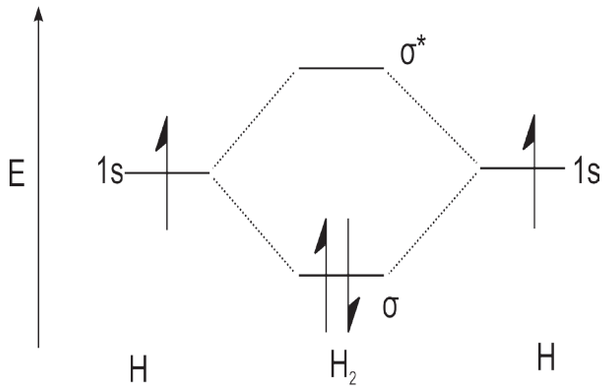


Fig. 5.8 : MO diagram for H_2 molecule

Hydrogen molecule is formed by the linear combination of two Hydrogen atoms, each having one electron in its 1s orbital. Linear combination of two 1s orbitals gives two molecular orbitals σ1s and σ*1s. The two electrons from the hydrogen atoms occupy the σ1s molecular orbital and σ*1s remains vacant.

Electronic configuration of Hydrogen molecule is written as $\sigma 1s^2$

Bond order = (bonding electron – antibonding electrons) ÷ 2

For hydrogen Bond order=(2-0)÷2=1

So in H_2 molecule there exists one covalent bond between the two hydrogen atoms. The bond length is 74 pm and the bond dissociation energy is 438 kJ mol. As there are no unpaired electrons present the H_2 molecule is diamagnetic.

2. Lithium molecule. Li_2 :

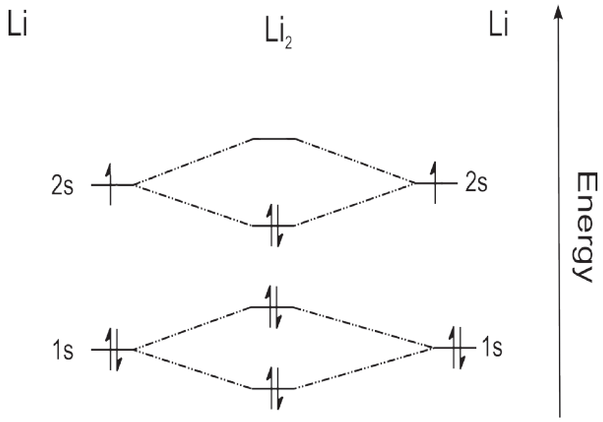


Fig. 5.9 : MO diagram for Li_2

Each Lithium atom has 3 electrons with electronic configuration $1s^2, 2s^1$, so Li_2 molecule will have 6 electrons. Linear combination of atomic orbitals gives four molecular orbitals σ1s, σ*1s, σ2s, σ*2s

Electronic configuration of Li_2 molecule will be $(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2$

Bond order=(4-2)÷2=1,

This means in Li_2 molecule there is one bond between the two Lithium atoms. Such Li_2 molecules are found in the vapour state. As there are no unpaired electrons the molecule is diamagnetic.

3. N_2 molecule : $_7$

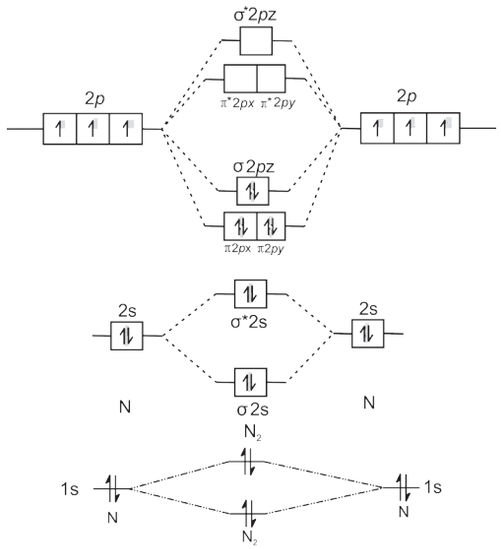


Fig. 5.10 : MO diagram for N_2

N : $1s^2\ 2s^2\ 2p^3$

Electronic configuration of N_2 molecule (14 electrons) is

$(\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma^*\ 2s)^2\ (\pi_x)^2\ (\pi_y)^2 (\sigma\ 2p_z)^2$

Bond order of N_2 molecule = $\frac{10-4}{2} = 3$

N_2 molecule is diamagnetic.

4. O_2 molecule :

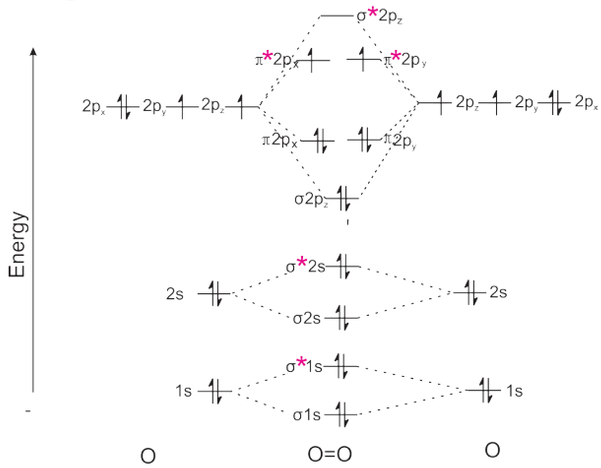


Fig. 5.11 : MO diagram for O_2

$_8$O : $1s^2\ 2s^2\ 2p^4$

The electronic configuraton of O_2 molecule (16 electrons) is

$(\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma\ 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2 (\pi 2p_x)^2$
$(\pi 2p_y)^2\ (\pi^* 2p_x)^1\ (\pi^* 2p_y)^1$

Bond order of O_2 molecule = $\frac{10-6}{2} = 2$

O_2 molecule is paramagnetic due to presence of 2 unpaired electrons in the π* orbitals.

5. F_2 molecule :

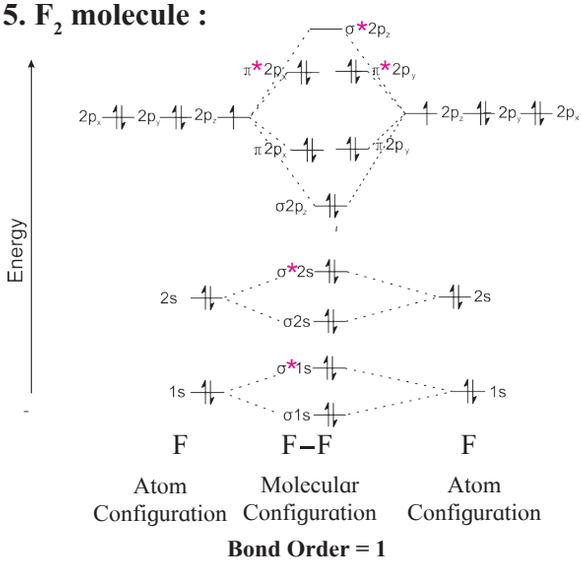


Fig. 5.12 : MO diagram for F_2

$_9F$: $1s^2\ 2s^2\ 2p^5$

The electronic configuration of F_2 molecule (18 electrons) is $(\sigma\ 1s)^2\ (\sigma^*1s)^2\ (\sigma\ 2s)^2\ (\sigma^*2s)^2\ (\sigma 2p_z)^2 (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi^* 2p_x)^2\ (\pi^* 2p_y)^2$

Bond order of F_2 molecule $= \frac{10-8}{2} = 1$

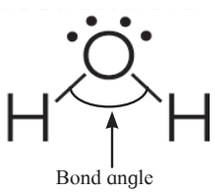
F_2 molecule is diamagnetic

Can you tell?

Why He_2 molecule is not stable ?
Draw MO diagram for it

5.6 Parameters of covalent bond : A covalent bond is characterised by different parameters. These parameters help to understand how strong is the bond between the two atoms, what is the distance between them and what is the shape of the molecule.

5.6.1 Bond angle : The electrons which participate in bond formation are present in orbitals. The angle between the orbitals holding the bonding electrons is called the bond angle.



Bond angle can be determined experimentally using spectroscopic techniques. Value of bond angle gives an idea about the arrangement of orbitals around the central atom and the shape of the molecule.

Table 5.5 bond angles of some molecules

	Molecule	Bond of angle
1	H_2O	104^028^1
2	NH_3	107
3	BF_3	120

5.6.2 Bond Enthalpy : The amount of energy required to break one mole of bond of one type, present between two atoms in the gaseous state is termed as Bond Enthalpy. For diatomic molecules the dissociation energy is the same as bond enthalpy. Bond enthalpy for H_2 molecule is 435.8 kJ mol^{-1}. The bond enthalpy is a measure of strength of the bond between two atoms and can be measured experimentally. N-N bond in N_2 is stronger than the O-O bond in O_2. Larger is the bond dissociation energy stronger is the bond in the molecule. For heteronuclear diatomic molecule HCl the bond enthalpy was found to be 431.0 kJ mol^{-1}.

In case of polyatomic molecules the bond enthalpy and bond dissociation energy are not identical. Bond enthalpy is the average of the sum of successive bond dissociation energies. For example dissociation of water.

$H_2O(g) \longrightarrow H(g) + \dot{O}H(g)\ \ \Delta H_1 = 502$ kJ mol^{-1}

$\dot{O}H\ (g) \longrightarrow H\ (g) + O\ (g)\ \Delta H_2 = 427$ kJ mol^{-1}

Average bond enthalpy of O-H bond in H_2O :

$$\Delta_a H = \frac{502 + 427}{2} = 464.5\ \text{kJmol}^{-1}.$$

In both the above equations the bond between O and H is broken but the amount of energy required to break the bond is different, i.e. enthalpies of two O-H bonds in water are different.

This difference arises due to the fact that cleavage of the two O-H bonds in water takes place in two steps. In the first step one O-H bond breaks leaving behind OH radical. Now the electronic enviornment around oxygen to

which hydrogen is attached is different than that around oxygen in H_2O molecule and this causes a change in the successive bond dissociation energy.

Same difference is observed in enthalpy values of O-H bond in C_2H_5OH. Oxygen here is attached to C_2H_5 group therefore hydrogen of O-H is in different environment than hydrogen of H-O-H.

In the same way, the bond enthalpy value of any covalent bond is slightly different for each bond of that kind in a given molecule and also different molecules. The average values of bond enthalpy, $\Delta_a H$, are determined from the experimentally measured values of large number of compounds containing a particular bond. Average bond enthalpy data are given in Table 5.4. In general stronger bond implies larger bond enthalpy.

Do you know ?

Among diatomic molecules the bond order and bond enthalpy of N_2 is highest. Bond order = 3, Bond enthalpy = 946 kJ mol^{-1}

Table 5.6 Bond enthalpies

Bond	$\Delta_a H$ / kJ mol^{-1}
C - H	400 - 415
N - H	390
O - H	460-464
C - C	345
C- N	290 -315
C-O	355 - 380
C - Cl	330
C - Br	275
O - O	175 - 184
C = C	610 - 630
C ≡ C	835
C = O	724 - 757
C ≡ N	854

5.6.3 Bond length : Bond length implies the equilibrium distance between the nuclei of two covalently bonded atoms in a molecule. Bond lengths are measured by X-ray and Electron diffraction techniques.

Table 5.7 Average bond lengths for some single, double and triple bonds

Type of bond	Covalent bond length (pm)	Type of bond	Covalent bond length (pm)
O-H	96	H_2(H-H)	74
C-H	107	F_2(F-F)	144
N-O	136	Cl_2(Cl-Cl)	199
C-O	143	Br_2(Br-Br)	228
C-N	143	I_2(I-I)	267
C-C	154	N_2(N≡N)	109
C = O	121	O_2(O=O)	121
N = O	122	HF (H-F)	92
C = C	133	HCl (H-Cl)	127
C = N	138	HBr (H -Br)	141
C ≡ N	116	HI (H-I)	160
C ≡ C	120		

Each atom of the bonded pair contributes to the bond length. Bond length depends upon the size of atoms and multiplicity of bonds.

It increases with increase in size of atom and decreases with increase in multiplicity of bond. It is generally measured in picometre (pm) or in Angstrom unit ($\overset{0}{A}$) – > = > ≡ >, so C - C single bond is longer and C ≡ C triple bond is shorter.

Some typical average bond lengths of C - C single double and triple bond and others are shown in table 5.4.

5.6.4 Bond Order : According to the Lewis theory the bond order is equal to the number of bonds between the two atoms in a molecule. The bond order in H_2, O_2 and N_2 is 1, 2 and 3 respectively. Isoelectronic molecules and ions have identical bond order. For example N_2, CO and NO^+ each have bond order 3. F_2 whereas O_2^{2-} has bond order 1. Stabilities of molecules can be determined by knowing the bond order. As bond order increases, bond enthalpy increases and bond length decreases.

5.6.5 Polarity of a Covalent Bond : Covalent bonds are formed between two atoms of the same or different elements. Thus covalent bond is formed between atoms of some elements of H-H, F-F, Cl-Cl etc. The shared pair of electrons is attracted equally by both atoms and is situated midway between two atoms. Such covalent bond is termed as Nonpolar Covalent bond.

H : H — electron pair at the centre

H-H — Non polar covalent bond

When a covalent bond is formed between two atoms of different elements and have different electronegativities the shared electron pair does not remain at the centre. The electron pair is pulled towards the more electronegative atom resulting in the separation of charges. This give rise to as Dipole. The more electronegative atom acquires a partial -ve charge and the other atom gets a partial +ve charge. Such a bond is called as **polar covalent bond.** The examples of polar molecules include. HF, HCl etc.

$H : F \quad {}^{\delta+}H–F^{\delta-}$ H-F

Polar covalent bond

Fluorine is more electronegative than Hydrogen therefore the shared electron pair is more towards fluorine and the atoms acquire partial +ve and -ve charges, respectively. Polarity of the covalent bond increases as the difference in the electronegativity between the bonded atoms increases. When the difference in elctronegativities of combining atom is about 1.7 ionic percentage in the covalent bond is 50%.

Can you tell?

Which molecules are polar ?
H-I, H-O-H, H-Br, Br_2, N_2, I_2, NH_3

5.7 Dipole moment

Definition : Dipole moment (μ) is the product of the magnitude of charge and distance between the centres of +ve and -ve charges.

$\mu = Q \times r$

Q : charge ; r : distance of separation.

unit of dipole moment is Debye (D)

$1\ D = 3.33564 \times 10^{-30}\ Cm$

C : coulomb ; m : meter

Dipole moment being a vector quantity is represented by a small arrow with the tail on the positive centre and head pointing towards the negative centre.

$^{\delta+}H \longrightarrow F^{-\delta}$ (μ =1.91 D). The crossed arrow ($\longrightarrow$) above the Lewis structural indicates the direction of the shift of electron density towards the more electronegative atom.

Dipole moments of polyatomic molecules : Each polar bond in a polyatomic molecule has its own dipole. The resultant dipole of the molecule is decided by (i) shape of the molecule that is the spatial arrangement of bonds (ii) contribution of the individual dipoles and those of the lone pair of electrons, if any

The dipole moment of polyatomic molecule is the vector sum of the dipole moments of various bonds and lone pairs.

Consider BeF_2 and BF_3.

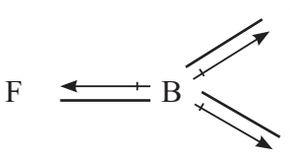
BeF_2 is a linear molecule and the dipoles are in opposite direction and are of equal strengths, so net dipole moment of $BeF_2 = 0$

F ⟵ Be ⟶ F $\qquad \longleftarrow + \longrightarrow = 0$

Bond dipoles $\qquad$ net dipole in $BeF_2 = 0$

BF_3 is angular

In BF_3 bond angle is 120^0 and molecule is symetrical. The three B-F bonds are oriented at 120^0 with each other and sum of any two is equal and opposite to the third therefore sum of three B-F dipoles = 0.



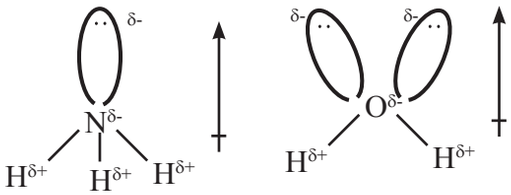
$\longleftarrow + \longrightarrow = 0$

Bond dipoles $\qquad$ net dipole in $BF_3 = 0$

In case of angular molecules both lone pairs and electonegativity difference contribute to dipole moment.

Lone pairs and dipole moment : In some molecules the central atom has unshared or lone pairs of electrons. These lone pairs also contribute to overall dipole of the molecule. Nitrogen in NH_3 and Oxygen in H_2O posses

lone pairs, these reinforce the dipoles due to N-H and O-H bonds. Both these molecules are highly polar.

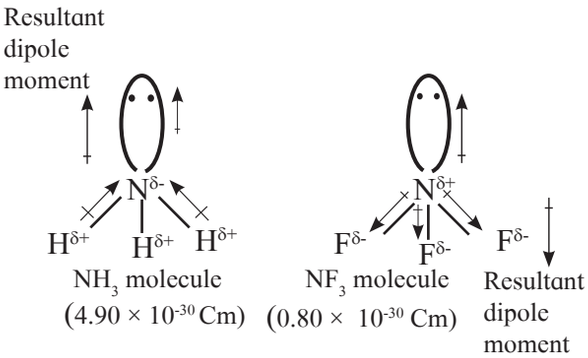


μ= 1.48 D μ= 1.85 D

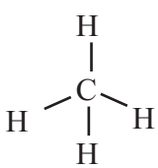
Nitrogen has only one lone pair while oxygen has two lone pairs which reflects in the higher dipole moment of water.

Consider NH_3 and NF_3

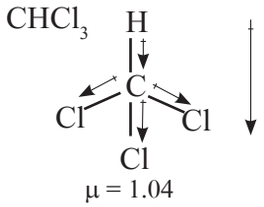
Both have pyramidal shape with a lone pair of electrons on nitrogen atom. Here hydrogen is less electronegative while, fluorine is more electronegative than nitrogen. The resultant dipole moment of NH_3 is 4.90×10^{-30} Cm while that of NF_3 is 0.80×10^{-30} Cm. This difference is because in case of NH_3 the orbital dipole due to lone pair is in the same direction as that of resultant dipole moment of N-H bonds hence gets added whereas in NF_3, the orbital moment is in the direction opposite to the resultant dipole moment of three N-F bonds. The orbital dipole because of lone pair decreases the effect of the resultant N-F bond moments, which results in its low dipole moment.



CH_4 : The central atom carbon has no lone pair and the molecule is non-polar.



In $CHCl_3$ the dipoles are not equal and do not cancel hence $CHCl_3$ is polar with a non zero dipole moment.



Dipole moments of some molecules are shown in table 5.8.

Table 5.8 dipole moments and geometry of some molecules

Types of molecule	Example	Dipole moment μ (D)	Geometry
Molecule AB	HF	1.91	linear
	HCl	1.03	linear
	HBr	0.79	linear
	H_2	0	linear
Molecule AB_2	H_2O	1.85	bent
	H_2S	0.95	bent
	CO_2	0	linear
Molecule AB_3	NH_3	1.47	trigonal pyramidal
	NF_3	0.23	trigonal pyramidal
	BF_3	0	trigonal planar
Molecule AB_4	CH_4	0	tetrahedral
	$CHCl_3$	1.04	tetrahedral
	CCl_4	0	tetrahedral

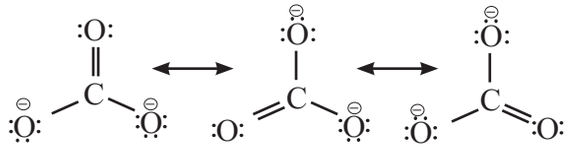
5.8.7 Covalent character of ionic bond :

Several ionic compounds possess partial covalent character and show properties similar to covalent compounds. For example LiCl is ionic but it is more soluble in organic solvents than water. To explain the partial covalent character in ionic bonds Fajans put forth the following rules :

1. The smaller size of the cation and larger the size of the anion renders, greater covalent character to ionic bond. For example $Li^{\oplus}Cl^{\ominus}$ is more covalent than $Na^{\oplus}Cl$. Similarly $Li^{\oplus}I^{\ominus}$ is more covalent than $Li^{\oplus}Cl^{\ominus}$.
2. Greater the charge on cation, more is covalent character of the ionic bond. For example, covalent character of $AlCl_3$, $MgCl_2$ and NaCl decreases in the following order $Al^{3\oplus}(Cl^{\ominus})_3 > Mg^{2\oplus}(Cl^{\ominus})_2 > Na^{\oplus}Cl^{\ominus}$
3. A cation with the outer electronic configuration of the $s^2p^6d^{10}$ type possess a greater polarising power compared to the cation having the same size and same charge but having outer electronic configuration of s^2p^6 type.

This is because d- electrons of the $s^2\ p^6\ d^{10}$ shell screen nuclear charge less effectively compared to s and p electrons of s^2p^6 shell. Hence the effective nuclear charge in a cation having $s^2\ p^6\ d^{10}$ configuration is greater than that of the one having s^2p^6 configuration. For example : $Cu^{\oplus}Cl^{\ominus}$ is more covalent than $Na^{\oplus}Cl^{\ominus}$. Here ($Cu^{\oplus}$ $1s^2\ 2s^22p^6\ 3s^23p^63d^{10}$; $Na^{\oplus}$ $1s^2\ 2s^22p^6$)

5.8 Resonance : Many polyatomic molecules can be represented by more than one Lewis structures. Consider for example, three structures written for $CO_2^{2\ominus}$. Each structure differs from the other only in the position of electrons without changing positions of the atoms.



None of these individuals structures is adequate to explain the properties. The actual structure of $CO_3^{2\ominus}$ is a combination of three Lewis structures and is called as the **resonance hybrid**. Resonance signifies that there is more than one possible way in which the electrons can be assigned in a Lewis structure. The various structures are called canonical forms.

Now consider the example of O_3. It is the resonance hybrid of the following structures.

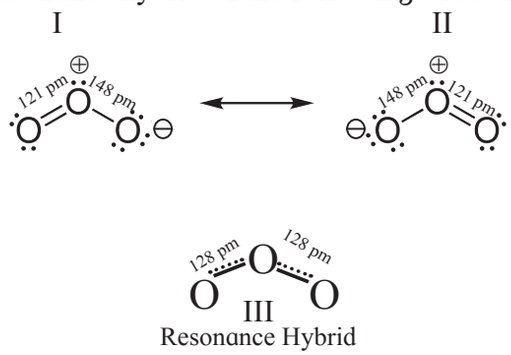


Fig. 5.13 Resonance in the O_3 molecule

(structure I and II are canonical forms while structure III is the resonance hybrid.)

Resonance Energy :

We have seen that many polyatomic ions and molecules can be represented by different canonical forms and each form has a different energy. Energy of the resonating forms is different from the most stable structure, **resonance hybrid**. The difference in energy of the stable contributing structure and the resonating forms is usually defined as Resonance energy.

To summarize it can be stated that

a. Energy of the resonance hybrid structure is less than the energy of any single canonical form hence, resonance stabilizes certain polyatomic molecules or ions.
b. The average of all resonating structures contributes to overall bonding characteristic features of the molecule.

This will be clear from the example of ozone. Ozone can be represented by two cannonical forms (shown earlier) I and II. III is the resonance hybrid. The energy of III is less than that of I and II.

Exercises

1. Select and write the most appropriate alternatives from the given choices.

A. Which molecule is linear?
   a. SO_3 b. CO_2
   c. H_2S d. Cl_2O

B. When the following bond types are listed in decreasing order of strength (strongest first). Which is the correct order ?
   a. covalcnt > hydrogen > vander waals'
   b. covalent > vander waal's > hydrogen
   c. hydrogen > covalent > vander waal's
   d. vander waal's > hydrogen > covalent.

C. Valence Shell Electron Pair repulsion (VSEPR) theory is used to predict which of the following :
   a. Energy levels in an atom
   b. the shapes of molecules and ions.
   c. the electrone getivities of elements.
   d. the type of bonding in compounds.

D. Which of the following is true for CO_2?

	C=O bond	CO_2 molecule
A	polar	non-polar
B	non-polar	polar
C	polar	polar
D	non-polar	non-polar

E. Which O_2 molecule is pargmagnetic. It is explained on the basis of :
   a. Hybridisation b. VBT
   c. MOT d. VSEPR

F. The angle between two covalent bonds is minimum in:
   a CH_4 b. C_2H_2
   c. NH_3 d. H_2O

2. Draw

A. Lewis dot diagrams for the folowing
   a. Hydrogen (H_2)
   b. Water (H_2O)
   c. Carbon dioxide (CO_2)
   d. Methane (CH_4)
   e. Lifthium Fluoride (LiF)

B. Diagram for bonding in ethene with sp^2 Hybridisation.

C. Lewis electron dot structures of
   a. HF b. C_2H_6 c. C_2H_4
   d. CF_3Cl e. SO_2

D. Draw orbital diagrams of
   a. Fluorine molecule
   b. Hydrogen fluoxide molecule

3. Answer the following questions

A. Distinguish between sigma and pi bond.

B. Display electron distribution around the oxygen atom in water molecule and state shape of the molecule, also write H-O-H bond angle.

C. State octel rule. Explain its inadequecies with respect to
   a. Incomplete octel b. Expanded octel

D. Explain in brief with one example:
   a. Ionic bond b. covalend bond
   c. co-ordinate bond

E. Give reasons for need of Hybridisation

F. Explain geometry of methane molecule on the basis of Hybridisation.

G. In Ammonia molecule the bond angle is 107^0 and in water molecule it is $104^0 35'$, although in both the central atoms are sp^3 hybridized Explain

H. Give reasons for:
   a. Sigma (σ)bond is stronger than Pi (π)bond.
   b. HF is a polar molecule
   c. Carbon is a tetravalent in nature.

I. Which type of hybridization is present in ammonia molecule? Write the geometry and bond angle present in ammonia.

J. Identify the type of orbital overlap present in
   a. H_2 b. F_2 c. H-F molecule.
   Explain diagramatically.

K. F-Be-F is a liner molecule but H-O-H is angular. Explain.

L. BF_3 molecule is planar but NH_3 pyramidal. Explain.

M. In case of bond formation in Acetylene molecule :
   a. How many covalend bonds are formed ?
   b. State number of sigma and pi bonds formed.
   c. Name the type of Hybridisation.

N. Define :
   a. Bond Enthalpy
   b. Bond Length

O. Predict the shape and bond angles in the following molecules:
   a. CF_4 b. NF_3
   c. HCN d. H_2S

4. Using data from the Table, answer the following :

Examoles	C_2H_6 Ethane	C_2H_4 Ethene	C_2H_2 Ethyne
Structure	-C - C-	C = C	-C ≡ C -
Type of bond between carbons	single	double	triple
Bond length (nm)	0.154	0.134	0.120
Bond Enthalpy kJ mol^{-1}	348	612	837

a. What happens to the bond length when unsaturation increases?
b. Which is the most stable compound?
c. Indicate the relation between bond strength and Bond enthalpy.
d. Comment on overall relation between Bond length, Bond Enthalpy and Bond strength and stability.

5. Complete the flow chart

Molecular Formula	Structural Formula	Shape/ Geometry	Bond angle
$BeCl_2$			180^0
	O=C=O -	Linear	
C_2H_2			

7. Answer in one sentence:

A. Indicate the factor on which stalility of ionic compound is measured?
B. Arrange the following compounds on the basis of lattice energies in decreasing (descending) order: BeF_2, $AlCl_3$, LiCl, $CaCl_2$, NaCl
C. Give the total number of electrons around sulphur (S) in SF_6 compound.
D. Covalant bond is directional in nature. Justify.
E. What are the interacting forces present during formation of a molecule of a compound ?
F. Give the type of overlap by which pi (π) bond is formed.
G. Mention the steps involved in Hybridization.
H. Write the formula to calculate bond order of molecule.
I. Why is O_2 molecule paramagnetic?
J. What do you mean by formal charge ? Explain its significance with the help of suitable example.

Activity :

Practice the bonding structure with the help of structure set of chemistry.

6. Complete the following Table

Molecule	Type of Hybridisation	Type of bonds	Geometry	Bond angle
CH_4	-	4C-H 4σ bonds	Tetrahedral	-
NH_3	sp^3	3N-H 3σbonds 1 lone pair	-	-
H_2O	-	-	angular	104.5^0
BF_3	sp^2	-	-	120^0
C_2H_4	-	-	-	120^0
BeF_2	-	2 Be-F	Linear	-
C_2H_2	sp	(3σ+2π) 1C-C σ 2C-H σ 2C-C π	-	-

6. Redox Reactions

6.1 Introduction

Can you tell?

1. Why does cut apple turn brown when exposed to air ?
2. Why does old car bumper change colour?
3. Why do new batteries become useless after some days ?

Redox is an abbreviation used for the terms 'oxidation and reduction'. A large number of phenomena such as respiration, rusting, combustion of fuel involve redox reactions.

Can you recall?

1. What is combustion reaction?
2. Write an equation for combustion of methane.
3. What is the driving force behind reactions of elements?

6.1.1 Classical ideas of redox reactions

Classically oxidation refers to combination of an element or a substance with oxygen.

For example, Oxidation of carbon

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \cdots\cdots (6.1)$$

Oxidation of magnesium

$$2\,Mg + O_2 \longrightarrow 2\,MgO(s) \quad \cdots\cdots (6.2)$$

In reaction (6.1) and (6.2) the carbon and magnesium are oxidized on reacting with oxygen. Now consider the reaction :

$$2\,Fe_2O_3 + 3\,C(s) \rightarrow 4\,Fe(s) + 3\,CO_2(g) \quad \cdots\cdots (6.3)$$

In this reaction there is removal of oxygen from Fe_2O_3. Hence it is a **reduction reaction**.

Further

$$2H_2S(g) + O_2(g) \longrightarrow 2\,S(s) + 2\,H_2O(l) \quad \cdots\cdots (6.4)$$

In this reaction there is removal of hydrogen and is also called **oxidation**. Here the sulfur in H_2S loses hydrogen and undergoes oxidation while oxygen accepts hydrogen and undergoes reduction.

Oxidants/ Oxidising agent : A reagent/ substance which itself undergoes reduction and causes oxidation of another species is called **oxidant /oxidising agent**. Now consider some more examples.

$$Mg(s) + F_2(g) \longrightarrow Mg\,F_2(s) \quad \cdots\cdots (6.5)$$

$$Mg(s) + S(s) \longrightarrow MgS(s) \quad \cdots\cdots (6.6)$$

The above reactions are also examples of oxidation though no oxygen is involved and thus scope of oxidation can be expanded. Combination with electronegative element is oxidation. Oxidation can also be looked upon as the **removal of electropositive element**.

For example

$$Hg_2Cl_2(s) \longrightarrow HgCl_2(s) + Hg(s) \quad \cdots\cdots (6.7)$$

Now let us consider some examples of **reduction**.

a. Removal of oxygen from mercuric oxide

$$2\,HgO(s) \longrightarrow 2\,Hg(l) + O_2(g) \quad \cdots\cdots (6.8)$$

b. Removal of electronegative element from $FeCl_3$ as in

$$2\,FeCl_3 + H_2(g) \longrightarrow 2FeCl_2(aq) + 2\,HCl \quad \cdots\cdots (6.9)$$

c. Addition of hydrogen

$$CH_2 = CH_2(g) + H_2(g) \longrightarrow CH_3 - CH_3(g) \quad \cdots\cdots (6.10)$$

d. Addition of an elctropositive element

$$2\,HgCl_2(aq) + SnCl_2(aq) \rightarrow Hg_2Cl_2(s) + SnCl_4(aq) \quad \cdots\cdots (6.11)$$

In eq. (6.8) there is removal of oxygen from mercuric oxide Eq (6.9) shows removal of electronegative element from $FeCl_3$ Eq (6.10) involves addition of hydrogen. Equation (6.11) involves addition of an electropositive element Hg to $HgCl_2$. All these reactions represent **reduction**.

Reductant / reducing agent : A reagent / reducing agent is defined as a substance/ reagent which itself undergoes oxidation bringing about the reduction of another species. Now consider again equation (6.11). The equation (6.11) involves simultaneous oxidation and reduction. In this reaction $HgCl_2$ is reduced to Hg_2Cl_2 and $SnCl_2$ is oxidized to $SnCl_4$. Hence it is redox reaction.

Key points

Oxidation it is defined as:

a. addition of oxygen.
b. addition of electronegative element.
c. removal of hydrogen.
d. removal of electropositive element.
e. loss of electrons by any species.

Reduction it is defined as:

a. removal of oxygen.
b. removal of electronegative element.
c. addition of hydrogen.
d. addition of electropositive element.
e. gain of electrons by any species.

6.1.2 Redox reaction in terms of electron transfer : Redox reaction can be described as electron transfer as shown below.

$$Mg + \frac{1}{2} O_2 \longrightarrow Mg^{2\oplus} + O^{2\ominus} \quad \text{..... (6.12)}$$

$$Mg + F_2 \longrightarrow Mg^{2\oplus} + 2F^{\ominus} \quad \text{..... (6.13)}$$

Development of charges on the species produced suggest the reactions 6.12 and 6.13 can be written as :

Loss of $2e^{\ominus}$

$$Mg(s) + O_2(g) \longrightarrow Mg^{2\oplus} + O^{2\ominus}$$

Gain of $2e^{\ominus}$

Loss of $2e^{\ominus}$

$$Mg(s) + F_2(g) \longrightarrow Mg^{2\oplus} + 2F^{\ominus}$$

Gain of $2e^{\ominus}$

When Mg is oxidised to MgO, the neutral Mg atom loses electrons to form $Mg^{2\oplus}$ in MgO. The elemental oxygen gains electrons and forms $O^{2\ominus}$ in MgO.

Each of the above steps represents a half reaction which involves electron transfer (loss or gain). Sum of these two half reactions or the overall reaction is a redox reaction. Now consider the following half reactions.

$$Fe(s) \longrightarrow Fe^{2\oplus}(aq) + 2e^{\ominus} \quad \text{..... (6.14)}$$

$$Cu^{2\oplus}(aq) + 2e^{\ominus} \longrightarrow Cu(s) \quad \text{..... (6.15)}$$

$$Fe(s) + Cu^{2\oplus}(aq) \longrightarrow Fe^{2\oplus}(aq) + Cu(s) \quad \text{..... (6.16)}$$

In the half reaction (6.14) Fe acts as a reducing agent whereas $Cu^{2\oplus}$ acts as oxidising agent which accepts electrons from Fe. The half reaction involving loss of electrons is called oxidation reaction and that involving gain of electrons is called reduction. Thus eq. (6.14) is oxidation, eq. (6.15) is reduction and eq. (6.16) is a redox reaction.

Key points : Oxidant / oxidizing agent : A reagent / substance which itself undergoes reduction and causes oxidation of another species is called oxidant or oxidizing agent. This is an **electron acceptor**.

Reductant / Reducing agent : A reagent / reducing agent is defined as a substance / reagent which itself undergoes oxidation and brings about reduction of another species. A reductant is electron donor.

Displacement reactions can also be looked upon as redox reactions. In such reactions an ion (or atom) in a compound is replaced by an ion (or on atom) of another element.

$$X + YZ \longrightarrow XZ + Y$$

The reaction (6.16) is displacement reaction.

Try this

Complete the following table of displacement reactions. Identify oxidising and reducing agents involved.

Reactants	Products
Zn (s) + ... (aq)	..... (aq) + Cu (s)
Cu (s) + 2 Ag^{+} (aq)	..... + ...
..... + ...	Co^{2+} (aq) + Ni (s)

6.2 Oxidation number : Description of redox reaction in terms of electron transfer suggest involvement of only ionic species in it. But many reactions involving only covalent bonds also fulfil the classical definition of oxidation and reduction. For example:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \quad \text{..... (6.17)}$$

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \quad \text{..... (6.18)}$$

Eq (6.17) represents oxidation of H_2 as it is combination with oxygen. An electronegative element Cl is added to H_2, and therefore, eq (6.18) also represents oxidation of H_2. As products of both these oxidations are polar covalent molecules, there is an electron shift rather than complete electron transfer from one species to the other.

A practical method based on **oxidation number** is developed to describe all the redox reactions, which are either ionic involving complete electron transfer or covalent which refer to shift of electrons. In this method the electron pair in a covalent band is assumed to belong to more electronegative element, that is, it shifts completely to more electronegative element.

Oxidation number of an element in a compound **is defined** as the number of electrical charges it carries (assuming complete electron transfer in the case of covalent bond). The following rules have been formulated to determine the oxidation number of an element in a compound.

6.2.1 Rules to assign oxidation number

1. The **oxidation number** of each atom of an **element** in free state is zero. For example : each atom in H_2, Cl_2, O_3, S_8, P_4, O_2, Ca, etc. has oxidation number of zero.
2. The **oxidation number** of an atom in a **monoatomic** ion is equal to its charge. Thus alkali metals have oxidation number +1 in all their compounds (NaCl, KCl, etc.). Alkaline earth metals have oxidation number +2 in all their compouds ($CaCO_3$, $MgCl_2$, etc.). Al is considered to have +3 as its oxidation number in all its compounds.
3. The **oxidation number of O** is usually -2 in all of its compounds except in peroxide or peroxide ion where it has oxidation number of -1 and in superoxide each oxygen has oxidation number -1/2.

Ca-O	H-O-O-H	(O-O)	KO_2
+2 -2	+1 -1 -1 +1	-1 -1	+1 -1/2

In OF_2 oxidation number of oxygen is +2.

4. The **oxidation number of H** atom is either +1 or -1. When the H atom is bonded to nonmetals, its oxidation number is +1. When it is bonded to metals, it possesses oxidation number of -1.

$(O-H)^-$	H-O-H	Li-H	H-Ca-H
-2 +1	+1 -2 +1	+1 -1	-1 +2 -1

5. The oxidation number of F is -1 in all of its compounds. The other halogens Cl, Br and I usually exhibit oxidation number of -1 in their halide compounds. However in compounds in which halogens Cl, Br and I are bonded to oxygen, oxidation number of halogens is +1 For example,

H-F	KBr	Cl-O-Cl	H-O-Cl
+1-1	+1-1	+1 -2 +1	+1 -2 +1

6. The algebraic sum of oxidation numbers of all the atoms in a neutral molecule is zero.
7. The algebraic sum of oxidation numbers of all the atoms in a polyatomic ion is equal to net charge of the ion.
8. When two or more atoms of an element are present in molecule or ion, oxidation number of the atom of that element will be average oxidation number of all the atoms of that element in that molecules.

By applying rules 1 to 5 it is possible to determine oxidation number(s) of atoms of various elements in molecules or ions. For doing this the rules 6, 7 and 8 are useful.

Problem 6.1: Deduce the oxidation number of S in the following species:
i. SO_2 ii. $SO_4^{2\ominus}$

Solution:

i. SO_2 is a neutral molecule :

$\therefore$ Sum of oxidation number of all atom of SO_2 = 0 = (oxidation number of S) + 2 x (oxidation number of O)

$\therefore$ 0 = (oxidation number of S) + 2 x (-2)

$\therefore$ Oxidation number of S in SO_2 = 0 – (2x (-2)) = 0 – (-4) = + 4

ii. $SO_4^{2\ominus}$ is an ionic species.

$\therefore$ Sum of oxidation number of all atom of $SO_4^{2\ominus}$ = -2

= Oxidation number of S + 4 x (Oxidation number of O)

$\therefore$ Oxidation number of S in $SO_4^{2\ominus}$ = -2 -4 x (-2) = -2+8 = + 6

Remember

Oxidation number of an element can be positive or negative and a whole number or a fraction.

6.2.2 Stock notation : Oxidation number represents the oxidation state of an atom and is also denoted by Roman numeral in parentheses after the chemical symbol of the concerned element in the molecular formula. This representation is called **Stock notation** after the German Scientist Alfred Stock. For example :

1. $Au^{1\oplus}\ Cl^{1\ominus} \longrightarrow Au(I)Cl$
2. $Au^{3\oplus}Cl_3^{1\ominus} \longrightarrow Au(III)Cl_3$
3. $Sn^{4\oplus}Cl_4^{1\ominus} \longrightarrow Sn(IV)Cl_4$
4. $Sn^{2\oplus}Cl_2^{1\ominus} \longrightarrow Sn(II)Cl_2$
5. $Mn^{4\oplus}O_2^{2\ominus} \longrightarrow Mn(IV)O_2$

The Stock notation is used to specify the oxidation number of the metal. The idea of oxidation number is very convenient to define oxidation, reduction and the substances like oxidizing agent (oxidant) and reducing agent (reductant) of the redox reaction.

6.2.3 Redox reaction in terms of oxidation number :

Oxidation : An increase in the oxidation number of an element in a given substance.

Reduction : A decrease in the oxidation number of an element in a given substance.

Oxidizing agent : A substance which increases the oxidation number of an element in a given substance, and itself undergoes decrease in oxidation number of a constituent element.

Reducing agent : A substance that lowers the oxidation number of an element in a given substance, and itself undergoes an increase in the oxidation number of a constituent element in it.

Problem 6.2 : Assign oxidation number to each element in the following compounds or ions.

a. $KMnO_4$ b. $K_2Cr_2O_7$ c. $Ca_3(PO_4)_2$

Solution :

a. $KMnO_4$

1. Oxidation number of K = +1
2. Oxidation number of O = -2
3. Sum of the oxidation numbers of all atoms = 0

∴ Oxidation no. of K + oxidation of Mn + 4 x oxidation number of O = 0

(+1) + oxidation number of Mn + 4 x (-2) = 0
oxidation number of Mn + 1 - 8 = 0
oxidation number of Mn - 7 = 0
oxidation number of Mn = +7

b. $K_2Cr_2O_7$

1. oxidation number of K =+1
2. oxidation number of O = -2
3. sum of oxidation number of all atoms = 0

∴ 2 x oxidation no. of K + 2x oxidation number of Cr +7x oxidation number of O = 0
∴ 2 x (+1) + 2 x oxidation number of Cr + 7 x (–2) = 0
∴ +2 +2 x oxidation number of Cr - 14 = 0
∴ 2x oxidation number of Cr + 2 - 14 = 0
∴ 2x oxidation number of Cr - 12 = 0
∴ 2x oxidation number of Cr = +12
∴ oxidation number of Cr = +12 /2
∴ oxidation number of Cr = +6

c. $Ca_3(PO_4)_2$

1. oxidation number of Ca = +2 (alkaline earth metal ion)
2. oxidation number of O = -2
3. sum of oxidation number of all atoms = 0

∴ 3 x O.N. of Ca + 2 x oxidation number of P + 8 x oxidation number of O = 0
∴ 3 x(+2) + 2 x oxidation number of P + 8 x (-2) = 0
∴ (+6) + 2 x oxidation number of P -16 = 0
∴ 2 x oxidation number of P -16 + 6 = 0
∴ 2 x oxidation number of P -10 = 0
∴ 2 x oxidation number of P = +10
∴ oxidation number of P = +10/2
∴ oxidation number of P = + 5

Problem 6.3 : Assign oxidation number to the atoms other than O and H in the following species.

i. $SO_3^{2\ominus}$ ii. $BrO_3^{\ominus}$ iii. $ClO_4^{\ominus}$ iv. $NH_4^{\oplus}$ v. $NO_3^{\ominus}$ vi. $NO_2^{\ominus}$ vii. SO_3 viii. N_2O_5

Solution : The oxidation number of O atom bonded to a more electropositive atom is -2 and that of H atom bonded to electronegative atom is +1. Using these values the oxidation numbers of atoms of the other elements in a given polyatomic species are calculated.

i. $SO_3^{2\ominus}$

-2 = oxidation number of S + 3 x (oxidation number of O)

$\therefore$ Oxidation number of S = $-2 - 3(-2)$

$= -2 + 6 = 4$

ii. $BrO_3^{\ominus}$

-1 = oxidation number of Br + 3 x (oxidation number of O)

$\therefore$ Oxidation number of Br = $-1 - 3(-2)$

$= -1 + 6 = 5$

Similarly the oxidation number in the remaining species are found to be

iii. Cl in $ClO_4^{\ominus}$: +7 iv. N in $NH_4^{\oplus}$: -3

v. N in $NO_3^{\ominus}$: +5 vi. N in $NO_2^{\ominus}$: +3

vii. S in SO_3 : +6 viii. N in N_2O_5 : +5

Problem 6.4 : Identify whether the following reactions are redox or not. State oxidants and reductants therein.

a. $3H_3AsO_3(aq) + BrO_3^{\ominus}(aq) \longrightarrow Br^{\ominus}(aq) + 3H_3AsO_4(aq)$

1. Write oxidation number of all the atoms of reactants and products by doing required calculations. (a) stands for known O.N. and (b) for calculated O.N.

$3H_3AsO_3 + BrO_3^{\ominus} \rightarrow Br^{\ominus} + 3H_3AsO_4$

(a) 3 x(+1) | 3 x(-2) | 3 x (-2) -1 | 3 x (+1) | 4x(-2)

(b) +3 +5 +5

2. Identify the species that undergoes change in oxidation number

Loss of $2e^{\ominus}$

$3H_3AsO_3(aq) + BrO_3^-(aq) \longrightarrow Br^-(aq) + 3H_3AsO_4(aq)$

Gain of $6e^{\ominus}$

The oxidation number of As increases from +3 to +5 and that of Br decreases from +5 to -1. Because oxidation number of one species increases and that of other decreases, the reaction is therefore redox reaction.

The oxidation number of As increases by loss of electron. Thus As is a reducing agent and is itself oxidized. On the other hand, the oxidation number of Br decreases. Hence, it is reduced by the gain of electron and act as an oxidizing agent.

Result :

1. The reaction is redox reaction.
2. Oxidant/oxidizing agent - BrO_3^-
3. Reductant/Reducing agent - H_3AsO_3

Do you know ?

Some elements in a particular compound may possess fractional oxidation number. For example : C_3O_2, Br_3O_8, $Na_2S_4O_6$, C_8H_{18}, etc. In these compounds oxidation number of C, Br, S, C are 4/3, 16/3, 2.5, 9/4, respectively. These oxidation numbers are actually the average oxidation number of all the atoms of elements in that compound. Different atoms of the element in such species exhibit different oxidation states. For example : Tertra thionate ion has two S atoms with oxidation number +5 and two with zero (0). Therefore, the average oxidation number of S in these species is 10/4 = 2.5

$^{-}O - \overset{O}{\overset{\|}{S}}(+5) - \overset{0}{S^*} - \overset{0}{S^*} - \overset{O}{\overset{\|}{S}}(+5) - O^-$ structure of $S_4O_6^{2-}$ (tetrathionate ion)

6.3 Balancing of redox reactions : Two methods are used to balance chemical equation for redox processes : Oxidation number method and Half reaction method or Ion electron method.

6.3.1 The Oxidation number method is illustrated in the following steps :

Step I : Write the unbalanced equation for redox reaction. Balance the equation for all atoms in the reactions, except H and O. Identify the atoms which undergo change in oxidation number and by how much. Draw the bracket to connect atoms of the elements that changes the oxidation number.

Step II : Show an increase in oxidation number per atom of the oxidised species and hence the net increase in oxidation number. Similarly show a decrease in the oxidation number per atom of the reduced species and the net decrease in oxidation number. Determine the factors which will make the total increase and decrease equal. Insert the coefficients into the equation.

Step III : Balance oxygen atoms by adding H_2O to the side containing less O atoms, One H_2O is added for one O atom. Balance H atoms by adding $H^{\oplus}$ ions to the side having less H atoms.

Step IV : If the reaction occurs in basic medium, then add $OH^{\ominus}$ ions, equal to the number of $H^{\oplus}$ ions added in step III, on both the sides of equation. The $H^{\oplus}$ and $OH^{\ominus}$ on same sides of reactions are combined to give H_2O molecules.

Step V : Check the equation with respect to both, the number of atoms of each element and the charges. It is balanced.

Note : For acidic medium step IV is omitted.

Problem 6.5 : Using the oxidation number method write the net ionic eqvation for the reaction of potassium permanganate, $KMnO_4$, with ferrous sulphate, $FeSO_4$.

$MnO_4^{\ominus}(aq) + Fe^{2\oplus}(aq) \longrightarrow Mn^{2\oplus}(aq) + Fe^{3\oplus}(aq)$

Solution :

Step 1 : The skeletal ionic equation is

$MnO_4^{\ominus}(aq) + Fe^{2\oplus}(aq) \longrightarrow Mn^{2\oplus}(aq) + Fe^{3\oplus}(aq)$

Step 2 : Assign oxidation number to Mn and Fe, and calculate the increase and decrease in the oxidation number and make them equal. (a) stands for known O.N. and (b) for calculated O.N.

$$\underset{\substack{(a)\\(b)}}{\overset{\uparrow\ \uparrow}{MnO_4^{\ominus}}} + \underset{\uparrow}{Fe^{2\oplus}} \longrightarrow \underset{\uparrow}{Mn^{2\oplus}} + \underset{\uparrow}{Fe^{3\oplus}}$$

(a) 4 x (-2) +2 +2 +3

(b) +7

increase in oxidation number :

$Fe\ (+2) \longrightarrow Fe\ (+3)$

increase per atom = 1

decrease in oxidation number :

$Mn(+7) \longrightarrow Mn(+2)$

decerase per atom = 5

to make the net incerase and decrease equal we must take 5 atoms of $Fe^{2\oplus}$

$MnO_4^{\ominus}(aq) + 5Fe^{2\oplus}(aq) \longrightarrow Mn^{2\oplus}(aq) + 5Fe^{3\oplus}(aq)$

Step 3 : Balance the 'O' atoms by adding $4H_2O$ to the right hand side.

$MnO_4^{\ominus}(aq) + 5Fe^{2\oplus}(aq) \longrightarrow Mn^{2\oplus}(aq) + 5Fe^{3\oplus}(aq) + 4H_2O(l)$

Step 4: The medium is acidic. To make the charges and hydrogen atoms on the two sides equal, add $8H^{\oplus}$ on the left hand side.

$MnO_4^{\ominus}(aq) + 5\ Fe^{2\oplus}(aq) + 8H^{\oplus}(aq) \longrightarrow Mn^{2\oplus}(aq) + 5Fe^{3\oplus}(aq) + 4H_2O(l)$

Step 5: Check the two sides for balance of charges and atoms. The net ionic equation obtained in step 4 is the balanced equation.

$$\mathbf{MnO_4^{\ominus}(aq) + 5\ Fe^{2\oplus}(aq) + 8H^{\oplus}(aq) \longrightarrow Mn^{2\oplus}(aq) + 5Fe^{3\oplus}(aq) + 4H_2O}$$

Problem 6.6 : Balance the following reaction by oxidation number mathod.

$CuO + NH_3 \longrightarrow Cu + N_2 + H_2O$

Solution :

Step I : Write skeletal equation and balance the elements other that O and H.

$CuO + 2\ NH_3 \longrightarrow Cu + N_2 + H_2O$

Step II : Assign oxidation number to Cu and N. Calculate the increase and decrease in the oxidation number and make them equal. (a) stands for known O.N. and (b) for calculated O.N.

$$\underset{\substack{(a)\\(b)}}{\overset{\uparrow\ \uparrow\ \uparrow\ \uparrow}{CuO + 2NH_3}} \longrightarrow \underset{\uparrow\ \uparrow}{Cu + N_2 + H_2O}$$

(a) -2 3x(+1) 0 0

(b) +2 -3

increase in oxidation number :

$$\underset{\uparrow}{2NH_3} \longrightarrow \underset{\uparrow}{N_2}$$

-3 0

increase per atom = 3

decrease in oxidation number

$$\underset{\uparrow}{CuO} \longrightarrow \underset{\uparrow}{Cu}$$

+2 0

decrease per atom = 2

to make the net increase and decrease equal we must take 3 atoms of Cu and 2 atoms of N

$3CuO + 2NH_3 \longrightarrow 3Cu + N_2 + H_2O$

Step III : Balance 'O' atoms by addition $2H_2O$ to the right hand side.

$3CuO + 2NH_3 \longrightarrow 3Cu + N_2 + 3H_2O$

Step IV : Charges are already balanced

Step V : Check two sides for balanced of atoms and charges. The equation obtain in step IV is balanced.

$$\mathbf{3CuO + 2NH_3 \longrightarrow 3Cu + N_2 + 3H_2O}$$

6.3.2 Ion electron method (Half reaction method) : In this method two half equations are balanced separately and then added together to give balanced equation. Following steps are involved

Step I : Write unbalanced equation for the redox reaction. Assign oxidation number to all the atoms in the reactants and products. Divide the equation into two half equations. One half equation involves increase in oxidation number and another involves decrease in oxidation

number (Write two half equation separately)

Step II : Balance the atoms except O and H in each half equation. Balance oxygen atom by adding H_2O to the side with less O atoms.

Step III : Balance the H atom by adding H^+ ions to the side with less H atoms.

Step IV : Balance the charges by adding appropriate number of electrons to the right side of oxidation half equation and to the left of reduction half equation.

Step V : Multiply half equation by suitable factors to equalize the number of electrons in two half equations. Add two half equations and cancel the number of electrons on both sides of equation.

Step VI : If the reaction occurs in basic medium then add OH^- ions, equal to number of $H^\oplus$ ions on both sides of equation. The $H^\oplus$ and OH^- ions on same side of equation combine to give H_2O molecules.

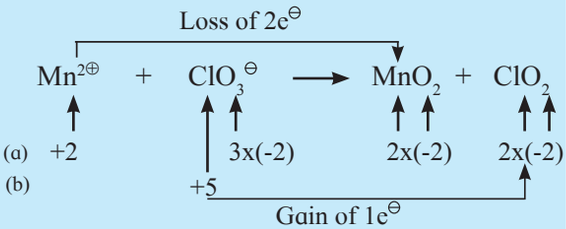
Step VII : Check that the equation is balanced in both, the atoms and the charges.

Problem 6.7 : Balance the following unbalanced equation (in acidic medium) by ion electron (half reaction method)

$Mn^{2\oplus}(aq) + ClO_3^{\ominus}(aq) \rightarrow MnO_2(s) + ClO_2(aq)$

Solution :

Step I : Write unbalanced equation for the redox reaction. Assign oxidation number to all the atoms in reactants and product then. Divide the equation into two half equations.



Oxidation half reaction

$Mn^{2\oplus}(aq) \longrightarrow MnO_2(s)$

Reduction half reaction

$ClO_3^{\ominus}(aq) \longrightarrow ClO_2(aq)$

Step II : Balance half equations for O atoms by adding H_2O to the side with less O atoms. Add $2H_2O$ to left side of oxidation and one H_2O to the right side of reduction.

Oxidation

$Mn^{2\oplus}(aq) + 2H_2O(l) \longrightarrow MnO_2(s)$

Reduction

$ClO_3^{\ominus}(aq) \longrightarrow ClO_2(aq) + H_2O(l)$

Step III : Balance H^- atoms by adding $H^\oplus$ ions to the side with less H. Hence add $4H^\oplus$ ions to the right side of oxidation and $2H^\oplus$ ions to the left side of reduction.

Oxidation

$Mn^{2\oplus}(aq) + 2H_2O(l) \longrightarrow MnO_2 + 4H^\oplus(aq)$

Reduction

$ClO_3^{\ominus}(aq) + 2H^\oplus(aq) \longrightarrow ClO_2(aq) + H_2O(l)$

Step IV : Now add 2 electrons to the right side of oxidation and 1 electron to the left side of reduction to balance the charges.

Oxidation

$Mn^{2\oplus}(aq) + 2H_2O(l) \longrightarrow MnO_2(s) + 4H^\oplus(aq) + 2e^{\ominus}$

Reduction

$ClO_3^{\ominus}(aq) + 2H^\oplus(aq) + e^{\ominus} \longrightarrow ClO_2(aq) + H_2O(l)$

Step V : Multiply reduction half equation by 2 to equalize number of electrons in two half equations. Then add two half equation.

Oxidation

$Mn^{2\oplus}(aq) + 2H_2O(l) \longrightarrow MnO_2(s) + 4H^\oplus(aq) + 2e^{\ominus}$ Reduction ..... (1)

$2ClO_3^{\ominus}(aq) + 4H^\oplus(aq) + 2e^{\ominus} \longrightarrow 2ClO_2(aq) + 2H_2O(l)$ ..... (2)

eq. (1) + eq. (2) gives the net reaction

$Mn^{2\oplus}(aq) + 2ClO_3^{\ominus}(aq) \longrightarrow MnO_2(s) + 2ClO_2(aq)$

The equation is balanced in terms of number of atoms and the charges.

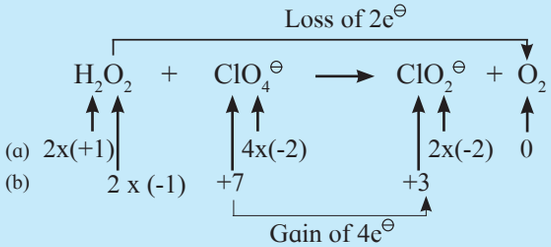
Problem 6.8 : Balance the following unbalanced equation by ion electron (half reaction method)

$H_2O_2(aq) + ClO_4^{\ominus}(aq) \longrightarrow ClO_2^{\ominus}(aq) + O_2(g)$

Solution :

Step I : Write unbalanced equation for the redox reaction and assign oxidation number to all the atoms in reactants and products. (a) stands for known O.N. and (b) for calculated O.N.

Divide the equation into two half equations.



Oxidation

$H_2O_2\,(aq) \longrightarrow O_2\,(g)$

Reduction

$ClO_4^{\ominus}(aq) \longrightarrow ClO_2^{\ominus}(aq)$

Step II : Balance the half equation for O atoms by adding H_2O to the side with less O atoms. Hence add 2 H_2O to the right side of reduction half equation and none to the oxidation half equation

Oxidation

$H_2O_2\,(aq) \longrightarrow O_2(g)$

Reduction

$ClO_4^{\ominus}(aq) \longrightarrow ClO_2^{\ominus}(aq) + 2\,H_2O(l)$

Step III : Balance H atoms by adding H^+ ions to the side with less H. Hence add $2H^{\oplus}$ ions to the right side of oxidation half equation and $4H^{\oplus}$ ions to the left side of reduction half equation.

Oxidation

$H_2O_2\,(aq) \longrightarrow O_2(g) + 2H^{\oplus}(aq)$

Reduction

$ClO_4^{\ominus}(aq) + 4H^{\oplus}(aq) \longrightarrow ClO_2^{\ominus}(aq) + 2H_2O\,(l)$

Step IV : Add 2 electrons to the right side of oxidation half equation and 4 electrons to the left side of reduction half equation to balance the charges.

Oxidation

$H_2O_2\,(aq) \longrightarrow O_2(g) + 2H^{\oplus}(aq) + 2e^{\ominus}$

Reduction

$ClO_4^{\ominus}(aq) + 4H^{\oplus}(aq) + 4e^{\ominus} \longrightarrow ClO_2^{\ominus} + 2H_2O$

Step V : Multiply oxidation half equation by 2 to equalize the number of electrons and then add two half equations.

Oxidation

$2\,H_2O_2\,(aq) \longrightarrow 2O_2(g) + 4H^{\oplus}(aq) + 4e^{\ominus}$

Reduction

$ClO_4^{\ominus}(aq) + 4H^{\oplus}(aq) + 4e^{\ominus} \longrightarrow ClO_2^{\ominus} + 2\,H_2O(l)$

$2\,H_2O_2\,(aq) + ClO_4^{\ominus}(aq) + 4H^{\oplus}(aq) + 4e^{\ominus} \longrightarrow 2\,O_2(g) + ClO_2^{\ominus}(aq) + 4\,H^{\oplus}(aq) + 4e^{\ominus} + 2\,H_2O(l)$

$2\,H_2O_2\,(aq) + ClO_4^{\ominus}(aq) \longrightarrow 2\,O_2(g) + ClO_2^{\ominus}(aq) + 2\,H_2O(l)$

This equation is balanced in terms of atoms and charges.

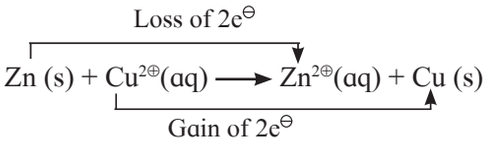
Try this

Classify the following unbalanced half equations as oxidation and reduction

Example	Type
$Cl^{\ominus}(aq) \longrightarrow Cl_2\,(g)$	oxidation
$OCl^{\ominus}(aq) \longrightarrow Cl^{\ominus}\,(g)$	
$Fe(OH)_2 \longrightarrow Fe(OH)_3$	
$VO^{2\oplus}\,(aq) \longrightarrow V^{3\oplus}\,(aq)$	

6.4 Redox reaction and electrode potential

We noted in the section 6.1.1 that displacement reaction can be looked upon as redox reaction. Consider the following displacement reaction.



..... (6.17)

This reaction can be brought about in two ways. The simpler method to observe this reaction is to take copper sulfate solution in a container and dip zinc rod in it. The redox reaction (6.17) takes place in that container. Zinc gets oxidized to $Zn^{2\oplus}$ ion and $Cu^{2\oplus}$ ions get reduced to metallic Cu. A direct transfer of electrons from zinc atom to cupric ions takes place in this case.

The electron transfer from Zn atom to $Cu^{2\oplus}$ ions can be demonstrated by carrying out two half reactions in two separate containers as shown in Fig. 6.1.

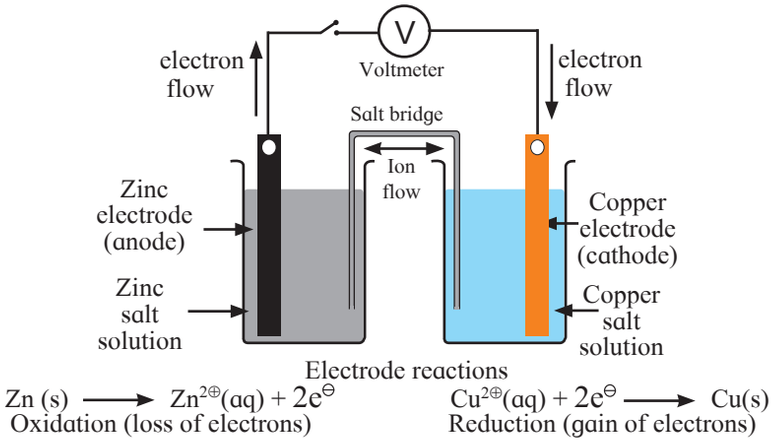


Fig. 6.1 : Daniel Cell

The set up in Fig. 6.1 is that of Daniel cell. The zinc and copper plates are connected by an electric wire through a switch and voltmeter. The solution in two containers are connected by salt bridge (U-shaped glass tube containing a gel of KCl or NH_4NO_3 in agar-agar). When switch is on, electrical circuit is complete as indicated by the deflection in the voltmeter. The circuit has two parts, one called external circuit, in the form of electrical wire which allows the flow of electrons and the other in the form of two solutions joined by salt bridge. In solution part of the circuit, the electric current is carried by movement of ions. When a circuit is complete, the zinc atoms on zinc plates spontaneously lose electrons which are picked up in the external circuit. The electrons flow from the zinc plate to copper plate through the wire. $Cu^{2\oplus}$ ions in the second container receive these electrons through the copper plate and are reduced to copper atoms which get deposited on the copper plate. Here, zinc plate acts as anode (negative electrode) and the copper plate acts as cathode (positive electrode). Thus, when two half reactions, namely, oxidation and reduction, are allowed to take place in separate containers and a provision is made for completing the electrical circuit, electron transfer takes place through the external circuit. This results in flow of electric current in the circuit as indicated by deflection in voltmeter. At the same time ions move within the solution resulting in completion of the electrical circuit. This is a simple electrochemical cell called Daniel cell, in which electricity is generated by redox reaction.

In an electrochemical cell electrons flow in the external circuit from anode to cathode while the conventional current flows from cathode to anode. An electrical potential is said to be established at the two electrodes of an electrochemical cell. It is called **electrode potential**. The magnitude and direction of the electrode potential depends upon the nature of the metal and ions, concentration of ions and temperature. The reaction associated with an electrode is called **electrode reaction**. The two chemical species linked by transfer of electrons form a **redox couple**.

6.4.1 Standard electrode potential : When concentration of each species taking part in the electrode reaction is unity and the temperature is 298 K, observed electrode potential is called standard electrode potential (E^0). By convention the standard electrode potential of hydrogen electrode is 0.00 Volt. Standard hydrogen electrode is used as reference electrode for determination of E^0 values of various redox couples.

Significance of E^0 value : The electrode reaction considered for the electrode potential is reduction reaction. Therefore, value and sign of standard electrode potential is a measure of the tendency of active species in the electrode reaction to remain in the oxidized / reduced form. A negative E^0 means redox couple is a stronger reducing agent than the $H^{\oplus}/H_2$ couple. Table 6.1 shows standard electrode potentials of reduction process of some redox couples.

Large negative value of E^0 means that redox couple is strong reducing agent. On the other hand, more positive value of E^0 means the redox couple is strong oxidizing agent. From the Table 6.1 it is seen that alkali metals have high negative value of E^0, which means that they are strong reducing agents. The alkali metals have great tendency to give away electron and form cations. On the other hand, fluorine has highly positive value of E^0 and thus great tendency to gain electron and is therefore, very strong oxidizing agents.

Table 6.1 : Standand electrode protentianls of some redox couples

Oxidised form + $ne^{\ominus}$ ⟶ reduced from	E^0/V
$F_2(g)+2e^{\ominus} \longrightarrow 2F^{\ominus}$	2.87
$H_2O_2+2H^{\oplus}+2e^{\ominus} \longrightarrow 2H_2O$	1.78
$MnO_4^{\ominus}+8H^{\oplus}+5e^{\ominus} \longrightarrow Mn^{2\oplus}+4H_2O$	1.51
$Cl_2(g)+2e^{\ominus} \longrightarrow 2Cl^{\ominus}$	1.36
$Cr_2O_7^{2\ominus}+14H^{\oplus}+6e^{\ominus} \longrightarrow 2Cr^{3\oplus}+7H_2O$	1.33
$O_2(g)+4H^{\oplus}+4e^{\ominus} \longrightarrow 2H_2O$	1.23
$Br_2+2e^{\ominus} \longrightarrow 2Br^{\ominus}$	1.09
$2Hg^{2\oplus}+2e^{\ominus} \longrightarrow Hg_2^{2\oplus}$	0.92
$Fe^{3\oplus}+e^{\ominus} \longrightarrow Fe^{2\oplus}$	0.77
$I_2(s)+2e^{\ominus} \longrightarrow 2I^{\ominus}$	0.54
$2H^{\oplus}+2e^{\ominus} \longrightarrow H_2(g)$	0.00
$Zn^{2\oplus}+2e^{\ominus} \longrightarrow Zn(s)$	-0.76
$Al^{3\oplus}+3e^{\ominus} \longrightarrow Al(s)$	-1.66
$Mg^{2\oplus}+2e^{\ominus} \longrightarrow Mg(s)$	-2.36
$Na^{\oplus}+e^{\ominus} \longrightarrow Na(s)$	-2.71
$Ca^{2\oplus}+2e^{\ominus} \longrightarrow Ca(s)$	-2.87
$K^{\oplus}+e^{\ominus} \longrightarrow K(s)$	-2.93
$Li^{\oplus}+e^{\ominus} \longrightarrow Li(s)$	-3.05

We shall learn more about electrode potential and electrochemical cells in the 12th standard.

Problem 6.9 : By using standard electrode potential table justify that the reaction between the following is spontaneous. (a) $Fe^{3\oplus}(aq)$ and $I^{\ominus}$ (aq), (b) $Ag^{\oplus}(aq)$ and Cu(s)

Solution : Write oxidation half reaction for one species and reduction half reaction for the other species. Change the sign of E^0 of oxidation half reaction. Take the sum of two E^0 values. If the sum is positive the reaction between two species is spontaneous.

(a) $Fe^{3\oplus}(aq)$ and $I^{\ominus}$ (aq)

Reduction : $2\,Fe^{3\oplus}(aq) + 2e^{\ominus} \longrightarrow 2\,Fe^{2\oplus}$, $E^0 = +0.77$ V

Oxidation : $2I^{\ominus}(aq) \longrightarrow I_2(s) + 2e^{\ominus}$, $E^0 = -0.54$ V

$2\,Fe^{3\oplus}(aq) + 2I^{\ominus}(aq) \longrightarrow 2\,Fe^{2\oplus}(aq) + I_2(s)$ Sum = + 0.23 V

The sum of E^0 values is positive, therefore the reaction is spontaneous.

(b) $Ag^{\oplus}(aq)$ and Cu(s)

Reduction : $2\,Ag^{\oplus}(aq) + 2e^{\ominus} \rightarrow 2Ag(s)$, $E^0 = +0.80$ V

Oxidation : $Cu(s) \longrightarrow Cu^{2\oplus}(aq) + 2e^{\ominus}$, $E^0 = -0.34$ V

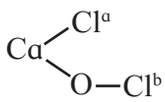
$2\,Ag^{\oplus}(aq) + Cu(s) \longrightarrow 2\,Ag(s) + Cu^{2\oplus}(aq)$ Sum = + 0.46 V

The sum of E^0 values is positive, therefore reaction is spontaneous.

Exercises

1. Choose the most correct option

A. Oxidation numbers of Cl atoms marked as Cl^a and Cl^b in $CaOCl_2$ (bleaching powder) are



a. zero in each

b. -1 in Cl^a and +1 in Cl^b

c. +1 in Cl^a and -1 in Cl^b

d. 1 in each

B. Which of the following is not an example of redox reacton ?

a. $CuO+H_2 \longrightarrow Cu+H_2O$

b. $Fe_2O_3+3CO_2 \longrightarrow 2Fe+3CO_2$

c. $2K+F_2 \longrightarrow 2KF$

d. $BaCl_2+H_2SO_4 \longrightarrow BaSO_4+2HCl$

C. A compound contains atoms of three elements A, B and C. If the oxidation state of A is +2, B is +5 and that of C is -2, the compound is possibly represented by

a. $A_2(BC_3)_2$

b. $A_3(BC_4)_2$

c. $A_3(B_4C)_2$

d. ABC_2

D. The coefficients p, q, r, s in the reaction

$p\ Cr_2O_7^{2\ominus} + q\ Fe^{2\oplus} \longrightarrow r\ Cr^{3\oplus} + s\ Fe^{3\oplus} + H_2O$

respectively are :

a. 1, 2, 6, 6

b. 6, 1, 2, 4

c. 1, 6, 2, 6

d. 1, 2, 4, 6

E. For the following redox reactions, find the correct statement.

$Sn^{2\oplus} + 2Fe^{3\oplus} \longrightarrow Sn^{4\oplus} + 2Fe^{2\oplus}$

a. $Sn^{2\oplus}$ is undergoing oxidation

b. $Fe^{3\oplus}$ is undergoing oxidation

c. It is not a redox reaction

d. Both $Sn^{2\oplus}$ and $Fe^{3\oplus}$ are oxidised

F. Oxidation number of carbon in H_2CO_3 is

a. +1 b. +2

c. +3 d. +4

G. Which is the correct stock notation for magenese dioxide ?

a. $Mn(I)O_2$ b. $Mn(II)O_2$

c. $Mn(III)O_2$ d. $Mn(IV)O_2$

I. Oxidation number of oxygen in superoxide is

a. -2 b. -1 c. $-\frac{1}{2}$ d. 0

J. Which of the following halogens does always show oxidation state -1 ?

a. F

b. Cl

c. Br

d. I

K. The process $SO_2 \longrightarrow S_2Cl_2$ is

a. Reduction

b. Oxidation

c. Neither oxidation nor reduction

d. Oxidation and reduction.

2. Write the formula for the following compounds :

A. Mercury(II) chloride

B. Thallium(I) sulphate

C. Tin(IV) oxide

D. Chromium(III) oxide

3. Answer the following questions

A. In which chemical reaction does carbon exibit variation of oxidation state from -4 to +4 ? Write balanced chemical reaction.

B. In which reaction does nitrogen exhibit variation of oxidation state from -3 to +5 ?

C. Calculate the oxidation number of underlined atoms.

a. $H_2\underline{S}O_4$ b. $H\underline{N}O_3$ c. $H_3\underline{P}O_3$
d. $K_2\underline{C}_2O_4$ e. $H_2\underline{S}_4O_6$ f. $\underline{Cr}_2O_7^{2-}$
g. $NaH_2\underline{P}O_4$

D. Justify that the following reactions are redox reaction; identify the species oxidized/reduced, which acts as an oxidant and which act as a reductant.

a. $2Cu_2O\,(s) + Cu_2S\,(s) \longrightarrow 6Cu\,(s) + SO_2\,(g)$

b. $HF\,(aq) + OH^{\ominus}(aq) \longrightarrow H_2O(l) + F^{\ominus}(aq)$

c. $I_2\,(aq) + 2\,S_2O_3^{2\ominus}(aq) \rightarrow S_4O_6^{2\ominus}(aq) + 2I^{\ominus}(aq)$

E. What is oxidation? Which one of the following pairs of species is in its oxidized state ?

a. $Mg / Mg^{2\oplus}$ b. $Cu / Cu^{2\oplus}$
c. $O_2 / O^{2\ominus}$ d. $Cl_2 / Cl^{\ominus}$

F. Justify the following reaction as redox reaction.

$2\,Na(s) + S(s) \longrightarrow Na_2\,S(s)$

Find out the oxidizing and reducing agents.

G. Provide the stock notation for the following compounds : $HAuCl_4$, Tl_2O, FeO, Fe_2O_3, MnO and CuO.

H. Assign oxidation number to each atom in the following species.

a. $Cr(OH)_4^{\ominus}$ b. $Na_2S_2O_3$
c. H_3BO_3

I. Which of the following redox couple is stronger oxidizing agent ?

a. Cl_2 ($E^0 = 1.36$ V) and Br_2 ($E^0 = 1.09$ V)
b. $MnO_4^{\ominus}$ ($E^0 = 1.51$ V) and
$Cr_2O_7^{2\ominus}$ ($E^0 = 1.33$ V)

J. Which of the following redox couple is stronger reducing agent ?

a. Li ($E^0 = -3.05$ V) and
Mg ($E^0 = -2.36$ V)
b. Zn ($E^0 = -0.76$ V) and
Fe ($E^0 = -0.44$ V)

4. Balance the reactions/equations :

A. Balance the following reactions by oxidation number method

a. $Cr_2O_7^{2\ominus}(aq) + SO_3^{2\ominus}(aq) \longrightarrow Cr^{3\oplus}(aq) + SO_4^{2\ominus}(aq)$ (acidic)

b. $MnO_4^{\ominus}(aq) + Br^{\ominus}(aq) \longrightarrow MnO_2\,(s) + BrO_3^{\ominus}(aq)$ (basic)

c. $H_2SO_4\,(aq) + C\,(s) \longrightarrow CO_2\,(g) + SO_2\,(g) + H_2O\,(l)$ (acidic)

d. $Bi\,(OH)_3\,(g) + Sn(OH)_3^{\ominus}(aq) \longrightarrow Bi\,(s) + Sn\,(OH)_6^{2\ominus}(aq)$ (basic)

B. Balance the following redox equation by half reaction method

a. $H_2C_2O_4\,(aq) + MnO_4^{\ominus}\,(aq) \longrightarrow CO_2(g) + Mn^{2\oplus}(aq)$ (acidic)

b. $Bi\,(OH)_3\,(s) + SnO_2^{2\ominus}(aq) \rightarrow SnO_3^{2\ominus}\,(aq) + Bi\,(s)$ (basic)

5. Complete the following table :

Assign oxidation number to the underlined species and write Stock notation of compound

Compound	Oxidation number	Stock notation
$\underline{Au}Cl_3$		
$\underline{Sn}Cl_2$		
$\underline{V}_2O_7^{4\ominus}$		
$\underline{Pt}Cl_6^{2\ominus}$		
$H_3\underline{As}O_3$		

Activity :

Perform redox reaction experiment with the help of Daniel cell under teacher guidance.

7. Modern Periodic Table

Can you recall?

- What was the basis of classification of elements before the knowledge of electronic structure of atom?
- Name the scientists who made the classification of elements in the nineteenth century.
- What is Mendeleev's periodic law?
- How many elements are discovered uptil now?
- How many horizontal rows and vertical columns are present in modern periodic table?

7.1 Introduction

In the early nineteenth century about 30 elements were known and were classified into three types on the basis of their physical properties as: **metals, nonmetals and metalloids**. Subsequent noteworthy attempts For classification of the increasing number of elements based on **atomic mass** were **Dobereiner's triads** and **Newlands' octaves**.

Just think

- How many days pass between two successive full moon nights?
- What type of motion does a pendulum exhibit?
- Give some other examples of periodic events.

In **1869, Russian chemist Dmitri Mendeleev** put forth periodic table of the 63 elements known at that time using the atomic mass and properties of elements. Mendeleev's periodic table was based on the as **Mendeleev's periodic law** which is stated as **"The physical and chemical properties of elements are periodic function of their atomic masses".**

Mendeleev arranged the elements known at that time in an increasing order of their atomic masses. The serial or ordinal number of an element in the increasing order of atomic mass was referred to as its atomic number. He folded this list in accordance with recurrence of properties of elements and formed his periodic table consisting of vertical groups and horizontal series (now called periods).

In Mendeleev's periodic table, elements belonging to the same group showed similar properties. Properties of elements in a series/ period showed gradual variation from left to right. Mendeleev left some gaps corresponding to certain atomic numbers in the periodic table so as to maintain the periodicity of the properties. Mendeleev's periodic table was accepted by the scientific community since the newly discovered elements fitted well into the gaps with their properties as predicted by Mendeleev's periodic law. Inert gases, not predicted by Mendeleev and discovered in later years also could be accommodated in this periodic table by creating an additional group.

After the discovery of atomic structure, the atomic number, which was an ordinal number assigned to element in Mendeleev's periodic table, was recognized as the proton number, Z, of that element. This was the outcome of **Henry Moseley's work (1913)** on x-ray spectroscopic study of a large number of elements. Moseley showed that the frequency of x-ray emitted by an element is related to atomic number, Z, rather than the atomic mass. The atomic number, Z, was considered as more fundamental property of the atom than the atomic mass. As a result, Mendeleev's periodic law was modified. It is called the **modern periodic law** and is stated as: **"The physical and chemical properties of elements are a periodic function of their atomic numbers"**.

Mendeleev's periodic table was revised in accordance with the modern periodic law. We will look into the final revised version known as the **modern periodic table** also called the **long form of periodic table** in the following sections.

7.2 Structure of the Modern Periodic Table

Over a long period of time many scientists have come up with different forms of periodic table. However, the so called **'long form of periodic table' or 'the modern periodic table',** which is a revised version of Mendeleev's periodic table, is the most convenient and widely used form of the periodic table of elements today.

The modern periodic table has horizontal rows intersecting the vertical columns giving rise to a number of boxes. The horizontal rows are called periods (which Mendeleev called series) and the vertical columns are called groups. There are **seven periods** (numbered 1 to 7) and **eighteen groups** (numbered 1 to 18) in the modern periodic table.

This numbering of the periods and groups is recommended by the **International Union of Pure and Applied Chemistry, IUPAC.** The boxes formed at the intersection of the periods and groups are the places for individual elements. Below the main table are placed **two series** containing fourteen elements each. There are in all 118 boxes to accommodate **118 elements** in the modern periodic table. As on today all the 118 boxes are filled as a result of discovery of manmade elements. IUPAC has approved names and symbols of all the 118 elements. (Refer to Fig. 7.1)

The overall shape of the modern periodic table shows that it is divided into four blocks. Two groups on left form the **s-block,** six groups on the right constitute the **p-block,** ten groups in the center form the **d-block** and the two series at the bottom constitute the **f-block** (Fig. 7.2).

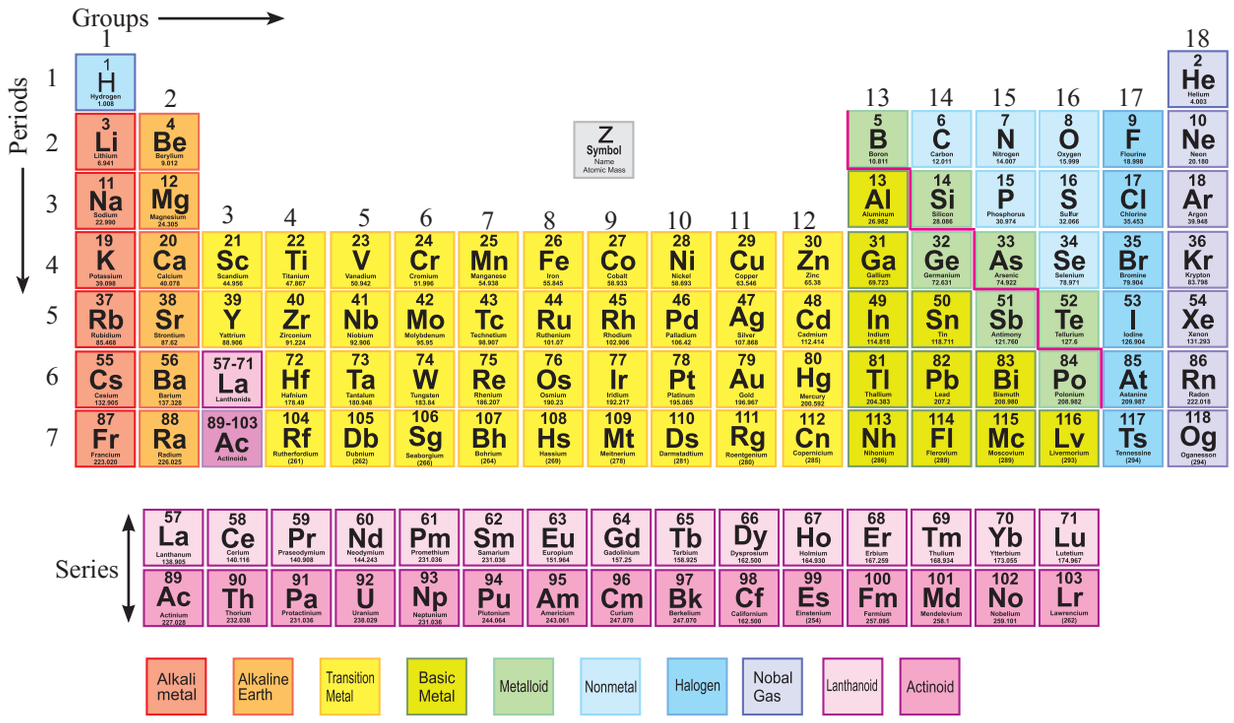


Fig. 7.1 : Modern Periodic Table

(Refer page 271)

7.3 Periodic Table and Electronic configuration

Can you recall?

- What do the principal quantum number '*n*' and azimuthal quantum number '*l*' of an electron belonging to an atom represent?
- Which principle is followed in the distribution of electrons in an atom?

When Mendeleev put forth his periodic table in 1869, the atomic structure was not known. He observed periodicity in the properties of elements on arranging them in an increasing order of atomic mass. Later, with the advent of quantum mechanical model of atom, the properties of elements were correlated to electronic configuration.

You have learnt in the Chapter 4 that the electrons in atom are distributed in shells and subshells in accordance with the **aufbau principle** which includes **increasing order of energy, Pauli exclusion principle and Hund's rule of maximum multiplicity**. When elements are arranged in an increasing order of atomic number (*Z*), periodicity is observed in their electronic configuration and which reflects in the characteristic structure of the modern periodic table. The location of elements in the modern periodic table is correlated to quantum numbers of the last filled orbital. Let us have a deeper look into the electronic configuration of the elements and the structure of the modern periodic table.

7.3.1 Electronic configuration in periods

We noted earlier that periods in the modern periodic table are numbered 1 to 7. On inspection of the electronic configurations (see Fig. 7.3) of elements in various periods we understand that the period number is same as the principal quantum number '*n*' of the outermost or valence shell of the elements.

Along a period the atomic number increases by one and one electron is added to outermost shell which forms neutral atom of the next element. Every period ends with complete octet configuration (or duplet in the case of the first period) of the valence shell and the next period begins with addition of electron to the next shell of higher energy compared to the previous period. The first shell, thus, gets filled along the **first period.** As the first shell can accommodate only two electrons, there are two elements in the first period, namely, H (Z=1) : $1s^1$ and He (Z=2) : $1s^2$. The first period ends at 'He' because 'He' has complete duplet.

Electrons are filled in the second shell along the **second period**. The second period, thus, begins with Li (Z=3) : $1s^2\ 2s^1$ and ends up with Ne (Z=10): $1s^2 2s^2 2p^6$. 'Ne' with 8 electrons in its outermost second shell has complete octet. The second shell has electron capacity of 8. It gets filled along the second period, as the atomic number increases. Thus there are eight elements in the second period.

Similarly there are eight elements Na (Z=11) to Ar (Z=18) having the condensed electronic configurations described together as $[Ne]3s^{1-2}3p^{1-6}$ in the **third period**, as a result of completion of the third shell.

The **fourth period** begins with filling of 4s subshell. The first two elements of the fourth period are K (Z=19) : [Ar] $4s^1$ and Ca (Z=20): $[Ar]4s^2$. According to the aufbau principle the next higher energy subshell is 3d, which can accommodate upto 10 electrons. Filling of the 3d-subshell results in the next 10 elements of the fourth period, from Sc (Z=21) : [Ar] $4s^2 3d^1$ to Zn (Z=30) : [Ar] $4s^2 3d^{10}$. After this the electrons enter the subshell 4p for the next six elements : Ga (Z = 31) : [Ar] $4s^2 3d^{10} 4p^1$ to Kr (Z=36) : [Ar] $4s^2 3d^{10} 4p^6$. The fourth period, thus, contains in all 18 elements (2+10+6=18).

The **fifth period** accomodates 18 elements as a result of successive filling of electrons in the 5s, 4d and 5p subshells.

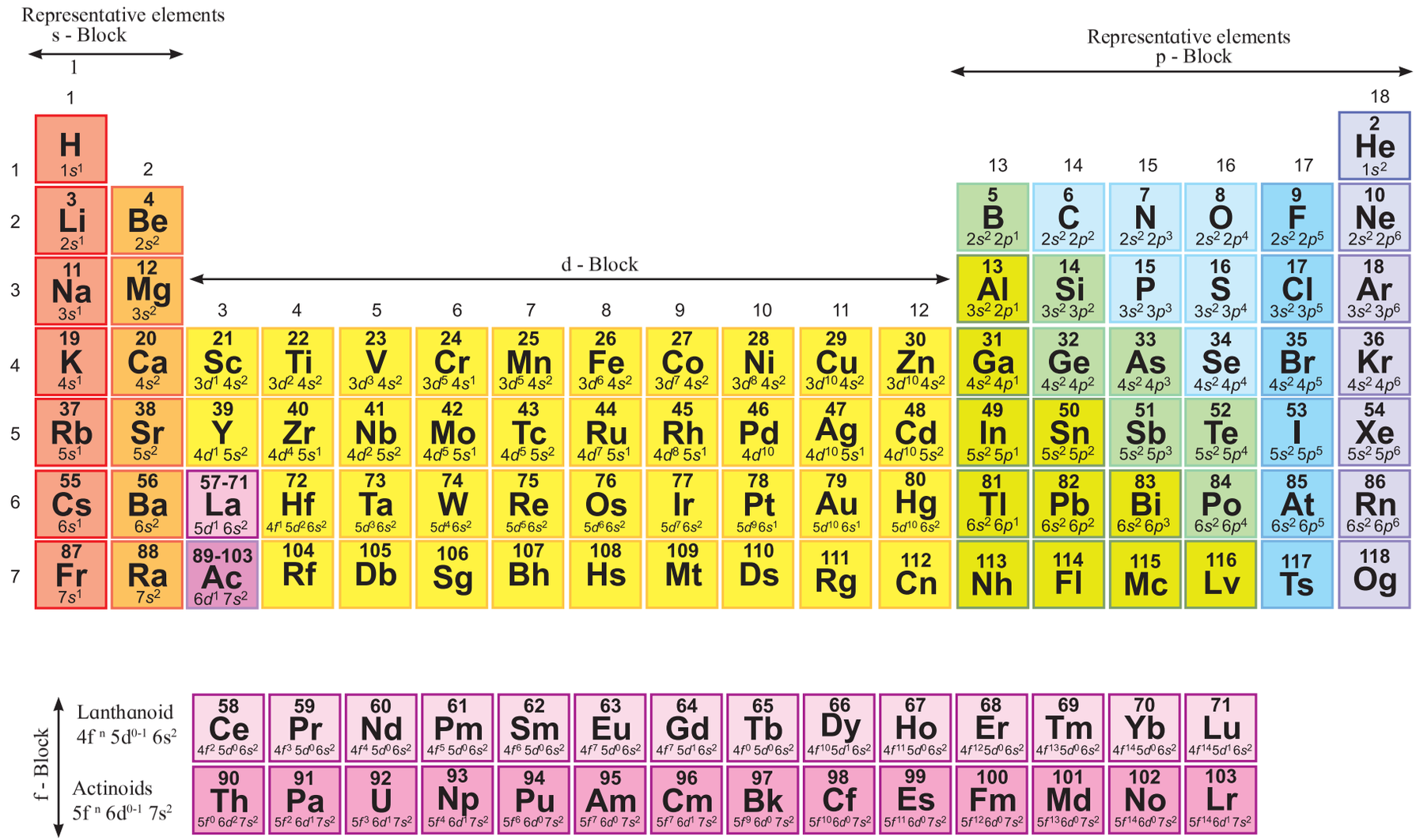


Fig. 7.2 : Outer electronic configuration of elements in the four blocks of the periodic table

Problem 7.1 : What is the subshell in which the last electron of the first element in the 6th period enters ?

Solution :

The 6th period begins by filling the last electron in the shell with n=6. The lowest energy subshell of any shell is 's'. Therefore the last electron of the first element in the 6th period enters the subshell '6s'.

Problem 7.2 : How many elements are present in the 6th period? Explain.

Solution :

The 6th period begins by filling the last electron in the subshell '6s' and ends by completing the subshell '6p'. Therefore, the sixth period has the subshells filled in increasing order of energy as 6s < 4f < 5d < 6p. The electron capacities of these subshells are 2, 14, 10 and 6, respectively. Therefore, the total number of elements in the 6th period are 2+14+10+6 = 32.

In short, a period begins by filling of one electron to the 's' subshell of a new shell and ends with an element having complete octet (or duplet) corresponding to the same shell. Between these two ends corresponding to 's' and 'p' subshell of the valence shell, the inner subshells 'd' and 'f' are filled successively following the aufbau principle.

7.3.2 Electronic configuration in groups

A new shell is added down a group. The general outer electronic configuration, therefore, is expected to be the same down any particular group. Indeed it is found to be so for the groups 1, 2 and 3. (See Fig. 7.2 and Table 7.1) In the groups 13 to 18 the appropriate inner 'd' and 'f' subshells are completely filled and the general outer electronic configuration is the same down the groups 13 to 18. (see Fig. 7.2 and Table 7.1).

In the groups 4 to 12, however, the 'd' and 'f' subshells are introduced at a later stage (4th period for 'd' and 6th period for 'f') down the group. As a result variation in the general outer configuration is introduced only at the later stage down the groups 4 to 12.

Table 7.1 : General outer electronic configuration in groups 1 to 3 and 13 to 18

Group number	General outer configuration	Examples
Group 1	ns^1	$_3$Li:$2s^1$, $_{11}$Na:$3s^1$
Group 2	ns^2	$_4$Be:$2s^2$, $_{12}$Mg:$3s^2$
Group 3	ns^2 $(n\text{-}1)d^1$	$_{21}$Sc:$4s^23d^1$, $_{39}$Y:$5s^24d^1$
Group 13	ns^2 np^1	$_5$B:$2s^22p^1$, $_{13}$A1:$3s^23p^1$
Group 14	ns^2 np^2	$_6$C:$2s^22p^2$, $_{14}$Si:$3s^23p^2$
Group 15	ns^2 np^3	$_7$N:$2s^22p^3$, $_{15}$P:$3s^23p^3$
Group 16	ns^2 np^4	$_8$O:$2s^22p^4$, $_{16}$S:$3s^23p^4$
Group 17	ns^2 np^5	$_9$F:$2s^22p^5$, $_{17}$C1:$3s^23p^5$
Group 18	ns^2 np^6	$_{10}$Ne:$2s^22p^6$, $_{18}$Ar:$3s^23p^6$

7.3.3 Electronic configuration in the four blocks: We noted in section 7.2 that structure of the modern periodic table shows four blocks. These blocks are formed in accordance with the subshell in which the last electron enters. Accordingly the four blocks are named as s-block, p-block, d-block and f-block.

s-Block : The last electron in the s-block elements is filled in a s-subshell. There being only one orbital in a s-subshell, the general outer electronic configuration of s-block elements is ns^{1-2}. Thus elements of the group-1 and group-2 belong to the s-block. The s-block is present on the left extreme of the modern periodic table.

p-Block: The last electron in the p-block elements is filled in p-subshell. There being three degenerate p-orbitals in a p-subshell, upto 6 electrons can be filled. Therefore, the elements belonging to six groups, namely, group 13, 14, 15, 16, 17 and 18 constitute the p-block. The p-block appears on the right in the modern periodic table. The p-block ends with the group 18 which represent the family of inert gases. Remarkably, the first element of the group 18, helium (He) does not have the p subshell as its valence shell has n =1 and its configuration is shown as $1s^2$. Yet 'He' is placed in the 18th group of the p –block because its valence shell is completely filled (which is a complete duplet), similar to complete valence shell of the other elements belonging to group 18 (which have complete octets). The general electronic configuration for the p-block (from the second to the seventh period) is $ns^2\ np^{1-6}$.

d-Block : The d-block in the modern periodic table is formed as a result of filling the last electron in d-orbital. A d-subshell is present in the shells with $n \geq 3$ and according to the $(n+l)$ rule (refer to Chapter 4) the energy of ns orbital is less than that of the $(n-1)$d orbital. As a result, the last electron enters a $(n-1)$d-subshell only after the ns subshell is completely filled. There being five orbitals in a d-subshell, 10 electrons can successively be accommodated. There are ten groups, namely, groups 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 in the d-block which appears in the centre of the modern periodic table. The general outer electronic configuration of the d-block elements is $ns^{0-2}\ (n-1)d^{1-10}$. Some variations in the configuration, consequent to the extra stability associated with half-filled and a fully filled subshell, are readilly observed. For example, the outer electronic configuration of Cr (Z = 24) is $4s^1 3d^5$ instead of $4s^2 3d^4$. This is because both 4s and 3d subshells are half-filled.

f-Block : In the f-block elements the last electron is filled in f-orbital. As there are seven orbitals in a f-subshell, the general outer electronic configuration of the f-block is $ns^2\ (n-1)d^{0-1}\ (n-2)f^{1-14}$. The variations as a result of the extra stability of half-filled and fully filled subshell need to be accounted for. For example, the outer electronic configuration of $_{63}$Eu is $6s^2 4f^7 5d^0$ because the 4f subshell is half-filled. The f-block constitutes two series of 14 elements called the **lanthanoid** and the **actinoid series**, put one below the other. The f-block is placed separately at the bottom of the periodic table.

Problem 7.3 : Outer electronic configurations of a few elements are given below. Explain them and identify the period, group and block in the periodic table to which they belong.

$_2$He : $1s^2$, $_{54}$Xe : $5s^2 5p^6$, $_{16}$S : $3s^2 3p^4$, $_{79}$Au : $6s^1 5d^{10}$

Solution :

$_2$He : $1s^2$

Here n = 1. Therefore, $_2$He belongs to the **1st period**. The shell n =1 has only one subshell, namely 1s. The outer electronic configuration $1s^2$ of 'He' corresponds to the maximum capacity of 1s, the **complete duplet**. Therefore, He is placed at the end of the **1st period in the group 18** of inert

gases, so 'He' belongs to **p-block.**

$_{54}$**Xe : 5s^{2}5p^6**

Here n = 5. Therefore, $_{54}$Xe belongs to the **5th period**. The outer electronic configuration 5s^{2}5p^6 corresponds to **complete octet**. Therefore $_{54}$Xe is placed in **group 18** and belongs to **p-block**.

$_{16}$**S : 3s^{2}3p^4**

Here n = 3. Therefore, $_{16}$S belongs to the **3rd period**. The 3p subshell in 'S' is partially filled and short of completion of octet by two electrons. Therefore 'S' belongs to (18-2) = **16th group** and **p – block**.

$_{79}$**Au : 6s^{1}5d^{10}**

Here n = 6. Therefore, 'Au' belongs to the **6th period**. The sixth period begins with filling of electron into 6s and then into 5d orbital. The outer configuration of 'Au' : 6s^1 5d^{10} implies that (1+10) = 11 electrons are filled in the outer orbitals to give 'Au'. Therefore 'Au' belongs to the **group 11**. As the last electron has entered 'd' orbital 'Au' belongs to the **d-block**.

7.4 Blockwise characteristics of elements

We have seen in the previous section that the 118 elements in the modern periodic table are distributed in four blocks having general electronic configuration according to their block. The elemental properties are characteristic of the block they belong.

7.4.1 Characteristics of s-block elements

The s-block contains the elements of **group 1 (alkali metals)** and **group 2 (alkaline earth metals)**. All these elements are **reactive metals,** and occur in nature only in combined state. Their **compounds,** with exception of Li and Be, are **predominantly ionic**. This is because they have only one or two valence electrons which they can lose readily forming $M^{\oplus}$ or $M^{2\oplus}$ ions. They have **low ionization enthalpies**, which decrease down the group resulting in increased reactivity.

7.4.2 Characteristics of p-block elements :

The p-block contains elements of **groups 13 to 18**. The **p-block elements together with s-block elements** are called **main group elements** or **representative elements**. The last group of the p-block, namely, the **18th group**, is the family of **noble/inert gases**. These have closed valence shells (complete duplet in the case of 'He' and complete octet in the case of the other noble gases) and therefore very low chemical reactivity. Elements of **group 17 (halogen family) and group 16 (chalcogens) include reactive nonmetals**. The **electron gain enthalpies** being **highly negative**, they gain one or two electrons readily and form anions ($X^{\ominus}$ or $X^{2\ominus}$) which have complete octet. The p-block contains **all the three traditional types of elements**. The metals on the left, the nonmetals on the right and the metalloids along a **zig-zag line** (see Fig. 7.1) which separates metals from nonmetals. The nonmetallic character increases as we move from the left to the right, whereas it decreases as we go down a group.

7.4.3 Characteristics of d-block elements

The d-block contains elements of the **groups 3 to 12**. They are **all metals**. The d-block elements are known as **transition elements** or **transition metals.** They form a bridge between chemically reactive s-block elements and less reactive elements of groups 13 and 14. Most of d-block elements possess Partially filled inner d-orbitals. As a result the d-block elements have properties such as **variable oxidation state**, **paramagnetism**, **ability to form coloured ions.** They can be used as **catalysts**. Zn, Cd, and Hg with configuration ns^2 (n-1) d^{10}, (completely filled s - and d - subshells) do not show the properties typical of transition metals.

7.4.4 Characteristics of f-block elements

The f-block contains elements **all** of which are **metals** and are placed in the two rows called **lanthanoid series** ($_{58}$Ce to $_{71}$Lu) and **actinoid**

series ($_{90}$Th to $_{103}$Lr). These series are named after their preceding elements lanthanum ($_{57}$La) and actinium ($_{89}$Ac) in the third group of the d-block of the 6th and 7th period respectively. The lanthanides are also known as **rare earth elements**. The last electron of the elements of these series is filled in the (*n*-2)f subshell, and therefore, these are called **inner-transition elements**. These elements have very similar properties within each series. The actinide elements beyond $_{92}$U are called **transuranium elements**. All the transuranium elements are manmade and radioactive.

Problem 7.4 : Chlorides of two metals are common laboratory chemicals and both are colourless. One of the metals reacts vigorously with water while the other reacts slowly. Place the two metals in the appropriate block in the periodic table. justify your answer.

Solution

Metals are present in all the four blocks of the periodic table. Salts of Metals in the f-block and p-block (except $AlCl_3$) are not common laboratory chemicals. Therefore, the choice is between s- and d-block. From the given properties their placement is done as shown below:

s-block: Metal that reacts vigorously with water

d-block: Metal that reacts slowly with water.

The colourless nature of the less reactive metal in the d-block implies that the inner d-subshell is completely filled.

7.5 Periodic trends in elemental properties

The original structure of the periodic table was based on empirically observed periodicity in the elemental properties. Thus, elemental properties show similarity in a group and show gradual variation across a period. The quantum mechanical model of atom explains the observed periodic trends of elemental properties. We will now discuss in this section the periodic trends in some physical and chemical properties of elements, correlating them with electronic configuration and the nuclear charge. These trends are explained in terms of two fundamental factors, namely, attraction of extranuclear electrons towards the nucleus and repulsion between electrons belonging to the same atom. These attractive and repulsive forces operate simultaneously in an atom. This results in two interrelated phenomena called effective nuclear charge and screening effect.

7.5.1 Effective nuclear charge and screening effect :

In a multi-electron atom the positively charged nucleus attracts the negatively charged electrons around it, and there is mutual repulsion amongst the negatively charged extranuclear electrons. The repulsion by inner-shell electrons is particularly important. This results in pushing the outer-shell electrons further away from the nucleus. The outer-shell electrons are, thus, held less tightly by the nucleus. In other words, the attraction of the nucleus for an outer electron is partially cancelled. It means that an outer-shell electron does not experience the actual positive charge present on the nucleus. The net nuclear charge actually experience by an electron is called the **effective nuclear charge**, $\boldsymbol{Z_{eff}}$. The effective nuclear charge is lower than the actual nuclear charge, *Z*. In other words, the inner electrons shield the outer electrons from the nucleus to a certain extent. This effect of the inner electrons on the outer electrons is called **screening effect** or **shielding effect** of the inner/core electrons.

Effective nuclear charge $= Z_{eff}$

$= Z$ - electron shielding

$= Z - \sigma$

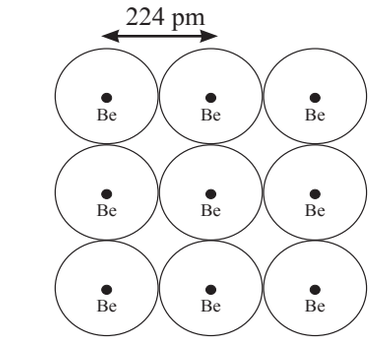
Here σ (sigma) is called **shielding constant** or **screening constant** and the value of σ depends upon type of the orbital that the electron occupies.

As we move across a period actual nuclear charge increases by +1 at a time, the valence shell remains the same and the newly added electron gets accommodated in the same shell. There is no addition of electrons to the core. Thus, shielding due to core electrons remains the same though the actual nuclear charge, Z, increases. The net result is that **the effective nuclear charge, Z_{eff}, goes on increasing across a period**. On the other hand, the Z_{eff} decreases down a group. This is because, as we move down a group, a new larger valence shell is added. As a result, there is an additional shell in the core. The shielding effect of the increased number of core electrons outweighs the effect of the increased nuclear charge; and thereby **the effective nuclear charge felt by the outer electrons decreases largely down a group**.

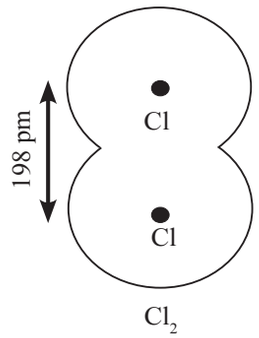
7.5.2 Periodic trends in physical properties

Many physical properties of elements such as melting point, boiling point and density show periodicity. In this section we are going to consider the periodic trends in physical properties with reference to atomic radius, ionic radius, ionization enthalpy, electron gain enthalpy and electronegativity.

a. Atomic radius : You have learnt in chapter 4 that the quantum mechanical model of atom describes the extranuclear part of atom as the electron cloud. As a direct implication of this, the atom has no definite boundary. The atomic size or atomic radius, therefore, can be estimated from the internuclear distance under different circumstances. In the case of nonmetals (except noble gases), the atoms of an element are bonded to each other by covalent bonds. (Refer to Chapter 5). Bond length of a single bond is taken as sum of radii of the two single bonded atoms. This is called covalent radius of the atom. For example : (i) Bond length of C-C bond in diamond is 154 pm. Therefore, atomic radius of carbon is estimated to be 77 pm. (ii) Bond length of Cl-Cl bond in Cl_2 is measured as 198 pm. Therefore, the atomic radius of Cl is estimated to be 99 pm. (see Fig. 6.3)



Atomic radius of Be $= \frac{224 \text{ pm}}{2} = 112 \text{ pm}$



Cl_2

Atomic radius of Cl $= \frac{198 \text{ pm}}{2} = 99 \text{ pm}$

Fig 6.3 : Estimation of atomic radii of metals and nonmetals

In the case of metals, distance between the adjacent atoms in metallic sample is measured. One half of this distance is taken as the metallic radius. **Thus, atomic radius is one half of the internuclear distance between two adjacent atoms of a metal or two single bonded atoms of a nonmetal.**

Do you know ?

Atomic radius is estimated in terms of the electron density surface which encloses typically 95 % (or more, which is orbitary of the electron density.

Table 7.2 : Atomic radii of some elements

Element symbol (atomic radius / pm)							
Group / Period	1	2	13	14	15	16	17
2	Li (152)	Be (111)	B (88)	C (77)	N (74)	O (66)	F (64)
3	Na (186)	Mg (160)	Al (143)	Si (117)	P (110)	S (104)	Cl (99)
4	K (231)						Br (114)
5	Rb (244)						I (133)
6	Cs (262)						At (140)

It can be seen from Table 7.2 that atomic radius decreases across a period (upto group 17) and increases down a group. Greater the effective nuclear charge stronger is attraction of the nucleus for the outer electrons and smaller is the atomic radius. As we move across a period, screening effect caused by the core electrons remains the same, on the other hand the effective nuclear charge goes on increasing (see section 6.5.1). The valence electrons are, therefore, more tightly bound and in turn the atomic radius goes on decreasing along a period. The effective nuclear charge decreases and shielding effect increases down a group (see section 7.5.1). The valence electrons are, thus, held by weaker attractive force and the atomic radius increases down a group.

b. Ionic radius: An atom forms a positively charged ion, cation, on the removal of one or more electrons whereas a negatively charged ion, anion, is formed with gain of one or more electrons. Measurements of distances between neighbouring cations and anions in ionic crystals have been useful for estimation of ionic radii. The ionic radii show the same trends as of atomic radii.

A cation is smaller than the atom from which it is formed, because it contains fewer electrons than atom, though the nuclear charge is the same. As a result the shielding effect is less and effective nuclear charge is larger within a cation.

An anion has a larger radius than the corresponding atom, as it has more number of electrons than the atom. These additional electrons result in increased electron repulsion, decreased effective nuclear charge and in turn, the increased size.

Some atoms and ions contain the same number of electrons and are called **isoelectronic species**. (See chapter 4) The actual nuclear charge of the isoelectronic species is, however, different. The radii of isoelectronic species vary according to actual nuclear charge. Larger nuclear charge exerts greater attraction for the electrons and the radius of that isoelectronic species becomes smaller. For example, $F^{\ominus}$ and $Na^{\oplus}$ both have 10 electrons, their radii are 133 pm and 98 pm respectively, as the nuclear charge of $F^{\ominus}$ is + 9 which is smaller than that of $Na^{\oplus}$ which is, + 11.

c. Ionization enthalpy : Removal of an electron from the neutral atom X results

Problem 7.5 : Identify the species having larger radius from the following pairs : (i) Na and $Na^{\oplus}$, (ii) $Na^{\oplus}$ and $Mg^{2\oplus}$

Solution :

(i) The nuclear charge is the same in Na and $Na^{\oplus}$. But $Na^{\oplus}$ has less number of electrons and less number of occupied shells (two shells in $Na^{\oplus}$ while three shells in Na). Therefore, radius of Na is larger. (ii) $Na^{\oplus}$ and $Mg^{2\oplus}$ are isoelectronic species. $Mg^{2\oplus}$ has larger nuclear charge than $Na^{\oplus}$. Therefore, $Na^{\oplus}$ has larger radius.

in formation of cation $X^{\oplus}$. **The energy required to remove an electron from the isolated gaseous atom in its ground state is called ionization enthalpy ($\Delta_i H$).** Ionization enthalpy is the quantitative measure of tendency of an element to lose electron and expressed in kJ mol^{-1}. Since electrons are lost one at a time, we have first ionization enthalpy, second ionization enthalpy, and so on, for a given element.

$$X(g) \rightarrow X^{\oplus}(g) + e^{\ominus} \; ; \; \Delta_i H_1$$

$$X^{\oplus}(g) \rightarrow X^{2\oplus}(g) + e^{\ominus} \; ; \; \Delta_i H_2$$

Ionization enthalpy is always positive since the energy always need to be supplied to knock out electron from atom.

The second ionization enthalpy, $\Delta_i H_2$, is larger than the first ionization enthalpy, $\Delta_i H_1$, as it involves removal of electron from the positively charged species. Tables 7.3 and 7.4 show the values of first ionization enthalpy down the group 1 and across the period 2 respectively.

It is seen from Table 7.3 that on moving down the group the first ionization enthalpy decreases. This is because electron is to be removed from the larger valence shell. Screening due to core electrons goes on increasing and the effective nuclear charge decreases down the group. (See section 7.5.1) The removal of the outer electron, therefore, becomes easier.

Table 7.3 : First ionization enthalpy values of elements of group 1

Elements of Group 1	Atomic Number *Z*	Outer electronic configuration	$\Delta_i H_1$ /kJ mol^{-1}
Li	3	$2s^1$	520
Na	11	$3s^1$	496
K	19	$4s^1$	419
Rb	37	$5s^1$	403
Cs	55	$6s^1$	374

An overall increase of the first ionization enthalpy across the period 2 (see table 7.4) can be notice. This is because the screening is the same and the effective nuclear charge increases across a period. (See section 7.5.1) As a result the outer electron is held more tightly. The first ionization enthalpy, therefore, increases across a period. The alkali metal displays the lowest first ionization enthalpy. The inert gas shows the highest first ionization enthalpy across a period.

Some irregularities are noticed for the first ionization enthalpies as we move across a period. For example, the first ionization enthalpy of 'B' is smaller than that of 'Be'. This is because 'Be' loses the electron from 2s orbital while 'B' loses the electron from 2p orbital which has less penetration (see shapes of orbitals in chapter 4) than the 2s orbital and therefore it is easier to remove a 2p electron than a 2s electron. Similarly, first ionization enthalpy of 'O' is smaller than that of 'N'. This is because 'O' loses the electron from a doubly occupied '2p' orbital. Due to

Table 7.4 : First ionization enthalpy values of elements of period 2

Element of period 2	Li	Be	B	C	N	O	F	Ne
Atomic number *Z*	3	4	5	6	7	8	9	10
Outer electronic Configuration	$2s^1$	$2s^2$	$2s^2\,2p^1$	$2s^2\,2p^2$	$2s^2\,2p^3$	$2s^2\,2p^4$	$2s^2\,2p^5$	$2s^2\,2p^6$
$\Delta_i H_1$ / kJ mol^{-1}	520	899	801	1086	1402	1314	1681	2080

electron-electron repulsion it is easier to lose this electron than an electron from the singly occupied 2p orbital in nitrogen atom. (This is a consequence of Hund's rule of maximum multiplicity, described in Chapter 4.)

Problem 7.6 :
The first ionization enthalpy values of Si, P and C1 are 780, 1060 and 1255 kJ mo1^{-1} respectively. Predict whether the first ionization enthalpy of S will be closer to 1000 or 1200 kJ mol^{-1}.

Solution :
As we move across the period 3 from left to right the elements Si, P, S, C1 come in a sequence. Their outer electronic configurations are $3s^23p^2$, $3s^23p^3$, $3s^23p^4$ and $3s^23p^5$ respectively and 'P' loses an electron from a singly occupied 3p orbital whereas 'S' loses an electron from a doubly occupied 3p orbital. Therefore, the first ionization enthalpy value of 'S' has to be lower than that of 'P'. Thus, first ionization enthalpy of 'S' would be less than 1060 kJ mol^{-1}, and therefore, should be close to 1000 kJ mol^{-1} and not 1200 kJ mo1^{-1}.

d. Electron gain enthalpy: Addition of an electron to a neutral atom (X) results in formation of an anion ($X^{\ominus}$). **The enthalpy change that takes place when an electron is added to an isolated gaseous atom in its ground state is called the electron gain enthalpy,** $\Delta_{eg}H$. Electron gain enthalpy is a quantitative measure of the ease with which an atom adds an electron forming the anion and is expressed in units of kJ mol^{-1}.

$$X(g) + e^{\ominus} \rightarrow X^{\ominus}(g); \Delta_{eg}H.$$

$\Delta_{eg}H$ may be positive or negative depending upon whether the process of adding electron is endothermic or exothermic. Elements of **group 17** have very high negative values of electron gain enthalpy. This is because of they attain stable noble gas electronic configuration on the addition of one electron. Elements of **group 18**, noble gases have, on the other the hand, exhibit high positive values for electron gain enthalpy. Since, the added electron has to enters the next higher shell with larger principal quantum number, this is very unstable electronic configuration due to very low effective nuclear charge and high shielding from the core electrons. The **alkali metals** have very low negative electron gain enthalpy values. **In general,** electron gain enthalpies are large negative for elements of the upper right of the periodic table, excluding the group 18 of noble gases.

The trends for electron gain enthalpy values of the elements in the periodic table are less regular than the ionization enthalpies. An **overall trend** reveals that electron gain enthalpy becomes more negative with increase of atomic number along the period upto the second last element, because the effective nuclear charge increases across the period and it is easier to add an electron to a smaller atom. Down the group, the electron has to be add to farther shell and the electron gain enthalpy, thus, becomes less negative.

Problem 7.7 :
Identify the element with more negative value of electron gain enthalpy from the following pairs. Justify.
(i) C1 and Br (ii) F and O

Solution :
(i) CI and Br belong to the same group of halogens with Br having higher atomic number than Cl. As the atomic number increases down the group the effective nuclear charge decreases. The increased shielding effect of core electrons can be noticed. The electron has to be added to a farther shell, which releases less energy and thus electron gain enthalpy becomes less negative down the group. Therefore, Cl has more negative electron gain enthalpy than Br. ....CONTD on next page

(ii) F and O belong to the same second period, with F having higher atomic number than O. As the atomic number increases across a period, atomic radius decreases, effective nuclear charge increases and electron can be added more easily. Therefore more energy is released with gain of an electron as we move to right in a period. Therefore, F has more negative electron gain enthalpy.

e. Electronegativity: When two atoms of different elements form a covalent bond, the electron pair is shared unequally. **The ability of a covalently bonded atom to attract the shared electrons toward itself is called electronegatively (*EN*).** It is not an experimentally measurable quantity. A number of numerical scales of electronegativity were developed by many scientists. Pauling scale of electronegativity is the one used most widely. **Linus Pauling** assigned **(1922)** arbitrarily a value of 4.0 for fluorine which is expected to have the highest value of electronegativity. Table 7.5 shows the values of electronegativity assigned to some other elements.

Electronegativity represents attractive force exerted by the nucleus on shared electrons. Electron sharing between covalently bonded atoms takes place using the valence electron. The electronegativity depends upon the effective nuclear charge experienced by electron involved in formation of the covalent bond. Electronegativity increases as we move across the period. This is because the effective nuclear charge increases steadily across the period. The *EN* decreases down the group. The size of the valence shell goes on increasing, the shielding effect of the core electron goes on increasing and in term the effective nuclear charge decreases down the group.

Electronegativity predicts the nature of the bond, or, how strong is the force of attraction that holds two atoms together. (Refer Chapter 5).

7.5.3 Periodic trends in chemical properties:

The most fundamental chemical property of an element is its combining power. This property is numerically expressed in terms of **valency** or **valence**. Valency of an element indicates the number of chemical bonds that the atom can form giving a molecule. Another frequently used term related to valence is the **oxidation state** or **oxidation number**. Valence does not have any sign associated with it, but oxidation number does, and can be either + or –, which is decided by electronegativities of atoms that are bonded.

The second aspect of chemical property is the **chemical reactivity**. The chemical reactivity is related to the ease with which an element loses or gains the electrons.

The chemical properties of elements are relate to electronic configuration.

Table 7.5 : Electronegativity *(EN)* values of some elements (Pauling scale)

Element symbol (*EN*)							
Group / Period	1	2	13	14	15	16	17
1	H (2.1)						
2	Li (1.0)	Be (1.5)	B (2.0)	C (2.5)	N (3.0)	O (3.5)	F (4.0)
3	Na (0.9)	Mg (1.2)	Al(1.5)	Si (1.8)	P (2.1)	S (2.5)	Cl (3.0)
4	K (0.8)						Br (2.8)
5	Rb (0.8)						I (2.5)
6	Cs (0.7)						At (2.2)

Table 7.6 : Periodic trends in valency of main group elements

Group	1	2	13	14	15	16	17	18
General outer electronic configuration	ns^1	ns^2	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
Number of valence electrons	1	2	3	4	5	6	7	8
Valency	1	2	3	4	3,5	2,6	1,7	0
Formula of hydride	LiH	BeH_2	B_2H_6	CH_4	NH_3	H_2O	HF	
	NaH	MgH_2	AlH_3	SiH_4	PH_3	H_2S	HCI	
	KH	CaH_2	GaH_3	GeH_4	AsH_3	H_2Se	HBr	
Formula of oxide	Li_2O	BeO	B_2O_3	CO_2	N_2O_3 N_2O_5		OF_2	
	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6, P_2O_5,	SO_2, SO_3	CI_2O_7	
	K_2O	CaO	Ga_2O_2	GeO_2	As_2O_3, As_2O_5	SeO_2, SO_3	Br_2O	

a. Periodic trends in valency: Valency of the main group elements is usually equal to the number of valence electrons (outer electrons) and/or equal to difference between 8 and the number of valence electrons. Table 7.6 shows the periodic trends in the valency of main group elements by taking examples of hydrides and some oxides.

As may be notice form Table 7.6 that the valency remains the same down the group and shows a gradual variation across the period as atomic number increases from left to right.

b. Periodic trends in metallic–nonmetallic character : The metals, nonmetals and metalloids appear in separate regions of modern periodic table: metals on the left, nonmetals on the right and metalloids along a zig-zag line separating the two. Metals are characterized by good electrical conductivity and ability to form compounds by loss of valence electrons. Nonmetals are characterized by their poor electrical conductivities and ability to form compounds by gain of valence electrons in valence shell. This can be explained in terms of ionization enthalpy and electron gain enthalpy.

The ionization enthalpy decreases down the group. The tendency to lose valence electrons, thus, increases down the group and the **metallic character increases down a group**. The ionization enthalpy increases across the period and consequent **metallic character decreases across a period**. Electron gain enthalpy becomes more and more negative across the period, it tends to be less negative down the group. Thus, **nonmetallic character increases across the period and decreases down the group**.

c. Periodic trends in chemical reactivity: Chemical reactivity of elements is decided by how easily it attains electronic configuration of the nearest inert gas by gaining or loosing electrons.

The elements preceding an inert gas react by gaining electrons in the outermost shell, whereas the elements which follow an inert gas in the periodic table react by loss of valence electrons. Thus the chemical reactivity is decided by the electron gain enthalpy and ionization enthalpy values, which in turn, are decided by effective nuclear charge and finally by the atomic size. The ionization enthalpy is smallest for the element on the extreme left in

a period, whereas the electron gain enthalpy is most negative for the second last element on the extreme right, (preceding to the inert gas which is the last element of a period). Thus, the most reactive elements lie on the extreme left and the extreme right (excluding inert gases) of the periodic table.

Apart from the metallic-nonmetallic character the chemical reactivity can be illustrated by comparing their reaction with oxygen to form oxides and the nature of the oxides. The reactive elements on the extreme left (that is, alkali metals) react vigorously with oxygen to form oxides (for example Na_2O) which reacts with water to form strong bases (like NaOH). The reactive elements on the right (that is, halogens) react with oxygen to form oxides (for examples Cl_2O_7) which on reaction with water form strong acids (like $HClO_4$). The oxides of the elements in the center of the main group elements are either amphoteric (for example Al_2O_3), neutral (for example CO, NO) or weakly acidic (for example CO_2)

The change in atomic radii of transition metals and inner transition elements is rather small. Therefore, the transition metals and inner transition elements belonging to the individual series have similar chemical properties. Their ionization enthalpies are intermediate between those of s-block and p - block.

Problem 7.8 :

Ge, S and Br belong to the groups 14, 16 and 17, respectively. Predict the empirical formulae of the compounds those can be formed by (i) Ge and S, (i) Ge and Br.

Solution :

From the group number we understand that the general outer electronic configuration and number of valence electrons and valencies of the three elements are :

Element	Group	Outer electronic configuration	Number of Valence electron	Valency
Ge	14	ns^2np^2	4	4
S	16	ns^2np^4	6	8 - 6 = 2
Br	17	ns^2np^5	7	8 - 7 = 1

(i) S is more electronegative than Ge. Therefore, the empirical formula of the compound formed by these two elements is predicted by the method of cross multiplication of the valencies :

Element: Ge S

Valency: 4 2

Formula: Ge_2S_4

Empirical formula: GeS_2

(ii) Br is more electronegative than Ge. The empirical formula of the compound formed by these two elements in predicted by the method of cross multiplication of valencies :

Element: Ge Br

Valency: 4 1

Formula: $GeBr_4$

Empirical formula: $GeBr_4$

Problem 7.9

Write the chemical equations for reaction, if any, of (i) Na_2O and (ii) Al_2O_3 with HCl and NaOH both. Correlate this with the position of Na and Al in the periodic table, and infer whether the oxides are basic, acidic or amphoteric.

Solution

(i) $Na_2O + 2HCl \rightarrow 2NaCl + H_2O$

$Na_2O + NaOH \rightarrow$ No reaction

As Na_2O reacts with an acid to form salt and water it is a basic oxide. This is because Na is a reactive metal lying on the extreme left of the periodic table.

(ii) $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$

$Al_2O_{3\oplus} 2NaOH \rightarrow 2Na\,AlO_2 + H_2O$

As Al_2O_3 reacts with an acid as well as base to form a salt and water. It is an amphoteric oxide. Al is a moderately reactive element lying in the centre of main group elements in the periodic table.

Exercises

1. Explain the following

A. The elements Li, B, C, Be and N have the electronegativities 1.0, 2.0, 1.5 and 3.0, respectively on the Pauling scale.

B. The atomic radii of Cl, I and Br are 99, 133 and 114 pm, respectively.

C. The ionic radii of $F^{\ominus}$ and $Na^{\oplus}$ are 133 and 98 pm, respectively.

D. $_{13}Al$ is a metal, $_{14}Si$ is a metalloid and $_{15}P$ is a nonmetal.

E. Cu forms coloured salts while Zn forms colourless salts.

2. Write the outer electronic configuration of the following using orbital notation method. Justify.

A. Ge (belongs to period 4 and group 14)

B. Po (belongs to period 6 and group 16)

C. Cu (belongs to period 4 and group 11)

3. Answer the following

A. La belongs to group 3 while Hg belongs to group 12 and both belong to period 6 of the periodic table. Write down the general outer electronic configuration of the ten elements from La to Hg together using orbital notation method.

B. Ionization enthalpy of Li is 520 kJ mol^{-1} while that of F is 1681 kJ mol^{-1}. Explain.

C. Explain the screening effect with a suitable example.

D. Why the second ionization enthalpy is greater than the first ionization enthalpy ?

E. Why the elements belonging to the same group do have similar chemical properties ?

F. Explain : electronegativity and electron gain enthalpy. Which of the two can be measured experimentally?

4. Choose the correct option

A. Consider the elements B, Al, Mg and K predict the correct order of metallic character :

a. B > Al > Mg > K

b. Al > Mg > B > K

c. Mg > Al > K > B

d. K > Mg > Al > B

B. In modern periodic table, the period number indicates the :

a. atomic number

b. atomic mass

c. principal quantum number

d. azimuthal quantum number

C. The lanthanides are placed in the periodic table at
   a. left hand side
   b. right hand side
   c. middle
   d. bottom

D. If the valence shell electronic configuration is ns^2np^5, the element will belong to
   a. alkali metals
   b. halogens
   c. alkaline earth metals
   d. actinides

E. In which group of elements of the modern periodic table are halogen placed ?
   a. 17 b. 6
   c. 4 d. 2

F. Which of the atomic number represent the s-block elements ?
   a. 7, 15
   b. 3, 12
   c. 6, 14
   d. 9, 17

G. Which of the following pairs is NOT isoelectronic ?
   a. $Na^{\oplus}$ and Na
   b. $Mg^{2\oplus}$ and Ne
   c. $Al^{3\oplus}$ and $B^{3\oplus}$
   d. $P^{3\ominus}$ and $N^{3\ominus}$

H. Which of the following pair of elements has similar properties ?
   a. 13, 31
   b. 11, 20
   c. 12, 10
   d. 21, 33

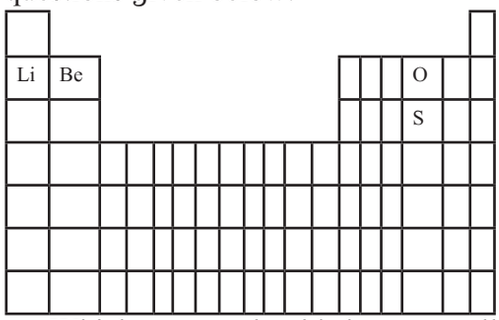
5. Answer the following questions

A. The electronic configuration of some elements are given below:
   a. $1s^2$ b. $1s^2\ 2s^2\ 2p^6$
   In which group and period of the periodic table they are placed ?

B. For each of the following pairs, indicate which of the two species is of large size :
   a. Fe^{2+} or Fe^{3+} b. Mg^{2+} or Ca^{2+}

C. Select the smaller ion form each of the following pairs:
   a. K^+, Li^+ b. N^{3-}, F^-

D. With the help of diagram answer the questions given below:



   a. Which atom should have smaller ionization enthalpy, oxygen or sulfur?
   b. The lithium forms +1 ions while berylium forms +2 ions ?

E. Define : a. Ionic radius
   b. Electronegativity

F. Compare chemical properties of metals and non metals.

G. What are the valence electrons ? For s-block and p-block elements show that number of valence electrons is equal to its group number.

H. Define ionization enthalpy. Name the factors on which ionisation enthalpy depends? How does it vary down the group and across a period?

I. How the atomic size vary in a group and across a period? Explain with suitable example.

J. Give reasons.
   a. Alkali metals have low ionization enthalpies.
   b. Inert gases have exceptionally high ionization enthalpies.
   c. Fluorine has less electron affinity than chlorine.
   d. Noble gases possess relatively large atomic size.

K. Consider the oxides Li_2O, CO_2, B_2O_3.
   a. Which oxide would you expect to be the most basic?
   b. Which oxide would be the most acidic?
   c. Give the formula of an amphoteric oxide.

Activity :

Prepare a wall mounting chart of the modern periodic table.

8. Elements of Groups 1 and Group 2

We have seen in chapter 7 that the element of group 1 and group 2 belong to the s-block of the modern periodic table.

Can you recall?

1. Which is the first element in the periodic table ?
2. What are isotopes ?
3. Write the formulae of the compounds of hydrogen formed with sodium and chlorine.

Hydrogen is the first element in the periodic table. Hydrogen appears at the top of group 1 of the alkali metals. But it differs from alkali metals in a number of respects and, therefore, is studied separately.

8.1 Hydrogen : Hydrogen has the simplest atomic structure of all the elements. A hydrogen atom consists of a nucleus of charge +1 and one extranuclear electron. Hydrogen has a little tendency to lose this electron however can pair with the other electron easily forming a covalent bond. It exists in diatomic form as H_2 molecule; therefore it is often called **dihydrogen**.

8.1.1 Occurrence : In the free state hydrogen exists as dihydrogen gas. Hydrogen is most abundant element in the universe; it makes 70 % of the total mass of the universe. Hydrogen is also the principal element in the solar system. On the earth, hydrogen is the tenth most abundant element on mass basis and the third most abundant element on atom basis.

8.1.2 Position of hydrogen in the periodic table : Position of hydrogen in the periodic table has been a subject of discussion.

Can you tell?

In which group should hydrogen be placed ? In group 1 or group 17 ? Why ?

Electronic configuration of hydrogen is $1s^1$ which is similar to ns^1 which is the outer electronic configuration of alkali metals belonging to the group 1. But $1s^1$ also resembles the outer electronic configuration of group 17 elements, which is ns^2np^5. By adding one electron to H we get electronic configuration of the inert gas He which is $1s^2$ and by adding one electron to ns^2np^5 we get ns^2np^6 which is the outer electronic configuration of the remaining inert gases. Some chemical properties of hydrogen are similar to those of alkali metals while some resemble halogens. The uniqueness of hydrogen is that $H^{\oplus}$ formed by loss of the electron from hydrogen atom does not exist freely. It is always associated with other molecules. For example:

$$H^{\oplus} + H_2O \longrightarrow H_3O^{\oplus}$$

This is because $H^{\oplus}$ is nothing else but a proton. Hydrogen is, therefore, placed separately above the group 1. It may be noted, here, that metastable metallic hydrogen was discovered at Harvard university, USA, in January 2017.

8.1.3 Isotopes of Hydrogen : If different atoms of the same element have different mass numbers they are called isotopes of each other. (Refer to chapter 4). Hydrogen has three isotopes with mass numbers 1, 2 and 3. They all contain one proton and one electron but different number of neutrons in the nucleus. (see figure 8.1 and table 8.1)

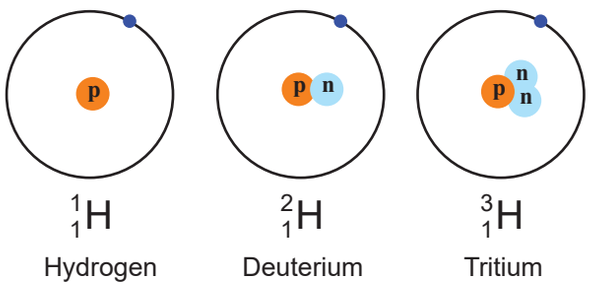


Figure 8.1 Isotopes of hydrogen

Table 8.1 : Characteristics of isotopes of hydrogen

Name of the Isotope	Symbol	Atomic number *Z*	Atomic mass number *A*	Neutron number *N*	Abundance	Stability
Hydrogen	H or $_1^1H$ or H-1	1	1	0	99.98 %	Stable
Deuterium	D or $_1^2H$ or H-2	1	2	1	0.015 %	Stable
Tritium	T or $_1^3H$ or H-3	1	3	2	Trace	Ratio active

Do you know ?

Tritium $_1^3H$ is a radioactive nuclide with half life period 12.4 years and emits low energy $\beta^{\ominus}$ particles.

8.1.4 Preparation of dihydrogen

Hydrogen can be prepared using many methods.

A. Laboratory methods

i. Dihydrogen is prepared in laboratory by the action of dilute hydrochloric acid on zinc granules.

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

ii. Dihydrogen can be prepared by the action of aqueous solution of sodium hydroxide on zinc.

$$Zn(s) + 2NaOH(aq) \rightarrow Na_2ZnO_2(aq) + H_2(g)$$

B. Industrial methods

i. By electrolysis of pure water: Pure water is a poor conductor of electricity. Therefore a dilute aqueous solution of acid or alkali is used to prepare dihydrogen by electrolysis. For example, electrolysis of dilute aqueous solution of sulphuric acid yields two volumes of hydrogen at cathode and one volume of oxygen at anode.

$$2H_2O\,(l) \xrightarrow[\text{trace of acid or akali}]{\text{electrolysis}} 2H_2\uparrow + O_2\uparrow$$

Pure dihydrogen (> 99.5% purity) gas is obtained by electrolysis of warm solution of barium hydroxide between nickel electrodes.

ii. From carbon or hydrocarbon: Three stages are involved in this industrial process of preparation of dihydrogen.

Stage 1 : Reaction of steam on hydrocarbon or coke (C) at 1270 K temperature in presence of nickel catalyst, gives water-gas, which is a mixture of carbon monoxide and hydrogen.

$$CH_4(g) + H_2O(g) \xrightarrow[Ni]{1270\ K} \underbrace{CO(g) + 3H_2(g)}_{\text{water-gas}}$$

As water-gas is used for synthesis of CH_3OH and a number of hydrocarbons, it is also called **'syngas'**. Production of syngas is also the first stage of gasification of coal.

$$C(s) + H_2O\,(g) \xrightarrow{1270\ K} CO(g) + H_2(g).$$

Sawdust, scrapwood, etc. can also be used in place of carbon.

Stage 2 : Water-gas shift reaction: The carbon monoxide in the watergas is transformed into carbondioxide by reacting with steam in presence of iron chromate as catalyst. This is called water-gas shift reaction.

$$CO(g) + H_2O(g) \xrightarrow[\text{iron chromate catalyst}]{673\ K} CO_2(g) + H_2(g)$$

Stage 3 : Carbon dioxide is removed by scrubbing with sodium arsenite solution.

Today major industrial production of dihydrogen is from petrochemicals (~ 77 %), about 18 % from coal, about 4 % by electrolytic methods and about 1 % by other methods.

8.1.5 Properties of dihydrogen

A. Physical properties : Dihydrogen is colourless, tasteless and odourless gas. It burns with a pale blue flame. It is a nonpolar water insoluble gas, lighter than air.

B. Chemical properties :

i. Reaction with metals : Dihydrogen combines with all the reactive metals such as alkali metals, calcium, strontium and barium at high tempereture, to form metal hydrides. For example :

$$2Na(s) + H_2(g) \xrightarrow{\Delta} 2NaH(s)$$

(In this respect dihydrogen is similar to halogens which also react with metals and form metal halides.)

Just think

In the above chemical reaction which element does undergo oxidation and which does undergo reduction ?

Do you know ?

The bond dissociation energy of H-H bond is high, which is 436 kJ mol^{-1}. Therefore reactions of dihydrogen take place at high temperature and /or in the epresence of catalyst.

ii. Reaction with dioxygen: Dihydrogen reacts with dioxygen in the presence of catalyst or by heating to form water. This reaction is highly exothermic.

$$2H_2(g) + O_2(g) \xrightarrow[\text{or heating}]{\text{catalyst}} 2H_2O(l) ;$$

$$\Delta H = -235 \text{ kJ mol}^{-1}$$

iii. Reaction with halogens: Dihydrogen inflames with fluorine even at -250^0 C in dark, whereas it requires catalyst to react with iodine. The vigour of reaction of dihydrogen decreases with increasing atomic number of halogen.

$$H_2(g) + X_2(g) \rightarrow 2HX(g)$$

(In this respect dihydrogen resembles alkali metals which also react with halogens to form halides.)

iv. Reducing nature of dihydrogen :

a. Dihydrogen reduces oxides and ions of metals those are less reactive than iron, to the corresponding metals at moderate temperature. For example :

$$CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(l)$$

$$Fe_3O_4(s) + 4H_2(g) \longrightarrow 3Fe(s) + 4H_2O(l)$$

$$Pd^{2\oplus}(aq) + H_2(g) \longrightarrow Pd(s) + 2H^{\oplus}(aq)$$

b. Hydrogenation of unsaturated organic compound

The hydrogenation of unsaturated organic compounds such as oil using nickel caralyst gives saturated organic compounds such as solid fat (vanaspati Ghee).

$$\underset{\text{(Vegetable oil)}}{>C=C<} + H_2 \xrightarrow[\Delta]{Ni} \underset{\text{(Saturated fat)}}{>CH-CH<}$$

7.1.6 Uses of dihydrogen

i. Largest use of dihydrogen is in production of ammonia.

ii. Dihydrogen is used in formation of vanaspati ghee by catalytic hydrogenation of oils.

iii. Liquid dihydrogen is used as a rocket fuel.

iv. Dihydrogen is used in preparation of important organic compounds like methanol in bulk quantity.

$$2H_2(g) + CO(g) \xrightarrow[\text{Cobalt catalyst}]{} CH_3OH(l)$$

v. Dihydrogen is used for preparation of hydrogen chloride (HCl) and metal hydrides.

Problem 8.1 : Justify the placement of hydrogen in the group of alkali metals with the help of reaction with halogens.

Solution :

Hydrogen on reaction with halogen (X_2) gives compounds with general formula HX. For example : $H_2 + Cl_2 \longrightarrow 2HCl$ similarly alkali metals (M) on reaction with halogens (X_2) give compounds with general formula MX.

For examples : $2Na + Cl_2 \longrightarrow 2NaCl$

Thus, H_2 and alkali metal are monovalent elements more electropositive than halogens. This similarily justifies the place of hydrogen in the group 1.

Can you recall?

1. What is the name of the family of reactive metals having valancy one?
2. What is the name of the family of reactive metals having valancy two?

8.2 Alkali metals and alkaline earth metals

8.2.1 Introduction : The elements of the groups 1 and 2 are placed on the left in the periodic table. Here the last electron enters into '*ns*' subshell. Thus they belong to the s-block of the periodic table. **Group 1** of the periodic table consists of the elements: **hydrogen, lithium, sodium, potassium, rubidium, caesium and francium**. These elements **except hydrogen** are collectively called **alkali metals**. We have already looked at hydrogen in the section 8.1. Two elements of Group 1, namely, sodium and potassium are the sixth and seventh most abundant elements in earth crust but francium does not occur appreciably in nature because it is radioactive and has short half-life period.

Group 2 of the periodic table consists of elements : **beryllium, magnesium, calcium, strontium, barium and radium**. These elements are collectively called **alkaline earth metals** because they occur as minerals in rocks. The elements magnesium and calcium are found abundantly in earth crust but radium is not easy to find. Radium is one of the first two radioactive elements discovered by Madame Curie.

8.2.2 Electronic configuration of elements of group 1 and group 2

The general outer electronic configuration of the group 1 elements is ns^1 and that of the group 2 elements is ns^2. The loosely held s-electrons in valence shell of these elements can be easily removed to form metal ions. Hence these elements are never found in free state in nature. Tables 8.2 and 8.3 show the electronic configurations of the elements of group 1 and group 2 elements, respectively.

Table 8.2 : Electronic configuration of group 1 elements

Name	Symbol	Atomic number	Condensed electronic configuration	Electronic Configuration.
Hydrogen	H	1	$1s^1$	$1s^1$
Lithium	Li	3	[He] $2s^1$	$1s^2\ 2s^1$
Sodium	Na	11	[Ne] $3s^1$	$1s^2\ 2s^2\ 2p^6\ 3s^1$
Potassium	K	19	[Ar] $4s^1$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$
Rubidium	Rb	37	[Kr] $5s^1$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^1$
Caesium	Cs	55	[Xe] $6s^1$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^1$
Francium	Fr	87	[Rn]$7s^1$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^{10}\ 6p^6\ 7s^1$

Table 8.3 : Electronic configuration of group 2 elements

Name	Symbol	Atomic number	Condense electronic configuration	Electronic Configuration.
Beryllium	Be	4	[He] $2s^2$	$1s^2\ 2s^2$
Magnesium	Mg	12	[Ne] $3s^2$	$1s^2\ 2s^2\ 2p^6\ 3s^2$
Calcium	Ca	20	[Ar] $4s^2$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$
Strontium	St	38	[Kr] $5s^2$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2$
Barium	Ba	56	[Xe] $6s^2$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2$
Radium	Ra	88	[Rn] $7s^2$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ \ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^{10}\ 6p^6\ 7s^2$

8.2.3 Trends in atomic and physical properties of elements of group 1 and group 2

All the **alkali metals** are silvery white and soft. Due to their large atomic size these elements have low density. They are the most electropositive elements. The **alkaline earth** are **metals** also in general silvery white lustrous and soft, but harder than the alkali metals. They are also strongly electropositive in nature. But comparatively less electropositive than the alkali metals. Some atomic and physical properties of the alkali metals and the alkaline earth metals are listed in the tables 8.4 and 8.5 respectively.

Table 8.4 : Physical properties of group 1 elements (except hydrogen)

Symbol	Atomic radius (pm)	Ionic radius (pm)	Density (g/cm^{-3})	Ionization enthalpy ($kJ\ mol^{-1}$)	Electro-negativity	Melting point (K)	Abundance in the lithosphere	Standard reduction potential E^{o} (V)
Li	152	76	0.54	520	1.0	454	18 ppm	-3.04
Na	186	102	0.97	496	0.9	371	2.27 %	-2.714
K	227	138	0.86	419	0.8	336	1.84 %	-2.925
Rb	248	152	1.53	403	0.8	312	78.12 ppm	-2.930
Cs	265	167	1.90	376	0.7	302	2.6 ppm	-2.927
Fr	-	(180)	-	~375	-	-	-10^{-18} ppm	-

Table 8.5 : Physical properties of group 2 elements

Symbol	Atomic radius (pm)	Ionic radius (pm)	Density (g/cm^{-3})	Ionization enthalpy ($kJ\ mol^{-1}$)		Electro-negativity	Melting point (K)	Abundance in the lithosphere	Standard reduction potntial E^{0} (V)
				1^{st}	2^{nd}				
Be	111	31	1.84	899	1757	1.5	1560	2 ppm	-1.97
Mg	160	72	1.74	737	1450	1.2	924	2.76 %	-2.36
Ca	197	100	1.55	590	1145	1.0	1124	4.6 %	-2.84
Sr	215	118	2.63	549	1064	1.0	1062	384 ppm	-2.89
Ba	222	135	3.59	503	965	0.9	1002	390 ppm	-2.92
Ra	-	148	(5.5)	509	979	-	973	10^{-6} ppm	-2.92

Unipositive ions of all the elements of group 1 have inert gas configuration. Thus they have no unpaired electron and their compounds are diamagnetic and colourless. The divalent ions of group 2 elements also have inert gas configuration with no unpaired electron, and therefore their compounds are also diamagnetic and colourless. Lithium and beryllium differ from the rest of the elements of the groups 1 and 2, respectively because of their extremely small size and comparatively high electronegativity.

The physical properties of group 1 and group 2 elements show reasonable regularity in the periodic trends. Thus the atomic and ionic radii and densities increase down both the groups. Ionization enthalpies and electronegativities decrease down both the groups. The elements of both these groups, in general, have high negative values of standard reduction potentials.

8.2.4 Chemical properties of elements of group 1 and group 2

The alkali metals and alkaline earth metals are very reactive in nature. As a result of this they are always found in combined state. Their reactivity is due to their low ionization ehthalpy values in general. The reactivity of these metals increases with increasing atomic radius and corresponding lowering of lonization enthalpy down the groups 1 and 2 can be noticed.

Problem 8.2:
Sodium forms ionic compounds having formulae NaCl, NaH and Na_2CO_3. Explain
Solution: Let us rewrite the formulae of the compounds of sodium showing charges on the concerned cation and basic anion.
$Na^{\oplus}Cl^{\ominus}$, $Na^{\oplus}H^{\ominus}$, $2Na^{\oplus}\ CO_3^{2\ominus}$
It is seen that in all these compounds Na carries one positive charge. The $Na^{\oplus}$ is formed from Na atom by losing one electron. $Na \rightarrow Na^{\oplus} + e^{\ominus}$
This happens because the electronic configuration of Na is $[Ne]3s^1$. There is only one electron in the valence shell of Na. It can easily be lost as the ionization enthalpy is low. And $Na^{\oplus}$ ion so formed is stable as it has stable electronic configuration of the inert gas Ne.

Problem 8.3 : Explain the observed values 496 kJ/mol and 737 kJ/mol of the first ionization enthalpies of Na and Mg, respectively.
Solution : The electronic configuration of Na is $[Ne]3s^1$ and that of Mg is $[Ne]3s^2$. During the first iouization only one electron is removed from a neutral atom.

$$Na \xrightarrow{1^{st}\ ionisation} Na^{\oplus} + e^{\ominus}$$

$$Mg \xrightarrow{1^{st}\ ionisation} Mg^{\oplus} + e^{\ominus}$$

The resulting Na is isoelectronic with Ne, and therefore, is stable. Thats why Na has low value of 1st ionization enthalpy. However, to form the unipositive $Mg^{\oplus}$ ion energy is required to unpair these electrons in the valency shell and also remove one electron to form the ion having electronic configuration [Ne] $3s^1$. It is not as stable as Na since it does not correspond to any inert gas. Therefore the first ionization enthalpy of Mg is higher than that of Na.

Problem 8.4:
What is the oxidation state of Na in Na_2O_2?
Solution: The peroxide species is represented as O_2^{2-}. Any compound is electrically neutral. Therefore oxidation state of each Na is (+2/2 = +1) in Na_2O_2.

Problem 8.5 :
The atomic radii of Na, K and Mg are 186, 227 and 160 pm, respectively. Explain the differences.
Solution : Na and K both belong to the group 1. K has larger valence shell than Na. Therefore the atomic radius of K is larger than that of Na. Na and Mg belong to the same period. Therefore both have the same valence shell. But the nuclear charge of Mg is larger than that of Na. Therefore, the valence electrons of Mg are held more tightly and its atomic radius is smaller than that of Na.

The elements of group 1 and group 2 both being s-block elements, show similarily in their chemical properties. The differences are due to variation in the atomic radii, ionization enthalpies and valencies.

i. Reaction with oxygen/air

Group 1 - All the elements of group 1 rapidly lose their luster in air due to formation of a layer of oxide, on peroxide and in some cases superoxide by reaction with oxygen in air.

$2Li + O_2 \rightarrow 2LiO$
(Lithium oxide)

$2Na + O_2 \rightarrow Na_2O_2$
(Sodium peroxide)

$K + O_2 \rightarrow KO_2$
(Potassium superoxide)

Do you know ?

- The reaction of Na and K with oxygen is highly exothermic and these metals catch fire when exposed to air.

- Potassium superoxide has ability to absorb carbon dioxide and give out oxygen at the same time:

$$4KO_2 + 2CO_2 \rightarrow 2K_2CO_3 + 3O_2\uparrow$$

- This property of KO_2 has been made use of in breathing equipment used for mountaineers and in submarines and space.

The oxides of group 1 metals are strongly basic in nature. They dissolve in water forming aqueous solutions of strong alkali. For example

$$2LiO(s) + H_2O(l) \rightarrow 2LiOH(aq)$$

Group 2 : These metals are protected from air oxidation by an oxide film formed on their surface.

All the elements of group 2 burn when ignited in air forming MO type oxides. The product is a mixture of oxide and nitride.

$$2Mg + O_2 \rightarrow 2MgO$$
$$3Mg + N_2 \rightarrow Mg_3N_2$$

Further heating of the oxide in air results in formation of peroxide.

ii. Reaction with water

Group 1 : Lithium, sodium and potassium all float on water due to hydrogen bubbles released on reaction with water. Lithium reacts slowly but sodium and potassium react vigrously with water. Due to highly exothermic reaction sodium and potassium catch fire when put in water.

$$2Na + 2H_2O \rightarrow 2NaOH + H_2\uparrow$$

Group 2 : The elements of group 2 react with water to form metal hydroxide and hydrogen. Beryllium does not react with water. Magnesium decomposes hot water, other elements react with cold water forming metal hydroxide $M(OH)_2$ and hydrogen gas.

$$Ca + 2H_2O \rightarrow Ca(OH)_2\downarrow + H_2\uparrow$$

iii. Reaction with Hydrogen

Group 1 : Alkali metals react with hydrogen at high tempereture to form the corresponding metal hydrides.

$$2M + H_2 \xrightarrow{673\ K} 2M^+H^-$$

Group 2 : All the metals of group 2, except beryllium, when heated with hydrogen form MH_2 type hydrides.

$$M + H_2 \xrightarrow{\Delta} MH_2$$

Problem 8.6 : NaCl is an ionic compound but LiCl has some covalent character, explain.

Solution: $Li^{\oplus}$ ion has very small size, therefore the charge density on $Li^{\oplus}$ is high. Therefore it has high tendency to distort the electron cloud around the negatively charged large chloride ion. This results in partial covalent character of the LiCl bond. $Na^{\oplus}$ ion cannot distort the electron cloud of $Cl^{\ominus}$ due to the bigger size of $Na^{\oplus}$ compared to $Li^{\oplus}$.

iv. Reaction with Halogens

Group 1 : All the alkali metals react vigorously with halogens to produce their ionic halide salts.

$$2M + X_2 \longrightarrow 2M^+X^-$$

Group 2: All the alkaline earth metals combine with halogens at high temperature to form halides.

$$M + X_2 \longrightarrow MX_2$$

v. Reducing nature

Group 1 : The reducing power of an element is measured in terms of standard electrode potential (E^0) corresponding to the transformation $M^{\oplus}(aq) + e^{\ominus} \rightarrow M(s)$. All the alkali metals have high negative values of E^0 indicative of their strong reducing nature, lithium is the most powerful and sodium is the least powerful in the group. (see Table 8.4)

Group 2 : All the alkaline earth metals have high negative values of standard reduction potential (E^0). (see Table 8.5), and are strong reducing agents. However their reducing power is less than those of alkali metals.

vi Solution in liquid ammonia

Group 1 : The alkali metals are soluble in liquid ammonia giving deep blue coloured solutions which show electrical conductivity.

$$M + (x + y)NH_3 \rightarrow [M(NH_3)_x]^{\oplus} + [e(NH_3)_y]^{\ominus}$$

The ammoniated electron is responsible for the deep blue colour of these solutions. These solutions are paramagnetic and on standing liberate hydrogen slowly, resulting in formation of the metal amide. The blue colour changes to bronze and the solution becomes diamagnetic.

$$M^{\oplus}(am) + e^{\ominus}(am) + NH_3(l) \rightarrow MNH_2(am) + H_2(g)^{\ominus}$$

(Here (am) denotes solution in ammonia.)

Group 2 : Similar to alkali metals the alkaline earth metals are also soluble in liquid ammonia which give deep blue black coloured solutions.

$$M + (x + 2y)\ NH_3 \rightarrow [M(NH_3)_x]^{2\oplus} + 2[e(NH_3)_y]^{\ominus}$$

8.2.5 Diagonal Relationship : It is expected that elements belonging to the same group exhibit similarity and gradation in their properties. The first alkali metal lithium and the first alkaline earth metal beryllium do not fulfil this expectation. Thus, lithium shows many differences when compared with the remaining alkali metals and resembles with magnesium, the second alkaline earth metal. Likewise beryllium shows many differences with remaining alkaline earth metals and shows similarity with aluminium, the second element of the next main group (group 13). The relative placement of these elements with similar properties in the periodic table appears to be across a diagonal (see. Table 8.6) and is called diagonal relationship.

Table 8.6 : Diagonal relationship

Main Group / Period	1	2	13
2	Li	Be	B
3	Na	Mg	Al

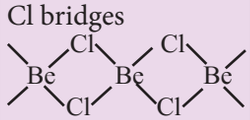
The table 8.7 shows some properties of lithium and magnesium which elucidate their diagonal relationship.

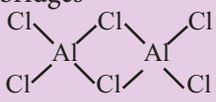
Table 8.7 : Ressemblence between Li and Mg

Criterion / Element	Products of reaction with air $M \xrightarrow{air} ?$	Products of thermal decomposition of carbonate $M_2CO_3/MCO_3 \xrightarrow{\Delta} ?$	Property of chloride	Formula of crystalline chloride
Li	$Li_2O + Li_3N$	$Li_2O + CO_2$	deliquescent	$LiCl.2H_2O$
Mg	$MgO + Mg_3N_2$	$MgO + CO_2$	deliquescent	$MgCl_2.8H_2O$
Group 1 (except Li)	$M_2O/M_2O_2/MO$	No reaction	Not deliquescent	MCl
Group 2	$MO + M_3N_2$	$MO + CO_2$	deliquescent	$MCl_2.xH_2O$

In table 8.8 some properties of Be and Al are shown which indicate the diagonal relationship

Table 8.8 : Resemblence between Be and Al

Criterion / Element	Properties of chloride			Properties of oxide Acidic/Basic/Amphoteric
	Nature of bonding	Whether Lewis acid	Solubility in organic solvent	
Be	**Covalent** chain structure with Cl bridges 	$BeCl_2$ is strong **Lewis acid**	**Soluble**	**Amphoteric** $BeO + 2HCl \rightarrow BeCl_2 + H_2$ $BeO + 2NaOH \rightarrow Na_2BeO_2 + H_2O$

Al	**Covalent** dimer with Cl bridges 	$AlCl_3$ is strong **Lewis acid**	**Soluble**	**Amphoteric** $Al_2O_3 + 6HCl \rightarrow 2AlCl_3+3H_2O$ $Al_2O_3+2NaOH \rightarrow 2NaAlO_2+H_2O$
Group 2	**Ionic**	**Not Lewis acid**	**Insoluble**	**Basic** $MO+HCl \rightarrow MCl_2 + H_2$ $MO + NaOH \rightarrow$ No reaction
Group 13	**Covalent**	**Lewis acid**	**Soluble**	*Amphoteric*

The diagonal relationship between the elemental pairs belonging to different groups and periods is due to the similarity in some of their atomic properties. Thus atomic and ionic radii of Li and Mg are very similar. (see the table 8.4). In the case of Be and Al the charge to radius ratio of their ions is very similar. (Be : $\frac{2}{31}$ and Al : $\frac{3}{53.55}$)

8.2.6 Uses of elements of group 1 and group 2

Group 1

i. Lithium metal is used in long-life batteries used in digital watches, calculators and computers.
ii. Liquid sodium has been used for heat transfer in nuclear power station.
iii. Potassium chloride is used as a fertilzer.
iv. Potassium is used in manufacturing potassium superoxide (KO_2) for oxygen generation. It is good absorbent of carbon dioxide.
v. Caesium is used in photoelectric cells.

Group 2

i. Beryllium is used as a moderator in nuclear reactors.
ii. Alloy of magnesium and aluminium is widely used as structural material and in aircrafts.
iii. Calcium ions are important ingredient in biological system, essential for healthy growth of bones and teeth.
iv. Barium sulphate is used in medicine as barium meal for intestinal x-ray.
v. Radium is used in radiotherapy for cancer treatment.

8.2.7. Biological importance of elements of group 1 and group 2

Group 1

i. Sodium ion is present as the largest supply in all extracellular fluids. These fluids provide medium for transportting nutrients to the cells.
ii. The concentration of sodium ion in extracellular fluids regulates the flow of water across the membrane.
iii. Sodium ions participate in the transmission of nerve signals.
iv. Potassium ions are the most abundant ions within cells. These are required for maximum efficiency in the synthesis of proteins and also in oxidation of glucose.

Group 2

i. $Mg^{2\oplus}$ ions are important part of chlorophyll in green plants.
ii. $Mg^{2\oplus}$ ions play an important role in the breakge of glucose and fat molecules, in synthesis of proteins with enzymes, and in regulation of chlolesterol level.
iii. $Ca^{2\oplus}$ ions are important for bones and teeth in the form of apatite $[Ca_3(PO_4)_2]$
iv. $Ca^{2\oplus}$ ions play important role in blood clotting.
v. $Ca^{2\oplus}$ ions are required for contraction and stretching of muscles.
vi. $Ca^{2\oplus}$ ions are also required to maintain the regular beating of heart.

Problem 8.7 : Magnesium strip slowly tarnishes on keeping in air but metallic calcium is readily attacked by air. Explain.

Solution: Mg and Ca belong to group 2, but periods 2 and 3, respectively. During the reaction with air the metallic Mg and Ca lose their valence electrons. The tendency to lose valence electron is the metallic character, which increases down the group. Thus, calcium has higher metallic character, greater tendency to lose valence electron and lower ionization enthalpy than magnesium. Therefore Mg reacts slowly with air, forming a thin film of oxide, resulting into tarnishing, whereas Ca reacts readily at room temperature with oxygen and nitrogen in the air.

8.3 Some important compounds of elements of s-block

In this section we consider five important compounds of s-block elements with reference to their prepartion, properties and uses.

8.3.1. Sodium Carbonate (washing soda) $Na_2CO_3.10H_2O$

Prepartion: Sodium Carbonate is commercially prepared by **Solvay process**. In the **first stage** of process CO_2 is passed into a concentrated solution of NaCl which is saturated with NH_3. Crystals of sodium bicarbonate separate as a result of the following reactions.

Reactions in the first stage:

$2\ NH_3(aq) + H_2O + CO_2(g) \rightarrow (NH_4)_2\ CO_3(aq)$

$(NH_4)_2CO_3(aq) + H_2O + CO_2(aq) \rightarrow 2\ NH_4HCO_3(aq)$

$NH_4HCO_3(aq) + NaCl(aq) \rightarrow NH_4Cl(aq) + NaHCO_3(s)$

Sodium bicarbonate has low solubility, and therefore its crystals precipitate out which are formed as a result of the double decomposition reaction between ammonium bicarbonate and sodium chloride.

In the **second stage** the separated crystals of sodium bicarbonate are heated to obtain sodium carbonate.

$2\ NaHCO_3(s) \xrightarrow{\Delta} Na_2CO_3(s) + H_2O(g) + CO_2(g)$

In this process the **recovery of ammonia** is done by treating the solution of NH_4Cl obtained with slaked lime, $Ca(OH)_2$. The byproduct of this reaction is calcium chloride.

$2\ NH_4Cl(aq) + Ca(OH)_2(s) \longrightarrow 2\ NH_3(g) + CaCl_2(aq) + H_2O(l)$

Do you know ?

Potassium carbonate can not be prepared by Solvay process because potassium hydrogen carbonate is highly water soluble and cannot be precipitated by reaction with potassium choride.

Properties : Sodium carborate (washing soda) is a white crystalline solid having the formula Na_2CO_3, $10H_2O$. It is highly soluble in water. On heating the decahyadrate loses water molecules to form monohydrate. On heating above 373 K temperature monohydrate further loses water and changes into white anhydrous powder called soda-ash.

$Na_2CO_3.10H_2O(s) \xrightarrow{373\ K} Na_2CO_3.H_2O(s) + 9H_2O(g)$

$Na_2CO_3.H_2O(s) \xrightarrow{> 373\ K} Na_2CO_3(s) + H_2O(g)$

Aqueous solution of sodium carbonate is alkaline because of its hydrolysis by the following reaction:

$Na_2CO_3 + H_2O \rightarrow NaHCO_3 + NaOH$

Uses

i. The alkaline properties of sodium carbonate are responsible for emulsifying effect on grease and dirt. It is used as cleaning material.

ii. It is used to make hard water soft (as a water softener), as it precipitates out the soluble calcium and magnesium salts in hard water as carbonates. For example : $Ca(HCO_3)_2(aq) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + 2NaHCO_3(aq)$

iii. It is used for commercial production of soap and caustic soda.

iv. It is an important laboratory reagent.

8.3.2 Sodium hydroxide (caustic soda) NaOH

Preparation : Sodium hydroxide is commercially obtained by the electrolysis of saturated aqueous solution of sodium chloride. Brine solution is subjected to electrolysis in Castner-Kellner cell. Mercury is used as cathode and carbon rod as anode. Metallic sodium liberated at the cathode forms sodium amalgam. Chlorine gas is evolved at the anode.

Cathode reaction: $Na^{\oplus} + e^{\ominus} \xrightarrow{Hg} Na\text{-amalgam}$

Anode reaction: $Cl^{\ominus} \longrightarrow 1/2\ Cl_2 + e^{\ominus}$

Sodium hydroxide is obtained by treating sodium amalgam with water, when hydrogen gas is liberated.

$$2Na\text{-}Hg + 2H_2O \longrightarrow 2NaOH + 2Hg + H_2$$

Properties : Sodium hydroxide is a white deliquescent solid, having melting point 591 K. It is highly water soluble and gives a strongly alkaline solution. The surface of the solution absorbs atmospheric CO_2 to form Na_2CO_3.

Uses

i. Sodium hydroxide is used in purification of bauxite (the aluminium ore).
ii. It is used in commercial production of soap, paper, artificial silk and many chemicals.
iii. It is used for mercerising cotton fabrics.
iv. It is used in petroleum refining.
v. It is an important laboratory reagent.

8.3.3 Calcium Carbonate ($CaCO_3$)

Calcium carbonate is found in nature as chalk, lime stone, marble.

Preparation

i. When carbon dioxide is bubbled through solution of calcium hydroxide (slaked lime) water insoluble solid calcium carbonate is formed.

$$Ca(OH)_2(aq) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O(l)$$

Excess carbon dioxide transforms the precipitate of $CaCO_3$ into water soluble calcium bicarbonate and therefore has to be avoided.

ii. When solution of calcium chloride is added to a solution of sodium carbonate, calcium carbonate is formed as precipitate.

$$CaCl_2(aq) + Na_2CO_3(aq) \longrightarrow CaCO_3(s) + 2NaCl(aq)$$

Properties

Calcium carbonate is soft, light, white powder. It is practically water insoluble. On heating to 1200 K calcium carbonate decomposes into calcium oxide and carbon dioxide.

$$CaCO_3(s) \xrightarrow{1200\ K} CaO(s) + CO_2\uparrow$$

It reacts with dilute acids to give the corresponding calcium salt and carbon dioxide.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2\uparrow + H_2O$$
$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2\uparrow + H_2O$$

Uses:

i. Calcium carbonate in the form of marble is used as building material.
ii. Calcium carbonate is used in the manufacture of quicklime (CaO) which is the major ingredient of cement.
iii. A mixture of $CaCO_3$ and $MgCO_3$ is used as flux in the extraction of metals from ores.
iv. It is required for the manufacture of high quality paper.
v. It is an important ingredient in toothpaste, chewing gum, dietary suppliments of calcium and filler in cosmetics.

8.3.4 Hydrogen peroxide (H_2O_2) : Hydrogen peroxide is a low cost, clean and mild oxidising agent. A 30% aqueous solution hydrogen peroxide is commercially available.

Preparation :

i. Hydrated barium peroxide is treated with ice cold dilute sulfuric acid. The precipitate of barium sulphate formed is filtered off to get hydrogen peroxide solution.

$$BaO_2.8H_2O(s) + H_2SO_4(aq) \xrightarrow[273\ K]{low\ temp} BaSO_4\downarrow + H_2O_2(aq) + 8H_2O(l)$$

ii. Small quantity of sodium peroxide is added to ice-cold solution of dilute sulfuric acid with strirring gives hydrogen peroxide (Merck process).

$$Na_2O_2(aq) + H_2SO_4(aq) \xrightarrow{273\ K} H_2O_2(aq) + Na_2SO_4(aq)$$

iii. A 50 % solution of sulfuric acid is subjected to an electrolytic oxidation to form peroxydisulfuric acid at anode.

$$2HSO_4^{\ominus} \xrightarrow{Electrolysis} H_2S_2O_8 + 2e^{\ominus}$$

Hydrolysis of the peroxydisulfuric acid yields hydrogen peroxide.

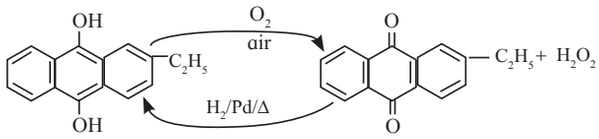
$HO\text{-}SO_2\text{-}O\text{-}O\text{-}SO_2\text{-}OH + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2$

This method can be extended to laboratory preparation of D_2O_2

iv. Industrially hydrogen peroxide is prepared by air-oxidation of 2-ethylanthraquinol.

The 2-ethylanthraquinol is regenerated by catalytic hydrogenation of 2-ethylanthraquinone.

2-ethylanthraquinol $\xrightarrow[\text{air}]{O_2}$ H_2O_2 + 2 - ethylanthraquinone



Properties

i. Pure H_2O_2 is a very pale blue coloured liquid, having b.p. 272.4 K.

ii. H_2O_2 is miscible in water and forms a hydrate ($H_2O_2 . H_2O$)

iii. Strength of aqueous solution of H_2O_2 is expressed in 'volume' units. The commercially marketed 30% (by mass) solution of H_2O_2 has volume strength of 100 volume. It means that 1 mL of 30% solution of H_2O_2 will give 100 mL oxygen at STP.

iv. H_2O_2 acts as a mild oxidising as well as reducing agent.

a. Oxidising action of H_2O_2 in acidic medium

$2Fe^{2\oplus}(aq) + 2H^{\oplus}(aq) + H_2O_2(aq) \rightarrow 2Fe^{3\oplus}(aq) + 2H_2O(l)$

b. Reducing action of H_2O_2 in acidic medium

$2\ MnO_4^{\ominus} + 6H^{\oplus} + 5H_2O_2 \rightarrow 2Mn^{2\oplus} + 8H_2O + 5O_2$

Uses

i. Hydrogen peroxide is used as mouthwash, germicide, mild antiseptic, preservative for milk and wine and bleaching agent for soft materials due to its mild oxidising property.

ii. Hydrogen peroxide, due to its reducing property, is used as an antichlor to remove excess chlorine from fabrics which have been bleached by chlorine.

iii. Now a days it is also used in environmental chemistry for pollution control, restoration of aerobic condition to sewage water.

Promblem 8.8 : Calculate % (by mass) of a H_2O_2 solution which is 45.4 volume.

Solution: 45.4 Volume H_2O_2 solution means 1L of this solution will give 45.4 L O_2 at STP

$$\underset{(2\times34)\ g}{2\ H_2O_2} \rightarrow \underset{22.7\ L\ at\ STP}{2\ H_2O + O_2}$$

Thus, 22.7 L O_2 at STP is produced by 68 g H_2O_2

$\therefore$ 45.4 L O_2 at STP is produced by $\frac{68\times45.4}{22.7}$ = 136 g H_2O_2

$\therefore$ Strength this H_2O_2 solution = 136 g/L

$$= \frac{136\ g\ H_2O_2}{1000\ g\ water} = 13.6\%\ (by\ mass)$$

8.3.5 Lithium aluminium hydride ($LiAlH_4$)

Lithium aluminium hydride is commonly abbreviated as LAH. It has chemical formula $LiAlH_4$.

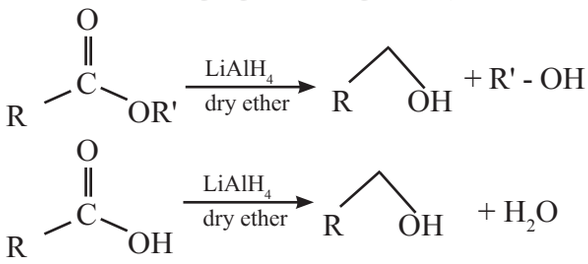
Prepartion : Lithium hydride is treated with aluminium chloride to give lithium aluminium hydride

$$4LiH + AlCl_3 \rightarrow LiAlH_4 + 3LiCl$$

Properties: Lithium aluminium hydride is a colourless solid. It reacts violently with water and even atmospheric moisture.

Uses

(i) LAH is a source of hydride and therefore used as reducing agent in organic synthesis.



(ii) LAH is useful to prepare PH_3(phosphine)

$4\ PCl_3 + 3LiAlH_4 \rightarrow 4\ PH_3 + AlCl_3 + Li\ Cl$

Exercises

1. Explain the following

A. Hydrogen shows similarity with alkali metals as well as halogens.

B. Standard reduction potential of alkali metals have high negative values.

C. Alkaline earth metals have low values of electronegativity; which decrease down the group.

D. Sodium dissolves in liquid ammonia to form a solution which shows electrical conductivity.

E. $BeCl_2$ is covalent while $MgCl_2$ is ionic.

F. Lithium floats an water while sodium floats and catches fire when put in water.

2. Write balanced chemical equations for the following.

A. CO_2 is passed into concentrated solution of NaCl, which is saturated with NH_3.

B. A 50% solution of sulphuric acid is subjected to electrolyte oxidation and the product is hydrolysed.

C. Magnesium is heated in air.

D. Beryllium oxide is treated separately with aqueous HCl and aqueous NaOH solutions.

3. Answer the following questions

A. Describe the diagonal relationship between Li and Mg with the help of two illustrative properties.

B. Describe the industrial production of dihydrogen from steam. Also write the chemical reaction involved.

C. A water sample, which did not give lather with soap, was found to contain $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$. Which chemical will make this water give lather with soap? Explain with the help of chemical reactions.

D. Name the isotopes of hydrogen. Write their atomic composition schematically and explain which of these is radioactive ?

4. Name the following

A. Alkali metal with smallest atom.

B. The most abundant element in the universe.

C. Radioactive alkali metal.

D. Ions having high concentration in cell sap.

E. A compound having hydrogen, aluminium and lithium as its constituent elements.

5. Choose the correct option.

A. The unstable isotope of hydrogen is .....

a. H-1 b. H-2

c. H-3 d. H-4

B. Identify the odd one.

a. Rb b. Ra

c. Sr d. Be

C. Which of the following is Lewis acid ?

a. $BaCl_2$ b. KCl

c. $BeCl_2$ d. LiCl

D. What happens when crystalline Na_2CO_3 is heated ?

a. releases CO_2

b. loses H_2O

c. decomposes into $NaHCO_3$

d. colour changes.

Activity :

1. Collect the information of preparation of dihydrogen and make a chart.

2. Find out the s block elements compounds importance/uses.

9. Elements of Groups 13, 14 and 15

Can you recall?

If the valence shell electronic configuration of an element is $3s^2 3p^1$ in which block of periodic table is it placed ?

9.1 Introduction : You have learnt in Chapter 7 that in the p-block elements the diffrentiating electron (the last filling electron) enters the outermost p orbital. You also know that maximum six electrons can be accommodated in p-subshell (or three p orbitals). This gives rise to six groups, group 13 to 18, in the p-block. The p-block elements show greater variation in the properties than 's' block, which you learnt in the previous chapter. In this chapter you are going to study the elements of the groups 13, 14 and 15 in some details.

The elements boron ($_5$B), aluminium ($_{13}$Al), gallium ($_{31}$Ga), indium ($_{49}$In) and thallium ($_{81}$Tl) constitute the group 13, called the **boron family**. The elements carbon ($_6$C), silicon ($_{14}$Si), germanium ($_{32}$Ge), tin ($_{50}$Sn) and lead ($_{82}$Pb) form the group 14 called the **carbon family**. The elements nitrogen ($_7$N), phosphorous ($_{15}$P), arsenic ($_{33}$As), antimony ($_{51}$Sb) and bismuth ($_{83}$Bi) belong to group 15 of the periodic table called the **nitrogen family**.

9.2 Electronic configuration of elements of groups 13, 14 and 15

The general outer electronic configuration of the group 13 elements is $ns^2\ np^1$, those of the group 14 elements is ns^2np^2 while the group 15 elements are shown as ns^2np^3. These electronic configurations differ from their nearest inert gas by 3 or 4 electrons. These elements do not occur in free monoatomic state and found as compounds with other elements or as polyatomic molecules (such as N_2, P_4, C_{60}) or polyatomic covalent arrays (such as graphite, diamond). Table 9.1 shows the condensed electronic configuration of the elements of group 13, group 14 and group 15.

Table 9.1 : Condensed electronic configuration of elements of groups 13, 14 and 15

Group 13 (Boron family)		Group 14 (Carbon family)		Group 15 (Nitrogen family)	
Element	**Condesed electronic configuration**	**Element**	**Condesed electronic configuration**	**Element**	**Condesed electronic configuration**
$_5$B	$[He]2s^2 2p^1$	$_6$C	$[He]2s^2 2p^2$	$_7$N	$[He]2s^2 2p^3$
$_{13}$Al	$[Ne]3s^2 3p^1$	$_{14}$Si	$[Ne]3s^2 3p^2$	$_{15}$P	$[Ne]3s^2 3p^3$
$_{31}$Ga	$[Ar]3d^{10} 4s^2 4p^1$	$_{32}$Ge	$[Ar]3d^{10} 4s^2 4p^2$	$_{33}$As	$[Ar]3d^{10} 4s^2 4p^3$
$_{49}$In	$[Kr]4d^{10} 5s^2 5p^1$	$_{50}$Sn	$[Kr]4d^{10} 5s^2 5p^2$	$_{51}$Sb	$[Kr]4d^{10} 5s^2 5p^3$
$_{81}$Tl	$[Xe]4f^{14} 5d^{10} 6s^2 6p^1$	$_{82}$Pb	$[Xe]4f^{14} 5d^{10} 6s^2 6p^2$	$_{83}$Bi	$[Xe]4f^{14} 5d^{10} 6s^2 6p^3$

Problem 9.1 : Atomic numbers of the group 13 elements are in the order B < Al < Ga < In < Tl. Arrange these elements in increasing order of ionic radii of $M^{3\oplus}$.

Solution : The given elements are in an increasing order of atomic number. As we go down the group 13, their general outer electronic configuration is ns^2np^1. $M^{3\oplus}$ is formed by removal of three electrons from the outermost shell 'n'. In the $M^{3\oplus}$ the 'n-1' shell becomes the outermost. Size of the added 'n-1' shell increases down the group. Therefore the ionic radii of $M^{3\oplus}$ also increase down the group as follows :

$B^{3\oplus} < Al^{3\oplus} < Ga^{3\oplus} < In^{3\oplus} < Tl^{3\oplus}$

Problems 9.2 Why the atomic radius of Gallium is less than that of aluminium ?

Solution : Atomic radius increases down the group due to added new shell. 'Al' does not have 'd' electrons. As we go from Al down to 'Ga' the nuclear charge increase by 18 units. Out of the 18 electrons added, 10 electrons are in the inner 3d subshell. 'd' Electrons offer poor shielding effect. Therefore, the effects of attraction due to increased nuclear charge is experienced prominently by the outer electrons of 'Ga' and thus its atomic radius becomes smaller than that of 'Al'.

9.3 Trends in atomic and physical properties of elements of groups 13, 14 and 15. : The elements of group 13 show a wide variation in properties. In group 13 boron is a metalloid.It is glossy and hard solid like metal but a poor electrical conductor (like nonmetals). The other elements in this group are fairly reactive metals. Aluminium is the third most abundant element in the earth's crust. Some physical and atomic propeties of group 13 elements are given in Table 9.2

Table 9.2 : Physical properties of elements of group 13

Element	Atomic number	Atomic mass	Atomic radius (pm)	Ionic radius (pm) $M^{3\oplus}$	Ionization enthalpy (kJ mol^{-1})			Electronegativity	Density (g/cm^3)	Melting point (K)	Boiling point (K)
					1^{st}	2^{nd}	3^{rd}				
B	5	10.81	88	27	801	2427	3659	2.0	2.35	24.53	3923
Al	13	26.98	143	53.5	577	1816	2744	1.5	2.70	933	2740
Ga	31	69.72	135	62.0	579	1979	2962	1.6	5.90	303	2676
In	49	114.82	167	80.0	558	1820	2704	1.7	7.31	430	2353
Tl	81	204.38	170	88.5	589	1971	2877	1.8	11.85	576	1730

Problem 9.3 : The values of the first ionization enthalpy of Al, Si and P are 577, 786 and 1012 $kJmol^{-1}$ respectively. Explain the observed trend.

Solution : The trend shows increasing first ionization enthalpy from Al to Si to P. Al, Si and P belong to 13 period in the periodic table. They have same valence shell. Due to the increased nuclear charge electrons in the valence shell are more tightly held by the nucleus as we go from Al to Si to P. Therefore more energy is required to remove an electron from its outermost shell.

Table 9.3 enlists atomic and physical properties of the elements of carbon family (group 14). In this group all the three traditional types of elements are present. Carbon is a nonmetal, silicon is a metalloid which is brittle like nonmetal, it is hard and has metallic luster. Germanium is also brittle but hard and lustrous metalloid. Tin or lead down the group are corrosion resistant and moderately reactive.

Table 9.3 : Some atomic and physical properties of group 14 elements

Element	Atomic number	Atomic mass	Atomic radius (pm)	Ionic radius (pm) $M^{3\oplus}$	Ionization enthalpy (kJ mol^{-1})				Electro-negativity	Density (g/cm^3)	Melting point (K)	Boiling point (K)
					1^{st}	2^{nd}	3^{rd}	4^{th}				
C	6	12.01	77		1086	2352	4620	6220	2.5	3.51	4373	
Si	14	28.09	118	40	786	1577	3228	4354	1.8	2.34	1693	3550
Ge	32	72.60	122	53	761	1537	3300	4400	1.8	5.32	1218	3123
Sn	50	118.71	140	69	708	1411	2942	3929	1.8	7.26	505	2896
Pb	82	207.2	146	78	715	1450	3081	4082	1.9	11.34	600	2024

Table 9.4 : Some atomic and physical properties of group 15 elements

Element	Atomic number	Atomic mass	Atomic radius (pm)	Ionic radius (pm)	Ionization enthalpy (kJ mol^{-1})			Electronegativity	Density (g/cm^3)	Melting point (K)	Boiling point (K)
					1st	2nd	3rd				
N	7	14.01	70	171 ($M^{3\ominus}$)	1402	2856	4577	3.0	0.879	6.3	77.2
P	15	30.97	110	212 ($M^{3\ominus}$)	1012	1903	2910	2.1	1.823	317	554
As	33	74.92	121	222($M^{3\ominus}$)	947	1798	2736	2.0	5.778	1089	-
Sb	51	121.75	141	76 ($M^{3\oplus}$)	834	1595	2443	1.9	6.697	904	1860
Bi	83	208.98	148	103($M^{3\oplus}$)	703	1610	2466	1.9	9.808	544	1837

Group 15 is the nitrogen family. Table 9.4 shows atomic and physical properties of the elements of group 15. This group also include the three traditional types of elements: The gaseous nitrogen and brittle phosphorous are nonmetals. Arsenic and antimony are metalloids while bismuth is moderately reactive metal.

9.4 Chemical properties of the elements of the groups 13,14 and 15

9.4.1 Oxidation state : Oxidation state is the primary chemical property of all elements. The highest oxidation state exhibited by the p-block elements is equal to total number of valence electrons (sum of s- electrons and p-electrons). This is sometimes called the group oxidation state. In boron, carbon and nitrogen families the group oxidation state is the most stable oxidation state for the lighter elements. Besides, the elements of groups 13, 14 and 15 exhibit other oxidation states which are lower than the group oxidation state by two units. The lower oxidation states become increasingly stable as we move down to heavier elements in the groups. Table 9.5 shows various oxidation states exhibited by elements belonging to these groups.

Remember

The increased stability of the oxidation state lowered by 2 units than the group oxidation state in heavier p-block elements is due to **inert pair effect**. In these elements, the two s-electrons are involved less readily in chemical reactions. This is because the s-electrons of valence shell in p-block elements experience poor shielding than valence p- electron, due to ten inner d-electrons.

Table 9.5 : Oxidation states of the elements of groups 13, 14 and 15

Group	13	14	15
Outer electronic configuration	$ns^2\ np^1$	$ns^2\ np^2$	$ns^2\ np^3$
Group oxidation state	+3	+4	+5
Other oxidation states	+1	+2, -4	+3, -3
Examples of stable compounds	BF_3, $AlCl_3$, $GaCl_3$, $InCl_3$, TlBr	CH_4, CO_2, CCl_4, $SiCl_4$, $GeCl_4$, $SnCl_2$, $PbCl_2$	N_2O_5, NH_3, NF_3, PH_3, PCl_5, AsH_3, SbH_3, $SbCl_3$, $BiCl_3$

Problem 9.4 : Why $Tl^{\oplus 1}$ ion is more stable than $Tl^{\oplus 3}$?

Solution : Tl is a heavy element which belongs to group 13 of the p-block. The common oxidation state for this group is 3. In p-block, the lower oxidation state is more stable for heavier elements due to inert pair effect . Therefore, $Tl^{\oplus 1}$ ion is more stable than $Tl^{\oplus 3}$ ion.

9.4.2 Bonding in compounds of group 13, 14 and 15 elements : The lighter elements in groups 13, 14 and 15 have small atomic radii and high ionization enthalpy values. They form covalent bonds with other atoms by overlapping of valence shell orbitals. As we move down the group, the ionization enthalpies are lowered. The atomic radii increase since the valence shell orbitals are more diffused. The heavier elements in these group tend to form ionic bonds. The first member of these groups belongs to second period and do not have d orbitals. B, C and N cannot expand their octet. The subsequent elements in the group possess vacant d orbital in their valence shell, which can expand their octet forming a variety of compounds.

9.4.3 Reactivity towards air/oxygen

a. Group 13 elements : Elements of group 13 on heating with air or oxygen produce oxide of type E_2O_3 (where E = element)

$4\ E\ (s) + 3O_2(g) \xrightarrow{\Delta} 2\ E_2O_3\ (s)$

$2\ E\ (s) + N_2\ (g) \xrightarrow{\Delta} 2\ EN\ (s)$

b. Group 14 elements : The elements of group 14 on heating in air or oxygen form oxide of the type EO and EO_2 in accordance with the stable oxidation state and availability of oxygen.

$E\ (s) + 1/2\ O_2(g) \xrightarrow{\Delta} EO$

$E\ (s) + O_2\ (g) \xrightarrow{\Delta} EO_2$

c. Group 15 elements : The elements of group 15 on heating in air or oxygen forms two types of oxide E_2O_3 and E_2O_5.

$P_4 + 3\ O_2 \longrightarrow P_4O_6$

$P_4 + 5\ O_2 \longrightarrow P_4O_{10}$

$As_4 + 3\ O_2 \longrightarrow As_4O_6$

$2Bi + 3\ O_2 \longrightarrow Bi_2O_3$

Increase in metallic character down all these groups 13, 14 and 15 reflects their oxides which gradually vary from acidic through amphoteric to basic. (see Table 9.6)

The nature of stable oxides from groups 13, 14 and 15 are given in Table 9.6.

Table 9.6 : Nature of stable oxides of groups 13, 14 and 15 elements

Group	Element	Oxide	Nature
13	B	B_2O_3	Acidic
	Al	Al_2O_3	Amphoteric
	Ga	Ga_2O_3	Amphoteric
	In	In_2O_3	Basic
	Tl	Tl_2O_3	Basic
14	C	CO_2	Acidic
	Si	SiO_2	Acidic
	Ge	GeO_2	Acidic
	Sn	SnO_2	Amphoteric
	Pb	PbO_2	Amphoteric
15	N	N_2O_5	Acidic
	P	P_2O_5	Acidic
	As	As_4O_6	Amphoteric
	Sb	Sb_2O_3	Amphoteric
	Bi	Bi_2O_3	Basic

Do you know ?

Boron nitride is also called inorganic graphite.

9.4.4 Reaction with water

Most of the elements of groups 13,14 and 15 are **unaffected by water**. Aluminium reacts with water on heating and forms hydroxide while tin reacts with steam to form oxide.

$2\ Al\ (s) + 6\ H_2O\ (l) \xrightarrow{\Delta} 2\ Al\ (OH)_3\ (s) + 3\ H_2\ (g)$

$Sn\ (s) + 2\ H_2O\ (g) \xrightarrow{\Delta} SnO_2\ (s) + 2\ H_2\ (g)$

Lead is unaffected by water, due to formation of a protective film of oxide.

Do you know ?

Phosphorous is stored under water because it catches fire when exposed to air.

9.4.4 Reaction with halogens

All the elements of **group 13** react directly with halogens to form trihalides (EX_3). Thallium is an exception which forms mono halides (TlX)

$2\ E\ (s) + 3\ X_2\ (g) \longrightarrow 2\ EX_3\ (s)$

All the elements of **group 14** (except carbon) react directly with halogens to form

tetrahalides (EX_4). The heavy elements Ge and Pb form dihalides as well. Stability of di halides increases down the group. (Refer to 9.3.1, inert pair effect). The ionic character of halides also increases steadily down the group.

Problem 9.5 : $GeCl_4$ is more stable than $GeCl_2$ while $PbCl_2$ is more stable than $PbCl_4$. Explain.

Solution : Ge and Pb are the 4th and 5th period elements down the group 14. The group oxidation state of group 14 is 4 and the stability of other oxidation state, lower by 2 units, increases down the group due to inert pair effect. The stability of the oxidation state 2 is more in Pb than in Ge.

Elements of the **group 15** reacts with halogens to form two series of halides: EX_3 and EX_5 . The pentahalides possess more covalent character due to availability of vacant d orbitals of the valence shell for bonding. (Nitrogen being second period element, does not have d orbitals in its valence shell, and therefore, does not form pentahalides). Trihalides of the group 15 elements are predominantly covalent except BiF_3. The only stable halide of nitrogen is NF_3.

Problem 9.6 : Nitrogen does not form NCl_5 or NF_5 but phosphorous can. Explain.

Solution : Phosphorous and other members of the group can make use of d-orbitals in their bonding and thus compounds MX_3, as well MX_5 are formed Nitrogen can not form NCl_5 or NF_5 since it is void of d-orbitals in its second shell.

9.5 Catenation : The property of self linking of atoms of an element by covalent bonds to form chains and rings is called catenation. The catenation tendency of an element depends upon the strength of the bond formed.

Among the group 14 elements, carbon shows the maximum tendency for catenation because of the stronger C - C bond (348 kJ mol^{-1})

The order of catenation of group 14 elements is C >> Si > Ge = Sn. Lead does not show catenation.This can be clearly seen from the bond enthalpy values.

Bond	Bond enthalpy ($kJmol^{-1}$)
C -C	348
Si - Si	297
Ge - Ge	260
Sn - Sn	240

Can you recall?

What is common between diamond and graphite?

9.6 Allotropy : When a solid element exists in different crystalline forms with different physical properties such as colour, density, melting point, etc. the phenomenon is called allotropy and individual crystalline forms are called allotropes. Diamond and graphite are well known allotropes of carbon. Fullerenes, graphene and carbon nanotubes are other allotropes of carbon. Elements such as boron, bismuth, silicon, etc. of group 13, 14, and 15 exhibit allotropy. In this chapter we are going to look at some aspects of allotropes of carbon and phosphorous .

9.6.1 Allotropes of Carbon :

a. Diamond : In diamond each carbon atom is linked to four other carbon atoms (via. sp^3 hybrid orbitals) in tetrahedral manner.

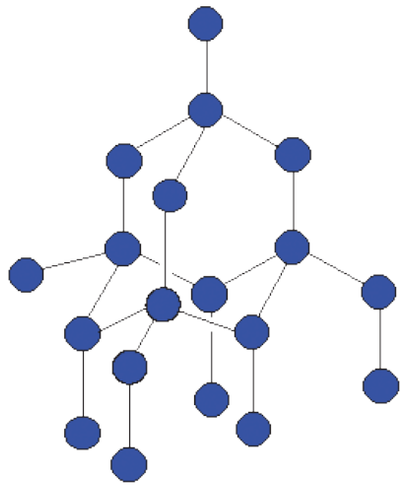


Fig 9.1 Structure of diamond

The C-C bond distance is 154 pm. The tetrahedra are linked together forming a three dimensional network structure (Fig. 9.1) involving strong C-C single bonds. Thus diamond is the hardest natural substance with abnormally high melting point (3930 ^{0}C). Diamond is bad conductor of electricity.

Uses : Diamond is used

- for cutting glass and in drilling tools.
- for making dies for drawing thin wire from metal.
- for making jewellery.

b. Graphite : Graphite is composed of layers of two dimensional sheets of carbon atoms (Fig. 9.2) each being made up of hexagonal net of sp^2 carbons bonded to three neighbours forming three sigma bonds. The fourth electron is in the unhybrid p-orbital of each carbon. The p-orbitals on all the carbons are parallel to each other. These overlap laterally to form π bonds. The π electrons are delocalised over the whole layer. The C- C bond length in graphite is 141.5 pm. The individual layers are held by weak van der Waals forces and separated by 335 pm. This makes graphite soft and slippery.

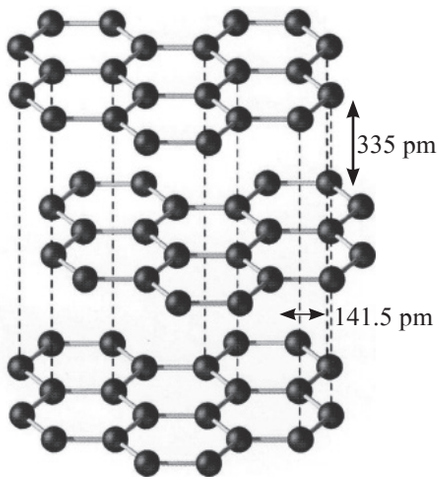


Fig 9.2 Structure of graphite

Remember

Graphite is thermodynamically most stable form (allotrope) of carbon.

c. Fullerene : Fullerenes are alltropes of carbon in which carbon molecules are formed by linking a definite numbers of carbon atoms. For example : C_{60}. Fullerenes are produced, when an electric arc is struck between the graphite electrodes in an inert atmosphere of argon or helium. The soot formed contains significant amount of C_{60} fullerene and smaller amounts of other fullerenes C_{32}, C_{50}, C_{70} and C_{84}.

C_{60} has a shape like soccer ball and called Buckminsterfullerene or bucky ball. (Fig. 9.3) It contains twenty hexagonal and twelve pentagonal fused rings of carbons.

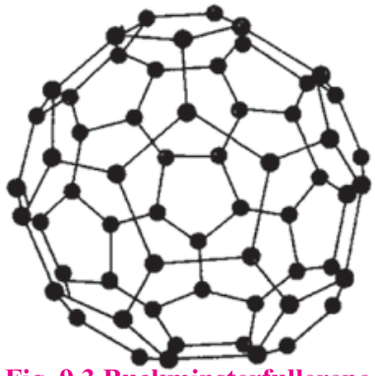


Fig. 9.3 Buckminsterfullerene

Unlike diamond and graphite, the C_{60} fullerene structure exhibits two distinct distances between the neighbouring carbons, 143.5 pm and 138.3 pm. Fullerenes are covalent molecules and soluble in organic solvents. Fullerene C_{60} reacts with group 1 metals forming solids such as K_3C_{60}. The compound K_3C_{60} behaves as a superconductor below 18 K, which means that it conducts electric current with zero resistance.

d. Cabon nanotubes : Carbon nanotubes are cylindrical in shape, consisting of rolled-up graphite sheet (Fig. 9.4). Nanotubes can be single-walled (SWNTs) with a diameter of less than 1 nm or multi-walled (MWNTs) with

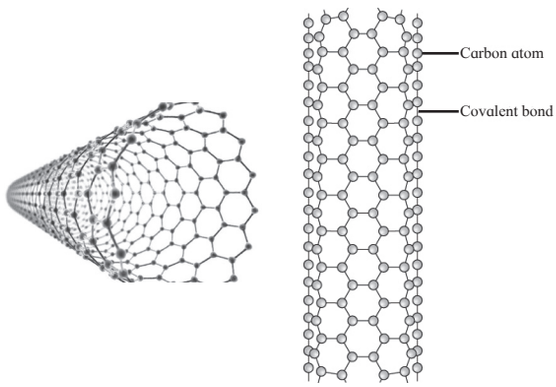


Fig. 9.4 Carbon nanotubes

diameter reaching more than 100 nm. Their lengths range from several micrometres to millimetres.

Carbon nanotubes are robust. They can be bent, and when released, they will spring back to the original shape.

Carbon nanotubes have high electrical and heat conductivities and highest strength to weight ratio for any known material to date. The researchers of NASA are working on combining carbon nanotubes with other matertials to obtain composites those can be used to build light weight space craft.

e. Graphene : Isolated layer of graphite is called graphene (Fig. 9.5). Graphene sheet is a two dimensional solid. Graphene has unique electronic properties.

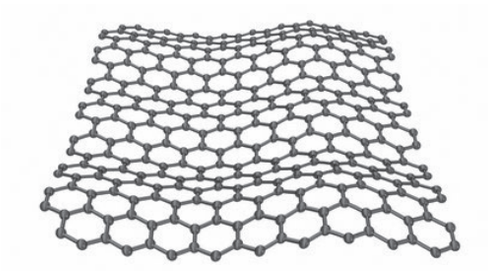


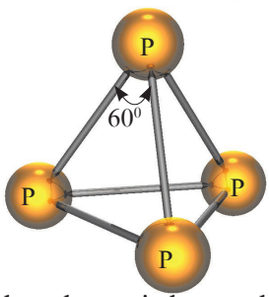
Fig. 9.5 Graphene

Do you know ?

The discovery of graphene was awarded with the Nobel prize to Geim and Novoselov (2010).

9.6.2 Allotropes of phosphorus : Phosphorus is found in different allotropic forms, the important ones being white and red phosphorus.

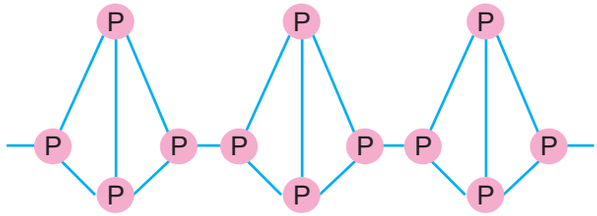
a. White (yellow) phosphorus : White (yellow) phosphorus consists of discrete tetrahedral P_4 molecules. The P-P-P bond angle is 60^o.



White phosphorus is less stable and hence more reactive, because of angular strain in the P_4 molecule.

- It is translucent white waxy solid.
- It glows in dark (chemiluminescence).
- It is insoluble in water but dissolves in boiling NaOH solution.
- It is poisonous.

b. Red phosphorus : Red phosphorus consists of chains of P_4 tetrahedra linked together by covalent bonds. Thus it is polymeric in nature.



- It is stable and less reactive.
- It is odourless. It possesses iron grey lustre
- It does not glow in dark.
- It is insoluble in water.
- It is non poisonous.

Remember

Red phosphorus is prepared by heating white phosphorus at 573 K in an inert atmosphere.

9.7 Molecular structures of some important compounds of the group 13, 14 and 15 elements

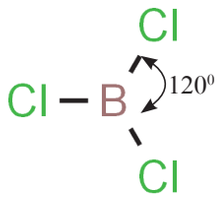
Can you recall?

- Which element from the following pairs has higher ionization enthalpy? B and Tl, N and Bi
- Does Boron form covalent compounds or ionic ?

You have seen in section 9.2 that lighter elements of groups 13, 14 and 15 have higher ionization enthalpy and because of smaller atomic radius do not form cation readily. These elements form covalent compounds. Covalent molecules have definite shape described with the help of bond lengths and bond angles. Inorganic molecules are often represented by molecular formulae indicating their elemental composition.

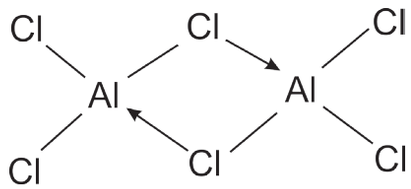
In the case of covalent inorganic molecules, the reactivity is better understood from their structures. In this section we will consider molecular structures of common compounds of elements of groups 13,14 and 15.

9.7.1 Boron trichloride (BCl_3) : Boron trichloride (BCl_3) is covalent. Here boron atom is sp^2 hybridised having one vacant unhybridised p orbital. B in BCl_3 has incomplete octet. The BCl_3 is nonpolar trigonal plannar molecule as shown.



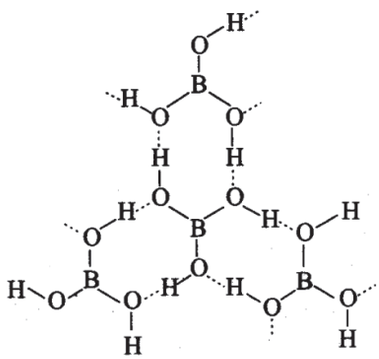
9.7.2 Aluminium Chloride ($AlCl_3$) :

Aluminium atom in aluminium chloride is sp^2 hybridised, with one vacant unhybrid p orbital. Aluminium Chloride ($AlCl_3$) exists as the dimer (Al_2Cl_6) formed by overlap of vacant 3d orbital of Al with a lone pair of electrons of Cl.



9.7.3 Orthoboric acid / boric acid (H_3BO_3) :

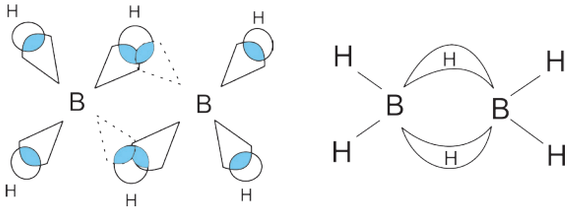
The orthoboric acid has central boron atom bound to three –OH groups. The solid orthoboric acid has layered crystal structure in which trigonal planar $B(OH)_3$ units are joined together by hydrogen bonds.



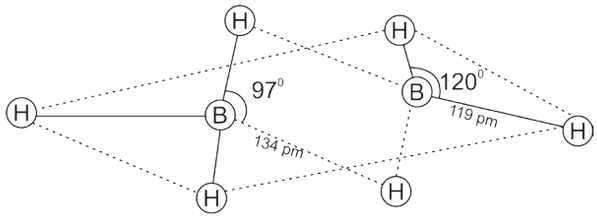
Orthoboric acid

9.7.4 Diborane (B_2H_6) : Boron has only three valence electron. In diborane each boron atom is sp^3 hybridized. Three of such hybrid orbitals are half filled, the fourth sp^3 hybrid orbital is vacant.

The two half filled sp^3 hybrid orbitals of each B atom overlap with 1s orbitals of two H atoms and form four B-H covalent bonds. Hydrogen atoms are located at the terminal. Besides, there are **2-centre - 2-electron** bonds where '1s' orbital of each of the remaining two H atoms simultaneouly overlap with half filled hybrid orbital of one B atom and the vacant hybrid orbital of the other B atom. This type of overlap produces two three centred - two electron bonds (3 c - 2e) or banana bonds. Hydrogen atoms involved in (3 c - 2 e) bonds are the bridging H- atoms. In diborane two B atoms and four terminal H atoms lie in one plane, while the two bridging H atoms lie symmetrically above and below this plane.



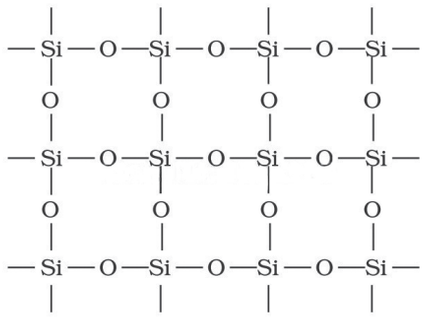
(3 centred - 2 electron bonds)



Bonding and structure of diborane

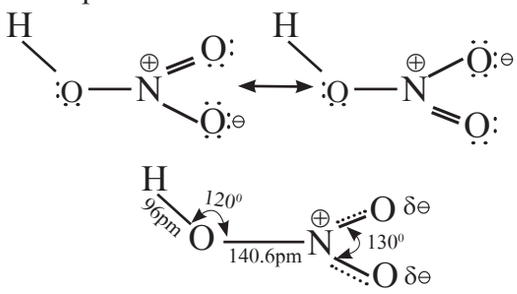
9.7.5 Silicon dioxide (SiO_2) : Silicon dioxide is commonly known as silica. Quartz, cristobalite and tridymite are different crystalline forms of silica. They are inter-convertible at a suitable temperature.

Silicon dioxide (silica) is a covalent three dimensional network solid, in which each silicon atom is covalently bound in tetrahedral manner to four oxygen atoms. The crystal contains eight membered rings having alternate silicon and oxygen atoms.



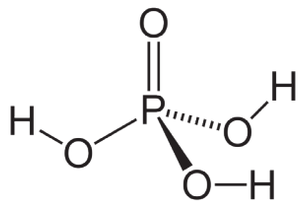
Structure of SiO_2

9.7.6 Nitric acid (HNO_3) : Nitric acid is a strong, oxidising mineral acid. The central nitrogen atom is sp^2 hybridised. HNO_3 exhibits resonance phenomenon.



Resonance Hybrid of HNO_3

9.6.7 Orthophosphoric acid/phosphoric acid (H_3PO_4) : Phosphorus forms number of oxyacids. Orthophosphoric acid is a strong non toxic mineral acid. It contains three ionizable acidic hydrogens. The central phosphorous atom is tetrahedral.



Try this

Find out the structural formulae of various oxyacids of phosphorus.

9.8 Chemistry of notable compounds of elements of groups 13, 14 and 15

9.8.1 Borax ($Na_2B_4O_7$) : It is one of the most important boron compound. The crystalline borax has formula $Na_2B_4O_7.10H_2O$ or $Na_2[B_4O_5(OH)_4].8H_2O$.

Borax naturally occurs as tincal (which contains about 90% borax) in certain inland lakes in India, Tibet and California (U.S.A).

Preparation :

Borax is prepared from the mineral colemanite by boiling it with a solution of sodium carbonate.

$$\underset{\text{Colemanite}}{Ca_2B_6O_{11}} + 2\,Na_2CO_3 \xrightarrow{\Delta} \underset{\text{Borax}}{Na_2B_4O_7} + 2\,NaBO_2 + 2\,CaCO_3\downarrow$$

Properties

i. Borax is white crystalline solid.

ii. Borax dissolves in water and gives alkaline solution due to its hydrolysis.

$$Na_2B_4O_7 + 7\,H_2O \longrightarrow 2NaOH + \underset{\text{Ortho boric acid}}{4\,H_3BO_3}$$

iii. On heating borax first loses water molecules and swells. On further heating it turns into a transparant liquid, which solidifies into glass like material known as borax bead.

$$Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underset{\text{Borax bead}}{2\,NaBO_2 + B_2O_3}$$

The borax bead consisting sodium metaborate and boric anhydride is used to detect coloured transition metal ions, under the name borax bead test. For example, when borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured $Co(BO_2)_2$ bead is formed.

iv. Borax when heated with ethyl alcohol and concentrated H_2SO_4 acid, give volatile vapours of triethyl borate which burn with green edged flame.

$$Na_2B_4O_7 + H_2SO_4 + 5\,H_2O \longrightarrow Na_2SO_4 + 4\,H_3BO_3$$

$$H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\text{Triethyl borate}}{B(OC_2H_5)_3} + 3\,H_2O$$

Remember

The above reaction is used as a test for detection and removal of borate in qualitative analysis.

Uses : Borax is used

i. in the manufacture of optical and hard borosilicate glass.
ii. as a flux for soldering and welding.
iii. as a mild antiseptic in the preparation of medical soaps
iv. in quanlitative analysis for borax bead test.
v. as a brightner in washing powder.

9.8.2 Silicones : Silicones represent organo-silicon polymers where $\{R_2SiO\}$ is a repeating unit. These are held together by $-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-$ linkage. Silicones have empirical formula R_2SiO ($R = CH_3$ or C_6H_5 group). This is similar to that of ketone (R_2CO) and hence the name silicones.

Preparation : The starting materials for manufacture of silicones are alkyl or aryl substituted silicon chlorides, $R_nSiCl_{(4-n)}$ where R is alkyl or aryl group.

When methyl chloride reacts with silicon in the presence of copper catalyst at a temperature 573 K, various types of methyl substituted chlorosilane of formulae $MeSiCl_3$, Me_2SiCl_2, Me_3SiCl with small amounts of Me_4Si are formed.

$$2CH_3Cl + Si \xrightarrow[573\ K]{Cu\ powder} Cl-\overset{CH_3}{\underset{CH_3}{Si}}-Cl$$

$$Cl-\overset{CH_3}{\underset{CH_3}{Si}}-Cl \xrightarrow[-2HCl]{2H_2O} HO-\overset{CH_3}{\underset{CH_3}{Si}}-OH$$

$$n\ HO-\overset{CH_3}{\underset{CH_3}{Si}}-OH \xrightarrow[-H_2O]{Polymerisation} \left(-\overset{CH_3}{\underset{CH_3}{Si}}-O-\right)_n$$

Hydrolysis of dimethyl dichlorosilane, $(CH_3)_2SiCl_2$ followed by condensation polymerisation yields straight chain silicone polymers.

The chain length of polymer can be controlled by adding $(CH_3)_3$ SiCl at the end as shown :

$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left(\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_n-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

Properties of silicones

i. They are water repellant.
ii. They have high thermal stability.
iii. They are good electrical insulators.
iv. They are resistant to oxidation and chemicals.

Uses of silicones

They are used as

i. insulating material for electrical appliences
ii. water proofing of fabrics
iii. sealant
iv. high temperature lubricants
v. For mixing in paints and enamels to make them resistant to high temperature, sunlight and chemicals.

9.8.3 Ammonia (NH_3)

Preparation

1. Ammonia is present in small quantities in air and soil where it is formed by the decomposition of nitrogeneous organic matter such as urea.

$$\underset{\text{(urea)}}{NH_2CONH_2} + 2\ H_2O \longrightarrow (NH_4)_2CO_3 \rightleftharpoons 2\ NH_3 + H_2O + CO_2$$

2. Ammonia is prepared on laboratory scale, by decomposition of the ammonium salts with calcium hydroxide or caustic soda.

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + 2H_2O$$

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + Na_2SO_4 + 2H_2O$$

3. On the large scale ammonia is prepared by direct combination of dinitrogen and dihydrogen. (Haber's process)

$$N_2(g) + 2H_2(g) \rightleftharpoons 2NH_3(g); \Delta_fH^\circ = -46.1\ kJ\ mol^{-1}$$

High pressure favours the formation of ammonia. The optimuim conditions for the production of ammonia are high pressure of 200 × 10^5 Pa (200 atm), temperature of ~700 K and use of a catalyst such as iron oxide with trace amounts of K_2O and Al_2O_3. Under these conditions equilibrium attains rapidly.

Properties

a. Physical properties

i. Ammonia is colourless gas with pungent odour.

ii. It has freezing point of 198.4 K and boiling point of 239.7 K.

iii. It is highly soluble in water. The concentrated aqueous solution of NH_3 is called liquor ammonia.

Remember

Ammonia has higher melting point and boiling point, because in the solid and liquid state NH_3 molecules get associated together through hydrogen bonding. Thus some more energy is required to break such intermolecular hydrogen bonds.

b. Chemical properties

i. Basic nature : The aqueous solution of ammonia is basic in nature due to the formation of OH^- ions.

$$NH_3(g) + H_2O(l) \rightleftharpoons NH^{\oplus}_4(aq) + OH^{\ominus}(aq)$$

ii. Ammonia reacts with acids to form ammonium salts.

$$NH_3 + HCl \longrightarrow NH_4Cl$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

iii. Aqueous solution of ammonia precipitates out as hydroxides (or hydrated oxides) of metals from their salt solutions.

$$ZnSO_4(aq) + 2\,NH_4OH(aq) \longrightarrow \underset{\text{White ppt}}{Zn(OH)_2(s)} + (NH_4)_2SO_4(aq)$$

$$FeCl_3(aq) + 2NH_4OH(aq) \longrightarrow Fe_2O_3.xH_2O + NH_4Cl(aq)$$

iv. Complex formation :

The lone pair of electrons on nitrogen the atom facilitates complexation of ammonia with transition metal ions.

$$Cu^{2\oplus}(aq) + 4NH_3(aq) \longrightarrow \underset{\text{deep blue}}{[Cu(NH_3)_4]^{2\oplus}(aq)}$$

$$AgCl(s) + 2NH_3(aq) \longrightarrow \underset{\text{colourless}}{[Ag(NH_3)_2]Cl(aq)}$$

Remember

This reaction is used for the detection of metal ions such as Cu^{2+}, Ag^+.

Uses

Ammonia is used in

i. manufacture of fertilizers such as urea, diammonium phosphate, ammonium nitrate, ammonium sulphate etc.

ii. manufacture of some inorganic compounds like nitric acid.

iii. refrigerant (liq. ammonia).

iv. laboratory reagent in qualitative and quantitative analysis (aq. solution of ammonia)

Remember

Ammonia gives brown ppt with Nessler's reagent (alkaline solution of K_2HgI_4).

$$2\,KI + HgCl_2 \longrightarrow HgI_2 + 2\,KCl$$

$$2\,KI + HgI_2 \longrightarrow K_2HgI_4 \text{ (Nesseler's reagent)}$$

$$2\,K_2HgI_4 + NH_3 + 3\,KOH \longrightarrow \underset{\text{Millon's base (Brown ppt)}}{H_2N\text{-}HgO\text{-}HgI} + 7\,KI + 2\,H_2O$$

Exercises

1. Choose correct option.

A. Which of the following is not an allotrope of carbon ?
   a. bucky ball b. diamond
   c. graphite d. emerald

B. ..... is inorganic graphite
   a. borax b. diborane
   c. boron nitride d. colemanite

C. Haber's process is used for preparation of .....
   a. HNO_3 b. NH_3
   c. NH_2CONH_2 d. NH_4OH

D. Thallium shows different oxidation state because .....
   a. of inert pair effect
   b. it is inner transition element
   c. it is metal
   d. of its high electronegativity

E. Which of the following shows most prominent inert pair effect ?
   a. C b. Si
   c. Ge d. Pb

2. Identify the group 14 element that best fits each of the following description.

A. Non metallic element
B. Form the most acidic oxide
C. They prefer +2 oxidation state.
D. Forms strong π bonds.

3. Give reasons.

A. $Ga^{3\oplus}$ salts are better reducing agent while $Tl^{3\oplus}$ salts are better oxidising agent.

B. $PbCl_4$ is less stable than $PbCl_2$

4. Give the formula of a compound in which carbon exhibit an oxidation state of

A. +4 B. +2 C. -4

5. Explain the trend of the following in group 13 elements :

A. atomic radii B. ionization enthalpy
C. electron affinity

6. Answer the following

A. What is hybridization of Al in $AlCl_3$?
B. Name a molecule having banana bond.

7. Draw the structure of the following

A. Orthophosphoric acid
B. Resonance structure of nitric acid

8. Find out the difference between

A. Diamond and Graphite
B. White phosphorus and Red phosphorus

9. What are silicones ? Where are they used ?

10. Explain the trend in oxidation state of elements from nitrogen to bismuth.

11. Give the test that is used to detect borate radical is qualitative analysis.

12. Explain structure and bonding of diborane.

13. A compound is prepared from the mineral colemanite by boiling it with a solution of sodium carbonate. It is white crystalline solid and used for inorganic qualitative analysis.

a. Name the compound produced.
b. Write the reaction that explains its formation.

14. Ammonia is a good complexing agent. Explain.

15. State true or false. Correct the false statement.

A. The acidic nature of oxides of group 13 increases down the graph.
B. The tendency for cantenation is much higher for C than for Si.

16. Match the pairs from column A and B.

A	B
BCl_3	Angular molecule
SiO_2	linear covalent molecule
CO_2	Tetrahedral molecule
	Planar trigonal molecule

17. Give the reactions supporting basic nature of ammonia.

18. Shravani was performing inorganic qualitative analysis of a salt. To an aqueous solution of that salt, she added silver nitrate. When a white precipitate was formed. On adding ammonium hydroxide to this, she obtained a clear solution. Comment on her observations and write the chemical reactions involved.

Activity :

Prepare models of allotropes of carbon and phosphorous.