Government of Telangana

313

INTERMEDIATE

CHEMISTRY

1

TELANGANA OPEN SCHOOL SOCIETY, HYDERABAD

313

Intermediate (TOSS) Course
Senior Secondary Course

CHEMISTRY

1

(CORE MODULES)

Telangana Open School Society (TOSS), Hyderabad

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SENIOR SECONDARY COURSE
INTERMEDIATE (TOSS) COURSE
CHEMISTRY-ADDITIONAL CURRICULUM

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FOREWORD

Dear Learner,

The Department of Education is giving equal importance to non-formal education through Open Distance Learning (ODL) mode of the lines of formal education. This is the first State Open School established in the country in the year 1991 offering courses up to Upper primary Level till 2008. From the academic year 2008-2009 SSC Course was introduced and Intermediate Course from the year 2010-2011. The qualified learners from the Open School are eligible for both higher studies and employment. So far **4,88,853** learners were enrolled in the Open Schools and **2,86,663** learners have successfully completed their courses. The Open School system is providing a second chance of learning for those who could not fulfil their dreams of formal education.

Government of Telangana is keen in providing quality education by supplying study materials along with the text books to enable the learners to take the exam with ease. Highly experienced professionals and subject experts are involved in preparing curriculum and study material based on subject wise blue prints. The study material for the academic year 2023-24 is being printed and supplied to all the learners throughout the state.

Welcome to the Revised Chemistry Course of Telangana Open Schooling System (TOSS) based on the National Institute of Open Schooling and the National Common Core Curriculum. This Course has four volumes I, II and III consist of theory portion and volume IV is a practical manual. The first book is in your hands. This book comprises one lesson of module 1 on Some Basic Concepts of Chemistry, three lessons of Module 2 on Atomic Structure and Chemical Bonding, five lessons of Module 3 on States of Matter, two lessons of Module 4 on Chemical Energetics and five lessons of module 5 on Chemical Dynamics. In Module 1 you will learn about the various units used to calculate the number of atoms, molecules and ions involved in chemical reactions. Module 2 will enlighten you about what lies inside the atoms and the different types of chemical bonds through which atoms combine. Module 3 deals with the various aspects of three states of matter *viz*, solid, liquid and gas. You will also learn about the properties of solutions and colloids. Module 4 deals with chemical reactions accompanied with energy changes and basic concepts like internal energy, enthalpy, entropy and spontaneity. Module 5 highlights on the Characteristics of Chemical Dynamics, catalysis inter conversion of Chemical energy into electrical energy in electrochemistry, electrochemical cells and fuel cell. We hope you will enjoy the course and find it interesting.

WE wish the learners of Open School make best use of the study material to brighten their future opportunities and rise up to the occasion in building Bangaru Telangana.

Wishing you happy chemistry learning ….

With best wishes.....

-WRITERS

HOW TO USE THE STUDY MATERIAL

Your learning material has been developed by a team of chemistry experts in open and distance learning. A consistent format has been developed for self-study. The following points will give you an idea on how to make best use of the print material.

Title is an advance organiser and conveys an idea about the contents of the lesson. *Reflect on it.*

Introduction highlights the contents of the lesson and correlates it with your prior knowledge as well as the natural phenomena in operation in our immediate environment. *Read it thoroughly.*

Objectives relate the contents to your desired achievements after you have learnt the lesson. Remember these.

Content of the lesson has been divided into sections and sub-sections depending on thematic unity of concepts. Read the text carefully and make notes on the side margin of the page. After completing each section, answer intext questions and solve numerical problems yourself. This will give you an opportunity to check your understanding. You should continue reading a section till such time that you gain mastery over it. At some places you will find some text in ***italics and bold***. This indicates that it is important. You must learn them.

Solved Examples will help you to understand the concepts and fix your ideas. In fact, problem solving is an integral part of training in physics. Do them yourself and note the main concept being taught through a particular example.

Activities are simple experiments which you can perform at your home or work placeusing readily available (low cost) materials. These will help you to understand physics by doing. Do them yourself and correlate your findings with your observations.

Intext questions are based on the concepts discussed in every section. Answer these questions yourself in the space given below the question and then check your answers with the model answers given at the end of the lesson. This will help you to judge your progress. If you are not satisfied with the quality and authenticity of your answers, turn the pages back and study the section again.

What have you learnt is essentially summary of the learning points for quick recapitulation. You may like to add more points in this list.

Terminal exercises in the form of short, long and numerical question will help you to develop a perspective of the subject, if you answer these meticulously. Discuss your responses with your peers or counsellors.

Answers to in text questions: These will help you to know how correctly you have answered the intext questions.

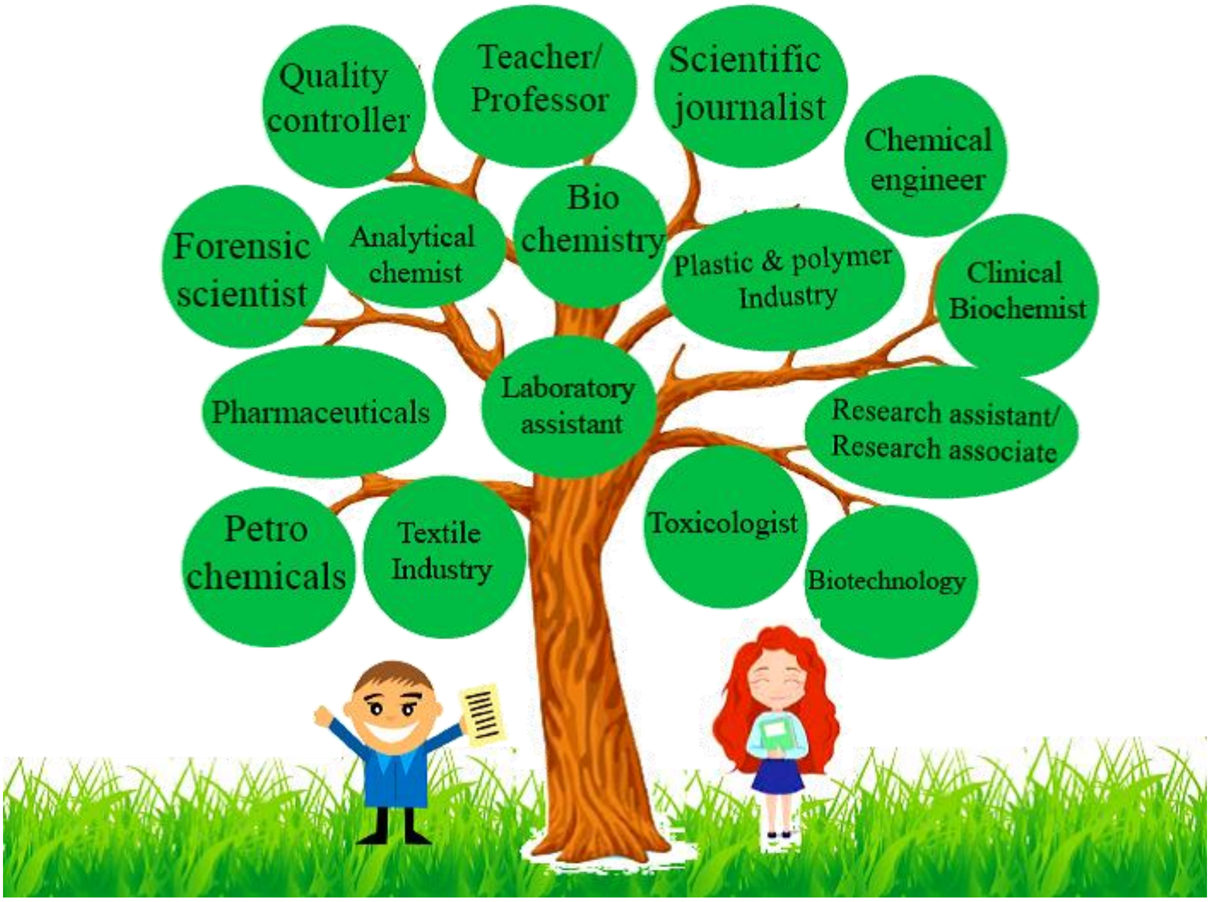
Audio: For understanding difficult or abstract concepts, audio programmes are available on certain content areas. You may listen to these on FM Gyanvani or may buy the CDs from Priced Publication Unit, NIOS.

Video: Video programmes on certain elements related to your subject have been made to clarify certain concepts. You may watch these at your study centre or may purchase these CDs from Priced Publication Unit, NIOS.

www. These are few selected websites that you can access for extended learning. Studying at a distance requires self-motivation, self-discipline and self-regulation. Therefore, you must develop regular study habit. Drawing a daily schedule will help you in this endeavour. You should earmark a well-ventilated and well-lighted space in your home for your study. However, it should not be noisy or distract your concentration from your work.

CAREER OPPORTUNITIES AFTER STUDYING CHEMISTRY

Chemical sciences (Chemistry) offer access to a wide range of careers. Chemistry is the study of substances, their makeup and applications. In fact, it is the study of all materials and is vital to every aspect of our lives. Organic Chemistry, Inorganic Chemistry, Analytical chemistry and Biochemistry are the main branches of chemistry. The career options in chemistry are practically endless! However, employment options depend on how far the education, training and experience taken. A chemistry or biochemistry degree can lead to career paths in professions such as Medicine, pharmacology, agriculture, chemical engineering, forensic science, etc. Some of the important career opportunities after studying chemistry at senior secondary level is as



RATIONALE

According to present scheme of school education at Senior Secondary stage, chemistry emerges out as a separate discipline. It is this stage where major emphasis is to be laid on providing suitable conceptual foundation. The present Senior secondary level Chemistry (313) course at TOSS has now been revised as per the NIOS (National Institute of Open Schooling), Common Core Curriculum developed by COBSE (Council of Boards of School Education) and NCERT (National Council for Educational Research and Training) making it current and need based.

The present chemistry course has been developed basically around the themes: Why do chemical reactions occur? What is the quantitative relationship among reacting constituents in a chemical reaction? How far and how fast will a chemical reaction proceed under a given set of conditions? Can we predict whether a chemical reaction will occur or not? What is the relation between the structure of a chemical substance and its functions/properties? In what way is a chemical reaction relevant for getting new types of substances and materials for daily life and chemical industries? Some interdisciplinary aspects have also been provided to make the course more meaningful and functional.

OBJECTIVES OF THE COURSE

It is expected that a learner will be able to:

Understand the principles, theories and laws of chemistry responsible for various chemical processes/reactions,

- realise the role of chemistry in production of many elements (metals/non-metals) and compounds useful in industries and daily life,
- appreciate the chemical nature of inorganic and organic substances around him/her, choose various vocational, professional and applied courses of his/her choice based on knowledge of chemistry gained.
- Apart from this, the present course also aims at developing the following capacity in the learner:
- perform chemical calculations to know about the chemical reactions and chemical compounds,
- explain chemical reactions, concepts and phenomenon,
- develop awareness about uses and abuses of chemical substances,
- develop skills arranging/setting apparatus, handling apparatus and chemicals properly, and
- analyse and synthesise simple compounds.

SPECIAL FEATURES OF THE COURSE

The academic standard of the present chemistry course in comparable with the chemistry course of any State Education Board or Central Board of Secondary Education. The rationale behind the course is that every lesson has a role to play in understanding the holistic view of chemistry. The present course provides eight modules and a laboratory manual. A student appearing for senior secondary examination is expected to offer all the eight modules and practical.

COURSE STRUCTURE

The Revised Chemistry Course has three parts, I, II and III consist of theory portion and part IV is a practical manual. Part I, II and III of theory portion has eight modules. Part-I consists of five modules namely as: Some basic concepts of chemistry, Atomic Structure and Chemical Bonding, States of matter, Chemical Energetics, and Chemical Dynamics. Part-II consists of three modules namely: Chemistry of Elements and Chemistry of Organic Compounds, Part-III consists of two modules namely: Environmental Chemistry and Chemistry and Industry. Each module is further divided into different lessons.

Overview of the Learning Material

Book - 1

Module - I: Atoms, Molecules and Chemical Arithmetics

01. Mole Concept
02. Chemical Arithmatics

Module - II: Atomic Structure and Chemical Bonding

03. Atomic Structure
04. Periodic Table and Atomic Properties
05. Chemical Bonding

Module - III: State of Matter

06. The Gaseous state
07. The Liquid State
08. The Solid State
09. Solutions
10. Colloids

Module - IV: Chemical Energetics

11.Chemical Thermodynamics
12. Spontaneity of Chemical reactions

Module - V: Chemical Dynamics

13. Chemical Equilibrium
14. Ionic Equilibrium
15. Electro Chemistry
16. Chemical Kinetics
17. Adsorption and Catalysis

Book - 2

Module - VI: Chemistry of Elements

18. Occurance and Extraction of Metals
19. Hydrogen and *s* - block Elements
20. General Characteristics of the *p*-block Elements
21. *p*-block Elements and their Compounds - I
22. *p*-block Elements and their Compounds - II
23. d-block and f-block Elements
24. Coordination Compounds

Module - VII: Chemistry of Organic Compounds

25. Nomenclature and General Principles
26. Hydrocarbons
27. Compounds of Carbon Containing Halogens (Haloalkanes and Haloarenes)
28. Alcohols, Phenols and Ethers
29. Aldehydes, Ketones and CarboxylicAcids
30. Compounds of Carbon Containing Nitrogen
31. Biomlecules

Book - 3

Module VIIIA: Environmental Chemistry

32. Environmental Concerns
33. Air Pollution
34. Water Pollution
35. Heavy Metal Contamination
36. Radioactive Pollution

Module VIIIB: Chemistry and Industry

32. Petrochemicals
33. Polymers
34. Dyes, Paints and Pigments
35. Drugs and Medicines
36. Building Materials

CONTENTS

Module - I

Atoms, Molecules and Chemical Arithmatics

01. Mole Concept

02. Chemical Arithmatics

Chapter 01

MOLE CONCEPT

As you are aware, atoms and molecules are so small that we cannot see them with our naked eyes or even with the help of a microscope. Any sample of matter which can be studied consists of an extremely large number of atoms or molecules. In chemical reactions, atoms or molecules combine with one another in a definite number ratio. Therefore, it would be pertinent if we could specify the total number of atoms or molecules in a given sample of a substance. We use many units in our daily life. For example, we express the number of bananas or eggs in terms of 'dozen'. In chemistry, we use a number unit called a mole which is very large.

Objectives:

After studying this lesson, you will be able to:

- State the need for SI units;
- List base SI units;
- Explain the relationship between mass and number of particles;
- Define Avogadro's constant and state its significance;
- Calculate the molar mass of different elements and compounds and
- Define the molar volume of gases at STP.

1.1. SI Units (Revisited)

Measurement is needed in every walk of life. As you know for every measurement a 'unit' or a 'reference standard' is required. In different countries, different systems of units gradually developed. This created difficulties whenever people of one country had to deal with those of another country. Since scientists had to often use each other's data, they faced a lot of difficulties. For practical use, data had to be first converted into local units, and then only it could be used.

In 1960, the 'General Conference of Weights and Measures’ the international authority on units proposed a new system that was based upon the metric system. This system is called the ''International System of Units' which is abbreviated as SI units from its French name, Le Systeme Internationaled' Unites. You have learned about SI units in your earlier classes also and know that they are based upon seven base units corresponding to seven base physical quantities. Units needed for various other physical quantities can be derived from these base SI units. The seven base SI units are listed in Table1.1

Table 1.1: SI Base Units

Physical Quantity	Name of the SI Unit	Symbol of SI Unit
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric Current	Ampere	A
Temperature	Kelvin	K
Luminous Intensity	candela	cd
Amount of Substance	mole	mol

For measuring very large or very small quantities, multiples or sub-multiples of these units are used. Each one of them is denoted by a symbol which is **prefixed** to the symbol of the unit. For example, to measure long distances we use the unit **Kilometer** which is a multiple of meters, the base unit of length. Here **kilo** is the prefix used for the multiple 10^3. Its symbol is **k** which is prefixed to the symbol of meter, **m**. Thus, a symbol of a kilometer is **km** and

$$1 \text{ km} = 1.0\text{x } 10^3 \text{m} = 1000 \text{ m}$$

Similarly, for measuring small lengths we use centimeters (cm) and millimeters (mm) where

$$1\text{km} = 1.0 \text{ x } 10^{-2} \text{ m} = 0.01 \text{ m}$$

$$1\text{km} = 1.0 \text{ x } 10^{-3} \text{ m} = 0.001 \text{ m}$$

Some prefixes used with SI units are listed in Table 1.2.

Table 1.2: Some Prefixes used with SI Units

Prefix	Symbol	Meaning	Example
Tera	T	10^{12}	1Terameter(Tm)=1.0 x 10^{12}m
Giga	G	10^9	1Gigameter(Tm)=1.0 x 10^9m
Mega	M	10^6	1Megameter(Tm)=1.0 x 10^6m
Kilo	k	10^3	1Kilometer(Tm)=1.0 x 10^3m
Hecto	h	10^2	1Hectometer(Tm)=1.0 x 10^2m
Deca	da	10^1	1Decameter(Tm)=1.0 x 10^1m
Deci	d	10^{-1}	1Decimeter(Tm)=1.0 x 10^{-1}m
Centi	c	10^{-2}	1Centimeter(Tm)=1.0 x 10^{-2}m
Milli	m	10^{-3}	1Millimeter(Tm)=1.0 x 10^{-3}m
Micro	µ	10^{-6}	1Micrometer(Tm)=1.0 x 10^{-6}m
Nano	n	10^{-9}	1Nanometer(Tm)=1.0 x 10^{-9}m
Pico	p	10^{-12}	1Picometer(Tm)=1.0 x 10^{-12}m

Before proceeding further try to answer the following questions:

Intext Questions 1.1

1. Name the SI Unit of mass

....

2. What symbol will represent 1.0×10^2 g?

....

3. Name the prefixes used for (i) 10^2 and (ii) 10^{-9}

....

4. What do the following symbols represent?

i) Ms ....

ii) ms ....

1.2. Relationship between Mass and Number of Particles

Suppose you want to purchase 500 screws. How, do you think, the shopkeeper would give you the desired quantity? By counting the screws individually? No, he would give the screws by weight because it will take a lot of time to count them. If each screw weighs 0.8g, he would weigh 400g screws because it is the mass of 500 screws (0.8 x500 = 400g). You will be surprised to note that the Reserve Bank of India gives the desired number of coins by weight and not by counting. This process of counting by weighing becomes more and more labor-saving as the number of items to be counted becomes large. We can carry out the reverse process also. Suppose we take 5000 very tiny springs (used in watches) and weigh them. If the mass of the springs is found to be 1.5g, we can conclude that mass of each spring is $1.5/5000 = 3 \times 10^{-4}$g.

Thus, we see that mass and number of identical objects or particles are inter-related. Since atoms and molecules are extremely tiny particles it is impossible to weigh or count them individually. Therefore, we need a relationship between the mass and number of atoms and molecules (particles). Such a relationship is provided by 'mole concept'.

1.3. Mole - A Number Unit

Mass of an atom or a molecule is an important property. However, while discussing the quantitative aspects of a chemical reaction, the number of reacting atoms or molecules in more significant than their masses. Let us understand this with the help of the following activity.

Activity 1.1.

Aim: To study whether during a reaction, the reactants react with each other in a simple ratio by mass.

What is required?

China dish, sulfur powder, iron powder, a magnet and a magnifying glass.

What to do?

Mix *1g* each of iron and sulfur powders in a China dish and heat them till the reaction is complete and the mixture becomes a hard mass. Now break it into small pieces. Repeat the procedure with a mixture of *2g* of iron and *1g* of sulfur powder.

What to observe?

- Pieces obtained from the 'reaction mixture containing iron and sulfur in 1:1 ratio by mass (1g each) when observed through a magnifying glass show some yellowish particles of sulfur. When a magnet is brought near them, they are not attracted showing that there is no unreacted iron.
- Pieces obtained from the reaction mixture containing iron and sulfur in 2:1 ratio by mass (*2g* iron and *1g* sulfur) do not show yellow particles of unreacted sulfur but are attracted by the magnet. This shows the presence of some unreacted iron.

Conclusion

You can conclude that iron and sulfur do not react with each other in a simple mass ratio. When taken in 1:1 ratio by mass (Fe:S), some sulfur is left unreacted and when taken in 2:1 ratio by mass (Fe:S) some iron is left unreacted.

Let us now write the chemical equation of this reaction

$$\text{Fe} + \text{S} \rightarrow \text{FeS}$$

From the above chemical equation, it is clear that 1 atom of iron reacts with 1 atom of sulfur to form 1 molecule of iron(II) sulfide (FeS). It means that if we had taken equal *number* of atoms of iron and sulfur, both of them would have reacted completely. Thus, we may conclude that *substances react in a simple ratio by number of atoms or molecules*.

From the above discussion it is clear that the *number* of atoms or molecules of a substance is more relevant than their masses. In order to express their number, we need a number unit. One commonly used number unitis 'dozen', which, as you know, means a collection of 12. Other number units that we use are 'score' (20) and 'gross' (144 or 12 dozen). These units are useful in dealing with small numbers only. The atoms and molecules are so small that even in the minute sample of any substance, their number is extremely large. For example, a tiny dust particle contains about 10^{16} molecules. In chemistry such large numbers are commonly represented by a unit known as **mole**. Its symbol is 'mol' and it is defined as.

A mole is the amount of a substance that contains as many elementary entities (atoms, molecules or other particles) as there are atoms in exactly 0.012 kg or 12g of the carbon-12 isotope.

The term mole has been derived from the Latin word 'moles' which means a 'heap' or a 'pile'. It was first used by the famous chemist Wilhelm Ostwald more than a hundred years ago.

Here you should remember that one mole always contains the **same number of entities,** no matter what the substance is. Thus, *mole* is a number unit for dealing with elementary entities such as atoms, molecules, formula units, electrons etc., just as *dozen* is a number unit for dealing with bananas or oranges. In the next section you will learn more about this number.

1.4. Avogadro's Constant

In the previous section we have learned that a mole of a substance is that amount which contains as many elementary entities as there are atoms in exactly 0.012 kilogram or 12 grams of the carbon-12 isotope. This definition gives us a method by which we can find out the amount of a substance (in moles) if we know the number of elementary entities present in it or *vice versa*. Now the question arises how many atoms are there in exactly 12g of carbon-12.This number is determined experimentally and its currently accepted value is 6.022045×10^{23}. Thus 1mol = 6.022045×10^{23} entities or particles, or atoms or molecules. For all practical purposes this number is rounded off to 6.022×10^{23}.

The basic idea of such a number was first conceived by an Italian scientist **Amedeo Avogadro**. But whenever determined this number it was determined later and is known as Avogadro's constant in his honour.

This number was earlier known as Avogadro's number. This number along with the unit that is, 6.022×10^{23} mol^{-1} is known as Avogadro constant. It is represented by the symbol N_A. Here you should be clear that mathematically a number does not have a unit. Avogadro's number 6.022×10^{23} will not have any unit but Avogadro's constant will have unit of mol^{-1}. Thus Avogadro's constant, $N_A = 6.022 \times 10^{23}$ mol^{-1}.

Significance of Avogadro's Constant

You know that 0.012 kg or 12g of carbon-12 contains its one mole of carbon atoms. A mole may be defined as the amount of a substance that contains 6.022×10^{23} elementary entities like atoms, molecules or other particles. When we say one mole of carbon-12, we mean 6.022×10^{23} atoms of carbon-12 whose mass is exactly 12g. This mass is called the molar mass of carbon-12. The molar mass is defined as the mass (in grams) of 1mole of a substance. Similarly, a mole of any substance would contain 6.022×10^{23} particles or elementary entities. The nature of elementary entity, however, depends upon the nature of the substance as given below:

S. No.	Type of Substance	Elementary Entity
1	Elements like Na, K, Cu Which exist in atomic form	Atom
2	Elements like O, N, H which exist in molecular form (O_2, N_2 H_2)	Molecule
3	Molecular compounds like NH_3, H_2O, CH_4	Molecule
4	Ions like Na^+, Cu^{+2}, Ag^+, Cl^{-1}, O^{-2}	Ion
5	Ionic Compounds Like NaCl, $NaNO_3$, K_2SO_4	Formula Unit

Formula unit of a compound contains as many atoms or ions of different types as is given by its chemical formula. The concept is applicable to all types of compounds. The following examples would clarify the concept.

Formula	Atoms / ions present in one formula unit
H_2O	Two atoms of H and one atom of O
NH_3	One atom of N and three atoms of H
NaCl	One Na^+ ion and one Cl^- ion
$NaNO_3$	One Na^+ ion and one NO_3 ion
K_2SO_4	Two K^+ ions and one SO_4 ion
$Ba_3(PO_4)_2$	Three Ba^{2+} ions and two PO_4 ions

Now, let us take the examples of different types of substances and correlate their amounts and the number of elementary entities in them.

1 mole C = 6.022×10^{23} C atoms
1 mole O_2 = 6.022×10^{23} O_2 molecules
1 mole H_2O = 6.022×10^{23} H_2O molecules
1 mole NaCl = 6.022×10^{23} formula units of NaCl
1 mole Ba^{2+} ions = 6.022×10^{23} Ba^{2+} ions

We may choose to take amounts other than one mole and correlate them with number of particles present with the help of relation:

Number of elementary entities = number of moles x Avogadro's constant

1 mole O2 = $1 \times (6.022 \times 10^{23})$ = 6.022×10^{23} molecules of O_2
0.5 mole O2 = $0.5 \times (6.022 \times 10^{23})$ = 3.011×10^{23} molecules of O_2
0.1 mole O2 = $0.1 \times (6.022 \times 10^{23})$ = 6.022×10^{22} molecules of O_2

Intext Questions 1.2.

1. A sample of nitrogen gas consists of 4.22×10^{23} molecules of nitrogen. How many moles of nitrogen gas are there?

………

2. In a metallic piece of magnesium, 8.46×10^{24} atoms are present. Calculate the amount of magnesium in moles.

………

3. Calculate the number of Cl_2 molecules and Cl atoms in 0.25 mol of Cl_2 gas.

………

1.5. Mole, Mass and Number

You know that 1 mol = 6.022×10^{23} elementary entities
and Molar mass = Mass of 1 mole of substance
= mass of 6.022×10^{23} elementary entities.

As discussed earlier the elementary entity can be an atom, a molecule, an ion or a formula unit. As far as mole - number relationship is concerned it is clear that one mole of any substance would contain 6.022×10^{23} particles (elementary entities). For obtaining the molar mass, i.e., mole-mass relationship we have to use atomic mass scale.

1.5.1 Atomic Mass Unit

By international agreement, a unit of mass to specify the atomic and molecular masses has been defined. This unit is called *atomic mass unit* and its symbol is 'amu'. The mass of one C-12 atom, is taken as exactly 12 amu. Thus, C-12 atom serves as the *standard*. The **Atomic mass unit** is defined as a mass exactly equal to the 1/12th of the mass of one carbon-12 atom.

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

Atomic mass unit also called **unified atomic mass unit** whose symbol is ‘u’. Another name of atomic mass unit is **dalton** (symbol Da). The latter is mainly used in biological sciences.

1.5.2 Relative Atomic and Molecular Masses

You are aware that atomic mass scale is a *relative scale* with C-12 atom (also written as 12C) chosen as the standard. Its mass is taken as exactly 12. Relative masses of atoms and molecules are the number of times each atom or molecules is heavier than 1/12th of the mass of one C-12 atom. Often, we deal with elements and compounds containing isotopes of different elements. Therefore, we prefer to use *average* masses of atoms and molecules. Thus

$$\text{Relative atomic mass} = \frac{\text{Average mass of 1 atom of the element}}{{}^{1}/_{12}\text{th of the mass of one C-12 atom}}$$

$$\text{and Rleative molecular mass} = \frac{\text{Average mass of 1 molecule of the substance}}{{}^{1}/_{12}\text{th of the mass of one C-12 atom}}$$

Experiments show that one O-16 atom is 1.333 times as heavy as one C-12 atom. Thus Relative atomic mass of O-16 = 1.333 x 12 = 15.996 ~ 16.0

The relative atomic masses of all elements have been determined in a similar manner. Relative molecular masses can also be determined experimentally in a similar manner. In case we know the molecular formula of a molecule. we can calculate its relative molecular mass by adding the relative atomic masses of all its constituent atoms. Let us calculate the relative molecular mass of water, H_2O.

Relative molecular mass of water,

$$H_2O = (2 \text{ x relative atomic mass of H}) + (1 \text{ x relative atomic mass of O})$$
$$= (2 \text{ x } 1) + (1 \text{ x } 16) = 2 + 16 = 18.$$

The relative atomic and molecular masses are just numbers and dimension less, unit-less quantities.

1.5.3 Atomic, Molecular and Formula Masses

From the definition of atomic mass unit, we can calculate the atomic masses. Let us again take the example of oxygen-16 whose relative atomic mass is 16. By definition.

$$\text{Relative atomic mass of O-16} = 16 = \frac{\text{mass of one O-16 atom}}{{}^{1}/_{12}\text{th of the mass of one C-12 atom}}$$

$$\text{Since 1 amu} = {}^{1}/_{12}\text{th the mass of one C-12 atom}$$

$$\therefore 16 = \frac{\text{mass of one O-16 atom}}{1 \text{ amu}}$$

Mass of one O-16 atom = 16 amu

Or Atomic mass of O-16 = 16 amu

From this example we can see that numerical value of the relative atomic mass and atomic mass is the same. Only, the former has no unit while the latter has the unit *amu*.

Molecular and formula masses can be obtained by adding the atomic or ionic masses of all the constituent atoms or ions of the molecule of formula unit respectively. Let us understand these calculations with the help of following examples.

Example 1.1 : Calculate the molecular mass of ammonia, NH_3.

Solution : One molecule of NH_3 consists of one N atom and three H atoms.

Molecular mass of NH_3 = (Atomic mass of N) + 3 (Atomic mass of H)
= [14 + (3 x 1)] amu
= 17 amu

Example 1.2 : Calculate the formula mass of sodium chloride (NaCl).

Solution : One formula unit of sodium chloride consists of one Na^+ ion and one Cl^- ion.

Formula mass of NaCl = (Ionic mass of Na+) + Ionic mass of (Cl^-)
= 25 amu + 35.5 amu
= 58.5 amu

You would have noticed in the above example that ionic mass of Na^+ ion has been taken as 23 amu which is the same as the atomic mass of Na atom. Since loss or gain of few electrons does not change the mass significantly, therefore atomic masses are used as ionic masses. Similarly we have taken ionic mass of Cl^- as 35.5 amu which is the same as the atomic mass of Cl^- .

1.5.4. Molar Masses

We know that molar mass is the mass of 1 mol of the substance. Also, 1 mol of any substance is the collection of its 6.022 x 10^{23} elementary entities. Thus

Molar mass = Mass of 6.022 x 10^{23} elementary entities.

i. Molar mass of an element

You know that the relative atomic mass of carbon-12 is 12. A 12 g sample of it would contain 6.022 x 10^{23} atoms. Hence the molar mass of C-12 is 12 g mol^{-1}. Forgetting the molar masses of other elements we can see relative atomic masses.

Since the relative atomic mass of oxygen-16 is 16, a 16 g sample of it would contain 6.022x10^{23} oxygen atoms and would constitute its one mole. Thus, the molar mass of O-16 is 16g mol^{-1}. Relative atomic masses of some common elements have been listed the Table 1.3.

Table 1.3: Relative atomic masses of some elements (up to 1st place of decimal)

Element	Relative Atomic Mass
Hydrogen, H	1.0
Carbon, C	12.0
Nitrogen, N	14.0
Oxygen, O	16.0
Sodium, Na	23.0
Phosphorus, P	31.0
Sulphur, S	32.1
Chlorine, Cl	35.5
Potassium, K	39.1
Iron, Fe	55.9

ii. Molar mass of a molecular substance

The elementary entity in case of a molecular substance is the molecule. Hence, *molar mass of such a substance would be the mass of its 6.022 x 10^{23} molecules*, which can be obtained from its relative molecular mass or by multiplying the molar mass of each element by the number of its moles present in one mole of the substance and then adding them.

Let us take the example of water, H_2O. Its relative molecular mass is 18. Therefore, 18 g of it would contain 6.022 x 10^{23} molecules. Hence, its molar mass is 18g mol^{-1}. Alternately we can calculate it as:

Molar mass of water, H_2O = (2 x molar mass of H) + (molar mass of O)
= (2 x 1g mol^{-1}) + (16g mol^{-1})

Table1.4: Molecular masses and molar masses of some substances

Element (or) Compound	Molecular Mass (amu)	Molar mass (g mol^{-1})
O_2	32.0	32.0
P_4	124.0	124.0
S_8	256.8	256.8
H_2O	18.0	18.0
NH_3	17.0	17.0
HCl	36.5	36.5
CH_2Cl_2	85.0	85.0

iii. Molar masses of ionic compounds

Molar mass of an ionic compound is the mass of its 6.022 x 10^{23} formula units. It can be obtained by adding the molar masses of ions present in the formula unit of the substance. In case of NaCl it is calculated as.

Molar mass of NaCl = molar mass of Na^+ + molar mass of Cl^-
= (23g mol^{-1}) + (35.5g mol^{-1})
= 58.5g mol^{-1}

Let us take some more examples of ionic compounds and calculate their molar masses.

Example 1.3 : Calculate the molar mass of

i) K_2SO_4 ii) $Ba_3(PO_4)_2$

Solution :

i) Molar mass of K_2SO_4 = (2 x molar mass of K^+) + (molar mass of SO_4^{2-})
= (2 x molar mass of K^+) + (molar mass of of S + 4 x molar mass of O)
= [(2 x 39.1) + (32.1 + 4 x 16)] g mol^{-1}]
= (78.2 + 32.1 + 64) g mol^{-1} = 174.3 g mol^{-1}

ii) Molar mass of $Ba_3(PO_4)_2$ = (3 x molar mass of Ba^{2+}) + (molar mass of PO_4^{3-})
= (3 x molar mass of Ba^{2+}) + 2 (molar mass of P + 4 x molar mass of O)

$= [(3 \text{ x } 137.3) + 2 (31.0 + 4 \text{ x } 16.0)] \text{ g mol}^{-1}]$

$= (411.9 + 190.0) \text{ g mol}^{-1} = 601.9 \text{ g mol}^{-1}$

Now you have learned about the mole, mass and number relationships for all types of substances. The following examples would illustrate the usefulness of these relationships.

Example1.4: Find out the mass of carbon-12 that would contain 1.0 x 10^{19} carbon-12 atoms.

Solution: Mass of 6.022 x 10^{23} carbon-12 atoms = 12g

$$\text{Mass of 1.0 x 1019 carbon-12} = \frac{12 \text{ x } 1 \text{ x } 10^{19}}{6.022 \text{ x } 10^{23}} \text{ g}$$

$$= 1.99 \text{ x } 10^{-4} \text{ g}$$

Example 1.5 : How many molecules are present in 100g sample of NH_3 ?

Solution : Molar mass of NH_3 = (14 + 3) gm mol^{-1} = 17 g mol^{-1}

∴ 17g Sample of NH_3 contains 6.022 x 10^{23} molecules

$$\text{Therefore, 100g sample of } NH_3 \text{ would contain } \frac{6.022 \text{ x } 10^{23} \text{ molecule}}{17\text{g}} \text{ x } 100\text{g}$$

$$= 35.42 \text{ x } 10^{23} \text{ molecules}$$

$$= 3.542 \text{ x } 10^{24} \text{ molecules}$$

Example 1.6: Molar mass of O is 16g mol^{-1}. What is the mass of one atom and one molecule of oxygen?

Solution : Mass of 1 mol or 6.022 x 10^{23} atoms of O = 16g.

$$\text{Mass of 1 atom of O} = \frac{16\text{g}}{6.022 \text{ x } 10^{23}}$$

$$= 2.66 \text{ x } 10^{-23}\text{g.}$$

Since a molecule of oxygen contains two atoms (O2).

its mass = 2 x 2.66 x 10^{-23}g = 5.32 x 10^{-23}g.

Intext Questions 1.3.

1. Calculate the molar mass of hydrogen chloride, HCl.

....

2. Calculate the molar mass of argon atoms, given that the mass of single atom is 6.634 x10^{-26} kg.

....

3. Calculate the mass of 1.0 mol of potassium nitrate, KNO_3 (atomic masses: K=39 amu; N=14amu, O=16amu)

....

4. The formula of sodium phosphate is Na_3PO_4. What is the mass of 0.146 mol of Na_3PO_4? (Atomic masses: Na=23.0 amu, P=31.0 amu; O=16.0 amu)

....

1.6. Mass, Molar Mass and Number of Moles

Mass, molar mass number of moles of a substance are inter-related quantities. We know what:

Molar mass (M) = Mass of one mole of the substance.

Molar mass of water is 18g mol^{-1}. If we have 18g of water, we have 1mol of it. Suppose we have 36 g water (18 x 2), we have 2 mol of it. In general, in a sample of water of mass (*n* x 18)g, the number of moles of water would be *n*. We may generalize the relation as

$$\text{Number of moles (amount) of a substance} = \frac{\text{mass of the substance}}{\text{molar mass of the substance}}$$

$$n = \frac{m}{M} \qquad\qquad m = n \times M$$

These relations are useful in calculations involving moles of substance.

Example 1.7 : In a reaction, 0.5 mol of aluminium is required. Calculate the amount of aluminium required in grams? (atomic mass of Al = 27 amu)

Solution : Molar mass of Al = 27g mol^{-1}

Required mass = no. of moles x molar mass.

= (0.5 mol) x (27g mol^{-1})

= 13.5 g

1.7. Molar Volume,Vm

Molar volume *is the volume of one mole of a substance*. It depends upon temperature and pressure. It is related to the density, by the relation.

$$\text{Molar volume} = \frac{\text{Molar mass}}{\text{Density}}$$

In case of gases, we use their volumes at standard temperature and pressure (STP). For the purpose 0^0C or 273K temperature is taken as the standard temperature and 1bar pressure is taken as the standard pressure. At STP, the molar volume of an ideal gas is 22.7 liter*. You will study that gases do not behave ideally and therefore their molar volume is not exactly 22.7L. However, it is very close to 22.7 L and for all practical purposes we take the molar volume of all gases at STP as 22.7 L mol^{-1}.

*Earlier 1 atmosphere pressure was taken as the standard pressure and at STP (273K, 1 atm) the molar volume of an ideal gas was taken as 22.4L mol^{-1}. The difference in the value is due to the change in the standard pressure (1bar) which is slightly less than 1atm.

Intext Questions 1.4.

1. How many moles of Cu atoms are present in 3.05g of copper (Relative atomic mass of Cu = 63.5)

....

2. A piece of gold has a mass of 12.6 g. How many moles of gold are present in it? (Relative atomic mass of Au = 197)

....

3. In a combustion reaction of an organic compound, 2.5 mol of CO_2 were produced. What volume would it occupy at STP (273K,1bar)?

....

What You Have Learnt

- Mole is the amount of a substance which contains as may elementary entities as there are atoms present in 0.012 kg or 12g of C-12. Thus mole denotes a number.
- The number of elementary entities present in one mole of substance is 6.022×10^{23}.
- The mass of one mole of a substance is called its molar mass. It is numerically equal to relative atomic mass or relative molecular mass expressed in grams per mole (g mol^{-1}) or kilogram per mole (kg mol^{-1}).
- Molar volume is the volume occupied by one mole of a substance. One mole of an ideal gas at standard pressure and temperature, STP (273 K and 1 bar) occupies 22.7 litres.
- In ionic substances, molar mass is numerically equal to the formula mass of the compound expressed in grams.
- If the molar mass of a substance is known, then the amount of a substance present in a sample having a definite mass can be calculated. If M is the molar mass, then, the amount of substance n, present in a sample of mass m is expressed as $n = m/M$

Terminal Exercise

1. How many atoms are present in a piece of iron that has a mass of 65.0 g / (atomic mass; Fe = 55.9 amu).
2. A piece of phosphorus has a mass of 99.2 g. How many moles of phosphorus, P_4 are present in it? (atomic mass, P = 31.0 amu)
3. Mass of 8.46 x 1024 atoms of fluorine is 266.95g. Calculate the atomic mass of fluorine.
4. A sample of magnesium consists of 1.92×10^{22} Mg atoms. What is the mass of the sample in grams? (atomic mass - 24.3 amu)
5. Calculate the molar mass in g mol-1 for each of the following.
    i) Sodium hydroxide, NaOH
    ii) Copper Sulphate $CuSO_4.5H_2O$
    iii) Sodium Carbonate, $Na_2CO_3.10H_2O$
6. For 150 gram sample of phosphorus trichloride (PCl_3), calculate each of the following:
    i) Mass of one PCl_3 molecule.
    ii) The number of moles of PCl_3 and Cl in the sample.
    iii) The number of grams of C1 atoms in the sample.

iv) The number of molecules of $PC1_3$ in the sample

7. Find out the mass of carbon-12, that would contain 1×10^{19} atoms.
8. How many atoms are present in 100g sample of C-12 atom?
9. How many moles of $CaCO_3$ would weigh 5g?
10. If you require 1.0×10^{23} molecules of nitrogen for the reaction $N_2 + 3H_2 \rightarrow 2NH_3$.
    i) What is the mass (in grams) of N_2 required?
    ii) How many moles of NH_3 would be formed in the above reaction from 1.0×10^{23} molecules of N_2?
    iii) What volume would NH3 gas formed in ii) occupy at STP ?

Answers to Intext Questions

1.1

1. Kilogram   2. µg
3. i) h   ii) n
4. i) Megasecond, 106 s
   ii) millisecond, 10^{-3} s.

1.2

1. $$\text{Moles of } N_2 \text{ gas} = \frac{4.22 \times 10^{23} \text{ molecules}}{6.022 \times 10^{23} \text{ molecules mol}^{-1}} = 0.70 \text{ mol}$$

2. $$\text{Amount of magnesium (moles} = \frac{8.46 \times 10^{24} \text{ atoms}}{6.022 \times 10^{23} \text{ atoms mol}^{-1}} = 14.05 \text{ mol}$$

3. No. of Cl_2 molecules in 0.25 mol Cl_2 = $0.25 \times 6.022 \times 10^{23}$ molecules
   = 1.5055×10^{23} molecules
   Since each Cl_2 molecule has 2 Cl atoms, the number of Cl atoms
   = $2 \times 1.5055 \times 10^{23} = 3.011 \times 10^{23}$ atoms.

1.3

1. Molar mass of hydrogen chloride = molar mass of HCl
   = 1 mol of H + 1 mol of Cl
   = $1.0 \text{ g mol}^{-1} + 35.5 \text{ g mol}^{-1}$
   = 36.5 g mol^{-1}

2. Molar mass of argon atoms = mass of 1 mol of argon
   = mass of 6.022×10^{23} atoms of argon.
   = $6.634 \times 10^{-26} \text{ kg} \times 6.022 \times 10^{23} \text{ mol}^{-1}$
   = $39.95 \times 10^{-3} \text{ kg mol}^{-1}$
   = 39.95 g mol^{-1}

3. Molar mass of KNO_3 = mass of 1 mol of K + mass of 1 mol of N + mass of 3 mol of O.

Since molar mass of an element is numerically equal to its atomic mass but has the units of g mol^{-1} in place of amu = 39.1 g + 14.0 g + 3 x 16.0 g

∴ Molar mass of KNO_3 = 39.1 g + 14.0 g + 48.0 g = 101.1 g mol^{-1}

4. Mass of 1 mol of Na3PO4 = 3 x (mass of 1 mol of Na) + mass of 1 mol of P + 4 x (mass of 1 mol of oxygen)

= 3 (23.0 g) + 31.0 g + 4 (16.0) g

= 69.0 g + 31.0 g + 64.0 g = 164.0 g

∴ Mass of 0.146 mol of Na_3PO_4 = 0.146 x 164.0 g = 23.94 g

1.4

1. Moles of Cu atoms in 3.05 g copper = $\frac{3.05 g}{63.5 \text{ g mol}^{-1}}$ = 0.048 mol

2. Moles of gold, Au = $\frac{12.6 \text{ g}}{197 \text{ g mol}^{-1}}$ = 0.064 mol

3. Molar volume of any gas at STP (298 K, 1 bar) = 22.7 L

∴ Volume occupied by 2.5 mol CO_2 at STP = 2.5 x 22.7 L = 56.75 L

Chapter 02

CHEMICAL ARITHMETICS

We know that atoms of different elements combine in simple whole- number ratios to form molecules. For example, hydrogen and oxygen atoms combine in the mass ratio of 1:8 and form water, H_2O. However, it is impossible to deal with individual atoms because they are so tiny we can neither see nor weigh them. Therefore, we must increase the size of these quantities to the point where we can see them and weigh them. With the help of **mole concept** it is possible to take a desired number of atoms / molecules by weighing (please refer to lesson-1). Now, in order to study chemical compounds and reactions in the laboratory, it is necessary to have adequate knowledge of the quantitative relationship among the amounts of the reacting substances that take part and products formed in the chemical reaction. This relationship is known as **Stoichiometry**. **Stoichiometry** (derived from the Greek stoicheion = element and metron = measure) is the term we use to refer to all the quantitative aspects of chemical compounds and reactions. In the present lesson, you will see how chemical formulae are determined and how chemical equations prove useful in predicting the proper amounts of the reactants that must be mixed to carry out a complete reaction. In other words we can take reactants for a reaction in such a way that none of the reacting substances is in excess. This aspect is very vital in chemistry and has wide application in industries.

Objectives

After reading this lesson, you will be able to:

- Define empirical and molecular formulae;
- Differentiate between empirical and molecular formulae;
- Calculate percentage by mass of an element in a compound and also workout empirical formula from the percentage composition;
- Establish relationship between mole, mass and volume;
- Calculate the amount of substances consumed or formed in a chemical reaction using a balanced equation and mole concept, and
- Explain that the amount of limiting reagent present initially limits the amount of the products formed.

2.1. Molecular and Empirical Formulae

In your previous classes, you have studied how to write chemical formula of a substance. For example, water is represented by H_2O, carbon dioxide is represented by CO_2, methane is represented by CH_4, dinitrogen penta-oxide is represented by N_2O_5, and soon. You are aware, formula for a molecule uses a symbol and subscript number to indicate the number of each kind of atoms present in the molecule (subscript 1 is always omitted). Such a formula is called molecular formula as it represents a molecule of a substance. A molecule of water consists of two hydrogen atoms and one oxygen atom. So, its molecular formula is written as H_2O. Thus, a molecular formula shows the actual number of atoms of different elements in a molecule of a compound.

There is another kind of formula, the empirical formula of a compound, which gives only relative number of atoms of different elements. These numbers are expressed as the simplest ratio. For example, empirical formula of glucose, which consists of carbon, hydrogen and oxygen in the ratio of 1:2:1 is CH_2O (empirical formulae are also called simplest formulae). Molecular formula = X_n where X is empirical formula and n is an integer). For example molecular formula of glucose is $C_6H_{12}O_6$ which is 6 times of its empirical formula. Thus, while empirical formula gives only a ratio of atoms, the molecular formula gives the actual number of atoms of each element in an individual molecule. In some cases the ratio of atoms shown in a molecular formula cannot be reduced to smaller integers. In such cases molecular and empirical formulae are the same, for example, sucrose $C_{12}H_{22}O_{11}$ which is popularly known as cane-sugar. In case of certain elements, a molecule consists of several atoms for example P_4, S_8, etc. In such cases, empirical formula will be symbol of the element only.

As you know, common salt, which is chemically called sodium chloride is represented as NaCl. This salt is ionic in nature and does not exist in molecular form. Therefore, NaCl is its empirical formula which shows that sodium and chlorine atoms are present in NaCl in the ratio of 1:1. Similar is the case with all ionic substances. KCl, $NaNO_2$, MgO are examples of empirical formulae as these are all ionic compounds. Table 2.1 provides a few more examples.

Table2.1: Molecular and Empirical Formulae

Substance	Molecular Formula	Empirical Formula
Ammonia	NH_3	NH_3
Carbon Dioxide	CO_2	CO_2
Ethane	C_2H_6	C_2H_6
Fructose	$C_6H_{12}O_6$	$C_6H_{12}O_6$
Sulphur	S_8	S_8
Benzene	C_6H_6	C_6H_6
Sodium Chloride	---	NaCl
Calcium Oxide	---	CaO

2.2. Chemical Composition and Formulae

How much carbon is present in one kilogram of methane whose molecular formula is CH_4? How much nitrogen is present in one kilogram of ammonia, NH_3? If we have prepared a substance that is made of 58.8% carbon, 28.4% oxygen, 8.28% nitrogen and 6.56% hydrogen, what is its empirical formula? You have studied atomic masses, formulae, and the mole concept. Can we solve the problem using these basic concepts? The answer is ‘yes. Atomic masses, formulae and the mole concept are the basic tools needed to solve such problems. What is percentage composition? Let us take up this aspect in a little detail and try to understand.

2.2.1. Percentage Composition

If we know the formula of a compound, we can find out how much of each of the elements is present in a given quantity of the compound. Aluminum is obtained from its oxide. Al_2O_3 (Which is found as the ore, bauxite). From the formula we can calculate how much aluminum can be obtained, at least in principle, from a given amount of aluminum oxide. Calculation is done by making use of the idea of percentage composition.

Percentage mass of an element in a compound

$$\frac{\text{mass of element in one molecular formula or in one empirical formula}}{\text{molecular mass or empirical formula mass of compound}} = \text{x } 100$$

$$= \frac{\text{Mass of element in 1 mol of compound}}{\text{Molar mass of compound}} \text{ x } 100$$

Let us calculate percentage composition of aluminium oxide, Al_2O_3

$$\text{Percentage of Aluminium} = \frac{\text{Mass of aluminium in 1 mol } Al_2O_3}{\text{Molar mass of } Al_2O_3} \text{ x } 100$$

Molar mass of $A1_2O_3$ = (2 x 27.0) g + (3 x 16.0) g = 102.0 g

Since 1 mol of $A1_2O_3$ contains 2 mol of Al atoms, the mass of Al is 2 x 27.0 g = 54.0 g Al

$$\text{Percentage of Aluminium} = \frac{54.0 \text{ g}}{102.0 \text{ g}} \text{ x } 100 = 52.9\%$$

We can calculate percentage of oxygen in the same way. One mole of Al_2O_3 contains 3 moles of O atoms, that is, 3 x 16.0g oxygen therefore

$$\text{Percentage of oxygen} = \frac{3 \text{ x } 16.0 \text{ g}}{102.0 \text{ g}} \text{ x } 100 = 47.1\%$$

Example 2.1: Butanoic acid, has the formula $C_4H_8O_2$. What is the elemental analysis of butanoic acid?

Solution: Molecular formula of the butanoic acid is $C_4H_8O_2$.

In one mole of butanoic acid there are 4 mol of carbon atoms. 8 mol of hydrogen atoms and 2 mol of oxygen atoms. Thus, 1 molar mass of butanoic acid will be equal to the sum of 4 x molar mass of carbon atoms, 8 x molar mass of hydrogen atoms, and 2 x molar mass of oxygen atoms.

Molar mass of butanoic acid = 4 x 12.0g + 8 x 1.0g + 2 x 16.0g = 88.0g

Percentage of C by mass =

Percentage of H by mass = $\frac{8.0\ g}{88.0\ g}$ x 100 = 9.1%

Percentage of O by mass = $\frac{32.0g}{88.0\ g}$ x 100 = 36.4%

The percentage of O is butanoic acid can also be calculated as follows:

Percentage of O by mass = 100 - (Percentage of C by mass + Percentage of H by mass)

= 100 - (54.5 + 9.1) = 36.4%

2.3. Determination of Empirical Formulae Formula Stoichiometry

We have just seen that if we know the formula of a compound, we can calculate the percentage composition. Now the question arises, can we determine the formula of the compound if we know the percentage composition of compound. The answer will be ‘yes’, but this formula will not be molecular formula; instead, it would be empirical formula as it would give simplest ratio of different atoms present in a compound. Normally we determine the percentage composition of different elements present in an unknown compound and determine its formula. Let us take a simple example of water. Water consists of 11.11% hydrogen and 88.89% oxygen by mass. From the data, we can determine empirical formula of water. Now if we assume that we have a 100.0g sample of water, then the percentage composition tells us that 100.0g of water contains 11.11g of hydrogen atoms and 88.89g of oxygen atoms.

From the atomic mass table, we find that 1mol of hydrogen atoms has a mass of 1.0g, and 1 mol of oxygen atoms has a mass of 16.0g. Now we can write unit conversion factors so that the mass of hydrogen can be converted to moles of H atoms and the mass of oxygen can be converted to moles of O atoms. Since 1 mol of H atoms has a mass of 1.0g we get the conversion factor as

$$\frac{1\text{ mol of H atoms}}{1.0\text{g H}}$$

Therefore

$$11.11\text{ g H} = (11.11\text{ g H})\ \frac{1\text{ mol of H atoms}}{1.0\text{g H}} = 11.11\text{ mol H atoms}$$

Similarly conversion factor for oxygen will be

$$\frac{1\text{ mol of O atoms}}{16\text{g O}}$$

Therefore, $88.89\text{ g O} = (88.89\text{ g O})\ \frac{1\text{ mol of O atoms}}{16\text{g O}} = 5.55\text{ mol O atoms}$

Thus in water, the ratio of moles of hydrogen atoms to moles of oxygen atoms is 11.11:5.55.

Since a mole of one element contains the same number of atoms as a mole of another element, the ratio of moles of atoms in a compound is also the ratio of the number of atoms. Therefore, the ratio of hydrogen atoms to oxygen atoms is 11.1:5.55. Now by dividing each by the smaller of the two numbers we can convert both numbers to integers.

$$\frac{11.11}{5.55} = 2 \quad \text{and} \quad \frac{5.55}{5.55} = 1$$

Thus ratio hydrogen and oxygen atoms in water is 2:1 and empirical formula of water is H_2O.

Intext Questions 2.1

1. For the compound Fe_3O_4, calculate percentage of Fe and O.

....

2. State percent composition for each of the following :
   (a) C in $SrCO_3$ b) SO_3 in H_2SO_4

....

3. What are the empirical formulae of substances having the following molecular formulae? H_2O_2, C_6H_{12}, Li_2CO_3, $C_2H_4O_2$, S_8, H_2O, B_2H_6, O_3, S_3O_9, N_2O_3

....

4. A compound is composed of atoms of only two elements, carbon and oxygen. If the compound contains 53.1% carbon, what is its empirical formula

....

2.4. Chemical Equation and Reaction Stoichiometry

You have studied that a reaction can be represented in the form of a chemical equation. A balanced chemical equation carries a wealth of information qualitative as well as quantitative. Let us consider the following equation and learn what all information it carries.

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s) \qquad \text{...... (2.1)}$$

1) Qualitative Information

Qualitatively the equation (2.1) tells that iron reacts with oxygen to form iron oxide.

2) Quantitative Information

Quantitatively a balanced chemical equation specifies numerical relationship among the quantities of its reactants and products. These relationships can be expressed in terms of:

i) Microscopic quantities, namely, atoms, molecules and formula units.

ii) Macroscopic quantities, namely, moles, masses and volumes (*in case of gaseous substances*) of reactants and products.

Now let us again take the reaction (2.1) given earlier and get the quantitative information out of it.

2.4.1 Microscopic Quantitative Information

The reaction (2.1)

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s) \qquad \text{...... (2.1)}$$

tells that *4 atoms* of iron react with *3 molecules* of oxygen to form *2 formula units* of iron oxide. Often this information is written below each reactant and product for ready reference as shown below:

$4Fe(s)$	+	$3O_2(g)$	$\rightarrow$	$2Fe_2O_3(s)$	...... (2.1)
4 atoms of Fe		**3 molecules of O2**		**2 formula units of Fe2O3**	

2.4.2 Macroscopic Quantitative Information

The microscopic quantitative information discussed in the previous section can be converted into macroscopic information with the help of mole concept which you have learnt in unit 1.

a) Mole Relationships

We know that Avogadro number of elementary entities like atoms, molecules, ions or formula units of a substance constitute one mole of it. Let us multiply the number of atoms, molecules and formula masses obtained in the previous section (Eq. 2.1a) by Avogadro's constant, N_A

$4Fe(s)$	+	$3O_2(g)$	$\rightarrow$	$2Fe_2O_3(s)$	...... (2.1)
4 atoms of Fe		**3 molecules of O_2**		**2 formula units of Fe_2O_3**	
4 x N_A atoms of Fe		3 x N_A molecules of O_2		2 x N_A formula units of $Fe_2O_3(s)$	
4 mol of Fe		**3 mol of O_2**		**2 mol of Fe_2O_3**	

We may rewrite the above equation as

$4Fe(s)$	+	$3O_2(g)$	→	$2Fe_2O_3(s)$	...... (2.1b)
4 mol of Fe		**3 mol of O_2**		**2 mol of Fe_2O_3**	

The above equation (2.1b) gives us the mole relationship between reactants and products. Here *4mol of Fe* react with *3mol of O_2* and produce *2mol of Fe_2O_3*.

b) Mass Relationships

The mole relationships which you have learnt in the previous section can be converted into mass relationship by using the fact that mass of one mole of any substance is equal to its molar mass which can be calculated from its formula with the help of relative atomic masses of its constituent elements.

In the reaction that we are discussing, the relative atomic masses of iron and oxygen are 55.8 and 16.0 respectively. Therefore

i. Molar mass of Fe $= 55.8\ g\ mol^{-1}$
ii. Molar mass of O_2 $= 2 \times 16.0 = 32\ g\ mol^{-1}$
iii. Molar mass of Fe_2O_3 $= (2 \times 55.8 + 3\times16.0)\ g\ mol^{-1}$
$= 159.6\ g\ mol^{-1}$

Using these molar masses we can convert the mole relationship given by equation 2.1b into mass relationship as given below:

$4Fe(s)$	+	$3O_2(g)$	→	$2Fe_2O_3(s)$
4 mol Fe		**3 mol O_2**		**2 mol Fe_2O_3**
(4 x 55.8) g Fe		(3 x 32) g O_2	→	(2 x 159.6) g Fe_2O_3
223.2 g Fe		96 g O_2		319.2 g FeO_3

Thus 223.2g iron would react with 96g oxygen and produce 319.2g ironoxide, We may rewrite the above equation as:

$4Fe(s)$	+	$3O_2(g)$	→	$2Fe_2O_3(s)$
223.2g Fe		96g O_2		319.2g Fe_2O_3

c) Volume Relationships

We know that one mole of *any gas* occupies a volume of 22.7L at STP (standard temperature and pressure 0^0C and 1 bar pressure). We can use this information to arrive at volume relationships between gaseous substances. The reaction that we are considering involves only one gaseous substance, O_2. We may rewrite the equation (2.1b) as

$4Fe(s)$	+	$3O_2(g)$	→	$2Fe_2O_3(s)$	...... (2.1)
4 mol		**3 mol**		**2 mol**	
		(3 x 22.7) L at STP			
		68.1 L at STP			

Thus 4 mol of iron would react with 68.1 L of oxygen at STP to produce 2 mol of iron oxide. (The volume relationship becomes more useful for reactions involving 2 or more gaseous substances).

We can express microscopic as well macroscopic quantitative relationships involved in the above reaction as shown below.

$4Fe(s)$	+	$3O_2(g)$	→	$2Fe_2O_3(s)$
4 atoms		**3 molecules**		**2 formula units**
4 mol		3 mol		2 mol
223.2 g		96 g		319.2 g
		68.1 L at STP		

We may use even mixed relations. For example, we may say 4mol of iron would react with 68.1L (at STP) of oxygen to produce 319.2g of ironoxide.

Let us understand these, relationships with two more examples.

a) Let us work out the mole, mass, and volume relationships for the reaction involved in the manufacture of ammonia by Haber's process.

Microscopic relationship	N_2 (g)	+	$3H_2$ (g)	→	$2NH_3$ (g) ......(2.2)
Microscopic relationships	1 Molecules		3 Molecules		2 Molecules
i) Moles	1 mol		3 mol		2 mol
ii) Mass	28 g		(3x2.0) = 6.0g		(2x17.0) = 34 g
iii) Volume	1 x 22.7 L		(3 x 22.7)		(2 x 22.7)
	= 22.7 L		= 68.1 L		= 45.4 L
or	1 vol		3 vol		2 vol

b) Let us take one more reaction, the combustion reaction of butane and work out the different types of relationships. The reaction is :

$2C_4H_{10}$ (g)	+	$13O_2$ (g)	→	$8CO_2$ (g)	+	$10H_2O$ (g)
2 molecues		13 molecules		8 molecules		10 molecules
2 mol		13 mol		8 mol		10 mol
2x(4x12+10x1g)		(13x32) g		8x(12+2x16) g		10x(2x1+16)g
116g		416g		352 g		180g
2x22.7=45.4L		13x22.7=295.1 L		8x22.7=181.6 L		10x22.7=227 L
2 vol		13 vol		8 vol		10 vol

Now let us use the mole, mass and volume relationships to make some calculations.

Example 2.2: In the manufacture of ammonia by Haber process, nitrogen reacts with hydrogen at high temperature and high pressure in the presence of a catalyst and gives ammonia.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(s)$$

How much hydrogen would be needed to produce one metric ton of ammonia?

Solution: We should first find out the mass relationships for the reaction.

N_2 (g)	+	$3H_2$ (g)	→	$2NH_3$(s)
1 mol		**3 mol**		**2 mol**
1x28g = 28 g		3x2g = 6.0 g		2x17g = 34 g

We know that:

1 metric ton = 1000 kg = 103 kg = 106 g

From the mass relationship 34 g NH_3 requires 6.0 g H_2 for its manufacture.

∴ 10^6 g NH_3 would require $\frac{6.0\ x\ 10^6}{34}$ g = 1.76 x 10^5 g of H_2.

Thus 1 metric ton of ammonia will be obtained by using 1.176 x 10^5g of Hydrogen.

Example 2.3: In a rocket motor fuelled by butane, C_4H_{10}, how many kg of O_2 should be provided with each kg of butane to provide for complete combustion?

Solution: The combustion reaction of butane is

$2C_4H_{10}$ (g)	+	$13O_2$ (g)	→	$8CO_2$	+	$10H_2O$(s)
2 mol		**13 mol**				
2 x 58 = 116 g		**13 x 32 = 416 g**				

Thus, to completely burn 116g butane, Oxygen required is 416 g.
Therefore, to completely burn 1 kg (1000 g) butane, oxygen required will be

$$= \frac{416 \text{ x } 1000}{116} \text{ g } O_2$$

$= 3586 \text{ g } O_2$

$= 3.586 \text{ kg } O_2 \sim 3.59 \text{ kg } O_2$

Example 2.4: When lead sulphide; PbS and lead oxide, PbO, are heated together the product are lead metal and sulphur dioxide, SO_2.

$$PbS(s) \quad + \quad 2PbO(s) \xrightarrow{\text{heat}} 3Pb\ (1) \quad + \quad SO_2\ (g)$$

If 14.0 g of lead oxide reacts according to the above equation, how many (a) moles of lead (b) grams of lead, (c) atoms of lead and (d) grams of sulphur dioxide are formed?
(Atomic mass: Pb = 207.0, S = 32.1; O = 16.0)

Solution: For each part of the question we will use the balanced equation

$$\underset{\textbf{1 mol}}{PbS(s)} \quad + \quad \underset{\textbf{1 mol}}{2PbO(s)} \xrightarrow{\text{heat}} \underset{\textbf{3 mol}}{3Pb\ (1)} \quad + \quad \underset{\textbf{1 mol}}{SO_2\ (g)}$$

Now formula mass of PbO = (207.0 + 16.0) = 223.0 amu
Thus, one mole of lead oxide formula units has a mass of 223.0 g.

Therefore, 14.0 g of PbO is $\frac{14.0 \text{ g PbO}}{223.0 \text{ g mol}^{-1} \text{ PbO}} = 6.28 \text{ x } 10^{-2}$ mol PbO

a) The balanced equation show that 2 mol of PbO form 3 mol of Pb. Therefore, $6.28 \text{ x } 10^{-2}$ mol of PbO form

$$6.28 \text{ x } 10^{-2} \text{ mol PbO x } \frac{3 \text{ mol Pb}}{2 \text{ mol PbO}} = 9.42 \text{ x } 10^{-2} \text{ mol Pb}$$

b) The atomic mass of Pb is 207.0; this tells us that one mol of lead has a mass 207.0g.
Thus, $9.42 \text{ x } 10^{-2}$ mol of Pb has a mass of

$$9.42 \text{ x } 10^{-2} \text{ mol Pb x } \frac{207.0 \text{ g Pb}}{1 \text{ mol Pb}} = 19.5 \text{ g Pb}$$

c) $9.42 \text{ x } 10^{-2}$ mol of Pb is

$9.42 \text{ x } 10^{-2}$ mol of Pb x $6.022 \text{ x } 10^{23}$ atoms mol^{-1} = $5.67 \text{ x } 10^{22}$ Pb atoms

d) The balanced equation shows that 2 mol of PbO form 1 mol of SO2.

$$6.28 \text{ x } 10^{-2} \text{ mol PbO x } \frac{1 \text{ mol } SO_2}{2 \text{ mol PbO}} = 3.14 \text{ x } 10^{-2} \text{ mol } SO_2$$

Now the relative molecular mass of SO_2 = 32.1 + 2 (16.0) = 64.1
Molar mass of SO_2 = 64.1 g mol^{-1}
Therefore, $3.41 \text{ x } 10^{-2}$ moles of SO_2 molecules have a mass of

$$3.14 \text{ x } 10^{-2} \text{ mol x } 64.1 \text{ mol}^{-1} = 2.01 \text{ g}$$

Intext Questions 2.2

1. How many grams of NH_3 can be made according to the reaction

$$N_2\ (g) + 3H_2\ (g) \rightarrow 2NH_3(s)$$

from (a) 0.207 mol of N_2 (b) 22.6 g of H_2

....

2. In reaction $C_2H_4 (g) + 3O_2 (g) \longrightarrow 2CO_2 (g) + 2H_2O(l)$

How many (a) moles of O_2 are consumed and (b) moles of H_2O are formed when 4.16×10^{-2} mol of C_2H_4 react?

………

2.5. Limiting Reagents

We generally find that substances which react with each other are not present in exactly the same proportion a reaction mixture as stated by a balanced chemical equation. For example, if 2 mol each of hydrogen and oxygen are mixed and a spark is passed through the mixture, water is formed according to the equation.

$$\begin{array}{ccccc} 2H_2 & + & O_2 & \rightarrow & 2H_2O \\ \text{2 mol} & & \text{1mol} & & \text{2mol} \end{array}$$

Here, 2 mol of hydrogen react with only 1 mol of oxygen, and 1 mol of oxygen therefore remains unreacted. In this example hydrogen is said to be the limiting reagent or reactant because its amount becomes zero and the reaction therefore stops before the other reactant; that is, the oxygen is used up. The amount of hydrogen present initially limits the amount of product that is formed.

Example2.5: 3mol of Sulphur dioxide (SO_2) is mixed with 2 mole of O_2, and after reaction is over SO_3 is obtained?

i) Which is the limiting reagent?

ii) What is the maximum amount of SO_3 that can be formed?

Solution: i) we must first write the balanced equation

$$2SO_2 \quad + \quad O_2 \quad \rightarrow \quad 2SO_3$$

According to the above equation

a) 2mol of SO_3 that can be formed from 3 mol of SO_2.

Amount of SO_3 that can be formed from 3 mol of SO_2

$$= (3 \text{ mol } SO_2) \times \frac{2 \text{ mol } SO_3}{2 \text{ mol } SO_2} = 3 \text{ mol } SO_3$$

b) 2 mol of SO_3 can be formed from 1 mol of O_2. Therefore, the amount of SO_3 that can be formed from 2 mol of O_2.

$$= (2 \text{ mol } O_2) \times \frac{2 \text{ mol } SO_3}{1 \text{ mol } O_2} = 4 \text{ mol } SO_3$$

According to the definition, the limiting reactant is that reactant which gives the smallest amount.

In this case SO_2 is the limiting reactant.

(ii) The maximum amount of product that can be obtained is the amount formed by the limiting reagent. Thus the maximum amount of SO_3 that can be obtained is 3 mol.

Example 2.6: 2.3 g of sodium metal is introduced into a 2L flask filled with chlorine gas at STP (273 K, 1 bar). After reaction is over, find:

i) What is the limiting reagent in this reaction?

ii) How many moles of sodium chloride are formed?

iii) Which substance is left unconsumed at the end of the reaction? Find out its mass in grams.

iv) What percentage of the substance present in excess is converted into sodium chloride?

(Given: Na = 23, Cl = 35.5)

Solution:

	2 Na (s)	+	Cl_2 (g)	→	2NaCl
	2 mol		**1 mol**		**2 mol**
or			22.7 L at STP		

i) Moles of sodium introduced = $\frac{2.3\ g}{23\ g\ mol^{-1}}$ = 0.1 mol

From the above equation, it is clear that 2 mol NaCl is formed from 2 mol Na

Therefore 0.1 mol Na can produce = $\frac{2 \times 0.1}{2}$ = 0.1 mol NaCl

Molar volume at STP = 22.7 L

Therefore moles of chlorine in 2 L volume at STP = $\frac{2L}{22.7L\ mol^{-1}}$ = 0.088 mol

From equation: 1 mol Cl_2 can produce 2 mol NaCl

Therefore 0.088 mol Cl_2 can produce 2 x 0.088 = 0.176 mol NaCl.

ii) Sodium being the limiting reagent, as calculated in (i), the moles of NaCl produced = 0.1 mol

iii) From above equation, 2 mol NaCl is produced from 1 mol Cl_2

Therefore 0.1 mol NaCl is produced from $\frac{1 \times 0.1}{2}$ = 0.05 mol Cl_2

Initial moles of Cl_2 = 0.088 mol

Moles of Cl_2 left unconsumed = (0.088 - 0.05) mol = 0.038 mol

Therefore, mass of Cl_2 left unconsumed = 0.038 g x 71.0 g mol^{-1} = 2.698 g

(because molar mass of Cl_2 = 2 x 35.5 = 71.0 g mol^{-1})

iv) Moles of Cl_2 consumed = 0.05 mol out of 0.088 mol

∴ Percent of Cl_2 consumed and converted into NaCl = $\frac{0.05}{0.088}$ x 100 = 56.8%

Example 2.7: 2.0 g mixture of $MgCO_3$ and $CaCO_3$ are heated till no further loss of weight takes place. The residue weighs 1.04g. Find the percentage composition of the mixture.

(Mg = 24, Ca = 40, C = 12, O = 16)

Solution: Mixture of $MgCO_3$ and $CaCO_3$ taken = 2.0 g

Let the mass of $MgCO_3$ be = *x* g

Therefore the mass of $CaCO_3$ = (2.0 - *x*) g

The decomposition reactions are

$MgCO_3$ (g)	→	MgO (s)	+	CO_2 (g)	(i)
(24+12+48) g		**(24+16) g**			
84 g		**40 g (Residue)**			
$CaCO_3$ (g)	→	CaO (s)	+	CO_2 (g)	(ii)
(40+12+48) g		**(40+16) g**			
100 g		**56 g (Residue)**			

Form the equation (i)

84 g $MgCO_3$ leave a residue $= 40$ g

x g $MgCO_3$ will leave residue $= \frac{40x}{84}$ g

Form the equation (ii)

100 g $CaCO_3$ leave a residue $= 56$ g

$(2.0 - x)$ g $CaCO_3$ will leave residue $= \frac{56(2.0-x)}{100}$ g

Total mass of the residue $= \frac{40x}{84} + \frac{56(2.0-x)}{100} = 1.04$ g (given)

$40 \text{ x } 100x + 84 \text{ x } 56 \text{ x } 2 - 84 \text{ x } 56x = 84 \text{ x } 100 \text{ x } 1.04$

$4000x + 9408 - 4704x = 8736$

$9408 - 8736 = (4704 - 4000)x$

$672 = 704x$

Therefore, mass of $MgCO_3$ in the mixture $= x = \frac{672}{704} = 0.96$ g

Therefore, percentage of $MgCO_3 = \frac{0.96}{2.0} \text{ x } 100 = 48\%$

and percentage of $CaCO_3 = 100 - 48 = 52\%$

What You Have Learnt

- A chemical formula is used not only to represent the name of a compound but also to indicate its composition in terms (i) relative number of atoms and (ii) relative number of moles of atoms.
- A molecular formula of a substance shows (i) the number of atoms of different elements in one molecule. (ii) the number of moles of atoms of different elements in one mole of molecule.
- An empirical formula shows only a ratio of (i) number of atoms, and (ii) moles of atoms in a compound.
- Molecular formula is always an integral multiple of the empirical formula
- The empirical formula of a compound can be determined from its chemical analysis.
- In order to determine a compound's molecular formula, molecular mass also must be known.
- Stoichiometry is the quantitative study of the composition of chemical compounds (compound or formula stoichiometry) and of the substances consumed and formed in chemical reactions (reaction or equation stoichiometry).
- Chemical equations specify not only the identities of substances consumed and formed in a reaction, but also relative quantities of these substances in terms of (a) atoms, molecules and formula units and (b) moles of these entities.
- A balanced chemical equation demonstrates that all the atoms present in the reactants are accounted for in the product; atoms are neither created nor destroyed in a reaction.
- The stoichiometric rations among the moles of reactants shown in a balanced equation are useful for determining which substance is entirely consumed and which substance(s) is (are) left over.

Terminal Exercise

1. Write empirical formulae of the following compounds: CO, Na_2SO_3, C_4H_{10}, H_2O_2, KCl

....

2. The empirical formula of glucose is CH_2O which has a formula mass of 30 amu. If the molecular mass of glucose is 180 amu. Determine the molecular formula of glucose.

....

3. What is ratio of masses of oxygen that are combined with 1.0 gram of nitrogen in the compound NO and N_2O_3?

....

4. A compound containing sulphur and oxygen on analysis reveals that it contains 50.1% sulphur and 49.9% oxygen by mass. What is simplest formula of the compound?

....

5. Hydrocarbons are organic compound composed of hydrogen and carbon. A, 0.1647 g sample of a pure hydrocarbon on burning in a combustion tube produced 0.5694 g of CO_2 and 0.0845 g of H_2O. Determine the percentage of these elements in the hydrocarbon.

....

6. On combustion 2.4g of a compound of carbon, hydrogen and oxygen gave 3.52 of CO_2 and 1.44 g of H_2O. The molecular mass of the compound was found to be 60.0 amu.

a) What are the masses of carbon, hydrogen and oxygen in 2.4 g of the compound?

....

b) What are the empirical and molecular formulae of the compound?

....

7. (i) What mass of oxygen is required to react completely with 24g of CH_4 in the following reaction?

$C_2H_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (l)$

....

(ii) How much mass of CH_4 would react with 96 g of oxygen.

....

8. In the reaction $H_2 + Cl_2 \rightarrow 2HCl$

How many grams of chlorine, Cl_2 are needed to react completely with 0.245 g of hydrogen, H2, to give hydrogen chloride, HCl? How much HCl is formed?

……

9. 3.65 g of H_2 and 26.7 g of O_2 are mixed and reacted. How many grams of H_2O are formed?

……

10. Cuastic soda NaOH can be commercially prepared by the reaction of Na_2CO_3 with slaked lime, $Ca(OH)_2$. How many grams of NaOH can be obtained by treating 2.0 kg of Na_2CO_3 with $Ca(OH)_2$?

……

11. A potable hydrogen generator utilizes the reaction

$CaH_2 + H_2O \rightarrow Ca(OH)_2 + 2H_2$

How many grams of H_2 can be produced by a 100 g cartridge of CaH_2?

……

12. The reaction $2Al + 3MnO \rightarrow Al_2O_3 + 3Mn$ proceeds till the limiting substance is consumed. A mixture of 220g Al and 400g MnO was heated to initiate the reaction. Which initial substance remained in excess and by how much? (Al = 27, Mn = 55).

……

13. $KClO_4$ may be prepared by means of following series of reactions

$Cl_2 + 2KOH \rightarrow KCl + KClO + H_2O$
$3KClO \rightarrow 2KCl + KClO_3$
$4KClO_3 \rightarrow 3KClO_4 + KCl$

How much Cl_2 is needed to prepare 400 g $KClO_4$ by the above sequence?
(K = 39, Cl = 35.5, O = 16, H = 1)

……

14. 2.0 g of mixture of Na_2CO_3 and $NaHCO_3$ was heated when its weight reduced to 1.876 g. Determine the percentage composition of the mixture.

……

15. Calculate the weight of 60% sulphuric acid is required to decompose 150g of chalk (calcium carbonate). (Given Ca = 40, C = 12, O = 16, S= 32)

……

Answers to Intext Questions

1. Molar mass of Fe_3O_4 $= 3 \times 56.0 + 4 \times 16.0$

$= (168.0 + 64.0) = 232.0 \text{ g mol}^{-1}$

Percentage of Fe $= \frac{168.0}{232.0} \times 100 = 72.41\%$

Percentage of O $= \frac{64.0}{232.0} \times 100 = 27.59\%$

2. a) Molar mass of $SrCO_3 = 87.6 + 12.0 + 48.0 = 147.6 \text{ g mol}^{-1}$

Percentage of carbon C in $SrCO_3 = \frac{12.0}{147.6} \times 100 = 8.13\%$

b) Molar mass of $H_2SO_4 = 2.0 + 32.1 + 64.0 = 98.1 \text{ g mol}^{-1}$

Molar mass of $SO_3 = 32.1 + 48.0 = 80.1 \text{ g mol}^{-1}$

Percentage of SO_3 in H_2SO_4 $= \frac{80.1 \times 100}{98.1}$ x 81.65%

3.

Substance	**Empirical formula**
H_2O_2	HO
C_6H_{12}	CH_2
Li_2CO_3	Li_2CO_3
$C_2H_4O_2$	CH_2O
S_8	S
H_2O	H_2O
B_2H_6	BH_3
O_3	O_3
S_3O_9	SO_3
N_2O_3	N_2O_3

4. Percentage of carbon = 53.1%

Percentage of Oxygen = 46.9%

Suppose we take 100g of the substance then moles of carbon = $\frac{53.1}{12.0}$ g = 4.43 mol

mole of oxygen = $\frac{46.0}{16.0}$ = 2.93 mol

molar ration of C and O = $\frac{4.43}{2.93} : \frac{2.93}{2.93}$

= 1.50 : 1 or 3 : 2

Empirical formula of the compound is C_3O_2.

2.2

1. In equation

$$N_2\,(g) \quad + \quad 3H_2\,(g) \quad \longrightarrow \quad 2NH_3(s)$$

1 mol **3 mol** **2 mol**

0.207 mol N_2 gives 0.414 mol of NH_3

0.414 mol of NH_3 = 0.414 mol x 17.0 g mol^{-1} = 7.038 of NH_3

22.6 g of Hydrogen = $\frac{22.6}{2.0}$ = 11.3 mol of hydrogen

11.3 mol of hydrogen will give 2/3 x 11.3 mol of NH_3 = 7.53 mol

Therefore, Mass of NH_3 = 7.53 mol x 17.0 g mol^{-1} = 128.01 g

2. $$C_2H_4\,(g) \quad + \quad 3O_2\,(g) \quad \longrightarrow \quad 2CO_2\,(g) \quad + \quad 2H_2O(g)$$

1 mol **3 mol** **2 mol** **2 mol**

a) 4.16×10^{-2} mol of C_2H_4 will consume $3 \times 4.16 \times 10^{-2}$ mol of oxygen

= $12.48 \times 10^{-2} = 1.248 \times 10^{-1}$ mol of O_2

b) moles of H_2O formed = $2 \times 4.16 \times 10^{-2}$ mol

= 8.32×10^{-2} mol of H_2O

Module - II

Atomic Structure and Chemical Bonding

03. Atomic Structure

04. Periodic Table and Atomic Properties

05. Chemical Bonding

Chapter 03

ATOMIC STRUCTURE

Chemistry has been defined as the study of matter in terms of its structure, composition, and properties. As you are aware, matter is made up of atoms, and therefore an understanding of the structure of atom is very important. You have studied in your earlier classes that the earliest concept of atom (smallest indivisible part of matter) was given by ancient (600-400 BC) Indian and Greek philosophers. At that time there was no experimental evidence. The origin of the concept of atom was based on their thoughts on 'What would happen if we continuously keep dividing matter'. John Dalton revived the concept of atom at the beginning of nineteenth century in terms of his atomic theory which successfully explained the laws of chemical combination. Later experiments showed that the atom is not indivisible but hasan internal structure.

In this lesson you will learn about the internal structure of an atom which will help you to understand the correlations between is structure and properties. You would learn about thesein the later lessons.

Objectives

After reading this lesson you will be able to:

- Recognize the fundamental particles of atom;
- Describe Rutherford's experiment and explain its results;
- Define electromagnetic radiation;
- List and define the characteristic parameters of electromagnetic radiation;
- Discuss line spectrum of hydrogen;
- Explain Bohr's postulates and discuss his model;
- Draw energy level diagram of a hydrogen atom showing different series of lines inits spectrum;
- Explain wave particle duality of matter and radiation;
- Formulate Heisenberg's uncertainty principle;
- Explain the need for quantum mechanical model;
- Draw probability pictures of an electron in an atom;
- List quantum numbers and discuss their significance;
- Draw the shapes of s,p, and d orbitals;
- Recognize nodal plane;
- Explain Pauli's exclusion principle;
- Define Aufbau principle and
- Explain Hund's rule of maximum multiplicity.

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- Explain Hund's rule of maximum multiplicity.

3.1 Fundamental Particles of Atom

In 1897 J.J. Thomson discovered electron as a constituent of atom. He determined that an electron had a negative charge and had very little mass as compared to that of the atom. Since an atom was found to be electrically neutral it was inferred that some source of positive chargemust be present in the atom. This soon led to the experimental discovery of the proton, which is a positively charged subatomic particle. Proton was found approximately 1840 times heavier than an electron. Further experiments revealed that the atomic masses were more than that expected from the presence of just protons and electrons in the atom. For example, the mass of a helium atom was expected to be double that of hydrogen atom but was actually found to be almost four times the mass of hydrogen atom. This suggested the presence of neutral particles with mass comparable to that of protons in the atom. Sir James Chadwick discovered this neutral particle and called it **neutron** subsequently in 1932. Thus we may conclude that atoms are not indivisible but are made up of three fundamental particles whose characteristics are given in Table 3.1.

Table 3.1 Fundamental particles and their characteristics

Particle	Symbol	Mass / kg	Actual Charge / C	Relative charge
Electron	e	$9.109\ 389 \times 10^{-31}$	$-1.602\ 177 \times 10^{-19}$	-1
Proton	p	$1.672\ 623 \times 10^{-27}$	$+1.602\ 177 \times 10^{-19}$	+1
Neutron	n	$1.674\ 928 \times 10^{-27}$	0	0

Since atoms are made up of still smaller particles, they must have an internal structure. In the next section, we shall take up some of the earlier ideas about the internal structure of the atom.

Intext Questions 3.1

1. Compare the mass of an electron with that of the proton.

....

2. What is a fundamental particle?

....

3. What is the name given to neutral particles in the atom?

....

3.2 Earlier Models

Once it was established that the atom is not indivisible, the scientists made attempts to understand the structure of the atom. A number of models have been proposed for the internal structure of the atom. The first attempt to describe the structure of an atom in terms of a model was made by J.J. Thomson.

3.2.1 Thomson’s Model

On the basis of his experiments on discharge tubes. Thomson proposed that atoms can be considered as a large positively charged body with a number of small negatively charged electrons scattered throughout it. This model (Fig. 3.1) was called as plum pudding modelof the atom.

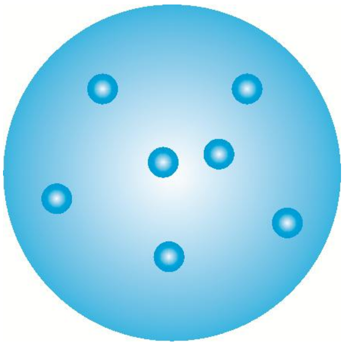
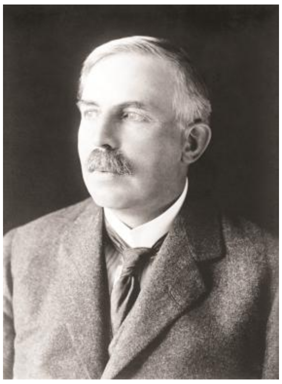


Fig 3.1 : *A pictorial representation of Thomson’s plum-pudding model*

The electrons represent the plums in the pudding made of positive charge. It is sometimes also called as **watermelon model.** In this, the juicy pulp of the watermelon represents the positive charge and the seeds represent the electrons.

J.J. Thomson (1871-1937)
Won Nobel Prize in Physics in 1906



Ernest Rutherford(1856-1940)
Won Nobel Prize in Chemistry in 1908

3.2.1 Rutherford’s Experiment

Ernest Rutherford performed an experiment called the ‘ Gold Foil Experiment’ or ‘a-ray scatteringexperiment’ to test the structure of an atom as proposed by Thomson. In this experiment a beam of fast moving alpha particles (positively charged helium ions) was passed through a very thin foil of gold. He expected that the alpha particles would just pass straight through the gold foil and could be detected by a photographic plate. But, the actual results of theexperiment (Fig. 3.2) were quite surprising. It was observed that most of the - particles did pass straight through the foil but a number of particles were deflected from their path. Some of these deflected slightly while a few deflected through large angles and about 1 in10,000 - particles suffered a rebound.

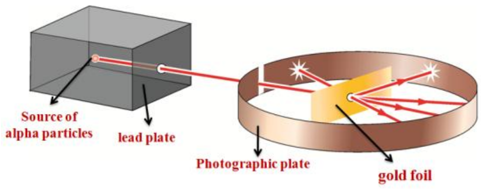


Fig. 3.2: *Schematic representation of Rutheford's α-particle scattering experiment.*

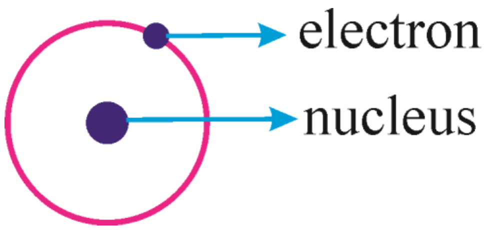


Fig. 3.3: *Schematic representation of of Rutherford's model*

These results led Rutherford to conclude that:

- the atom contained some dense and positively charged region located at the center of the atom that he called as **nucleus.**
- all the positive charge of the atom and most of its mass was contained in the nucleus.
- the rest of the atom must be empty space which contains the much smaller and negatively charged electrons (Fig. 3.3).

The model proposed by Rutherford explained the observation in the –ray scattering experiments as shown below in Fig. 3.4.

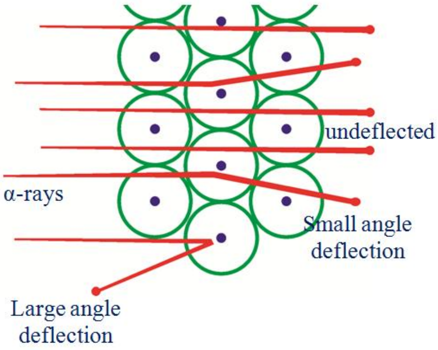


Fig. 3.4 *Explanation of the results of α-ray scattering experiment*

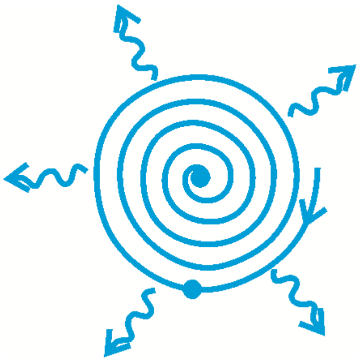


Fig. 3.5: *Failure of Rutherford's model*

However, there was a problem with the Rutherford's model. According to the Maxwell's theory of electromagnetic radiation, a charged particle undergoing acceleration would continuously emit radiation and lose energy. Since the electron in the atom is also a charged particle and is under acceleration, it is expected to continuously lose energy. As a consequence, the electron moving around the nucleus would approach the nucleus by a spiral path (Fig.3.5) and the atom would collapse. However, since it does not happen, we can say that the Rutherford's model failed to explain the stability of the atom.

The next attempt to suggest a model for atoms was made by Neils Bohr-a student of Rutherford. This model used the concept of quantization of the energy of electrons in the atom. Since this fact was suggested by line spectrum of hydrogen atom it is worthwhile to understand the meaning of a spectrum. For this we begin with the understanding of the nature of an electromagnetic radiation.

Intext Questions 3.2

1. List the three constituent particles of an atom.

....

2. What was the aim of Rutherford’s α-particle scattering experiment?

....

3. Briefly describe Rutherford’s model of an atom.

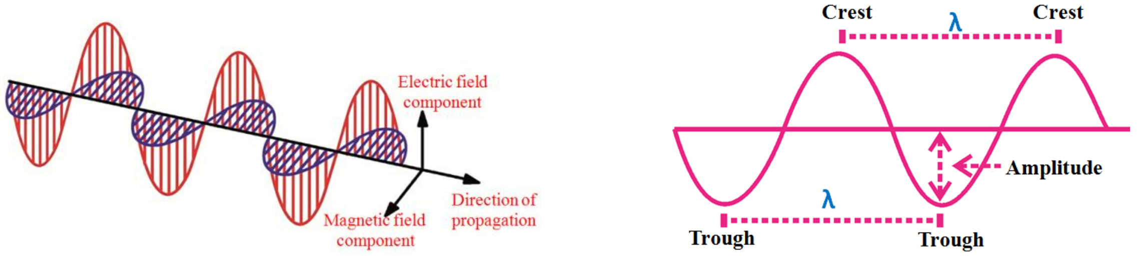
....

4. On what basis was the Rutherford’s model rejected?

....

3.3 Electromagnetic Radiations

Electromagnetic radiation is a kind of energy, which is transmitted through space in the form of electric and magnetic fields. These do not require any medium to propagate. Visible light, radiant heat, radio waves, X-rays and gamma radiation are some the examples of electromagnetic radradiationccording to the Maxwell’s theory, an electromagnetic radiation can be visualized as oscillating electric and magnetic fields. These travel as waves in the planes perpendicular to each other and also the direction of propagation. (Fig. 3.6 (a)) These radiations travel with the velocity of light (3.0 x 10^8 ms^{-1}).



(a) *(b)*

Fig. 3.6 : *(a) An electromagnetic wave showing electric and magnetic fields travellingin planes perpendicular to each other and also to the direction of propagation (b) Characteristics of electromagnetic wave*

3.3.1 Characteristic Parameters of Electromagnetic Radiations

The electromagnetic radiation is characterized by a number of parameters. These are

Amplitude: This is refers to the **maximum height to which the wave oscillates.** It equals the height of the crests or depth of the troughs.

Wavelength: It is the linear **distance between two consecutive wave-crests or wave-troughs** as shown in Fig. 3.6(b). It is represented by the Greek letter lambda (λ) and isexpressed in terms of m, cm, nm or Angstrom ($1A^0 = 10^{-10}$ m).

Frequency: It is defined as the **number of wave crests or wave troughs that pass through a given point per second.** It is represented by a Greek letter nu (v) and is expressed interms of s^{-1} (second inverse or per second). It is also called as Hz (Hertz).

Wave number: It equals **the number of waves per unit length.** It is denoted as v (nu bar) and is equal to the reciprocal of the wavelength. The SI of is m^{-1} (meter inverse). However, sometimes it is also expressed as cm^{-1} (centimeter inverse).

$$\bar{\nu} = \frac{1}{\lambda} \qquad .... (3.1)$$

Velocity: it is defined as the linear **distance traveled by the wave in one second.**

The velocity in meters per second can be obtained by multiplying frequency in Hertz (s^{-1}) with wavelength in meters.

$c = \nu\lambda$ **(or)** $\nu = \frac{c}{\lambda}$ …….(3.2)

The velocity of radiation depends on the medium. In a vacuum, the velocity is equal to 3.00 x 10^8 ms^{-1}.

Electromagnetic radiations also show the characteristics of particles. These are called *quanta*. These quanta are actually bundles of energy. A quantum of visible light is called a photon. The energy of the quantum (or photon) is proportional to the frequency of theradiation. The two are related as

$E = h\nu$ ………(3.3)

The energy of the quantum can also be related to the wavelength or wave number as

$E = h\frac{c}{\lambda}$ or $E = hc\bar{\nu}$ .... (3.4)

The energy of photon can be readily calculated from these equations if we know the frequency,wavelength, or wave number.

Example 3.1: A microwave radiation has a frequency of 12 gigahertz. Calculate the energy of the photon corresponding to this radiation. (h = 6.626 x 10^{-34} Js and 1 gigahertz = 10^9 Hz.)

Solution: The energy is given by the expression, $E = h\nu$

Substituting the values we get,

$$E = 6.626 \times 10^{-34}\ Js \times 1.2 \times 10^{10}\ s^{-1} = 7.95 \times 10^{-24}\ J$$

Example 3.2: The green light has a wavelength of 535 nm. Calculate the energy of a photon of green light.

Solution: We know that

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ Js) \times (3.0 \times 10^{8}\ ms^{-1})}{535 \times 10^{-9}\ m} = 3.71 \times 10^{-19}\ J$$

3.3.2 Electromagnetic Spectrum

Depending on their characteristics (wavelength, frequency and wave number) electromagnetic radiation is of many types and constitute what is called as an electromagnetic spectrum. (Fig. 3.7) The part of the spectrum that we can see is called visible spectrum and is a very small part of the overall spectrum.

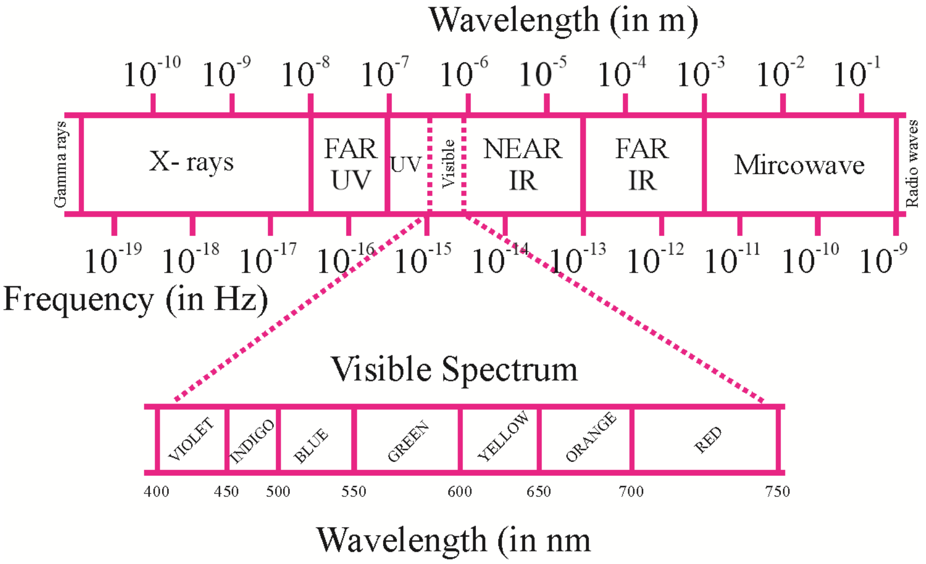


Fig. 3.7: *The electromagnetic spectrum*

Intext Questions 3.3

1. What is an electromagnetic radiation?

....

2. List any three characteristics of electromagnetic radiation.

....

3. What is wave number? How is it related to wave length?

....

4. What is the difference between a ‘quantum’ and a ‘photon’?

....

3.4 Line Spectrum

You know that when we pass a beam of sunlight through a prism we get a range of colours from violet to red (**VIBGYOR**) in the form of a spectrum (like a rainbow). This is called a ***continuous spectrum*** because the wavelengths of the light varies continuously, due to splitting of the white light into constituent colors which is known as dispersion of light, that is without any break. Let us take another example. You are aware of the flame tests for identifying cations in the qualitative analysis. Compounds of sodium impart a bright yellow colour to the flame, copper gives a green flame while strontium gives a crimson red coloured flame. If we pass such a light through a prism it gets separated into a set of lines. This is called as *line spectrum*. Fig. 3.8 differentiates between a continuous and a line spectrum.

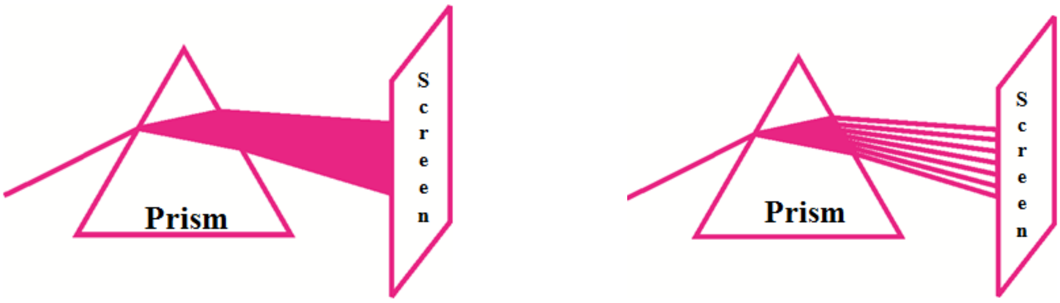
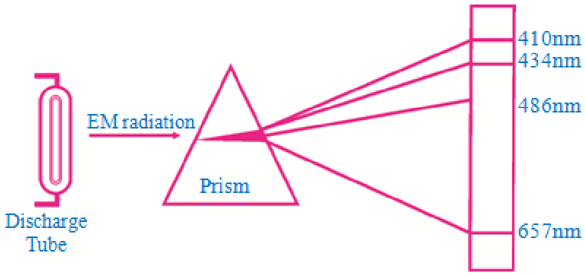


Fig. 3.8: *(a) a Continuous spectrum* *b) a Line spectrum*

3.4.1 Line Spectrum of Hydrogen Atom

When an electric discharge is passed through a discharge tube containing hydrogen gas at low pressure, it emits some light. When this light is passed through a prism it splits up into a set of five lines. This spectrum is called the *line spectrum of hydrogen* (Fig. 3.9).



Johann Balmer
(1825-1898)

Fig. 3.9: *A schematic diagram showing line spectrum of hydrogen in the visible range*

On careful analysis of the hydrogen spectrum, it was found to consist of a few sets of lines in the ultraviolet, visible and infrared regions. These sets of lines were observed by different scientists. These spectral emission lines could be expressed in the form of a general formula as:

$$\bar{\nu} = \frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{cm}^{-1}; R_H = 109677 \text{cm}^{-1} \qquad ...(3.5)$$

Where n_1 and n_2 are positive integers ($n_1 < n_2$) and R_H is called Rydberg's constant. The different sets of lines observed in the hydrogen atom spectrum, their discoveries and the values of n_1 and n_2 are given in the Table 3.2.

Table 3.2: Summary of the emission lines observed in hydrogen spectrum

Series	n_1	n_2	Region of spectrum
Lyman	1	2,3,4....	Ultraviolet
Balmer	2	3,4,5....	Visible
Paschen	3	4,5,6....	Infrared
Bracket	4	5,6,7....	Infrared
Pfund	5	6,7,8....	Infrared

The line Spectrum of hydrogen atom was explained by Bohr's model, which is discussed in section 3.5

Example 3.3: Calculate the wavelength of the Balmer line corresponding to $n_2 = 3$.

Solution: According to Balmer series = $= R_H\left[\frac{1}{2^2} - \frac{1}{n_2^2}\right]$

Where RH = 109,677 cm^{-1}

$$\text{For } n_2 = 3 : \bar{\nu} = 109,677\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = 109,677\left(\frac{5}{36}\right)$$

$$\text{Since} \quad \lambda = \frac{1}{\nu}; \lambda = \frac{36}{109,677 x 5}$$

$$= 6.56 \text{ x } 10^{-5} \text{ cm}$$

$$= 656 \text{ nm}$$

3.4.1.a Planck's Quantam Theory

The wave nature of light could explain the phenomenon of diffraction and interference. However, following are some of the observations which could not be explained with the help of electromagnetic theory. (called classical physics)

- The nature of emission of radiation from hot bodies.
- Reflection of electrons from metal surface when radiation strikes it.
- Variation of heat capacity of solids as a function of Temperature.
- Line spectra of atoms with special reference to hydrogen.

The First concrete explanation for the above observations was given by Max Planck in 1900. According to his theory light is emitted or absorbed in small packets of energy called photons. Each photon has a definite amount of energy associated with it.

The photons travel with a velocity, equal to velocity of light. The Energy of radiation (E) is proportional to its frequency (ν).

$$E \propto \nu; \quad E = h\nu$$

h is called the plank's constant.

$$h = 6.6256 \times 10^{-34}\ \text{Js} = 6.6256 \times 10^{-27}\ \text{erg.s}$$

Planck's theory successfully explains the emission of radiation from a hot body (black body radiations). When solids are heated they emit radiation over a wide range of wavelengths.

Example: When iron rod is heated in a furnace, it first turns to dull red and then becomes more and more red as the temperature increases. As this is heated further, the radiation emitted becomes white, then blue. In terms of frequency, it means that the radiation emitted goes from a lower frequency to a higher frequency region of electromagnetic spectrum. The ideal body, which emits and absorbs all frequencies, is called a black body and the radiation emitted by such a body is called black body radiation. A hollow sphere coated inside with platinum black and having a small hole in its wall acts as a near black body.

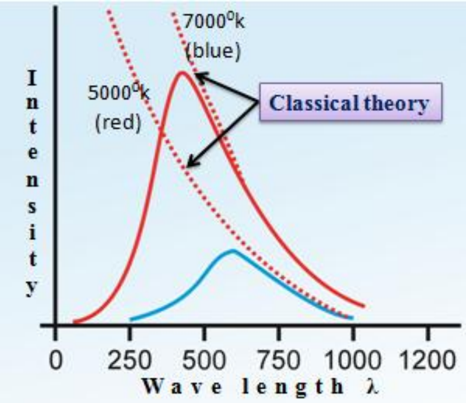


Fig. 3.9.a Radiations emitted by a black body at different temperatures

The exact frequency distribution of the emitted radiation i.e intensity of the radiation versus frequencygives curves. Such curves obtained at different temperatures of the black body are shown in Fig. 3.4.1(a).

The study of the curves shows that the nature of the radiation depends on the temperature of the blackbody. If the energy emitted is continuous the curve should be as shown by the dotted lines, but it is notso.

The following conclusions are drawn from the study of the shape of the curves.

- At a given temperature, the intensity of the radiant energy increases with the wave length,reaches a maximum, and then decreases.
- As the temperature increases, the peak of the curve shifts to lower wavelength.

The above experimental results could not be explained satisfactorily on the basis of the wave theory oflight. The salient features of Planck's theory are

* The oscillating particle in the black body does not emit energy continuously.

* Radiation is emitted only in discrete quantities, Planck gave the name QUANTUM to the smallest quantity that can be emitted or absorbed in theform of electromagnetic radiation.

* The phenomenon of wave propagation of radiant energy in the form of quanta is called quantization of energy.

* Energy is emitted or absorbed in simple integral multiples of a quantum. It cannot be in fractional values.

* $E = n.h\nu$; where n = an integer.

3.4.1.b Explanation of Photo Electric Effect

When a clean surface of an alkali metal (Ex: Potassium, Rubidium etc) is exposed to a beamof light, ejection of electrons from the metal surface takes place. Only if the frequency of incident light is greater than a certain minimumvalue, characteristic of the metal. This phenomenon is known as photo electric effect. It is observed that violet light is able to eject electrons from potassium but red light which is of lower frequency has no effect. The explanation for the frequency dependence of the photoelectric effect is given by **ALBERT EINSTEIN**. He could explain the photoelectric effect using Planck's quantum theory of electromagnetic radiation as a starting point. Einstein argued that the wave model of light cannot explain the observed facts. However, if light is regarded as consisting of particles (called photons) such that the energy (E) of a photon is related to the frequency (v) by the relation.

$E = h\nu$; where h = Planck's constant. It is easy to understand photoelectric effect.

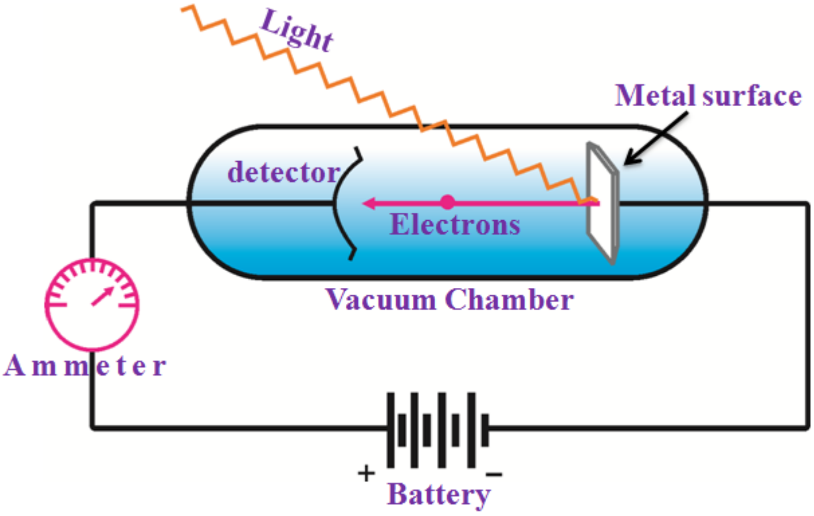


Fig. 3.9.b Equipment for studying the photoelectric effect. Light of a particular frequency strikes a clean metal surface inside a vaccum chamber. Electrons are ejected from the metal and are counted by a detector that measures their kinetic energy.

- When photon of sufficient energy strikes an electron in the atom of the metal, it transfers its energy instantaneously to the electron during the collision and the electron is ejected without any timelog or delay.
- Greater the energy possessed by the photon, greater will be the transfer of energy to the electron and greater the kinetic energy of the ejected electron.
- When a photon strikes the surface of the metal, the energy ($h\nu$) of the photon is absorbed by the electron in the metal and a part of this energy is used to set free the electron from the attractive forces in the metal. The remaining energy of the photon appears in the form of the kinetic energy of the released electron.

  Thus we can write $h\nu = W + K.E$ where, $h\nu$ = Energy of the photon.

  W = Energy required to overcome the attractive forces on the electron in the Metal and also called work function

  K.E = Kinetic energy of emitted electron.

  $\therefore\ h\nu = h\nu o + 1/2\, m_e V^2$

  M_e = mass of electron; ν = velocity of ejected electron.

  ν_0 = Threshold frequency.

3.5 Bohr's Model

In 1913, Niels Bohr (1885-1962) proposed another model of the atom where electrons move around the nucleus in circular paths. Bohr's atomic model is built upon a set of postulates, which are as follows:

1. The electrons move in a definite circular path around the nucleus (Fig. 3.10). He called these circular paths as **orbits** and postulated that ***as long as the electron is in a given orbit its energy does not change*** (or energy remains fixed). these orbits were therefore refered to as **stationary orbits** or **stationary states** or **non radiating orbits**.

Fig. 3.10 : *Bohr's model*

Bohr won the Nobel Prize in Physics in 1922 for his work.

2. The ***electron can change its orbit by absorbing or releasing evergy***. An electron at a lower (initial) state of energy, E_i can go to a (final) higher state of energy, E_f by absorbing (Fig 3.11) a single photon of energy given by

$E = hv = E_f - E_i$ ………… (3.6)

Similarly, when electron changes its orbit from a higher initial state of energy E_i to alower final state of energy E_f, a single photon of energy h_l is released.

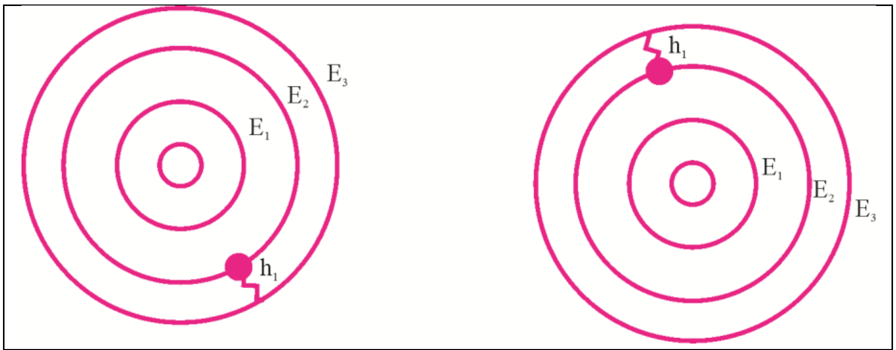


Fig. 3.11 : *Absorption and emission of photon causes the electron to change its energy level.*

3. The **angular momentum of an electron** of mass m_e moving in a circular orbit of radius r and velocity is an integral multiple of h/2.

$$m_e vr = \frac{nh}{2\pi}$$

where *n* is a positive integer, known as the **principal quantum number**.

Bohr obtained the following expressions for the energy of an electron in stationary states of hydrogen atom by using his postulates.

Energy of the orbit, $E_n = -R_H\left(\frac{1}{n^2}\right)$ .... (3.8)

Bohr could correlate R_H to other properties as $R_H = \frac{mz^2e^4}{8h^2\varepsilon_0^2}$; .... (3.9)

where,

m = mass of the electron

h = Plank's constant

z = nuclear charge

ε_0 = permitivitty of the medium

e = electronic charge

The negative sign in the energy expression means that the there is an attractive interaction between the nucleus and the electron. This means that certain amount of energy (called ionisation energy) would be required to remove the electron from the influence of the nucleus in the atom. You may note here that the energies of the Bohr orbits are inversely proportional to the square of the **quantum number** *n*. As *n* increase the value of the energy increases (becomes lesser negative or more positive). It means that as we go farther from the nucleus the energy of the orbit goes on increasing.

3.5.1 Bohr's Theory of Hydrogen Atom:

Hydrogen atom contains a single proton in its nucleus with +e. An electron with –e revolve round the nucleus in a circular orbit of radius 'r'. As per coulomb's law, electrostatic force of attraction between the nucleus and the electron is given by

Attractive force = $-e^2/r^2$

This is columbic force of attraction of the electron towards the nucleus. For the atom to be stable anequal centrifugal force must act away from the nucleus.

This centrifugal force arises as a result of the electron revolving around the nucleus in the circular orbit. It is equal to $\frac{mv^2}{r}$ where m is mass of electron revolving around the nucleus in the circular orbit and 'r' is the radius of the orbit.

Therefore alternative force of the electron revolving round the nucleus in a stationary orbit

$$\frac{-e^2}{r^2} = \frac{-mv^2}{r} \text{ or } \frac{e^2}{r} = mv^2 \qquad \text{---- (1)}$$

As per Bohr's quantum condition

$$mvr = \frac{nh}{2\pi}$$

$$\therefore V = \frac{nh}{2\pi mr} \text{ (or) } V^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \qquad \text{---- (2)}$$

Substitute the value of V2 in equation (1) above

$$\frac{-e^2}{r^2} = \frac{mn^2h^2}{4\pi^2m^2r^2} \text{ (or) } r = \frac{n^2h^2}{4\pi^2me^2}$$

If r is represented as r_n for n^th^ orbit

$$\text{Radius of nth orbit } (r_n) = \frac{n^2h^2}{4\pi^2me^2} \qquad \text{----- (3)}$$

Substitute the values of $h = 6.256 \times 10^{-27}$ erg.sec

$\pi = 3.14$

(Mass of electron) m = 9.1 x 10-28 g

(Charge on electron) $e = 4.802 \times 10^{-10}$ e.s.u in equation (3)

We get Radius of nth orbit (rn) = $0.529 \times 10^{-8}\ n^2$ cm

If n = 1 Bohr's orbit (r) = 0.529×10^{-8} cm = 0.529 A^0.

Since 'n' can have values 1,2,3…... a simple integer. It is obvious that orbits of only certain finite radii are possible and electrons could occupy possibly only these permitted orbits. These simple whole numbers denoted by 'n' are called Principal Quantum numbers.

Energy of electron:

The total energy of electron revolving in an orbit is obtained by summing up its kinetic energy and potential energy.

Kinetic energy due to motion of an electron = $\frac{1}{2}mv^2$

(m is the mass of electron and v is its velocity)

Potential energy of electron due to position = $-e^2 / r$

$$\text{Total energy of electron} = \text{K.E} + \text{P.E} = \frac{1}{2}mv^2 - \frac{-e^2}{r} = \frac{e^2}{2r} - \frac{e^2}{r} = \left[mv^2 = \frac{e^2}{r}\right]$$

$$\text{Therefore total energy of electron (E)} = \frac{-e^2}{2r}$$

$$\text{Substituting the value of 'r'} = \frac{n^2h^2}{4\pi^2me^2}$$

$$\text{Energy of electron in nth orbit} = E_n = \frac{-e^2 4\pi^2 me^4}{2n^2h^2}$$

$$E_n = \frac{-2\pi^2 me^4}{h^2} \times \frac{1}{n^2}$$

Except of 'n' all the other terms in the above equation are constant we can write

$$E_n = \frac{-K}{n^2} \quad \text{where } K = \frac{2\pi^2 me^4}{n^2}$$

Substituting the values of m,e,h and π we have

$$E_n = \frac{-21.72 \times 10^{-12}}{n^2}\ \text{erg} = \frac{-21.72 \times 10^{-19}}{n^2}\ \text{J or } \frac{-13.6}{n^2}\ \text{eV.}$$

Thus, we can conclude that the energy of an electron (E) can have only certain discrete restricted values depending upon the value of 'n'. This is termed as quantization of energy of the electron. An electron revolves only in certain orbits of fixed radii and also it has only certain allowed energy levels. These orbits are also termed as main energy levels or the principal quantum states.

In the equation energy of an electron $E_n = \frac{-K}{n^2}$

the energy of an electron is inversely proportional to the square of the principle quantum number n. As the value of n increases, radius of the orbit increase and the absolute value of energy of an electron also increase effectively.

As the value of n decrease, the radius of the orbit as well as the absolute value of its energy decreases. This increases the stability of the atom. When the electron of a hydrogen atom revolves in the first orbit, energy is at its lowest possible value and hence confers maximum stability to the hydrogen atom. This istermed as ground state of the hydrogen atom.

When the electron is free from the influence of the nucleus the energy is taken as zero. The electron in thissituation is associated with the stationary state of principle quantum number.

(n) = ∞ and is called as ionized hydrogen atom. When the electron is attracted by the nucleus and ispresent in orbit n the energy is emitted and its energy is lowered. This is the reason for the presence of negative sign in the equation for energy and depicts its stability relative to the reference state of zeroenergy and n =1

3.5.1 Explanation of Line Spectrum of Hydrogen Atom

As per the second postulate mentioned above, the energy emitted in the transition of a single electron from an initial stationary state of energy E_i to a final stationary state of energy E_f is given as h**ν** = E_i - E_f . Substituting the expressions for energy from Eq. 1.8 we can get the formula given in eg. 3.5. Thus Bohr's model provides an explanation for the observed line spectrum of hydrogen as summarized in Table 3.2 Fig. 3.12 shows the energy level diagramfor hydrozen atom and the transitions responsible for the observed line spectrum.

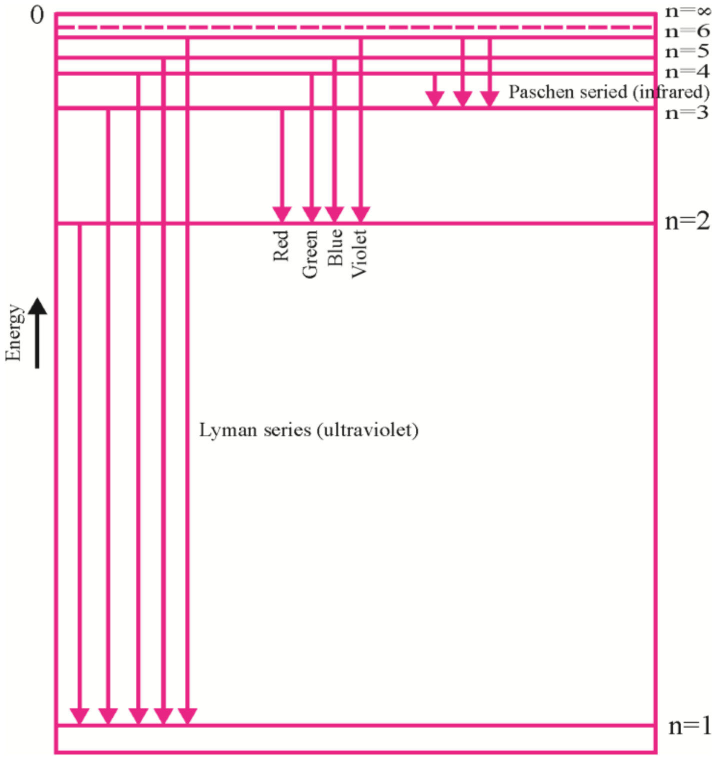


Fig. 3.12: *Energy level diagram for H-atom, showing various transitions responsible for the observed line spectrum.*

Intext Questions 3.4

1. What is the difference between a line spectrum and a continuous spectrum?

....

2. What are the main postulates of Bohr's model?

....

3. How does the energy of a Bohr orbit vary with the principle quantum number ‘n’?.

....

4. What is ‘Quantum’?

....

5. Give the value of Planck’s constant in S.I. system?

....

6. State photoelectric effect.

....

7. Define threshold energy.

....

3.6 Wave - Particle Duality

In section 3.3 you have learnt about the wave nature of light. As you are aware that some ofthe properties of light e.g. diffraction and interference can be explained based on its wave nature. On the other hand some other properties like photoelectric effect and scattering of light can be explained only on the basis of particle nature of light. Thus light has a dual nature possessing the properties of both a wave and a particle, i.e., light could under some conditions behave like a particle and other conditions behave as a wave.

In 1923 a young ~~F~~rench physicist, Louis de Broglie, argued that if light can show wave aswell as particle nature, why should particles of matter (e.g., electron) not posses wave like characteristics? He proposed that matter particles should indeed have a wave nature and said that a particle of mass *m* moving with a velocity *v* has an associated wavelength, ~~*e*~~ (sometimes called *de Broglie wavelength*) given by the formula;

$$\lambda = \frac{h}{mv} \quad \text{or} \quad \lambda = \frac{h}{p} \qquad \text{.... (3.10)}$$

Where p (= mv) is the momentum of the particle. The de Broglie wavelength of a body is inversely proportional to its momentum. Since the magnitude of *h* is very small, the wavelength of the objects of our everyday world would be too small to be observed. Let us make a calculation to see this.

Example 3.4: Calculate the de Broglie wavelength associated with a cricket ball weighing 380g thrown at a speed of 140 km per hour.

Solution: Mass of the cricket ball = 380 g

$= 380 \times 10^{-3}$ kg $= 0.38$ kg

Speed or Velocity = 140 km/hr

$= (140 \times 1000) / 3600 = 38.89$ m s^{-1}

The wavelength associated with the cricket ball will be

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\,\text{JS}}{(0.380\text{kg})(38.89\text{ms}^{-1})}$$

$= 4.48 \times 10^{-35}$ m (J = kg m_2 s^{-2})

Dr-Broglie (1892-1987)
de-Broglie proposed the theory of wave-particle dualism as a part of his PhDthesis in 1924. He got the physics Nobel Prize in 1929

If the electrons show wave nature then a beam of these electrons is expected to show diffraction which is a property of waves. In 1927 G.P. Thomson and C.J. Davidson demonstrated the diffraction of electron waves by the crystal lattice of nikel (Fig. 3.13). Thus electrons also show a dual nature. That is, sometimes this show particle nature while at some other times they show wave nature.

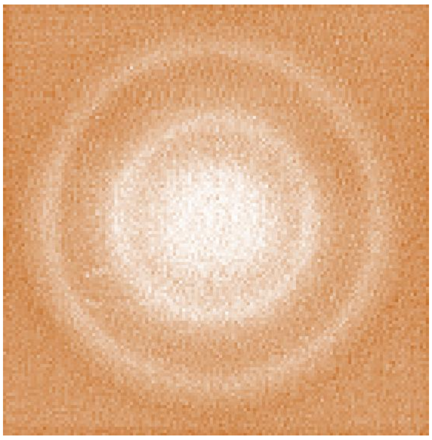


Fig. 3.13 : *Electron diffraction pattern from nickel crystal*

Werner Heisenberg (1901-1976)
Heisenberg got the phys.
Nobel Prize in 1932

3.7 Heisenberg's Uncertainty Principle

An important consequence of the wave-particle duality of matter and radiation was discovered by Werner Heisenberg in 1927 and is called the **uncertainty principle**. According to this principle it is not possible to simultaneously measure both the position and **momentum** (***or velocity***) of an electron accurately. In simple words we may state that more accurately you measure a particle's position, the less accurately you're able to measure its momentum, and vice versa. Mathematically, the Heisenberg principle can be expressed in terms of an inequality.

$$\Delta x \ \Delta p \ \geq \ \frac{h}{4\pi} \qquad \text{....(3.11)}$$

Where Δx and Δp are the uncertainties in the measurements of position and momentum respectively. If the position of an object is known exactly (i.e., $\Delta x = 0$), then the uncertainly in the momentum must be infinite, meaning that we cannot say anything about the velocity. Similarly, if the velocity is known exactly, then the position would be entirely uncertain and the particle could be anywhere. It means that we cannot say anything about the position of the particle. In actual practice none of the two properties can be measured with certainly. Due to the small value of Planck's constant, h (6.626 x 10^{-34} J s) this principle is not relevant while making measurements of large objects like car, bus or aeroplane etc. It is relevant, only when you are making measurements on very small objects such as electrons.

Heisenberg's principle questioned the validity of Bohr's model. It is so because accordingto Bohr's model we can precisely calculate the radius of the orbit (i.e., the position of the electron) and the velocity of electron in it. But it is not possible according to Heisenberg's principle. It motivated many scientists to develop newer models of the atom using the dual nature of the electron. This resulted into the development of a quantum mechanical or *Wave Mechanical Model* of the atom discussed in the next section.

Intext Questions 3.5

1. What do you understand by wave-particle duality?

....

2. Name the experiment that established the wave nature of electron.

....

3. Compute the de-Broglie wavelength associated with an electron moving which avelocity of 100 km / second? ($m_e = 9.1 \times 10^{-31}$ kg)

....

4. State Heisenberg's Uncertainty Principle?

....

3.8 Wave Mechanical Model of atom

Wave Mechanical Model of atom was proposed by Erwin Schrodinger - an Austrian physicist in 1926. This model is basically formalism or a mathematical recipe, which is based on some postulates that have no foundation in classical physics. The correctness of these postulates can be justified in terms of the correctness of the results predicted by them. According to this Model, the motion of electron inside the atom could be described in terms of a mathematical function called, **wave function**, φ (Greek letter, psi). The wave functions are assumed to contain all the information about the electron and are obtained by solving a differential equation called the Schrodinger wave equation (SWE). The square of the wave function φ^2 is a measure of the probability of finding an electron in a three dimensionalspace around the nucleus.

On solving the SWE for hydrogen atom we get a number of wave functions, which arecharacterized by three quantum numbers viz.,

- Principal quantum number, n
- Azimuthal quantum number, l
- Magnetic quantum number, m_l

These quantum numbers arise in the process of logically solving the wave equation. Every electron in an atom has a unique (different) set of quantum numbers which help to describe the three dimensional region where there is maximum probability of finding the electron. This region is called an ***atomic orbital*** or simply ***orbital***.

3.8.1 Significance of Quantum Numbers

The three quantum numbers describe the size, shape, and orientation of the atomic orbitals in space. There is an additional quantum number which does not follow from the Schrodinger wave equation but is introduced to account for electron spin. The fourth quantum number thus helps in designating the electrons present in the atom. Let us understand the significanceof each of these quantum numbers.

Principal quantum number, *n*

The principal quantum number, *n* describes the energy level (or principal shell) of the electron within the atom. n can have only positive non zero integral values (i.e., n = 1,2,3,4.....). This means that in an atom, the electron can have only certain energies.

Thuswe may say that n quantizes energy of the electron. The principal quantum number also determines the mean distance of the electron from the nucleus, i.e., its size. Greater thevalue of *n* farther is the electron from the nucleus.

Each principal shell can accommodate a maximum of $2n^2$ electrons, i.e. n = 1 number of electrons: 2

n = 2 number of electrons: 8
n = 3 number of electrons: 18 and so on...

Azimuthal quantum number, *l*

The azimuthal quantum number, *l* is related to the geometrical shape of the orbital. The value of *l* may be zero or a positive integer less than or equal to n-1 (n is the principal quantumnumber), i.e., *l* = 0,1,2,3....... (n-1). Different values of *l* correspond to different types of **subshells** and each subshell contains orbitals of a given shape.

l = 0	Corresponds to ***s***-subshell and contains the orbital with spherical shape called as ***s*-orbital**.
l = 1	Corresponds to ***p***-subshell and contains the orbitals with-a **dumb-bell shape** called as ***p*-orbitals**. There are three *p*-orbitals in each p-subshell.
l = 2	Corresponds to ***d***-subshell and contains the orbitals with a **clover leaf shape** called as***d*-orbitals**. There are five *d*-orbitals in each p-subshell.
l = 3	Corresponds to ***f***-subshell and contain **f orbitals.** There are seven *f*-orbitals in each ***f***-shubshell.

The shapes of s, p, and d orbitals will be discussed in the next subsection.

Magnetic quantum number, m_l

The quantum number, m_l describes the direction or orientation of the orbital in space. The quantum number m_l may have any integral value from - *l* to + *l*. For example, for *l* = 1; m_l can have the values as -1,0 and 1.

Magnetic quantum number, m_s

The quantum number, m_s describes the spin of the electron **i.e.,** whether it is clockwise or anticlockwise. The quantum number, m_s does not arise while solving SWE. The clockwise and anticlockwise direction of electron spin has arbitrarily been assigned the value as + 1/2and -1/2 respectively.

To sum up, let us take an example of an electron belonging to the third shell (n=3). This electron can be in as *s*-subshell (*l* = 0) or a *p*-subshell (*l* = 1) or a *d*-subshell (*l* = 2). If it happens to be in a *p*-shell it may be in any of the three possible *p*-orbitals (corresponding to m_1 = -1, 0 + 1 directed along *x*, *y* or *z* - axis. And within the orbital it may have clockwise (ms = + $\frac{1}{2}$) or anti-clockwise (ms = - $\frac{1}{2}$) direction of electron spin. The possible values of different quantum numbers for an electron belonging to the third shell are given in Table 3.3.

Table 3.3: The quantum numbers for an electron belonging to the third shell

Principal quantum number, n	Azimuthalquantum number, l	Magneticquantum number, m_l	Magnetic spinquantum number, m_s
3	0	0	**+1/2**
			-1/2
	1	-1	**+1/2**
			-1/2
		0	**+1/2**
			-1/2
		+1	**+1/2**
			-1/2
	2	-2	**+1/2**
			-1/2
		-1	**+1/2**
			-1/2
		0	**+1/2**
			-1/2
		+1	**+1/2**
			-1/2
		+2	**+1/2**
			-1/2

You may note here that the third shell can contain a maximum of 18 electrons and each ofthem, has a distinct set of four quantum numbers.

Intext Questions 3.6

1. What do you understand by a Wave Function?

....

2. What is the difference between an orbit and an orbital?

....

3. What are quantum numbers? List different quantum numbers obtained from Schrodinger Wave Equation?

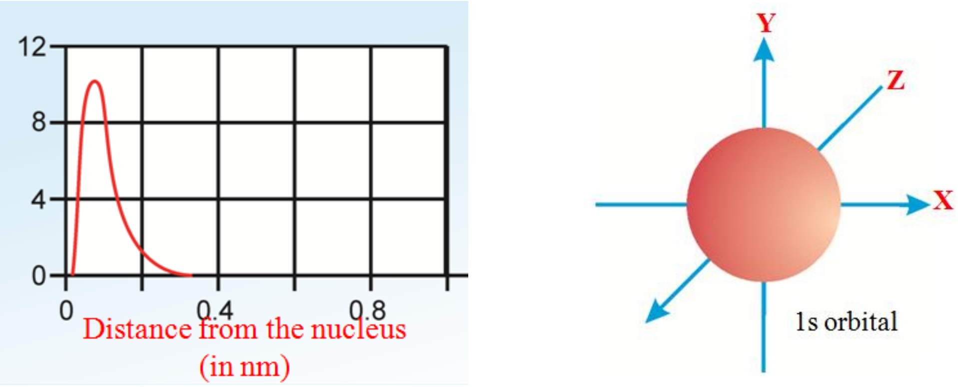
....

4. Give the significance of the Principal, azimuthal and magnetic quantum numbers?

....

3.8.1 Shapes of Orbitals

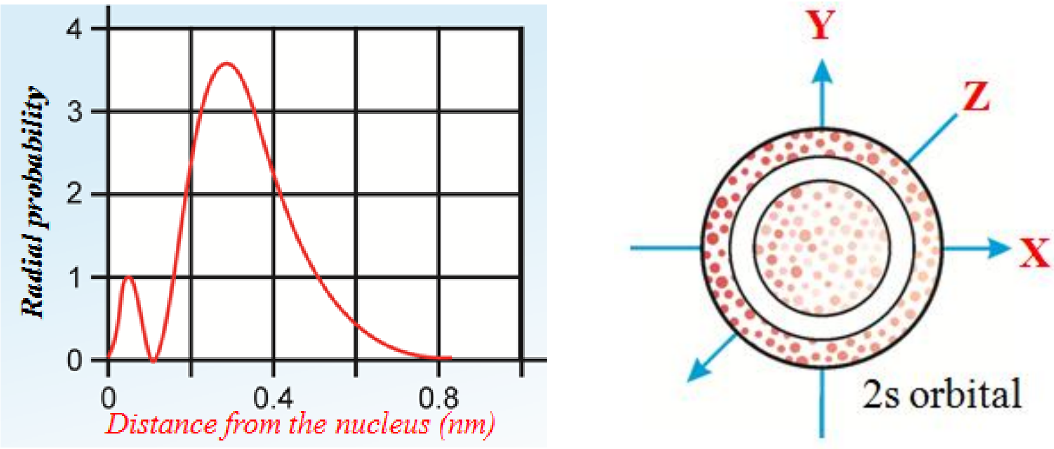
We have defined an orbital as "***the three dimensional region of space around the nucleus where there is maximum probability of finding the electron***". Lets us try to understand the meaning of an orbital by taking the example of 1s orbital ($n = 1$; $l = 0$). This can be understood in terms of a radial probability curve. Such a curve gives the variation of the probability of finding the electron as a function of distance from the nucleus. For 1s orbital the radial probability curve (Fig. 3.14 (a)) shows that the probability of finding the electron in 1s orbital increase as we move away from the nucleus and reaches a maximum at a certain distance (=0.0529 nm or 52.9 pm for hydrogen atom) and then decreases as we go further away from it and at a certain distance it becomes close to zero. The curve shows the radial probability for a given direction.



(a) (b)

Fig. 3.14: *(a) Radial probability curve for 1s orbital*
(b) Boundary surface diagram for 1s orbital

The probability would be same for all possible directions. if we put all such curves together it would give a spherical distribution of the electron probability. Since the radial probability does not become zero at any distance, we cannot specify the size of the sphere. Therefore, the orbital is represented as a boundary surface diagram, which may be thought as a region of space, which contains 95% of the probability of finding the electron, as indicated in Fig. 3.14 (b). Thus the 1s orbital is represented as a sphere.



(a) (b)

Fig. 3.15 : *(a) Radial probability curve for 2s orbital*
(b) Boundary surface diagram for 2s orbital

Similarly, the Fig 3.15 (a) gives the radial probability curve for a 2s orbital while the Fig 3.15 (b) shows the boundary surface diagram for the same. You can note two things here. First you may note that for a 2s orbital the boundary surface diagram is bigger as compared to a 1s orbital. Secondly, the radial probability curve shows two maxima. The probability initially increases, reaches a maxima then it decreases and comes close to zero. It increases again and decreases as we move further away from the nucleus. The region where the probability comes close to zero (before increasing again) is called a ***spherical node***. There are n-1 spherical nodes in an orbital.

A node is a region in space where the probability of finding the electron is close to zero.

p*-orbital:** Now when we draw the shape of a p orbital ($n = 1$; $l = 1$) we get a shape as shown in the Fig. 3.16. This picture shows the shape of one of the three possible p orbitals which is directed towards the z-axis; P_Z. You may note that the probability picture for a P_Z orbital consists of two lobes; one along the positive z-axis and the other along the negative z-axis. Another important feature of a p-orbital is the absence of the electron probability in the XY-plane. Such a plane is called a ***nodal plane. The shapes of the three p-orbitals are given inFig. 3.17

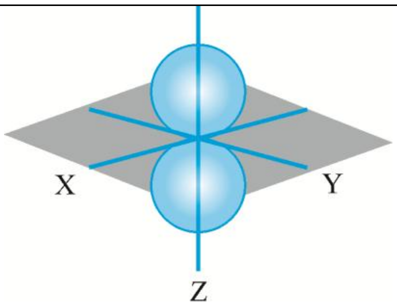


Fig. 3.16: *A p-orbital surface diagrams (shapes)*

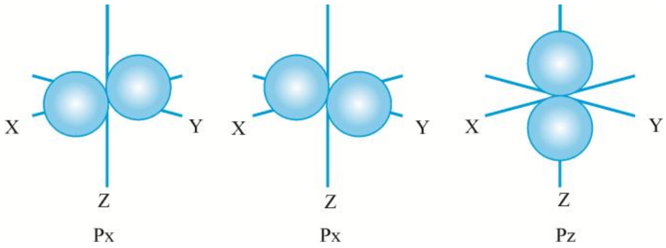


Fig. 3.17 : *The boundary showing a nodal plane of the p-orbitals*

The Fig. 3.18 gives shapes of five possible d-orbitals. The d-orbitals also contain nodal planes.The five d-orbitals have different shapes but they all have same energies i.e., these are degenerate.

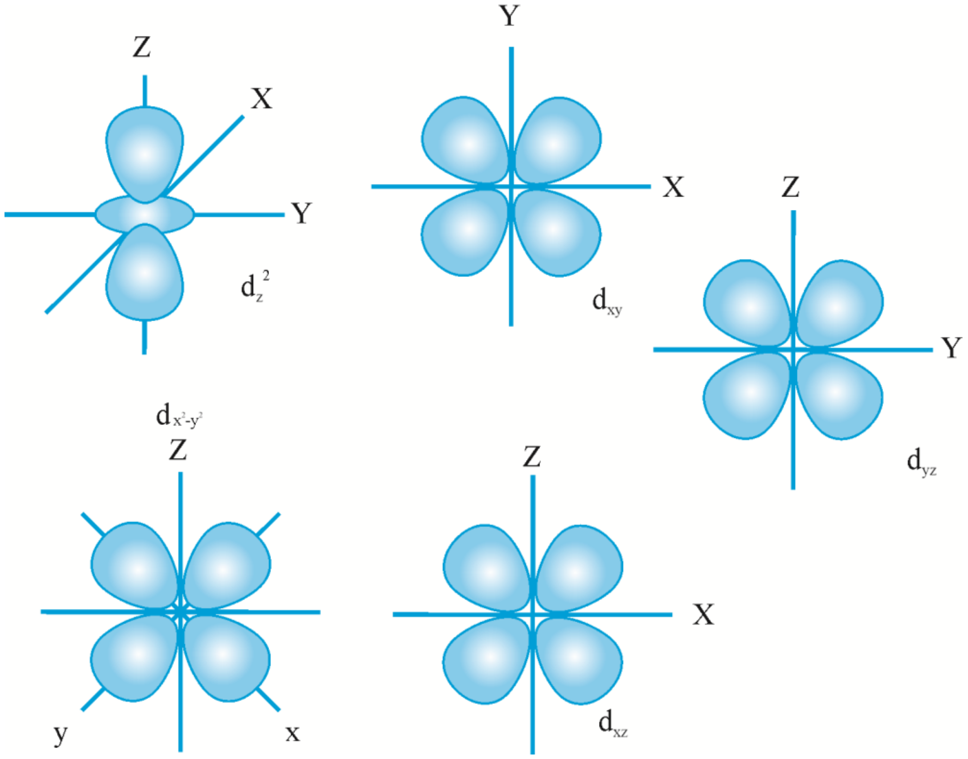


Fig. 3.18 : *The boundary surface diagrams (shapes) of the five d-orbitals*

Intext Questions 3.7

1. What are the shapes of s, p and d orbitals?

....

2. Describe the shape of a 2s orbital. How is it different from that of a 1s orbital?

....

3. What do you understand by

i) a spherical node ?

ii) a nodal plane ?

....

4. How many spherical nodes will be there in 3s orbtial ?

....

3.8 Electronic Configuration of Atoms

You have so far learn that an atom consists of a positively charged nucleus surrounded by electrons present in orbitals of different shapes and sizes. These orbitals are part of different shells and sub-shells and are characterized by the three quantum numbers viz. n, l and m_l. Let us now take up the distribution of electrons in these shells and sub-shells. Such a distribution of electrons is called **Electronic Configuration** and is governed by three basic rules or principles.

3.9.1 Aufbau (or building up) Principle

This principle is concerned with the energy of the atom and states that the electrons should occupy.–The electrons occupy the orbitals in such a way that the energy of atom is minimum. In other words, **the electrons in an atom are filled in the increasing order of their energies**. Now, how does one know the increasing order of the orbital energies? You have learnt above that the principal quantum number determines the energy of the orbitals. Higher the value of n higher the energy. This is true only for hydrogen atom. For other atoms, we need to consider both n and l. This means that **different sub-shells in a given shell have different energies**. The order of orbital energies can be determined by the following $(n + l)$ rules.

Rule 1 : An orbital with a lower value for $(n + l)$ has lower energy. For example, the 4s orbital$(n + l = 4 + 0 = 4)$ will fill before a 3d orbital $(n + l = 3 + 2 = 5)$.

Rule 2 : If the value of $(n + l)$ is same for two orbitals then the orbital with lower value of n will be filled first. For example, the 3d orbital $(n + l = 3 + 2 = 5)$ will fill before a 4p orbital $(n + l = 4 + 1 = 5)$.

Following these rules the increasing order of the orbital energies comes out to be

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s

3.9.1 Pauli's Exclusion Principle

This principle concerns the spin of electrons present in an orbital. According to the Pauli's principle, **no two electrons can have all the four quantum numbers to be same.**

For example, if a given electron in an atom has the set of four quantum numbers as $n = 2$, $l = 1$, $m_l = 1$ and $m_s = +1/2$ then no other electron in the atom can have the same set of quantum numbers.

As you know that an orbital is characterized by three quantum numbers so the electrons occupying a given orbital would have same values of these three quantum numbers. These electrons are distinguished in terms of their spin quantum number, m_S. Since the spin quantum number can have only two values so ***only two electrons can occupy a given orbital***. In fact this fourth quantum number was introduced through Pauli's principle only.

3.9.1 Hund's Rule

This rule concerns the distribution of electrons in a set of orbitals of the same energy, i.e. constituents of a subshell. According to this rule if a number of orbitals of the same sub-shell are available then the electrons distribute in such a way that each orbital is first singly occupied with same spin. For example, the six electrons in carbon distribute as

$1s^2\ 2s^2\ 2p^1_x\ 2p^1_y\ 2p^0_z$ and not as $1s^2\ 2s^2\ 2p^2_x\ 2p^0_y\ 2p^0_z$

Since electrons repel each other, they remain as far as possible from one another by occupying different orbitals. The rules discussed above can be used to write the electronic configuration of different elements.

There are two common ways of representing the electronic configurations. These are

a) **Orbital notation method:** In this method the filled orbitals are written in the order of increasing energies. The respective electrons in them are indicated as superscripts as shown in the example given below. For example, the electronic configuration of nitrogen atom (atomic number 7) is written as $1s^2\ 2s^2\ 2p^1_x\ 2p^1_y\ 2p^1_z$.

b) **Orbital diagram method:** In this method the filled orbitals are represented by circles or boxes and are written in the order of increasing energies. The respective electrons are indicated as arrows whose direction represents their spin. For example, the electronic configuration of nitrogen in the orbital diagram notation can be written as

Electronic configuration can also be written in a short hand form. In this method the last **completed orbital shell** is represented in terms of a noble gas. For example, the electronic configuration of lithium and sodium can be written as

Li	[He] $2s^1$
Na	[Ne] $2s^1$

The electrons in the noble gas configuration are termed as ***core electrons*** while the ones inthe outer shell are called ***valence electrons***.

Intext Questions 3.8

1. What do you understand by the electronic configuration of an atom?

....

2. What is Pauli's exclusion principle?

....

3. What is Aufbau principle? What are ($n + l$) rules?

....

4. Which of the following orbitals will be filled first?

a) $2p$ or $3s$ b) $3d$ or $4s$

....

What You Have Learnt

Atoms are made up of three fundamental particles namely, electrons, protons and neutrons.

J.J. Thomson made the first attempt to describe the structure of an atom in terms of a model called **plum pudding model**. According to this atoms can be considered as a large positively charged body (pudding) in which a number of small negatively charged electrons (plums) are scattered.

According to the Rutherford's model, the positive charge of the atom and most of its mass is contained in the nucleus and the rest of the atom is empty space which contains the much smaller and negatively charged electrons.

Electromagnetic radiation is a kind of energy, which is transmitted through space in the form of electric and magnetic fields. It travels with the speed of light and does not need any medium to travel.

The electromagnetic radiations are characterized by a number of parameters like, amplitude, wavelength, frequency, wave number and velocity.

In 1913, Niels Bohr proposed 'Planetary Model for atom. According to the model the electrons move in definite circular paths of fixed energy around a central stationary nucleus. The electrons can change their orbits by absorbing or emitting a photon of energy ($= h\nu$) equal to the difference of the energies of the orbits.

Bohr's model did explain for the stability of atom and the line spectrum of hydrogen. The model however was unable to explain the spectra of atoms other than hydrogen.

Louis de Broglie, argued for the dual nature of electron and proposed that matter particles should have a wave nature. The associated wave length, is given by the formula;

$$\lambda = \frac{h}{mv} \quad \text{or} \quad \lambda = \frac{h}{p}$$

This was experimentally verified by Thomson and Davisson by diffraction of electron waves by the crystal lattice of nickel.

The wave-particle duality of matter led Werner Heisenberg to propose the **uncertainty principle**. According to which it is not possible to measure simultaneously both the ***position*** and ***momentum*** of a particle with a infinite precision.

The dual nature of electron and Heisenberg's uncertainty principle led to the development of wave mechanical model.

According to the Wave Mechanical Model, the motion of electron inside the atom can be described in terms of a mathematical function called, wave function φ. This wave function contains all the information about the system and can be found by solving a wave equation called Schrodinger wave equation.

The square of the wave function, ψ^2 is a measure of the probability of finding the electron in a certain three dimensional space around the nucleus. This region is called as ***atomic orbital*** or simply ***orbital***.

These wave functions are characterized by three quantum numbers. These quantum numbers describe the size, shape and orientation of the atomic orbitals in space. Every electron in an atom has a unique set of quantum numbers.

The principal quantum number n concerns the quantisation of the energy of the electron while the Azimuthal quantum number, l is related to the shape of the orbital. The magnetic quantum number m_1 describes the direction or orientation of the orbital in space.

An additional quantum number, m_S is introduced to account for electron spin. This quantum number does not follow from the wave mechanical model and describes the spin of the electron.

Different orbitals have different shapes. An s orbital is spherical; p orbitals are dumb-bell shaped; *d* orbitals have cloverleaf shape while *f* orbitals have eight lobed shape.

The distribution of elections in the shells and subshells is called **Electronic Configuration**. If is governed by three rules which are Aufbau principle; Pauli's exclusion principle and Hund's Rule of maximum multiplicity.

According to Aufbau principle the electrons in an atom are filled in the increasing order of their energies which is determined by $(n + 1)$ rules.

According to the Pauli's exclusion principle, no two electrons can have all the four quantum numbers to be same.

While filling electrons in the orbitals of same subshell, according to Hund's rule, each orbital is first singly occupied with same spin then the pairing up takes place. The photons travel with a velocity equal to the velocity of light. The energy of radiation (E) is proportional to its frequency (v)

$E = hv$ where h is a Planck's constanth = 6.6256×10^{-34} JS

The phenomenon of ejection of electrons from the metal surface when light is exposed onit is called photo electric effect.

Terminal Exercise

1. a) What are the three fundamental particles that constitute an atom?

   b) Compare the charge and mass of an electron and of a proton.

2. What do you think is the most significant contribution of Rutherford to the developmentof atomic structure?

3. What experimental evidence shows the dual nature of light?

a) Compute the energy of FM radio signal transmitted at a frequency of 100 MHz.

b) What is the energy of a wave of red light with λ= 670 nm?

4. In what way was the Bohr's model better than the Rutherford's model?

5. What are the drawbacks of Bohr's Model?

6. What led to the development of Wave Mechanical Model of the atom?

7. What do you understand by an orbital? Draw the shapes of s and p-orbitals.

8. Explain the Hund's rule of maximum multiplicity with the help of an example.

9. Explain Planck’s Quantum theory.

10. The threshold energy (work function) of a metal is 4.2 ev. If radiation of 2000 A^0 falls onthe metal, what is the kinetic energy of the fastest photoelectron?

Answers to Intext Questions

3.1

1. Proton is heavier than electron. The ratio of their masses is

$$= m_p / m_c = \frac{1.672623 \text{ x } 10^{-27} \text{ kg}}{9.109389 \text{ x } 10^{-31} \text{ kg}}$$

$$= 1836$$

2. Main constituent particles like proton, neutron and electron etc. present in the atom come in the category of fundamental particles.
3. Neutron

3.2

1. Electron, proton and neutron
2. The aim of Rutherford’s experiment was to test the Thomson’s plum-pudding model.
3. According to Rutherford’s model for atom, the positive charge of the atom and most of its mass is contained in the nucleus. The rest of the atom is empty space which contains the much smaller and negatively charged electrons.
4. Rutherford’s model was rejected because it could not explain the stability of the atom.

3.3

1. Electromagnetic radiation is a kind of energy which is transmitted through space in the form of electric and magnetic fields. It travels with the speed of light and does not need any medium to travel.

2. The different characteristics of electromagnetic radiation are

i) Amplitude
ii) Wavelength,
iii) Frequency,
iv) Wave number and
v) Velocity

3. The wave number is defined as the number of waves per centimeter. It is equal to the reciprocal of the wavelength.

4. A quantum of visible light is called photon. The energy of the quantum (or photon) is proportional to the frequency of radiation.

3.4

1. A line spectrum consists of a series of discrete lines of characteristic wavelengths while a continuous spectrum contains a broad band of radiations containing all possible wavelengths in the range i.e., wavelengths of the radiation varies continuously.
2. The main postulates of Bohr’s model are:

i) The electrons move in a definite circular path called as **stationary orbits or stationary state** around a central stationary nucleus.

ii) The electrons can change their orbits by absorbing or emitting a photon of energy(= $h\nu$) equal to the difference of the energies of the orbits.

iii) The angular momentum of the electron is quantized.

3. The energy of a Bohr's orbit increases with an increase in the value of the principal quantum number, n. In fact it becomes lesser and lesser negative.

4. The smallest packet of energy is called quantum.

5. 6.625×10^{-34} Joules – second

6. When light is exposed to clean metallic surface, electrons are ejected from the surface. This effect is called as photo electric effect.

7. The minimum energy required for emission of photo electrons is called threshold energy.

3.5

1. The wave-particle duality refers to the fact that light and the material particles likeelectrons could sometimes behave as a particle and as a wave at other times.

2. The wave nature of electron was established by the diffraction of electron waves bythe crystal lattice of nickel.

3. Mass of the electron = 9.1×10^{-31} kg Speed or Velocity = 100 km s^{-1} = 105 m s^{-1} Using equation, the wavelength associated with the electron will be

4. According to Heisenberg's Uncertainty Principle it is not possible to measure both the *position* and *momentum* of a particle with any degree of certainty. More accurately we measure a particle's position, the less accurately we are able to measure it's momentum and vice versa.

3.6

1. It is a mathematical function that describes the motion of an electron inside the atom. It contains all the information about the system and can be found by solving a wave equation called Schrodinger wave equation.

2. An orbit refers to definite circular paths of fixed energy around a central stationary nucleus while an orbital refers to the three dimensional region of space around the nucleus where there is a probability of finding the electron.

3. The quantum numbers are integers that characterize the wave functions. These are obtained in the process of solving Schrodinger wave equation and every electron in an atom has a different set of quantum numbers. The three quantum numbers obtained from Schrodinger Wave Equation are

i. The principal quantum number, n

ii. Azimuthal quantum number, l and

iii. The magnetic quantum number m_1

4. The principal quantum number, n is concerned with the energy of the electron in a shell. The quantum number l is related to the geometrical shape of the orbital and the quantum, number, m_l describes the orientation of the orbital in space.

3.7

1. *s*-orbital : spherical;
p-orbitals : dumb-bell shaped ;
d-orbitals : cloverleaf shaped.

2. The 2s orbital is spherical in shape similar to the 1s orbital. However there are two differences. Firstly, the size of a 2s orbital is bigger as compared to a 1s orbital and secondly, it contains a spherical node.

3. i) It is a spherical region of zero probability in an s orbital (other than 1s).

ii) It is a planar region in an orbital (other than s orbitals) where the probability or finding the electron is zero.

4. The 3*s* orbtial will have **two** spherical nodes.

3.8

1. The distribution of electrons in the shells and subshells of an atom is called *Electronic Configuration*.

2. Pauli's principle states that an atom no two electrons can have same set of the four quantum numbers.

3. Aufbau principle states that the electrons in an atom are filled in the increasing order of their energies which is determined by $(n + l)$ rules.

4. There are two $(n + l)$ rules. These are

An orbital with a lower value for $(n + l)$ is filled first.

If the value of $(n + l)$ is the same for two orbitals then the orbital with lower value of n will be filled first.

4. i) 2p: $(n + l)$ for 2p = 2 + 1 = 3; for 3s $(n + l)$ = 3 + 0 = 3 ; Rule 2

ii) 4s : $(n + l)$ for 4s = 4 + 0 = 4; for 3d $(n + l)$ = 3 + 2 = 5 ; Rule 1

Chapter 04

PERIODIC TABLE AND ATOMIC PROPERTIES

We have seen different heaps of onions & potatoes at vegetable shop. Imagine, they are lying mixed and you want to buy 1kg of onion. What will happen? You will have to wait for long to sort that and then weight them. When you possess a variety of material substances, you have to keep them classified for an easy access and quick use. You cannot afford to mix clothes with eatables, cosmetics or books. Classification assures you that your eatables are in the kitchen, books on the study table or rack and your cosmetics are on the dressing table. Shopkeepers, business houses, storekeepers, administrators, managers, information technology experts and scientists etc. have to keep their materials duly classified.

Chemists faced a similar problem when they were to handle a large number of elements. The study of their physical and chemical properties and keeping a systematic record of them had been a great challenge to chemists. Classification of elements finally could be possible due to pioneering work of a few chemists. In the present lesson we shall discuss the need, genesis of classification and periodic trends in physical and chemical properties of elements.

Objectives

After reading this lesson you will be able to:

- recognise the need for classification of elements;
- recall the earlier attempts on classification of elements;
- define modern periodic law;
- name the elements with atomic number greater than 100 according to IUPAC nomenclature;
- corelate the sequence of arrangement of elements in the periodic table with the electronic configuration of the elements.
- recall the designations of the groups (1-18) in the periodic table;
- locate the classification of elements into s-, p-, d- and f- blocks of the periodic table and
- explain the basis of periodic variations of
  a) atomic size b) ionic size c) ionization enthalpy
  d) electron gain enthalpy within a group or a period
  e) chemical reactivity f) anamolous behavior

4.1 Early Attempts

Attempts were made to classify elements ever since the discovery of metals or may be even earlier. **J.W. Dobereiner** in 1817 discovered that when closely related elements are grouped in a set of three, the atomic weight of the middle element was almost the arithmetical mean of the two elements in the group e.g.,

Element	Lithium	Sodium	Potassium
Atomic weight	6.94	22.99	39.10
mean atomic weight	----	23.02	-----

He called such a group of three elements a triad. He could group only a few elements due to lack of knowledge of correct atomic weights of the elements at that time.

In 1863, **J.A.R. Newlands**, developed a system of classification of elements and entitled it as **Law of Octaves**. He arranged the elements are such a way that every eighth element had similar properties, like the notes of music. The law could not apply to a large number of known elements. However, the law indicated very clearly the recurrence of similar properties among the arranged elements. Thus the periodicity was visualised for the first time in a meaningful way.

Periodicity: Re-occurrence of properties after regular intervals.

More significant results were obtained when **Lother Meyer's** work reflecting the periodicity was found to be based on physical properties of the elements. He clearly showed that certain properties showed a periodic trend.

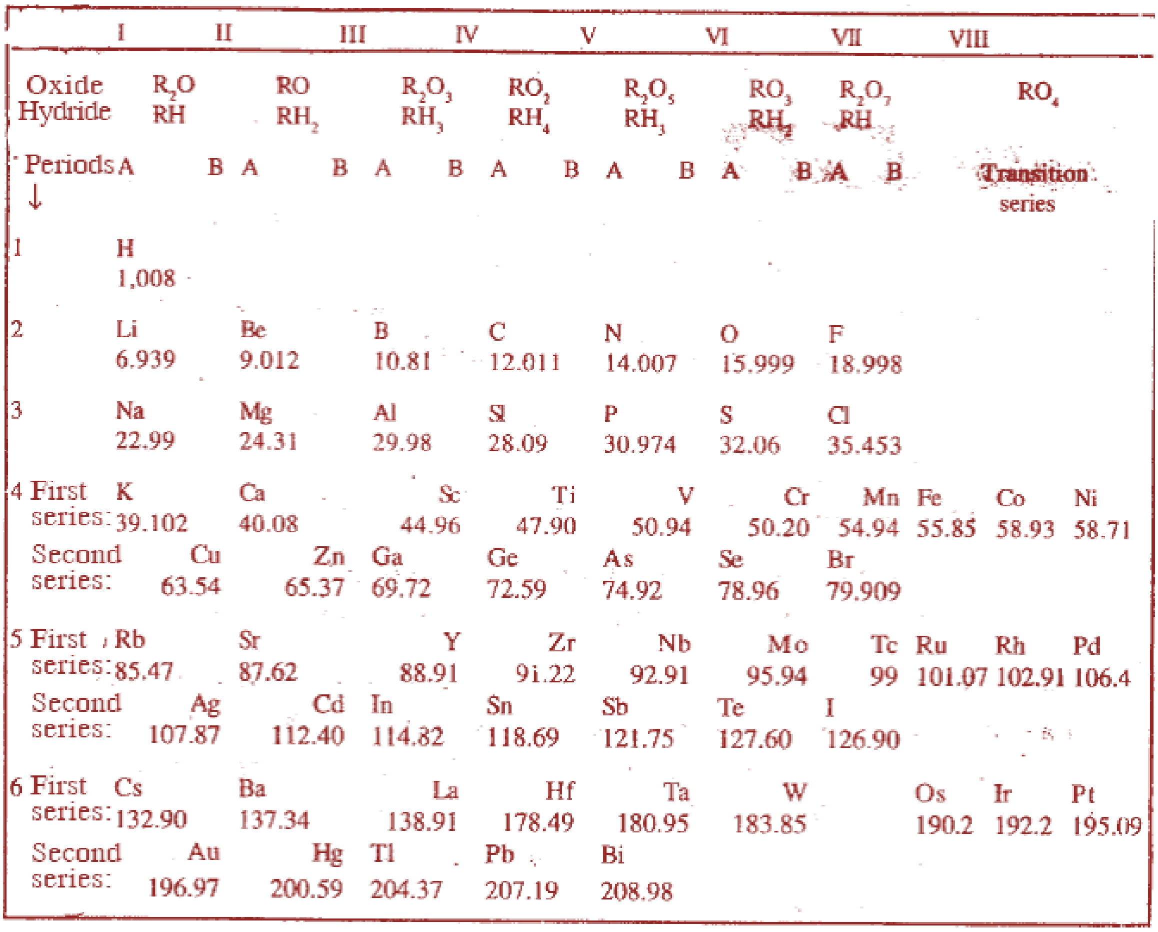
4.2 Mendeleev's Periodic Table

In 1869, Mendeleev's a Russain Chemist made a thorough study of the relation between the atomic weights of the elements and their physical and chemical properties. He then constructed a table in which elements were arranged in order of their increasing atomic weights. It was also found that every eighth elements had properties similar to that of the first element. Thus, there was a periodic occurrence of elements with similar properties.

One of the most striking applications of Mendeleev's classification of elements was that in his periodic table (Table 4.1) he left gaps for elements which were yet to be discovered. He also predicted the properties of these elements. However, Mendeleev's periodic table did not provide any place for isotopes and noble gases which were discovered later on.

This work laid strong foundation of the fundamental principles of the periodic law. One of his most important conclusions was that the elements if arranged according to their atomic weights, exhibit an evident systematic re-occurrence of properties (periodicity of properties) and even the properties of some elements were listed much before their discovery. Mendeleev's periodic Table (Table 4.1) was quite useful till the discovery of atomic number there existed certain inherent defects which opposed the system.

Table 4.1 Mendeleev's Table of 1871



	I	II	III	IV	V	VI	VII	VIII		
Oxide Hydride	R_2O RH	RO RH_2	R_2O_3 RH_3	RO_2 RH_4	R_2O_5 RH_3	RO_3 RH_2	R_2O_7 RH	RO_4		
Periods ↓	A B	A B	A B	A B	A B	A B	A B	Transition series		
1	H 1,008									
2	Li 6.939	Be 9.012	B 10.81	C 12.011	N 14.007	O 15.999	F 18.998			
3	Na 22.99	Mg 24.31	Al 29.98	Si 28.09	P 30.974	S 32.06	Cl 35.453			
4 First series:	K 39.102	Ca 40.08	Sc 44.96	Ti 47.90	V 50.94	Cr 50.20	Mn 54.94	Fe 55.85	Co 58.93	Ni 58.71
Second series:	Cu 63.54	Zn 65.37	Ga 69.72	Ge 72.59	As 74.92	Se 78.96	Br 79.909			
5 First series:	Rb 85.47	Sr 87.62	Y 88.91	Zr 91.22	Nb 92.91	Mo 95.94	Tc 99	Ru 101.07	Rh 102.91	Pd 106.4
Second series:	Ag 107.87	Cd 112.40	In 114.82	Sn 118.69	Sb 121.75	Te 127.60	I 126.90			
6 First series:	Cs 132.90	Ba 137.34	La 138.91	Hf 178.49	Ta 180.95	W 183.85		Os 190.2	Ir 192.2	Pt 195.09
Second series:	Au 196.97	Hg 200.59	Tl 204.37	Pb 207.19	Bi 208.98					

4.3 Modern Approach

Atomic number was discovered in 1913 by a team lead by Moseley. The periodic table based on atomic number is termed as Modern Periodic Table. Moseley arranged all the elements according to increasing atomic number and showed that the properties of elements are periodic function of their atomic numbers.

Modern periodic law: The properties of the elements are periodic function of their atomic numbers.

4.4 Long Form of Periodic Table

The arrangement of elements in the long form of periodic table is a perfect matching of electronic configuration of the elements on one hand and physical and chemical properties of the elements on the other. Some important considerations of the modern atomic structure applied to the classification of elements are discussed below:

i. An atom loses electrons from or gains electrons in the outermost shell of an atom during a chemical reaction.
ii. The sharing of an electron or electrons by an atom with other atom or atoms is largely through the outer most shell. Thus the electrons in the outermost shell of an atom largely determine the chemical properties of the elements.

We may therefore conclude that the elements possessing identical outer electronic configuration should possess similar physical and chemical properties and therefore they should be placed together for an easy and systematic study.

Keeping in mind the reasoning given above, when all the known elements are arranged in a table according to their increasing atomic number, the properties of the elements show periodicity (reappear at definite intervals). The periodicity is shown in Table in 4.2

4.5 Structural Features of the Long Form of Periodic Table

i. In this table there are 18 vertical columns called **GROUPS**. They are numbered from 1 to 18. Every group has a unique configuration.

ii. There are seven horizontal rows. These rows are called **PERIODS**. Thus the periodic table has seven periods, numbered from 1 to 7.

iii. There are a total of 114 elements known to us till today. Of all the known elements 90 are naturally occurring and others are made through nuclear transformations or are synthesised artificially. Either way they are **Manmade Elements**, but you will find the term specifically applied to transuranic elements (elements listed after uranium) only.

iv. First period consists of only two elements (very short period). Second and third periods consist of only eight elements each (short periods). Fourth and fifth periods consist of 18 elements each (long periods). Sixth period consists of 32 elements (long period). Seventh period is yet incomplete and more and more elements are likely to be added as the scientific research advances.

v. There are also nick names given to the groups or a cluster of groups on the basis of the similarly of their properties, as given below :

Group 1 elements except hydrogen, are called **Alkali Metals**
Group 2 elements are called **Alkaline Earth Metals**
Group 3 to 12 elements are called **Transition Metals.**
Group 16 elements are called **Chalcogens**
Group 17 elements are called **Halogens**
Group 18 elements are called **Noble Gases**.

Apart from what has been said above elements with atomic numbers 58 to 71 are called Lanthanoids - or Inner Transition elements (First series). Elements from atomic numbers 90 to 103 are called actinoids - Inner Transition elements (Second series). All elements except transition and inner transition elements are also collectively called Main Group Elements.

4.6 Position of Metals, Non-Metals and Metalloids

In order to locate the position of metals, non-metals and metalloids in the periodic table, you may draw a diagonal line joining the elements boron (At. no. 5) with that of tellurium (At. no. 52) and passing through silicon and arsenic. Now we are in a position to make the following observations.

i. The elements above the diagonal line and to the far right are non-metals (except selenium which shows slightly metallic character also). The non-metallic character is more marked the farther an element is from the diagonal line and up.

ii. The elements below the diagonal line and to the left are metals. (Hydrogen is a non-metal and is an exception) The metallic character is more marked the farther an element is from the diagonal line and down. All lathanoids and actinoids are metals.

iii. The elements along the diagonal line are metalloids and possess the characteristics of metals as well as of non-metals. In addition germanium, antimony and selenium also show the characteristics of metalloids.

Intext Questions 4.1

1. Classify the elements of group 14, 15 and 16 into metlas, non-metals and metalloids.
2. Compare the metallic character of aluminium and potassium.
3. Name the group number for the following types of elements. i) Alkaline earth metals ii) Alkali metals iii) Transition metals iv) Halogens v) Noble gases.
4. Name five man made elements.

Electronic configurations of elements and the periodic table

An electron in an atom is characterised by a set of four quantum numbers, and the principal quantum number (n) defines the main energy level known as shell. The filling of electrons into different subshells, also referred to as orbitals (*s, p, d, f*) in an atom. The distribution of electrons into orbitals of an atom is called its electronic configuration. An element's location in the Periodic Table reflects the quantum numbers of the last orbital filled. In this section we will observe a direct connection between the electronic configurations of the elements and the long form of the Periodic Table.

(a) Electronic Configurations in Periods: The period indicates the value of n for the outermost or valence shell. In other words, successive period in the Periodic Table is associated with the filling of the next higher principal energy level (n = 1, n = 2, etc.). It can be readily seen that the number of elements in each period is twice the number of atomic orbitals available in the energy level that is being filled.

The first period (n = 1) starts with the filling of the lowest level (1s) and therefore has two elements — hydrogen ($1s^1$) and helium ($1s^2$) when the first shell (K) is completed.

The second period (n = 2) starts with lithium and the third electron enters the 2s orbital. The next element, beryllium has four electrons and has the electronic configuration $1s^2\ 2s^2$. Starting from the next element boron, the 2p orbitals are filled with electrons when the L shell is completed at neon ($2s^2\ 2p^6$). Thus there are 8 elements in the second period.

The third period (n = 3) begins at sodium, and the added electron enters a 3s orbital. Successive filling of 3s and 3p orbitals gives rise to the third period of 8 elements from sodium to argon.

The fourth period (n = 4) starts at potassium, and the added electrons fill up the 4s orbital. Now you may note that before the 4p orbital is filled, filling up of 3d orbitals becomes energetically favourable and we come across the so called 3d transition series of elements. This starts from scandium (Z = 21) which has the electronic configuration $3d^1\ 4s^2$. The 3d orbitals are filled at zinc (Z=30) with electronic configuration 3d 104s 2 . The fourth period ends at krypton with the filling up of the 4p orbitals. Altogether we have 18 elements in this fourth period.

The fifth period (n = 5) beginning with rubidium is similar to the fourth period and contains the 4d transition series starting at yttrium (Z = 39). This period ends at xenon with the filling up of the 5p orbitals.

The sixth period (n = 6) contains 32 elements and successive electrons enter 6s, 4f, 5d and 6p orbitals, in the order — filling up of the 4f orbitals begins with cerium (Z = 58) and ends at lutetium (Z = 71) to give the 4f-inner transition series which is called the lanthanoid series.

The seventh period (n = 7) is similar to the sixth period with the successive filling up of the 7s, 5f, 6d and 7p orbitals and includes most of the man-made radioactive elements. This period will end at the element with atomic number 118 which would belong to the noble gas family.

Filling up of the 5f orbitals after actinium (Z = 89) gives the 5f-inner transition series known as the actinoid series. The 4fand 5f-inner transition series of elements are placed separately in the Periodic Table to maintain its structure and to preserve the principle of classification by keeping elements with similar properties in a single column.

(b) GroupWise Electronic Configurations Elements in the same vertical column or group have similar valence shell electronic configurations, the same number of electrons in the outer orbitals, and similar properties. For example, the Group 1 elements (alkali metals) all have ns 1 valence shell electronic configuration as shown below.

Table : Types of elements: Electronic configuration of alkali metals

Atomic Number	Symbol	Electronic Configuration
3	Li	$1s^2\ 2s^1$ or $[He]\ 2s^1$
11	Na	$1s^2\ 2s^2\ 2p^6\ 3s^1$or $[Ne]\ 3s^1$
19	K	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ or $[Ar]\ 4s^1$
37	Rb	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^1$ or $[Kr]\ 5s^1$
55	Cs	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^1$ or $[Xe]\ 6s^1$

4.7 Catagorisation of Elements into '*s*', '*p*', '*d*', and '*f*' Blocks

Grouping of elements in the periodic table can be done in another way also, which is more related to their electronic configuration. Under this categorisation, the location of the differentiating electron (the last electron) is most important. If, for example, the electron has gone to 's-subshell', the elements will fall in 's-block' and if the last electron goes to 'p-subshell', then the element will belong to p-block. Similarly if the defferentiating electron enters the d-subshells of an atom, then the elements comprising all such atoms will belong to d-block.

The salient features of the four types of elements marked in the Periodic Table:

The grouping of elements explained above can be related to the type of elements discussed earlier.

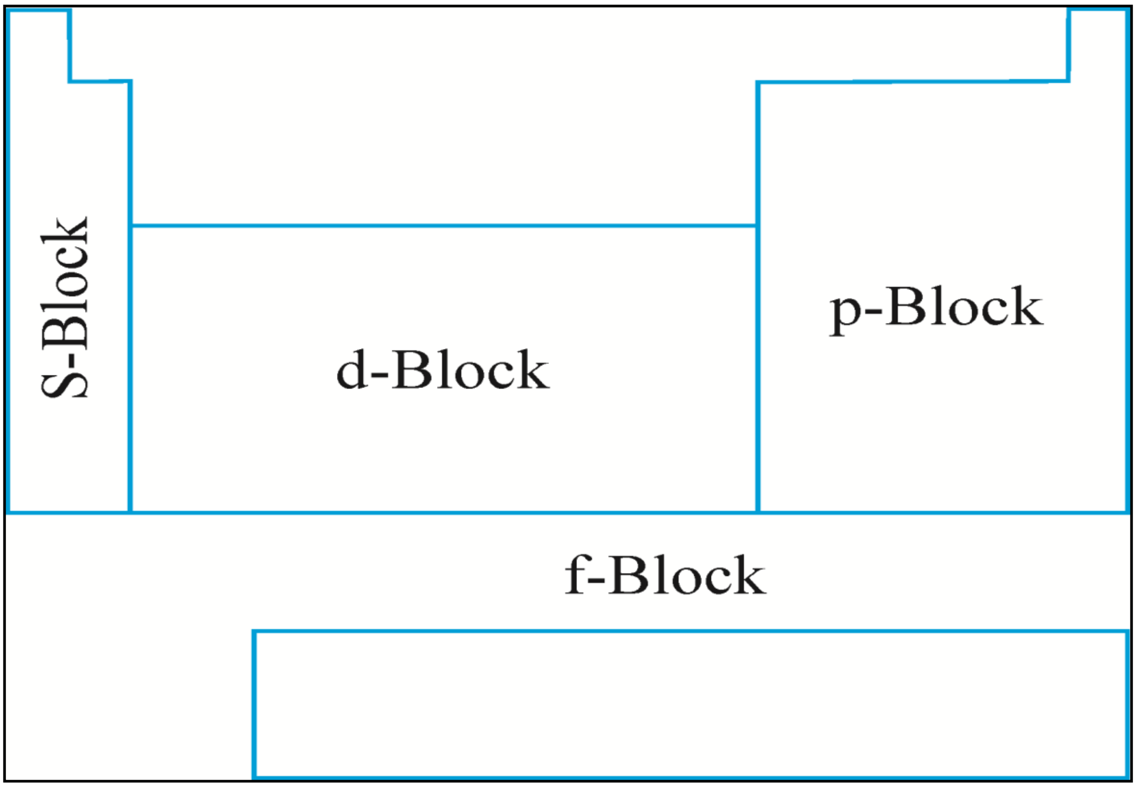
i. ***s*-block elements :** All alkali metals and, alkaline earth metals.

ii. ***p*-block elements :** All elements of group no. 13 to group no. 18.

iii. ***d*-block elements :** All elements from group no. 3 to group no. 12.

(Except Lanthanoids and Actinoides)

iv. ***f*-block elements :** Lanthanoids (at no 58 to 71) and Actinoids (at no. 90 to 103)



Blockwise categorization of elements

i) s-Block Elements:

- The elements of Group 1 (alkali metals) and Group 2 (alkaline earth metals) which have ns1 and ns2 outermost electronic configuration belong to the s-Block Elements.
- They are all reactive metals with low ionization enthalpies.
- They lose the outermost electron(s) readily to form 1+ ion (in the case of alkali metals) or 2+ ion (in the case of alkaline earth metals). The metallic character and the reactivity increases as we go down the group. Because of high reactivity they are never found pure in nature.
- The compounds of the s-block elements, with the exception of those of lithium and beryllium are predominantly ionic.

ii) The *p*-Block Elements: The *p*-Block Elements comprise those belonging to Group 13 to 18 and these together with the *s*-Block Elements are called the Representative Elements or Main Group Elements.

- The outermost electronic configuration varies from ns^2np^1 to ns^2np^6 in each period. non-metals.

- At the end of each period is a noble gas element with a closed valence shell ns^2np^6 configuration. All the orbitals in the valence shell of the noble gases are completely filled by electrons and it is very difficult to alter this stable arrangement by the addition or removal of electrons.
- The noble gases thus exhibit very low chemical reactivity.
- Preceding the noble gas family are two chemically important groups of non-metals.
- They are the halogens of Group 17 and the chalcogens of Group 16.
- These two groups of elements have highly negative electron gain enthalpies and readily add one or two electrons respectively to attain the stable noble gas configuration.
- The non-metallic character increases as we move from left to right across a period and metallic character increases as we go down the group.

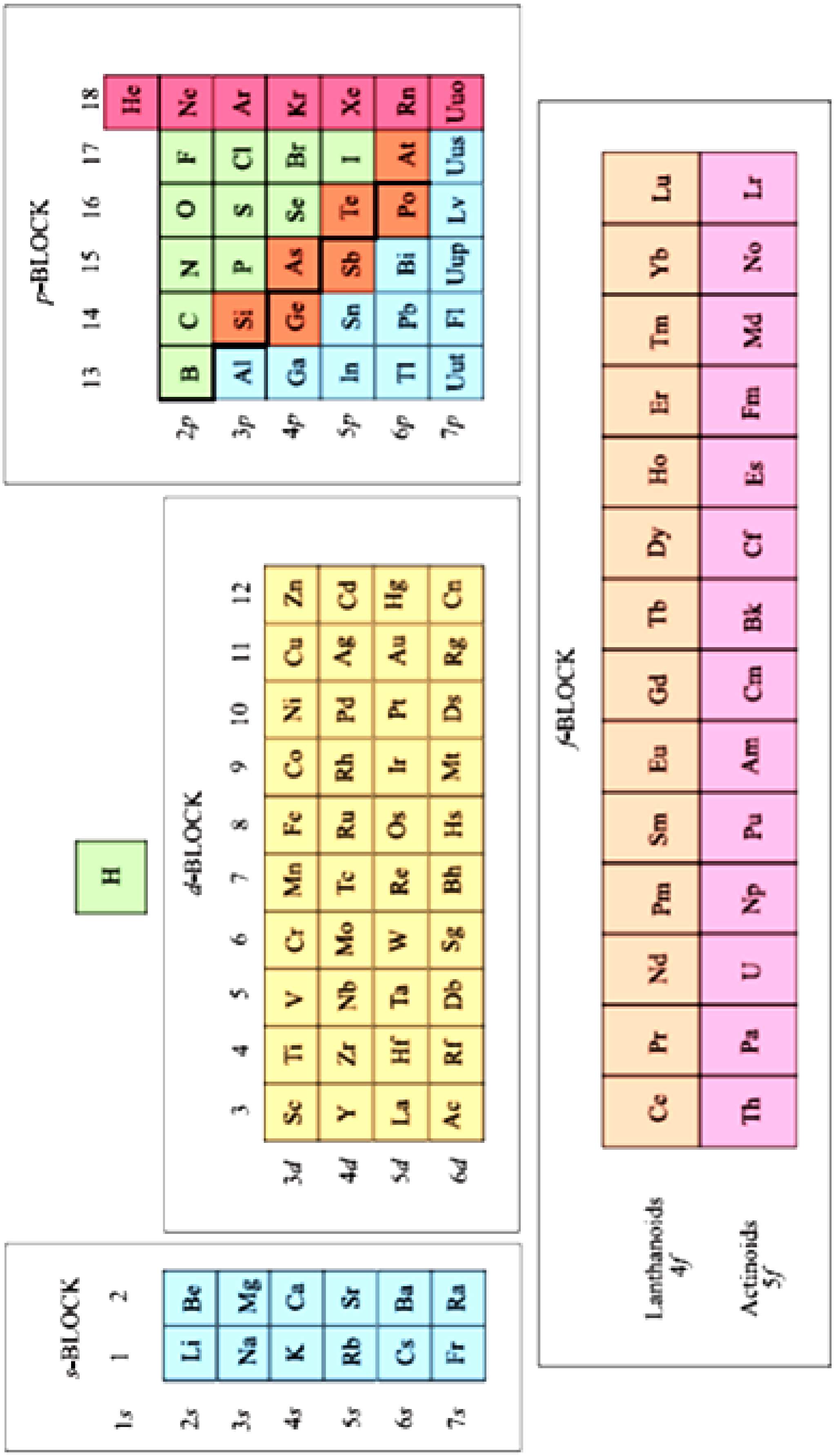
iii) The d-Block Elements also known as the Transition Elements: These are the elements of Group 3 to group 12 in the centre of the Periodic Table.

- These are characterized by the filling of inner d orbitals by electrons and are therefore referred to as d-Block Elements.
- These elements have the general outer electronic configuration $(n-1)d^{1-10}\ ns^{0-2}$. They are all metals.
- They mostly exhibit variable valence (oxidation states) and form coloured ions in solution. These show paramagnetism and are often used as catalysts.
- However, Zn, Cd and Hg which have the electronic configuration, $(n-1)d^{10}ns^2$ do not show most of the properties of transition elements.
- In a way, transition metals form a bridge between the chemically active metals of s-block elements and the less active elements of Groups 13 and 14 and thus take their familiar name "**Transition Elements**".

(iv) The f-Block Elements - Inner-Transition Elements: The two rows of elements at the bottom of the periodic table, called Lanthanides, Ce(Z = 58) – Lu(Z = 71) and Actinides, Th(Z = 90) – Lr (Z = 103).

- These are characterized by the outer electronic configuration $(n-2)f^{1-14}\ (n-1)d^{0-1}\ ns^2$.
- The last electron added to each element is filled in f-orbital.
- These two series of elements are hence called the **Inner-Transition Elements** (f-Block Elements) and these are all metals.
- Within each series, the properties of the elements are quite similar. The chemistry of the early actinides is more complicated than the corresponding lanthanides, due to the large number of oxidation states possible for the actinide elements.
- Actinide elements are radioactive and many of the actinide elements have been made only in nanogram quantities or even less by nuclear reactions and their chemistry is not fully studied. The elements after Uranium are called **Transuranium Elements**.

There are minor exceptions in Mn and Zn configurations. You will study more about the reasons for such exceptions in Lesson 23.



The types of elements in the Periodic Table based on the orbitals that are being filled. Also shown is the broad division of elements into METALS (🟦 🟨 🟧 🟪), NON METALS (🟩 🟥) and METALLOIDS (🟧).

Nomenclature of Elements with Atomic Numbers greater than 100

The naming of the new elements was earlier left entirely to its discoverer. The suggested names were then later ratified by IUPAC. But due to certain disputes that arose over the original discoverer of some of the elements of atomic numbers greater than 104, the IUPAC in 1994 appointed a Commission on Nomenclature of Inorganic Chemistry (CNIC). After consultation with the Commission and the chemists around the world, the IUPAC in 1997 recommended a nomenclature to be followed for naming the new elements with atomic numbers greater than 103 until their names are fully recognised. The names are derived directly from the atomic number of the element using the following numerical roots for 0 and number 1-9.

0 = nil   3 = tri   6 = hex   9 = enn
1 = un   4 = quad   7 = sept
2 = bi   5 = pent   8 = oct

The roots are put together in the order of the digits which make up the atomic number and ‘ium’ is added at the end.

Names, thus derives, and the IUPAC approved names of some elements with atomic numbers greater than 103 are listed in Table 4.3

Table 4.3 Nomenclature of elements with atomic numbers greater than 103

Atomic Numbe	Name	Symbol	IUPAC approved	IUPAC
104	Unnilquadiu	**Unq**	Rutherfordium	**Rf**
105	Unnilpentiu	**Unp**	Dubnium	**Db**
106	Unnilhexium	**Unh**	Seaborgium	**Sg**
107	Unnilseptium	**Uns**	Bohrium	**Bh**
108	Unniloctium	**Uno**	Hassium	**Hs**
109	Unnilennium	**Une**	Meitnerium	**Mt**
110	Ununnillium	**Uun**		
111	Unununnium	**Uuu**		
112	Ununbium	**Uub**		
113	Ununtrium	**Uul**		
114	Ununquadiu	**Uuq**		
115	Ununpentium	**Uup**		

4.8 Periodicity in Atomic Properties

The term periodicity is used to indicate that some characteristic properties occur in the periodic table after definite intervals, however with a varying magnitude. Thus after starting from a certain point on the periodic table, we are almost certain that the movement in particular direction will show steady increase or decrease of a said property.

4.9 Atomic Size

In homonuclear diatomic molecules the distance from the centre of one nucleus to the centre of another nucleus gives the bond length and half of this bond length is atomic radius.

(Fig. 4.2). The first number of each period is the largest in size. Thus we can say that the group 1 atom are the largest in their respective horizontal rows. Similarly, atoms of group 2 elements are large but are definitely smaller than the corresponding atoms of group 1. This is due to the reason that the extra charge on the nucleus draws the electrons inward resulting in smaller size for the atoms under reference. This trend of decrease in size of atoms, continues from left to right. An example is shown in Fig. 4.3. However there may be some exceptions and there will be other reasons to explain them.

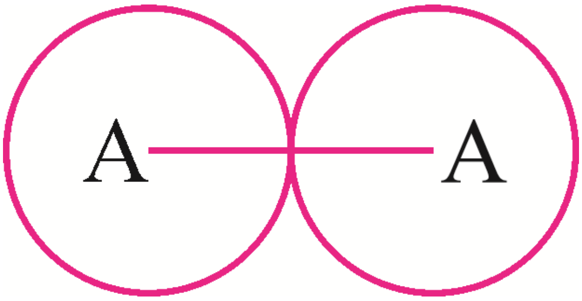


Fig. 4.2 : *Atomic radium = 1/2* $d_{AA} = r$

Fig. 4.3 : *From left to right, size of atoms decrease in the periodic table*

In going down the group of elements (in any particular column) the atomic size increases at each step.

This increase may be explained in terms of a new electron shell being added, when we pass from one element to another in a group.

4.9.a Types of atomic radius

The atomic radius cannot be determined exactly. But the inter-nuclear distance of the bonded atoms can be measured using x-ray diffraction or other methods.

The atomic radius depends on many factors like the number of bonds formed by the atom, nature of bonding, oxidation state etc.

The types of atomic radius are considered based on nature of bonding. They are

1. Crystal radius or Atomic radius
2. Vander Waal's radius.
3. Covalent radius .

Crystalline Radius :

This type of radius is applicable for metal atoms.

Half of the distance between the centres of the nuclei of two adjacent metal atoms in the metallic crystal is called crystal radius or atomic radius.

It is measured in $1A^0 = 10^{-8}$ cm = 10^{-10} m = 0.1 m

1 nm = 10^{-9} m

Example : The distance between two Na Atoms = $3.72\ A^0$

Crystal radius of Na = $3.72/2 = 1.86\ A^0$

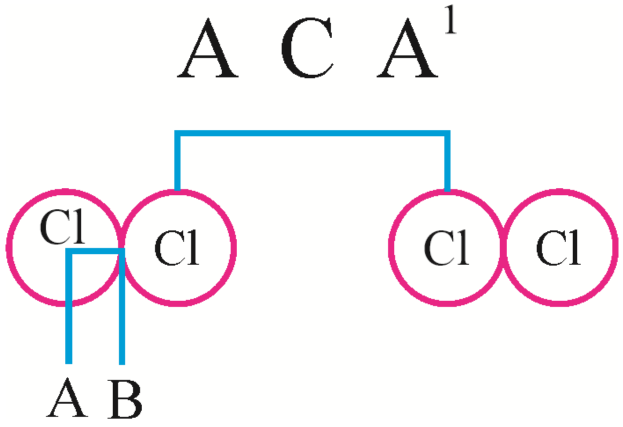
Vander Waal's radius :

- This type of radius is used only for molecular substances present in the solid state.
- ‘Vander Waal's radius is distance between the centres of two atoms of different molecules which are closest to each other.
- These atoms which approach closest to one another do not form chemical bond. But remain together due to Vander Waal's forces of attractions.
- For example the distance between two adjacent Chlorine atoms of different molecules is $3.6A^0$ – Then the Vander Waal's radius of Chlorine is $3.6/2 = 1.80\ A^0$
- Vander Waal forces of attraction are weak so it is found that Vander Waal's radius is 40% more than half of the distance between two nuclei of chemically bonded atoms.

Covalent radius :

- This radius is generally used while referring to non-metals.
- It is half of the distance between the nuclei of two atoms held together by a covalent bond.
- For Example the inter nuclear distance between Chlorine atoms in a molecule is 1.98A. The covalent radius of chlorine is one half of the inter nuclear distance.

ie. $1.98/2 = 0.99A^0$



Vander Waal and Covalent radii in chlorine.

Vander Waal's radius $= AC = A^1C = r = 1.8A^0$
Covalent radius $= AB = r = 0.99\ A^0$
The inter nuclear distance $= AA^1$ distance $= 3.6A^0$
Vander Waal's radius $= AA^1\ 1/2 = 3.6/2 = 1.80\ A^0$

Intext Questions 4.2

1. Give the order of penetration of orbitals toward, nucleus for a given principal quantum number.

....

2. Define shielding effect.

....

3. Define covalent radius of elements.

....

4.10 Ionic Size

An ion is formed when an atom undergoes a loss or gain of electron.

$M\ (g) \qquad M^+\ (g) + e^-$ (cation formation)
$M\ (g) + e^- \qquad M^-\ (g)$ (anion formation)

A cation is formed when an atom loses the most loosely bound electron from its outermost shell. The atom acquires a positive charge and becomes an ion (a cation). A cation is smaller than its atom. On the removal of an electron, the positive charge of the nucleus acts on lesser number of electrons than in the neutral atom and thus greater pull is exerted by the nucleus, resulting in a smaller size of the cation.

An anion is bigger than its atom because on receipt of an electron in the outermost orbit the number of negative charges increase and it out weights the positive charges. Thus the hold of the nucleus on the shells decrease resulting in an increase in the size of the anion.

A cation is always smaller than its atom and an anion is always bigger than its atom e.g. Na^+ is smaller than Na, Cl^- is bigger than Cl.

- In the main groups, the ionic radii increase on descending the group e.g., $Li^+ = 0.76\ A^o$, $Na^+ = 1.02\ A^o$, $K^+ = 1.38\ A^o$, etc. it is due to the addition of extra shell at each step.
- There is a decrease in the ionic radii of the positive ions on moving from left to right across a period in the periodic table. $Na^+ = 1.02\ A^o$, $Mg^{2+} = 0.72\ A^o$, $Al^{3+} = 0.535\ A^o$, etc. It is due to the increase in the number of charges on the nucles and also due to the increase in the charge on the ion.
- The ionic radii of the negative ions, also decrease on moving from left to right across a period. e.g. $O^{2-} = 1.40\ A^o$, $F^- = 1.33\ A^o$, etc. This is partly due to increase in the number of charges on the nucleus and also due to the decreasing change on the ion.

Intext Questions 4.3

1. Write the names of the elements with atomic numbers 105, 109, 112, 115 according to IUPAC nomenclature.

....

2. Arrange the following in the order of increasing size. Na^+, Al^{3+}, O^{2-}, F^-

....

3. How does the size of atoms vary from left to right in a period and on descending a group in the periodic table?

....

4.11 Ionization Enthalpy

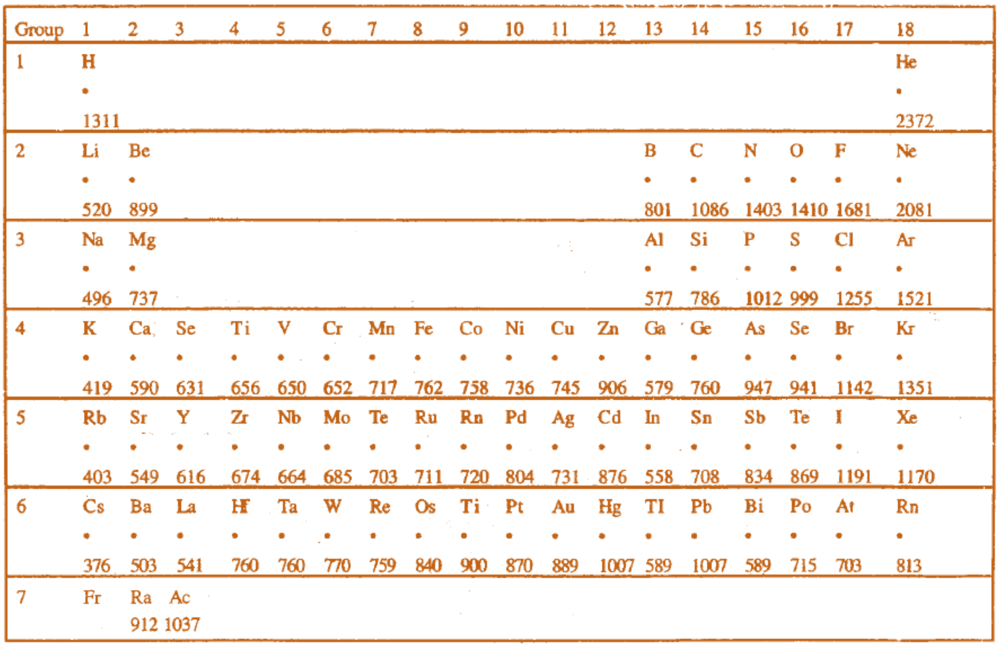
Ionization Enthalpy is the energy required to remove the most loosely bound electron from an isolated atom in the gaseous state for one mole of an element. It is expressed in kJ mol^{-1} (kilo joules per mole)

$$M(g) + IE \longrightarrow M+(g) + e^-$$

As we move from left to right in the periodic table, there is a nearly regular increase in the magnitude of the ionization enthalpy of elements.

Similarly, on moving down a group the magnitude of the ionization enthalpy indicates a regular decline. The ionization enthalpy of the first member of any group is the highest within that group and the ionization enthalpy of the last member in the same group, is the least. This is shown in table 4.4

Table 4.4: First ionization enthalpies of the elements (in kJ mol^{-1})



Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H • 1311																	He • 2372
2	Li • 520	Be • 899											B • 801	C • 1086	N • 1403	O • 1410	F • 1681	Ne • 2081
3	Na • 496	Mg • 737											Al • 577	Si • 786	P • 1012	S • 999	Cl • 1255	Ar • 1521
4	K • 419	Ca • 590	Se • 631	Ti • 656	V • 650	Cr • 652	Mn • 717	Fe • 762	Co • 758	Ni • 736	Cu • 745	Zn • 906	Ga • 579	Ge • 760	As • 947	Se • 941	Br • 1142	Kr • 1351
5	Rb • 403	Sr • 549	Y • 616	Zr • 674	Nb • 664	Mo • 685	Te • 703	Ru • 711	Rn • 720	Pd • 804	Ag • 731	Cd • 876	In • 558	Sn • 708	Sb • 834	Te • 869	I • 1191	Xe • 1170
6	Cs • 376	Ba • 503	La • 541	HF • 760	Ta • 760	W • 770	Re • 759	Os • 840	Ti • 900	Pt • 870	Au • 889	Hg • 1007	TI • 589	Pb • 1007	Bi • 589	Po • 715	At • 703	Rn • 813
7	Fr	Ra 912	Ac 1037															

The variation in the magnitude of ionization enthalpy of elements in the periodic table is mainly dependent on the following factors:

a. The size of the atom
b. The magnitude of the nuclear charge on the atom,
c. The extent of screening
d. The type of orbital involved (*s, p, d* or *f*)

i. In small atoms, the electrons are tightly held whereas in large atoms the electron are less strongly held. Thus, the ionization enthalpy decreases as the size of the atom increases.

ii. When an electron is removed from an atom, the effective nuclear charge, i.e., the ratio of the number of charges on the nucleus to the number of electrons, increases. As a result the remaining electrons come closer to the nucleus and are held more tightly. The removal of a second electron, therefore, requires more energy. e.g., Mg^+ is smaller than the Mg atom. The remaining electrons in Mg^+ are more tightly held. The second ionisation enthalpy is, therefore, more than the first ionisation enthalpy.

iii. Since the orbitals (s, p, d and f) have different shapes, the ionization enthalpy depends on the types of electrons removed. e.g. an electron in an s orbital is more tightly held as compared to an electron in a p orbital. It is because an s electron is nearer to the nucleus as compared to a p electron. Similarly a p-electron is more tightly held than a d-electron, and a d-electron is more tightly held than a f-electron. If all other factors are equal, the ionization enthalpies are in the order *s > p > d > f.*

These factors taken together contribute largely to decide the extent of the force of attraction between the nucleus and the electrons around it. The resultant of these factors thus determines the magnitude of ionization enthalpy of any element. You can see the variation in the magnitude of the ionization enthalpy of elements with atomic number in the Fig. 4.4.

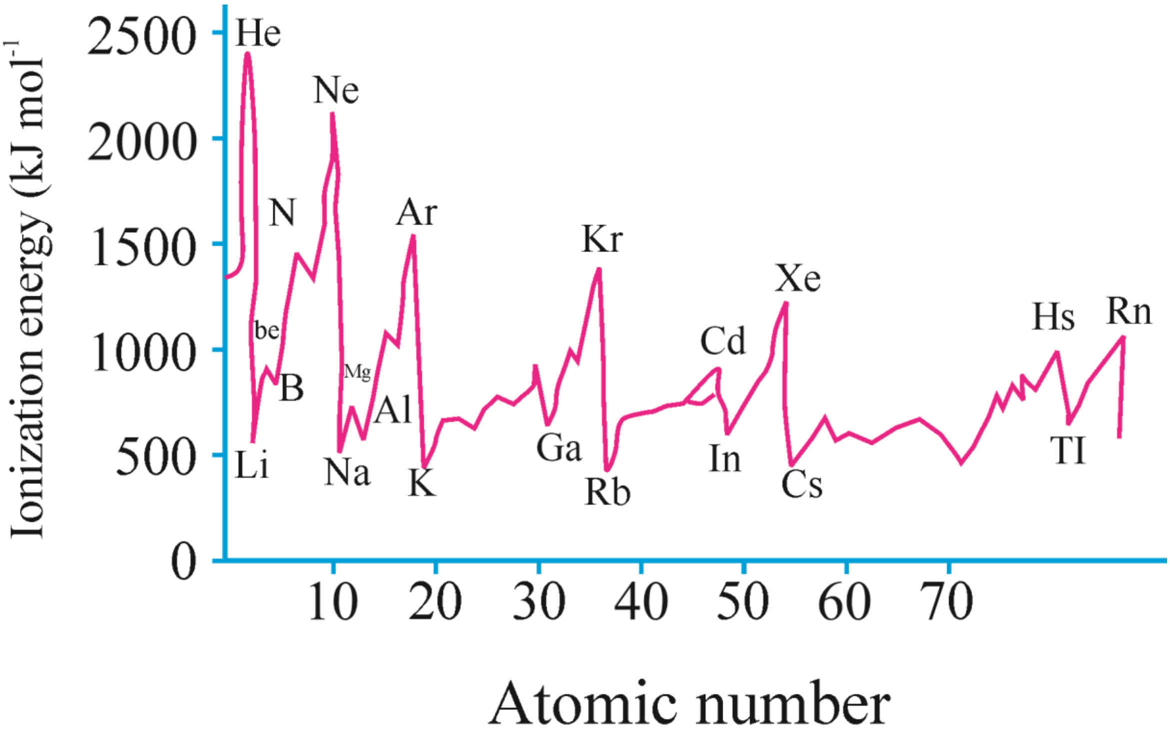


Fig. 4.4 : *Variation of ionization enthalpy of elements.*

It is clear from Fig. 4.4 that

i. The metals of group 1 (Li, Na, K, Rb, etc.) have the lowest ionization enthalpies in their respective periods.

ii. The noble gases (He, Ne, Ar, Kr, Ze and Rn) have the highest ionization enthalpies in their respective periods. It is because the energy required to remove an electron from a stable fully filled shell is very large.

iii. The values of ionization energies do not increase smoothly. e.g. the first ionization enthalpy of B (boron) is lower than that of Be (beryllium); the ionization enthalpy of Al (aluminium) is lower than that of Mg (magnesium); the first ionization enthalpy of O (oxygen) is lower than that of N (nitrogen). it can be explained as follows.

- The first ionization enthalpies of Be and Mg are higher than those of their preceding elements because the electrons are removed from the fully filled *s*-orbitals.
- The first ionization enthalpy of N is higher than that of O because from N, the electron is to be removed from a half-filled *p*-orbitals.
- Ionization enthalpy is the energy required to remove the most loosely bound electron form an atom (in the gaseous state) for one mole of an element. It is an absolute value and can be determined experimentally.

Factors effecting Ionization energy

The magnitude of Ionization potential of an atom depends on the following factors :

1. Atomic radius
2. Nuclear Charge

3. Screening or shielding effect on the outer electrons
4. Extent of penetration of orbitals of valence electrons.
5. The nature of sub shells; Whether half filled or completely filled with electrons or not.

1. **Atomic radius:** As the atomic size increases valence electrons move farther from the nucleus and so are held by weak nuclear attraction. So less energy is enough for the removal of the outer most electron of an atom. Hence, as the atomic radius increases, the Ionization energy decreases.
2. **Nuclear Charge:** The Number of electronic shells remain same, as the nuclear charge increase, the outer electrons are more strongly held by the nucleus due to attractive forces As a result, the energy required to remove the most loosely held electron from the atom is more. Hence IP increases, as the nuclear charge increases.

Element	Li	Be	C	N	F
Nuclear Charge	3	4	6	7	**9**
Ionization Potential *ev*$^-$	5.39	9.32	11.25	14.52	17.42

3. **Screening effect:** In an atom having more than one electron, the valance electrons are attracted by the nucleus and at the same time repelled by the inner core of electrons. The electrons present in the inner orbits screen the electrons present in the outer most orbit from being attracted by the nucleus. Hence, the nuclear attraction on the outer most electron decreases. This influence of the inner core of electrons on the attraction of the nucleus towards outer electrons is referred screening effect.

$$\text{Screening Effect} \quad \alpha \quad \frac{1}{1\text{p}}$$

The screening efficiency of orbitals falls off in the order ***s* > *p* > *d* > *f***

4. **Extent of penetration of Orbitals of valence electrons:** For a given quantum number the s-orbital penetrates more towards nucleus because of its spherical and symmetrical shape. So an electron of an s-orbital requires large amount of energy to be removed. In the same shell P-electrons require less energy to remove. Hence the Ionization energy follows the sequence of the extent of penetration of the orbitals ***s* > *p* > *d* > *f***.
5. **Completely filled or half filled sub shells:** Completely filled or half filled electronic sub energy levels impart greater stability to the atom *i.e.* the element. Such atoms required more energy for Ionization. Hence, they have more Ionization energy values.

4.12 Electron Gain Enthalpy

Every atom, in general, has a tendency to gain or lose electrons in order to acquire a noble gas configuration. The atoms which have five, six or seven electrons in their outer most shell, shows tendency to accept electrons and attain the nearest noble gas configuration. Halogens, for example, have seven electrons in their outermost orbit. Thus they show a tendency to accept one more electron and attain the nearest noble gas configuration. The energy change (E) for this process is called electron gain enthalpy of that atom.

Electron gain enthalpy is the energy released or adsorbed for one mole of neutral atoms in a gaseous state when electron is accepted by each atom.

$$X_{(g)} \quad + \quad e^- \quad \rightarrow \quad X^-_{(g)}$$

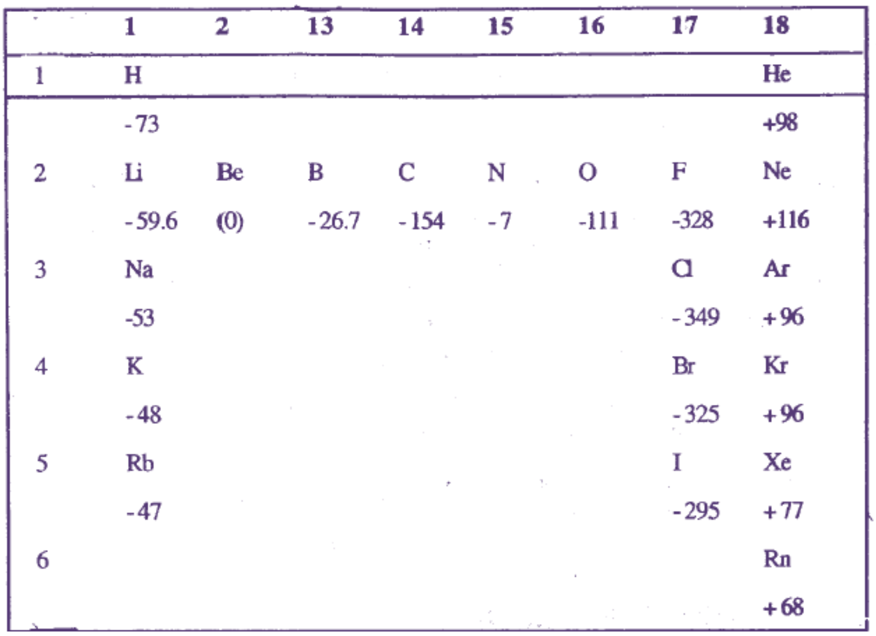
Where X represents an atom

$$Cl\ (g) \quad + \quad e^- \quad \rightarrow \quad Cl^-\ (g); \qquad \Delta E = -349\ \text{kJ mol}^{-1}$$

The negative value shows release of energy and hence tendency to greater stabilisation. The electron gain enthalpy becomes more in negative from left to right in a period. This is because it is easier to add an electron to a smaller atom since the added electron would be closer to the positively charged nucleus. Halogens release maximum energy when they accept an electron. On the other hand, metals do not accept electrons and show a high positive value for E. Thus electron enthalpy can be positive or negative.

Electron gain enthalpies becomes less in negative as we go down the group showing that the electropositive character of the atoms increases. This is because the size of the atom increases down the group and the electron added goes to the higher shells. Electron affinity values for some elements are shown in table 4.5, along with their position in the periodic table. The electron gain enthalpy of chlorine is more in negative value as compared to that of fluroine. This is due to the small size of the F atom. As the electron approaches near to the small F atom, it experiences repulsion from other electrons.

Table 4.5: Electron gain enthalpy in kJ mol^{-1}



	1	2	13	14	15	16	17	18
1	H							He
	-73							+98
2	Li	Be	B	C	N	O	F	Ne
	-59.6	(0)	-26.7	-154	-7	-111	-328	+116
3	Na						Cl	Ar
	-53						-349	+96
4	K						Br	Kr
	-48						-325	+96
5	Rb						I	Xe
	-47						-295	+77
6								Rn
								+68

4.13 Electro negativity

It is an indicator of the extent of attraction by which electrons of the bond pair are attract by an atom linked by this bond. The value of electro negativity is assigned arbitrarily to one atom such as hydrogen. Then the value of electro negativity is assigned to all other atoms with respect to hydrogen. One such scale is the **Pasuling Scale of electro negativity** (Table 4.6).

Electro negativity is defined as a measure of the ability of an atom to attract the electron pair in a covalent bond to itself.

In a homonuclear diatomic molecule such as hydrogen (H_2) or fluorine (F_2), the electron pair of the covalent bond in each molecule experiences equal attraction by each atom. Thus none of the two atoms is able to shift the bond pair of electrons to itself. However in a heteronuclear diatomic molecule, the bond pair electrons get shifted towards the atom which is more electronegative than the other. For example, in HF or HCl the bond pair of electrons are not shared equally but the more electronegative atom F or Cl is able to shift the bond pair towards itself, resulting in the polarization of the molecule.

A large difference between electro negativities of the two atoms indicates highly ionic character of the bond between them. For example, Cs^+F^-. On the other hand, zero difference in the electro negativities between the two atoms indicates that the percentage ionic character is zero. Therefore the molecule is purely covalent e.g. H_2, Cl_2, N_2 etc.

Table 4.6: Electro negativities of elements on Pauling Scale

Li	**Be**	**B**	**C**	**N**	**O**	**F**
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	**Ca**	**Se**	**Ge**	**As**	**Sc**	**Br**
0.8	1.0	1.3	1.7	1.8	2.1	2.5
Cs	**Ba**					
0.7	0.9					

The most electronegative elements have been placed on the farthest right hand upper corner (noble gases are not included). The value of electro negativity decreases as we go down in any group and increases from left to right in the period. Thus fluorine is the most electronegative and cesium is the least electronegative element. (We have not considered Francium being radioactive).

Intext Questions 4.4

1. What is the correlation between atomic size and ionization enthalpy?

....

2. Which species, in each pair is expected to have higher ionization enthalpy.

i) $_{3}$Li, $_{11}$Na ii) $_{7}$N, $_{15}$P iii) $_{20}$Ca, $_{12}$Mg iv) $_{13}$Al, $_{14}$Si

v) $_{17}$Cl, $_{18}$Ar vi) $_{18}$Ar and $_{9}$K vii) $_{13}$Al, $_{14}$C

....

3. Account for the fact that there is a decrease in first ionization enthalpy from Be to B and Mg to Al.

....

4. Why is the ionization enthalpy of the noble gases highest in their respective periods?

....

5. Name the most electronegative element.

....

Periodic Trends in Chemical Properties

Most of the trends in chemical properties of elements, such as diagonal relationships, inert pair effect, effects of lanthanide contraction etc. will be dealt with along the discussion of each group in later units. In this section we shall study the periodicity of the valence state shown by elements and the anomalous properties of the second period elements (from lithium to fluorine).

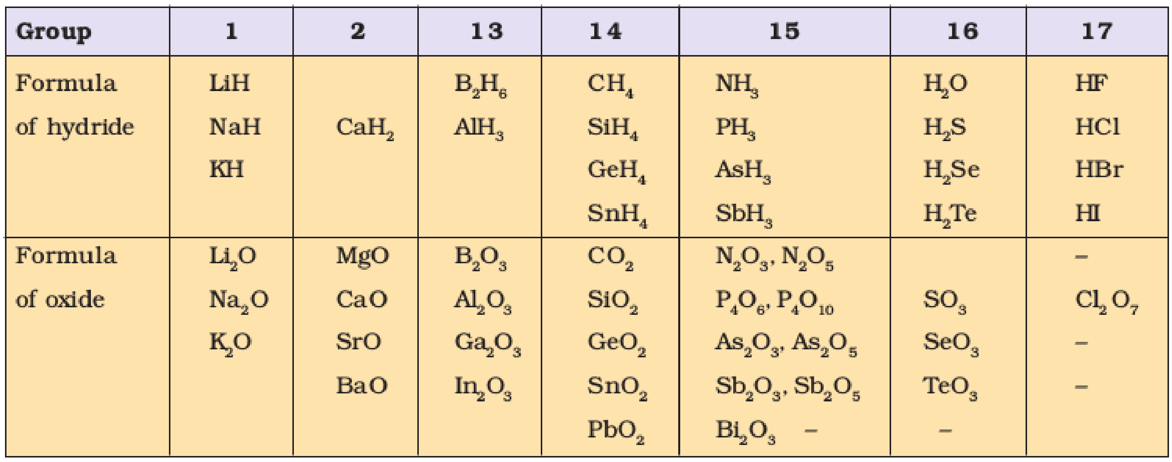
Periodicity of Valence or Oxidation States

The valence is the most characteristic property of the elements and can be understood in terms of their electronic configurations. The valence of representative elements is usually (though not necessarily) equal to the number of electrons in the outermost orbitals and / or equal to eight minus the number of outermost electrons as shown below.

Nowadays the term oxidation state is frequently used for valence. Consider the two oxygen containing compounds: OF_2 and Na_2O. The order of electro negativity of the three elements involved in these compounds is F > O > Na. Each of the atoms of fluorine, with outer electronic configuration $2s^2 2p^5$, shares one electron with oxygen in the OF_2 molecule. Being highest electronegative element, fluorine is given oxidation state –1. Since there are two fluorine atoms in this molecule, oxygen with outer electronic configuration $2s^2 2p^4$ shares two electrons with fluorine atoms and thereby exhibits oxidation state +2.

In Na_2O, oxygen being more electronegative accepts two electrons, one from each of the two sodium atoms and, thus, shows oxidation state –2. On the other hand sodium with electronic configuration 3*s*1 loses one electron to oxygen and is given oxidation state +1. Thus, the oxidation state of an element in a particular compound can be defined as the charge acquired by its atom on the basis of electronegative consideration from other atoms in the molecule.

Table 4.7: Periodic Trends in Valence of Elements as shown by the Formulas of Their Compounds



Group	1	2	13	14	15	16	17
Formula of hydride	LiH NaH KH	CaH_2	B_2H_6 AlH_3	CH_4 SiH_4 GeH_4 SnH_4	NH_3 PH_3 AsH_3 SbH_3	H_2O H_2S H_2Se H_2Te	HF HCl HBr HI
Formula of oxide	Li_2O Na_2O K_2O	MgO CaO SrO BaO	B_2O_3 Al_2O_3 Ga_2O_3 In_2O_3	CO_2 SiO_2 GeO_2 SnO_2 PbO_2	N_2O_3, N_2O_5 P_4O_6, P_4O_{10} As_2O_3, As_2O_5 Sb_2O_3, Sb_2O_5 Bi_2O_3 –	SO_3 SeO_3 TeO_3 –	– Cl_2O_7 – –

Anomalous Properties of Second Period Elements

The first element of each of the groups 1 (lithium) and 2 (beryllium) and groups 13-17 (boron to fluorine) differs in many respects from the other members of their respective group. For example, lithium unlike other alkali metals, and beryllium unlike other alkaline earth metals, form compounds with pronounced covalent character; the other members of these groups predominantly form ionic compounds. In fact the behaviour of lithium and beryllium is more similar with the second element of the following group i.e., magnesium and aluminium, respectively.

This sort of similarity is commonly referred to as diagonal relationship in the periodic properties. What are the reasons for the different chemical behaviour of the first member of a group of elements in the *s*- and *p*-blocks compared to that of the subsequent members in the same group?

The anomalous behaviour is attributed to their small size, large charge/ radius ratio and high electro negativity of the elements. In addition, the first member of group has only four valence orbitals (2*s* and 2*p*) available for bonding, whereas the second member of the groups have nine valence orbitals (3*s*, 3*p*, 3*d*). As a consequence of this, the maximum covalency of the first member of each group is 4 (e.g., boron can only form $[BF_4]^-$, whereas the other members of the groups can expand their valence shell to accommodate more than four pairs of electrons e.g., aluminium forms $[AlF_6]^{-3}$ Furthermore, the first member of *p*-block elements displays greater ability to form $p\pi - p\pi$ multiple bonds to itself (e.g., C = C, C ≡ C, N = N, N ≡ N) and to other second period elements (e.g., C = O, C = N, C ≡ N, N = O) compared to subsequent members of the same group.

Periodic Trends and Chemical Reactivity

The atomic and ionic radii, as we know, generally decrease in a period from left to right. As a consequence, the ionization enthalpies generally increase and electron gain enthalpies become more negative across a period. In other words, the ionization enthalpy of the extreme left element in a period is the least and the electron gain enthalpy of the element on the extreme right is the highest negative (***note:*** *noble gases having completely filled shells have rather positive electron gain enthalpy values*).

This results into high chemical reactivity at the two extremes and the lowest in the centre. Thus, the maximum chemical reactivity at the extreme left (among alkali metals) is exhibited by the loss of an electron leading to the formation of a cation and at the extreme right (among halogens) shown by the gain of an electron forming an anion.

This property can be related with the reducing and oxidizing behaviour of the elements which you will learn later. However, here it can be directly related to the metallic and non-metallic character of elements. Thus, the metallic character of an element, which is highest at the extremely left decreases and the non-metallic character increases while moving from, left to right across the period.

The chemical reactivity of an element can be best shown by its reactions with oxygen and halogens. Here, we shall consider the reaction of the elements with oxygen only. Elements on two extremes of a period easily combine with oxygen to form oxides.

The normal oxide formed by the element on extreme left is the most basic (e.g., Na_2O), whereas that formed by the element on extreme right is the most acidic (e.g., Cl_2O_7). Oxides of elements in the centre are amphoteric (e.g., Al_2O_3, As_2O_3) or neutral (e.g., CO, NO, N_2O). Amphoteric oxides behave as acidic with bases and as basic with acids, whereas neutral oxides have no acidic or basic properties.

Among transition metals (3*d* series), the change in atomic radii is much smaller as compared to those of representative elements across the period. The change in atomic radii is still smaller among inner-transition metals (4*f* series). The ionization enthalpies are intermediate between those of *s*- and *p*-blocks. As a consequence, they are less electropositive than group 1 and 2 metals.

In a group, the increase in atomic and ionic radii with increase in atomic number generally results in a gradual decrease in ionization enthalpies and a regular decrease (with exception in some third period elements) in electron gain enthalpies in the case of main group elements. Thus, the metallic character increases down the group and non-metallic character decreases. In the case of transition elements, however, a reverse trend is observed. This can be explained in terms of atomic size and ionization enthalpy.

What You Have Learnt

- The classification of elements makes their systematic.
- The arrangement of elements in the long form of the periodic table depends on their electronic configuration.
- The properties of the elements are periodic function of their atomic number.
- All the known elements are arranged in 18 groups in the long form of periodic table
- There are seven horizontal rows (periods) in the long form of the periodic table.
- Elements of groups 1 and 2 are known as alkali metals and alkaline earth metals respectively.
- *s, p, d and f* are the four blocks in the periodic table classified on the basis of their outer most electrons residing in s, p, d and f sub-shell.
- The elements can be classified into metals, non-metals and metalloids on the basis of their properties and their position in the periodic table.
- The atomic size, ionic size, ionization enthalpy, electron gain enthalpy and electro negativity show regular trends along a group and a period.
- Various type of atoms radius possible for atoms
- Factors which effect the Ionization potential of different atoms.

Terminal Exercise

1. Define modern periodic law.

2. Refer the periodic table in Table 4.2 and answer the following questions.

    i) The elements placed in group number 18 are called.....................

    ii) Alkali and alkaline earth metals are collectively called .... block metals.

    iii) The general configuration for halogens is………..............

    iv) Name a *p*-block elements which is a gas other than a noble gas or a halogen.

    v) Name the groups that comprise the 's' block of elements.

    vi) Element number 118 has not yet been established, to which block, will it belong?

    vii) How many elements should be there in total if all the 7s, 7p, 6d and 5f blocks are to be full ?

3. Describe the variation of Electron Affinity and Ionization Enthalpy in the periodic table.

4. Define the following:

    a) Electron gain enthalpy b) Ionization enthalpy

    c) Ionic radius d) Electro negativity

5. What is electro negativity? How is it related to the type of bond formed?

6. Why is the electron gain enthalpy of Cl more in negative value as compared to that of F?
7. Name the different types of atomic radius
8. What is shielding effect?
9. Explain 3 factors which influence the Ionization energy.

Answers to Intext Questions

4.1

1.

Metals	Non metals	Metalliods
Sn, Pb	C	Si, Ge
Sb, Bi	N, P	As
Te, Po	O, S	Se

2. Potassium is more metalic than aluminum.
3. i) 2 ii) 2 iii) 3-12 iv) 17 v) 18
4. Np, Lw, No, Rf, Hs.

4.2

1) *s > p > d > f*

2) Protection of outer electrons from nuclear attraction by electrons present in inner shells of an atom.

3) Covalent radius is half of the distance between the nuclei of two atoms held together by a covalent bond.

4.3

1. i) Unnilpentium ii) Unnilennium iii) Ununbium iv) Unnunpentium
2. Al3+, Na+, F^-, O^{2-}
3. The atomic size decreases from left to right across a period and increases on moving down the group.

i) s>p>d>f

ii) Protection of outer electrons from nuclear attraction by electrons present in inner shells of an atom.

iii) Covalent radius is half of the distance between the nuclei of two atoms held together by a covalent bond.

4.4

1. Ionization enthalpy decreases with increase in atomic size and vice-versa.

2 i) $_{3}$Li ii) $_{7}$N iii) $_{12}$Mg iv) $_{14}$Si v) $_{12}$Ar vi) $_{18}$Ar vii) $_{6}$C

3. The electronic configuration of Be is 1s2 2s2 whereas that of B is 1s2 2s2 2p1. In case of Be, the electron is to be removed from completely filled s orbital whereas in case of B it is to be removed from a singly occupied p orbital. Fully-filled orbitals are more stable. Hence, ionization enthalpy decreases from Be to B. Similarily, it decreases from Mg to Al.

4. The noble gases have fully filled and are stable. Hence, they have the highest ionization enthalpies in their respective periods.

5. Fluorine.

Chapter 05

CHEMICAL BONDING

In lesson 1 you have learnt about the structure of atom while in the lesson 2 you studied about the classification of elements and the variation in atomic properties. You know that molecules are obtained by the combination of two or more than two atoms of the same or different elements. In this lesson you will study

- Why do atoms combine?
- What are the different ways in which the atoms can combine? and
- What are the shapes of different molecules?

The answers to these questions are of fundamental importance to the study of chemistry, as you would discover while studying the later parts of this course.

Objectives

After reading this lesson you will be able to:

- explain the formation of bond in terms of potential energy diagram and octet rule;
- list different types of bonds;
- define ionic bond and cite some examples;
- write Lewis structures of some simple molecules;
- list the charateristics of ionic compounds;
- define covalent bond and cite some examples;
- list the characteristics of covalent compounds;
- state valence shell electron pair repulsion (VSEPR) theory;
- predict the geometry of molecules with the help of VSEPR thoery;
- explain the hybridization of atomic orbitals involving *s*, *p* and *d* orbitals and illustrate with examples;
- tabulate the geometry of some molecules showing sp, sp^2, sp^3, dsp^2 *and* dsp^3 hybridization;
- explain the formation of and bonds in CH_4, CH_2H_4 and C_2H_2;
- explain molecular orbital theory;
- write the molecular orbital configuration of H_2, N_2, O_2 and F_2 molecules;
- define bond length and bond order and relate them and
- explain hydrogen bonding with the help of examples.

5.1 What is a Chemical bond

A Chemical bond may be visualized as an effect that leads to the decrease in the energy. The combination of atoms leads to the formation of a molecule that has distinct properties different from that of the consituent atoms.

A question arises, “How do atoms achieve the decrease in energy to form the bond.” The answer lies in the electronic configuration. The formation of a bond between two atoms may be visualized in terms of their acquiring stable electronic configurations. That is when two atoms (other than that of noble gases) combine they will do so in such a way that they attain an electronic configuration of the nearest noble gas.

The stable electronic configuration of the noble gases can be achieved in a number of ways; by losing, gaining or sharing of electrons. Accordingly, there are different types of chemical bonds, like,

- Ionic or electrovalent bond
- Covalent bond
- Co-ordinate covalent bond

In addition to these we have a special kind of bond called hydrogen bond. Let us discuss about different types of bonds, their formation and the properties of the compounds so formed.

Kössel and Lewis approach to chemical bonding

In order to explain the formation of chemical bond in terms of electrons, a number of attempts were made, but it was only in 1916 when Kössel and Lewis succeeded independently in giving a satisfactory explanation. They were the first to provide some logical explanation of valence which was based on the inertness of noble gas.

Lewis pictured the atom in terms of a positively charged Kernel (the nucleus plus the inner electrons) and the outer shell that could accommodate a maximum of eight electrons. He further assumed that these eight electrons occupy the corners of a cube which surround the Kernel. Thus the single outer shell electron of sodium would occupy one corner of the cube, while in the case of a noble gas all the eight corners would be occupied.

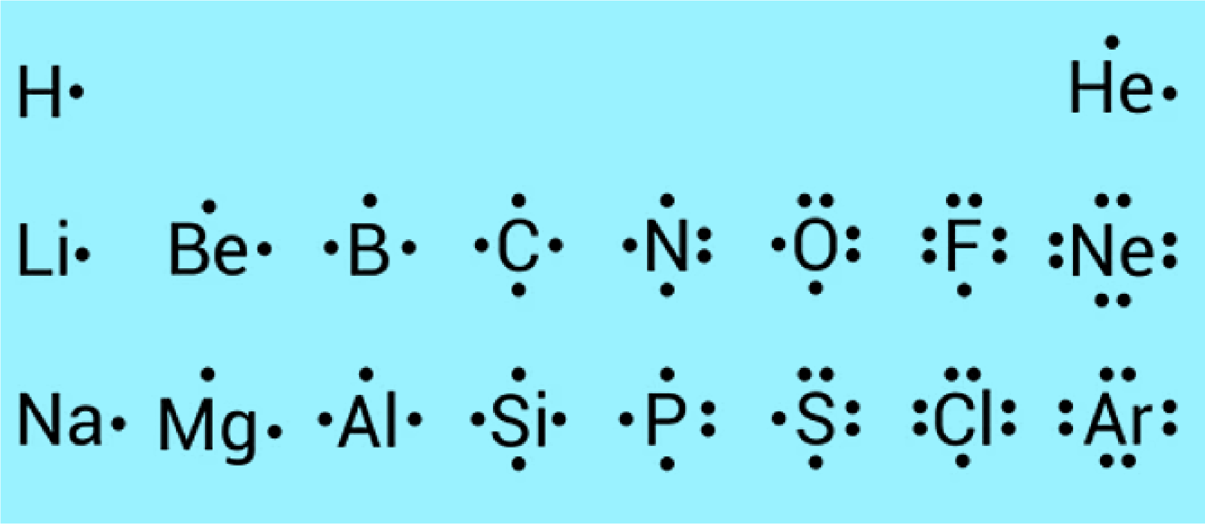
This octet of electrons represents a particularly stable electronic arrangement.

Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds.

In the case of sodium and chlorine, this can happen by the transfer of an electron from sodium to chlorine thereby giving the Na and CI ions. In the case of other molecules like Cl2. F2 etc., the bond is formed by the sharing of a pair of electrons between the atoms. In the process each atom attains a stable outer octet of electrons.

Octet rule: Kossel and Lewis in 1916 developed an important theory of chemical combination between atoms known as electronic theory of chemical bonding. According to this, atoms prefer to have eight electrons in their outermost orbit by losing, gaining or sharing electrons, in order to have an octet in their valence shell. This is known as Octet rule.

Lewis Symbols: In the formation of a molecule, only the outer shell electrons take part in chemical combination and they are known as valence electrons. The inner shell electrons are well protected and are generally not involved in the combination process. GN. Lewis, an American chemist introduced simple notations to represent valence electrons in an atom. These notations are called Lewis symbols. For example, the Lewis symbols for the elements of second period are as under



Significance of Lewis Symbols: The number of dots and the symbol represents the number of valence electrons, which is useful to calculate the common or group valence of the element. The group valence of an element is generally either equal number of dots in Lewis symbols or the number of dots or valence electrons.

Kössel, in relation to chemical bonding drew attention to the following

- In the periodic table. There exist highly electronegative halogens and highly electropositive alkali metals.
- The formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom are associated with gain and loss of an electron by the respective atoms:
- The negative and positive ions attain stable noble gas electronic configurations. The noble gases (with the exception of helium which has doublet of electrons) have a particularly stable outer shell configuration of eight (***octet***) electrons ns^2 np^6
- The negative and positive ions are brought together by electrostatic attraction between them.

Let us discuss about different types of bonds, their formation and the properties of the compounds so formed.

Ionic Bond formation

The electronic configuration of sodium atom (atomic number 11) is 2, 8, 1. Since it is highly electropositive, it readily loses an electron to attain the stable configuation of the nearest noble gas (neon) atom. It becomes a positively charged sodium cation (Na^+) in the process

$$\underset{2,8,1}{Na} \longrightarrow \underset{2,8}{Na^+} + e^- \qquad \Delta H = 493.8 \text{ k J mol}^{-1}$$

(ΔH is enthalpy change)

On the other hand, a chlorine atom (electronic configuration: 2, 8, 7) requries one electron to acquire the stable electronic arrangement of an argon atom. It becomes a negatively charged chloride anion (Cl^-) in the process.

$$\underset{2,8,7}{Cl} + e^- \longrightarrow \underset{2,8,8}{Cl^-} \qquad \Delta H = 397.5 \text{ k J mol}^{-1}$$

According to **Kossel's** theory, there is a **transfer of one electron** from sodium atom to chlorine atom and both the atoms attain noble gas configuration.

$$\begin{tikzcd}[column sep=small] Na & + & Cl \arrow[r] & Na^{+} & + & Cl^{-} \\ 2,8,1 \arrow[rr, bend right] & & 2,8,7 & 2,8 & & 2,8,8 \end{tikzcd}$$

The positively charged sodium ion and the negatively charged chloride ion are held together by electrostatic attractions. The bond so formed is called an **electrovalent** or an **ionic bond**. *Thus the ionic bond can be visualised as the electrostatic force of attraction that holds the cation and anion together*. The compounds so formed are termed as ionic or electrovalent compounds.

Factors favour the Ionic bond formation:

a) Cation formation

1) Lower ionization energy: Lower the ionization energy of an atom, greater is the case of formation of cation.

The IP of sodium is 519.82 kJ. mol^{-1} and that of Potassium is 495.57 kj. mol^{-1} so K^{+} ion can readily form than Na^{+} ion.

2) Large size of the atom: Large atom can easily lose the valence electrons. If the size is large, the distance between the nucleus and the valence electrons is more and therefore nuclear attraction is less. Therefore the electron can be removed easily from the atom forming cation.

3) Ion with lower change: Small magnitude of the charge favours the formation of ions easily. eg. : The ease of ion formation increases in the order $Na^{+} > Mg^{+2} > Al^{+3}$.

4) Cations with inert gas configuration: Ions pocessing electronic configuration similar to zero group elements are more stable than those ions which do not have such configuration.

e.g. Ca^{+2} (2,8,8) in more stable than Zn+2 (2,8,18) because Ca^{+2} has inert gas configuration.

b) Anion formation:

1) High Electron affinity: If the electron affinity of an element is high its anion can be easily formed.

e.g. $Cl^{-} > O^{2-} > N^{3-}$

2) Smaller size of atom: Smaller the atom lesser is the distance between the nucleus and the valance orbit. Hence the nuclear attraction on incoming electron is more So the anion is readily formed.

3) Lower change: Ions with lower change are more readily formed than those with higher charges. (like O^{-2} and N^{-3}).

$$Cl + e^{-} \longrightarrow Cl^{-} > O^{2-} > N^{3-}$$

c) Electro Negativity Values:

If the two bonded atoms differ by more than 1.70 in their EN values, the bond between them is ionic in nature.

The formation of NaCl from sodium and chlorine can be broken down into a number of steps as:

a) Sublimation of solid sodium to gaseous sodium atoms.

$$Na(s) \longrightarrow Na(g) \; ; \qquad \Delta H = 108.7 \text{ kJ mol-1}$$

b) Ionization of gaseous sodium atom to give sodium ion.

$$Na(s) \longrightarrow Na^{+}(g) + e^{-} \; ; \qquad \Delta H = 493.8 \text{ kJ mol-1}$$

c) Dissociation of gaseous chlorine molecule into chlorine atoms

$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$; $\Delta H = -120.9$ kJ mol-1

d) Conversion of gaseous chlorine atom to chloride ion **(addition of electron)**

$Cl(g) + e- \longrightarrow Cl-(g)$; $\Delta H = -379.5$ kJ mol-1

e) Formation of NaCl from sodium and chloride ions. **(Crystal or lattice formation)**.

$Na+(g) + Cl-(g) \longrightarrow Na+ Cl-(s)$; $\Delta H = -754.8$ kJ mol-1

The energy released in this step is **lattice energy.**

Lattice energy, U, is defined as the enthalpy required to dissociate one mole of crystalline solid in its standard state into the gaseous ions of which it is composed.

The net reaction would be

$Na(s) + \frac{1}{2}Cl\ (g) \longrightarrow Na+ Cl(s)$; $H = -4109.$ kJ mol-1

The overall energy change can be computed by taking the sum of all the energy changes;

$\Delta H = (180.7 + 493.8 + 120.9 - 379.5 - 754.8) = -410.9$ kJ mol-1

Thus we see that the net process of formation of NaCl from sodium and chlorine is accompanied by a large decrease in the energy. The approach we have just followed is based on the law of conservation of energy and is known as **Born-Haber cycle**.

Of the five different types of energies involved, two (sublimation and dissociation energies) have low values than the rest. Therefore, the three energy terms i.e., ionization energy, electron affinity and lattice energy are important in determining the formation of an ionic configuration the basis of the above discussion we can say that the formation of anion compound formed by

i. Low ionisation energy of the metal,
ii. High electron affinity of the other element (non-metal), and
iii. High lattice energy

5.2.2 Characteristic Properties of Ionic Compounds

- These exist as crystalline solids in which the ions are arranged in regular three dimensional structures. The ionic compounds are generally hard and brittle in nature.
- These compounds have high melting and boiling points due to strong electrostatic interactions between the ions.
- These are generally soluble in water and less soluble in non-polar solvents like ether, alcohol, etc.
- These conduct electricity when in molten state or in aqueous solutions.

Kossel's theory explain bonding quite well but only for a small class of solids composed of electropositive elements of Group 1 and 2 with highly eletronegative elements. Secondly, this theory is incapable of explaining the formation of compounds like, SO_2 or O_2, etc. For example in case of O_2, there is no reason to expect that one atom of oxygen would lose two electrons while the other accepts them. The problem was solved by Lewis theory of covalent bonding.

Properties of ionic compounds:

1) **Physical State:** Due to close packing of ions, ionic compounds are crystalline solids.
2) **Melting and Boiling points:** In ionic crystals the oppositely charged ions are bound by strong electrostatic force of attraction. To overcome these attractive force between

ions, more thermal energy is required. Hence the melting and boiling points of ionic compounds are high.

3) **Solubility:** Ionic compounds are soluble in polar solvents like water, liquid ammonia etc. But are insoluble in non-polar solvents like benzene, carbon disulphide etc.
4) **Reactivity:** Reaction between ionic compounds in aqueous solution is very fast due to strong attraction among ions.

e.g. When AgNO3 solution is added to NaCl solution, a white precipitate of AgCl is formed.

$$Ag^+ + NO^-_3 + Na^+Cl^- \longrightarrow AgCl + Na^+NO^-_3$$

5) **Isomerism:** Ionic bond is non directional so ionic compounds cannot exhibit isomersim.
6) **Electrical conductivity:** Ionic substances conduct electricity in molten state and in aqueous solution. The ionic compounds are, therefore, electrolytes.

5.3 Covalent Bond

Like Kossel, Lewis also assumed that atoms attain noble gas electronic configuration in the process of bond formation. However, the way the noble gas electronic configuration is achieved, is different. Lewis proposed that this is achieved by "*sharing of pair of electrons*" between the two atoms. Both the atoms contribute an electron each to this pair. For example, two hydrogen atoms form a molecule by sharing a pair of electrons. If electrons are indicated as dots, formation of hydrogen molecule can be shows as

$$H. + .H \longrightarrow H : H \longrightarrow H - H$$

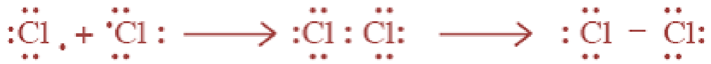
This shared pair of electrons contributes towards the stability of both the atoms and is said to be responsible for 'bonding' between the two atoms. Such a bond is called **covalent bond** and the compounds so obtained are called **covalent compounds**.

and the covalent bond formation in HF is represented as

Sometimes, the electrons contributed by different atoms are represented by different symbols. For example, formation of HF may also be shown as

In this case the hydrogen electron is shown as a cross while the electrons of fluorine are represented by dots. There is no differece between electrons; it is just a presentation for the sake of convenience.

In terms of Lewis structures the formation of a chlorine molecule from two chlorine atoms may be represented as



Here each chlorine atom with seven valence electrons, contributes one electron to the shared pair. In the process of bond formation both the chlorine atoms acquire the electronic configuration of argon. In the same way, the formation of oxygen molecule involves sharing of two pairs of electrons between the two oxygen atoms. In this case both the atoms contribute two electrons each and acquire eight electrons or an octet in their valence shell.

In a Lewis representation the electrons shown to be involved in the bond formation are called bonding Electrons the pair of electrons is called ‘bond pair’ and the pairs of electrons not involved in the bonding process are called ‘lone pairs’. The nature of the electron pair plays an important role in determining the shapes of the molecules. This aspect is discussed later in Section 5.4.

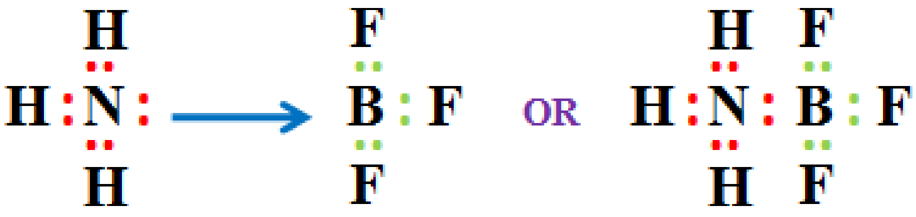
5.3.1 Polar Covalent Bond

In a chemical bond the shared electron pair is attracted by the nuclei of both the atoms. When we write the electron dot formula for a given molecule the shared electron pair is generally shown in the middle of the two atoms indicating that the two atoms attract it equally. However, actually different kinds of atoms exert different degrees of attraction on the shared pair of electrons. A more electronegative atom has greater attraction for the shared pair of electrons in a molecule. As a consequence in most cases the sharing is not equal and the shared electron pair lies more towards the atom with a higher electronegativity. For example, in HCl, the shared pair of electron is attracted more toward more electronegative chlorine atom. As a result of this unequal sharing of the electron pair, the bond acquires polarity or partial ionic character.

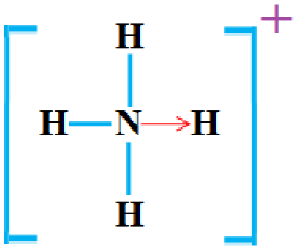
In an extreme case, the difference in the electronegativity may be so high that the electron pair is practically under the influence of a single atom. In other words the polarization of the bond is complete i.e., we have a case of ionic bonding. Thus, though the Lewis theory talks about covalent bonding it can account for the formation of ionic compounds also.

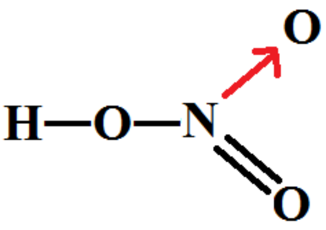
5.3.2 Coordinate Covalent Bond

You have learnt that in the formation of a covalent bond between the atoms, each atom contributes one electron to the shared electron pair, However, in some cases both the electrons of the shared pair are contributed by only one species (atom, molecule or ion) A common example is the formation of a bond between boron trifluoride (BF_3) and ammonia (NH_3).BF_3 is an electron deficient molecule and can accept a pair of electrons. The molecule of ammonia on the other hand is electron rich. It has a lone pair of electron on the nitrogen atom and that can be donated. Electron rich ammonia donates a pair of electron to electron deficient BF_3. Such electron donor-acceptor bonds are called **coordinate covalent** or **dative bonds**.



A coordinate bond is normally represented by an arrow pointing from a donor atom to the acceptor atom. A coordinate bond is identical to a covalent bond in terms of its polairty and strength. The two are different only in the way they are formed. We cannot distinguish between covalent and coordinate covalent bond, once these are formed. HNO_3 and NH_4^+ ion are some more common example of formation of a coordinate bond.



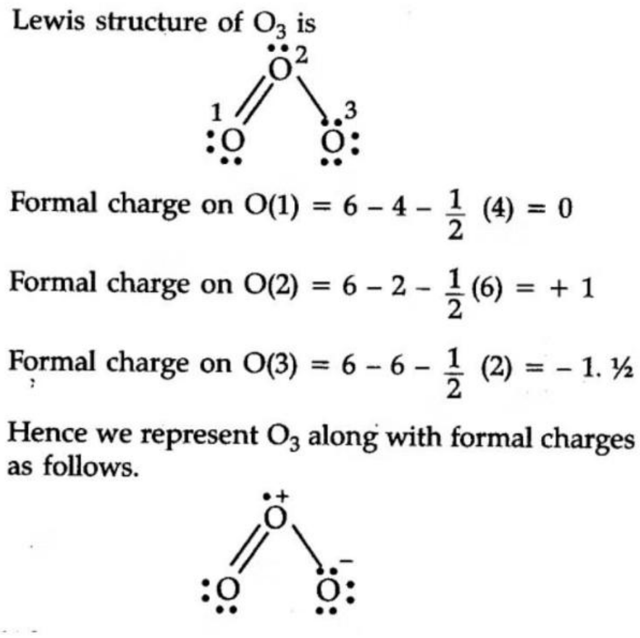


Formal Charge

Lewis dot structures, in general, do not represent the actual shapes of the molecules. In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom. It is, however, feasible to assign a formal charge on each atom. The formal charge of an atom in a polyatomic molecule or Ion may be defined as the difference between the number of valence electrons of that atom in an isolated or freestate and the number of electrons assigned to that atom in the Lewis structure.

Formal charge (F.C) on an atom in a Lewis structure	=	Number of valence electrons in the Free atom	-	Number of unshared electrons on the atom	-	number of bonds around the atom

Generally the lowest energy structure is the one with the smallest formal charge on the atoms. The formal charge is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighboring atoms.



Lewis structure of O_3 is

Formal charge on O(1) = $6 - 4 - \frac{1}{2}(4) = 0$

Formal charge on O(2) = $6 - 2 - \frac{1}{2}(6) = +1$

Formal charge on O(3) = $6 - 6 - \frac{1}{2}(2) = -1.$ ½

Hence we represent O_3 along with formal charges as follows.

Limitations of Octet Rule:

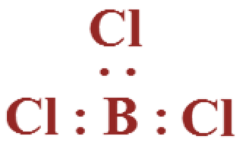
The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to elements in the second period of the periodic table. there are three types of exceptions to the octet rule as given below

The incomplete octet of the central atom

In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four electrons. Examples are LiCl, BeH_2 and BCl_3.

$Li : Cl$

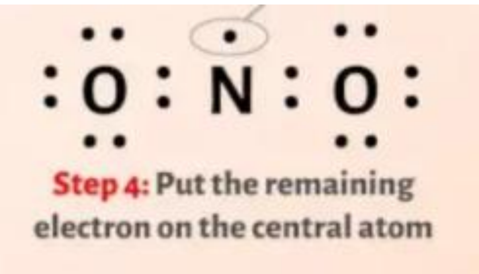
$H : Be : H$

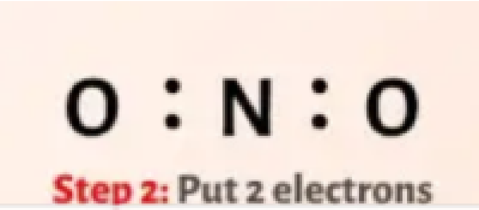


$$Cl : \overset{\overset{Cl}{\cdot\cdot}}{B} : Cl$$

Odd electron Molecules

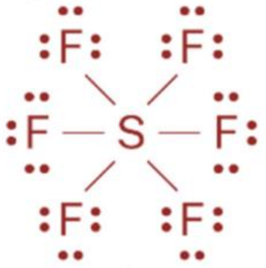
In molecules with an odd number of electrons like Nitric Oxide, NO and Nitrogen Dioxide NO_2, the octet rule is not satisfied for all atoms.





The expanded Octet:

Elements in and beyond the third period of the periodic table have apart from ns and np orbitals. n or (n-1) d orbitals are also available for bonding, in a number of compounds of these compounds there are more than eight valence elctrons around the central atom. this is termed as expanded octet.   Examples: PF_3, SF_6, H_2SO_3



Intext Questions 5.1

1. Define, electrovalent bond.

……………………………………………………………………………………………………

2. The formation of a nitrogen molecule from two nitrogen atoms in terms of Lewis theory.

……………………………………………………………………………………………………

3. What do you understand by a polar covalent bond? Give two example.

……………………………………………………………………………………………………

4. What is a coordinate covalent bond? How is it different from a covalent bond?

……………………………………………………………………………………………………

5. What are the factors which favour the formation of cation.

………

6. Ionic compounds do not exhibit isomerism why?

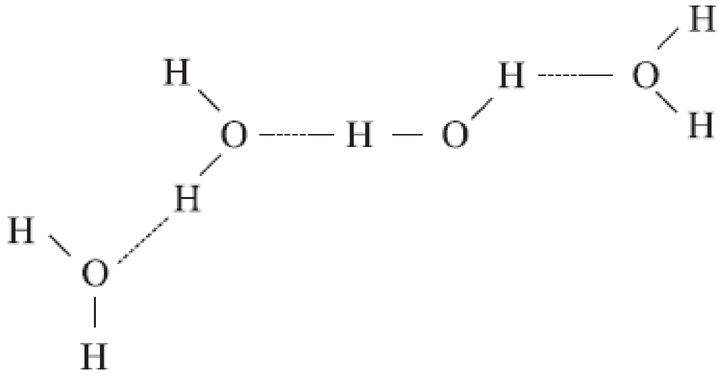
………

5.3.3 Characteristic Properties of Covalent Compounds

- The covalent compounds have low melting and boiling points due to weak forces of interaction between the molecules.
- The covalent compounds are poor conductors of electricity as these lack ionic species.
- The covalent compounds are generally insoluble in water and dissolve in nonpolar solvents like benzene, carbon tetrachloride etc.

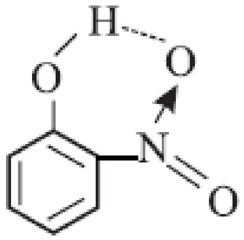
5.3.4 Hydrogen Bonding

It is a special type of attraction between a hydrogen atom bonded to a strongly electronegative atom (like nitrogen, oxygen or fluorine) and the unshared pair of electrons on another electronegative atom. Hydrogen bond is a weak bond, the strength being just about 4-25 kJ mol^{-1}. It is quite small as compared to the covalent bond, which needs a few hundreds of kJ mol^{-1} of energy to break. However, it is strong enough to be responsible for the high boiling points of H_2O and HF etc. In fact it is due to hydrogen bonding only that water exists as a liquid. The low density of ice also can be explained in terms of hydrogen bonding.

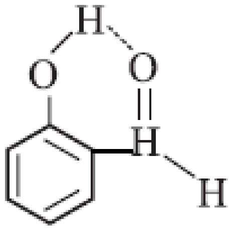


$$H - F \cdots\cdots H - F \cdots\cdots H - F$$

Due to the difference in the electronegativity between hydrogen and the other electronegative atom, the bond connecting them becomes polar. The hydrogen atom acquires a positive charge while the electronegative atom bears the negative charge. Hydrogen bonding results from the electrostatic interaction between the positively charged hydrogen atom and the negatively charged electronegative atom. The second electronegative atom may be a part of the same molecule or it may belong to a different molecule. Accordingly, there are two types of hydrogen bonds. If the hydrogen bond is formed between two different molecules it is called **intermolecular hydrogen bond**. When the hydrogen bond exists within the same molecule, it is called **intramolecular hydrogen bonding**. Salicyldehyde and o-nitrophenol are two common examples of the moelcules showing intramolecular hydrogen bonding whereas in water, intermolecular hydrogen bonding exists.



O-nitrophenol



Salicyldehyde

Hydrogen bonding plays an important role in the structure and function of many biomolecule like proteins and nucleic acids.

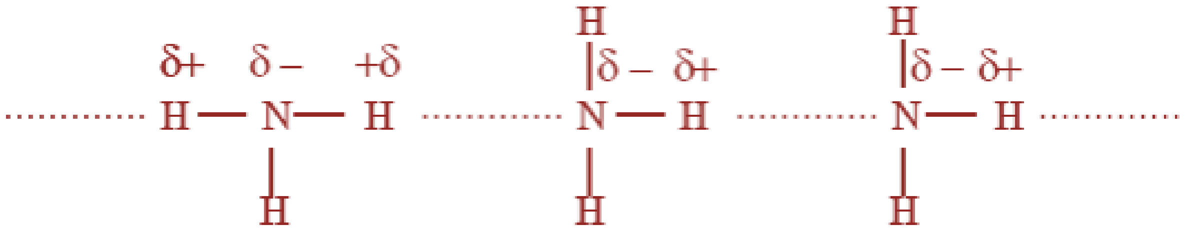
Effects of Hydrogen bond on some properties with example:

Ring formation or chelation through intramolecular H-bonding results in greater volatility lower boiling points and lower solubility in water. These properties can be utilized in the separation of the compounds with intramolecular hydrogen bonding.

The solubility of lower alcohols (ex. CH_3OH ; C_2H_5OH etc.) is due to H-bonding between molecules of alcohols and the molecules of water.

Intermolecular H-bonding has striking effect on the physical properties like metling points, boiling points, enthalpies of vapourization and sublimation.

Comparison of boiling points of NH_3 and HCl: NH_3 has higher boiling points has HCl even though nitrogen and chlorine have nearly same electronegatie values. NH_3 forms H-bonds while HCl does not. This is because of smaller size of Nitrogen atom compared to the chlorine atom.

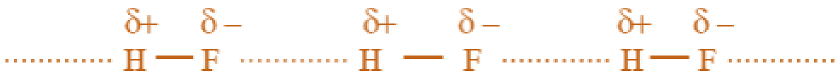


NH_3 as associated molecule

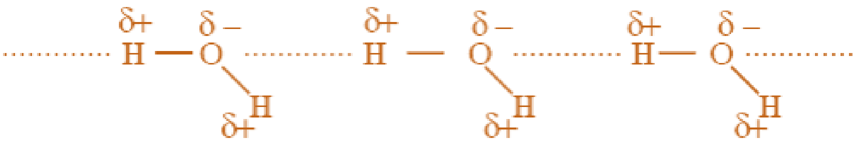
Comparison of boiling points of H_2O and HF:

The boiling point of H_2O is higher than that of HF even though both the compounds form associated molecules through intermolecular hydrogen bonding. They differ in the number of hydrogen atoms. The number of hydrogen bonds, are more in case of water due to the presence of two hydrogen atoms. But HF exists as $(HF)_6$ even in vapour state while water molecules exist as simple H_2O molecules in vapour state.

It means energy is not utilized to break the H-bonding in HF. But H-bonds in H2O consume energy for their cleave. Hence, the boiling point of water is higher than that of hydrogen flouride.



HF as associated molecule



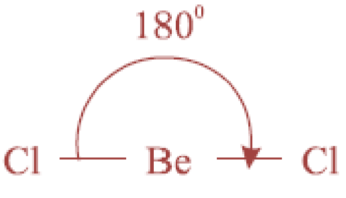
H_2O as associated molecule

5.4 Valence Shell Electron Pair Repulsion (VSEPR) Theory

In a molecule the constituent atoms have definite positions relative to one another i.e. the molecules have a definite shape. The theories of bonding that we have discussed so far do not say anything about the shape of the molecules. A simple theory called VSEPR theory was put forth by Sidgwick and Powell in 1940 to explain the shapes of molecules. It was later refined and extended by Nyholm and Gillespie in 1957. This theory focuses on the electron pairs present in the valence shell of the central atom of the molecule and can be started in terms of two postulates.

POSTULATE 1

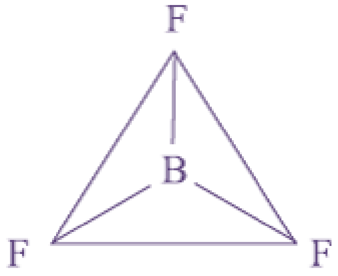
The electron pairs (both bonding and non-bonding) around the central atom in a molecule arrange themselves in space in such a way that they minimize their mutual repulsion. In other words, the chemical bonds in the molecule will be energetically most stable when they are as far apart from each other as possible. Let us take up some examples. $BeCl_2$ is one of the simple triatomic molecules. In this molecules, the central atom, beryllium has an electronic configuration of $1s^2\ 2s^2$. That is it has two electrons in its valence shell. In the process of covalent bond formation with two chlorine atoms two more electrons are contributed (one by each chlorine atom) to the valence shell. Thus there are a total of 4 valence electrons or two pairs of valence electrons. According to the postulate given above, these electron pairs would try to keep as far away as possible. It makes the two electron pairs to be at an angle of 180^0 which gives the molecule a linear shape.



linear molecule

Other molecules of this type would also have a similar shape.

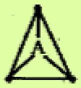
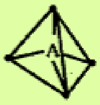
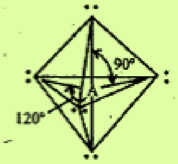
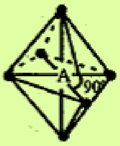
BF3: In boron trifluoride, the central atom, boron has an electronic configuration of $1s^2\ 2s^2\ 2p^1$. That is, it has three electrons in its valence shell. In the process of covalent bond formation with three fluorine atoms three more electrons are contributed (one by each fluorine atom) to the valence shell. Thus there are a total of 6 valence electrons or three pairs of valence electrons. According to the VSEPR postulate, these electron pairs would try to keep as far apart as possible. It makes the three electron pairs to be located at an angle of 120^0 which gives the molecule a planar trigonal shape.



Planar trigonal shape

Thus different molecules would have different shapes depending on the number of valence shell electrons involved. The geometric shapes associated with various numbers of electron pairs surrounding the central atom are given in Table 5.1.

Table 5.1: Geometric arrangements of electron pairs around central atom

Molecule Type	Number of electron pairs	Predicted geometry	Representative Structure	Example
AX_2	2	Linear		$HgCl_2$, BeH_2
AX_3	3	Planer trigonal		BF_3, BCl_3
AX_4	4	Tertahedral		CCl_4, CH_4, $SiCl_4$
AX_5	5	Trigonal bipyramidal		PCl_5, PF_5
AX_6	6	Octahedral		SF_6, PF_6^-

POSTULATE 2

The repulsion of a lone pair of electrons for another lone pair is greater than that between a bond pair and a lone pair which in turn is greater than that between two bond pairs.

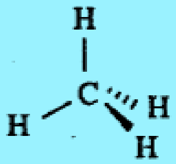
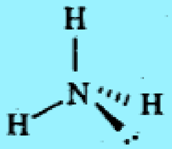
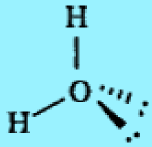
The order of repulsive force between different possibilities is as under.

Lone pair – lone pair > lone pair – bond pair > bond pair – bond pair

The shapes of the molecules given in Table 5.1 Correspond to the molecules containing only bond pair electrons. The shapes of molecules containing a combination of lone pairs and bond pairs would be distorted from above mentioned shapes.

Let us take an example of three molecules namely, methane, ammonia and water. All the three contain a total of 4 electron pairs around their central atom. But the nature of these is different in the three cases. In methane molecule the central carbon atom has 4 valence electrons and it shares 4 electrons with four hydrogen atoms. So there are a total of 4 bond pairs and according to Table 5.1 it should have a tetrahedral shape. In case of ammonia also there are four pairs of electrons but their nature is different. Three of these are bond pairs while one is a lone pair. Similarly, in case of water again there are four pairs of electrons; two are bond pairs while two are lone pairs. Due to the differences in the mutual repulsion between bond pair – bond pair and lone pair – bond pair the molecular shape would be slightly distorted from the expected tetrahedral shape. The number and nature of electron pairs and the geometries of these three molecules are given in Table 5.2.

Table 5.2: Molecular geometries of molecules with 4 electron pairs with different combinations of Ione pairs and bond pairs

Molecule	Number of bond pairs	Number of lone pairs	Molecular geometry	Molecular Shape	Bond angle (in degrees)
CH_4	4	0	tetrahedral		109.5
NH_3	3	1	trigonal pyramidal		107
H_2O	2	2	angular or bent		104.5

We have so far learnt that a chemical bond formation between two atoms can occur by transfer (ionic bonding) or sharing (covalent bonding) of electrons. The processes of bond formation and the bonding in simple molecules can be conveniently represented in terms of electron – dot structures. Further, the VSEPR theory provides a good idea of the shapes of the molecules. But! Have you noticed that we have been representing electrons as well defined dots i.e., localized particles. This is in contradiction with the probabilistic (orbital) representation of the electron that you have learnt in lesson 3. Let us learn, how we explain the process of bond formation in terms of modern theories that incorporate the wave mechanical representation of atom.

Intext Questions 5.2

1. What are the basic postulates of VSEPR theory?

....

2. Predict the shape of methane (CH_4) on the basis of VSEPR theory?

....

3. What is the effect of Hydrogen bond on boiling points?

....

5.5 Modern Theories of Chemical Bonding

The theories of chemical bonding proposed (in 1916) by Kossel and Lewis are called as classical theories of bonding. These do not take into account the wave mechanical or quantum mechanical principles. After the development of quantum mechanical description of atomic structure two more theories were proposed to explain the bonding between atoms. These are called modern theories of chemical bonding. These are Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT). Let us discuss these theories in brief.

5.5.1 Valence Bond Theory

VSEPR theory gives the geometry of simple molecules but it does not explain them. Also it has limited applications. To overcome these limitations, the Valence Bond Theory (VBT) and the Molecular Orbital Theory (MOT) are introduced. Both the theories are based on quantum mechanical principles.

Many attempts were made to apply this theory for the formation of covalent bonds. One such theory, valence bond theory (VBT) was postulated by Heitler and London. This was extended later by pauling and slater to explain the shapes of the molecules as well as the directions of the bonds in them. The important postulates of this theory are as follows:

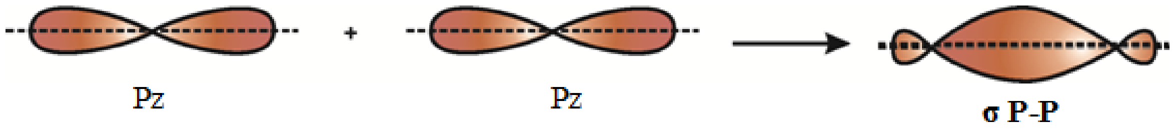
1) A covalent bond is formed by the overlap of two atomic orbitals.
2) The overlapping orbitals contain unpaired electrons of opposite spins.
3) Each of the bonded atoms retains its own atomic orbitals. But the electron pair in the overlapping orbitals is shared by both atoms.
4) Greater the extent of over of orbitals, stronger is the bond formed.
5) As the atomic orbitals are directional in nature (except '***s***' orbitals) the bonds that result due to the overlap of orbitals are also directional. This gives the definite geometry to the covalent molecule.
6) The increased electron density due to the overlap of atomic orbitals of the two combining atoms is along the internuclear axis and keeps two atoms attracted to each other. This gives stability to the molecule.

Examples:

i) Formation of H_2 molecules: Hydrogen molecule is formed due to overlapping of s-s orbitals. When two hydrogen atoms come together, 1s orbitals of the Hydrogen atoms overlap to form a strong "σ" bond this is $\sigma_{s\text{-}s}$.

Formation of H_2

ii) Formation of Cl_2 molecule: The electronic configuration of chlorine atom is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2{}_x\ 3p^2{}_y\ 3p^1{}_z$. It has one half filled $3p_z$ orbital. The Pz orbital of one chlorine atom overlaps the Pz orbital of the chlorine atom and the two electrons of opposite spins pair up to form covalent bond. As the overlap along inter nuclear axis is maximum a strong bond is formed. The bond is formed due to **σ P-P** overlap.

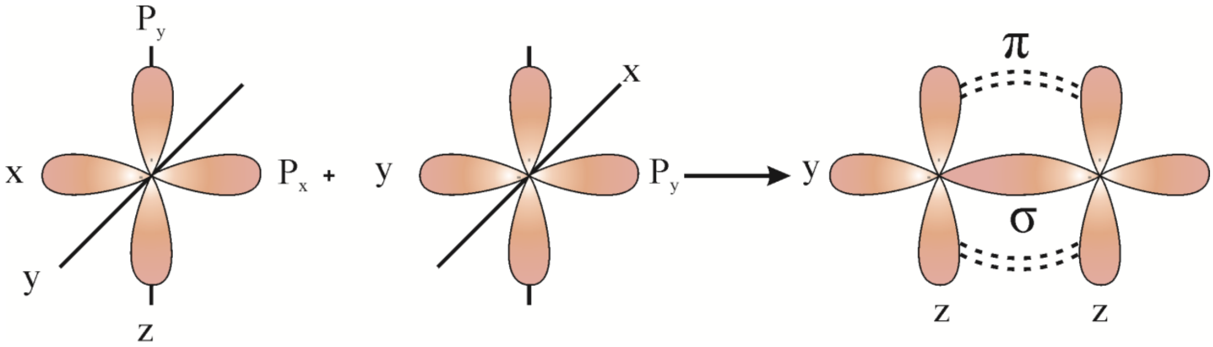


Formation of Cl_2

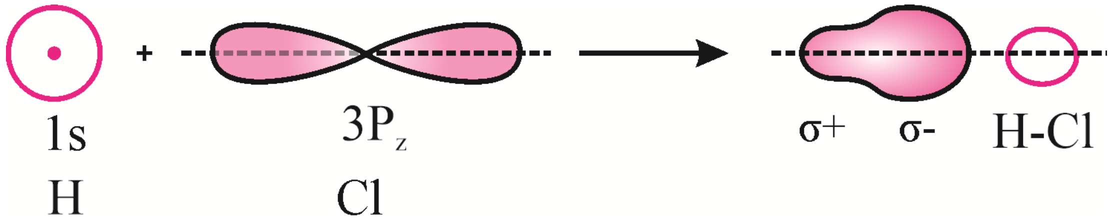
iii) Formation of O_2 molecule: The electronic configuration of oxygen atom is $1s^2\ 2s^2\ 2p^2{}_x\ 2p^1{}_y\ 2p^1{}_z$. It has two half filled 2p orbitals i.e., $2p_y$ and $2p_z$.

The P_y orbital of one atom overlaps the P_y orbital of the second atom to form a 'σ' bond σ P_y - P_y.

The P_z orbital in the two atoms will be at right angles to the internuclear axis. These two have lateral overlap. The electron density of the bonded pair is distributed in two banana like regions lying on either side of the internuclear axis. Thus the oxygen molecule has a double bond. The molecule has one σ P-P and one π P-P between the two atoms.



The electronic configuration of chlorine atom is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x\ 3p_y\ 3p_z$. It has one half filled 3pz orbital. The 3Pz orbital of chlorine overlaps 1s orbital of hydrogen atom and two electrons of opposite spins pair up to form covalant bond. As overlap along the internuclear axis is maximum a strong bond is formed. The bond is formed due to σ *s-p* overlap.



Suppose that the two hydrogen atoms are at infinite distance from each other. Their electrons are in their respective 1s orbitals and are under the influence of the corresponding nuclei. As the two atoms approach each other their 1s orbitals begin to overlap which lead to decrease in energy, Fig.5.1. At a distance equal to the bond length the overlapping is maximum and the energy is minimum. The overlapping can be equated to the sharing of electrons between the atoms. The electrons occupying the shared region of orbitals are under the influence of both the nuclei.

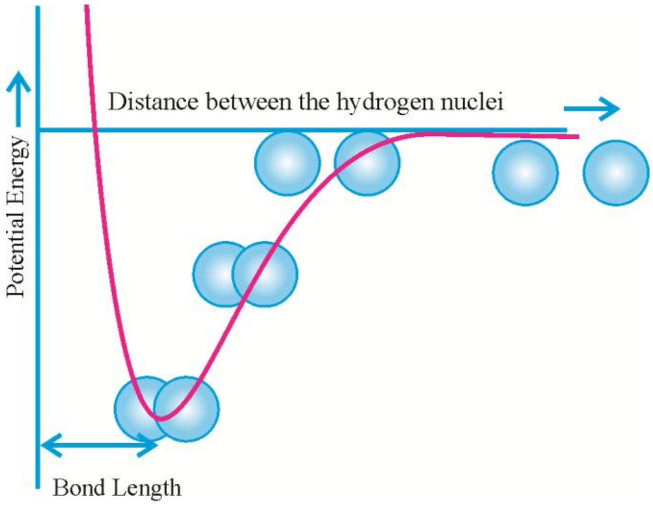
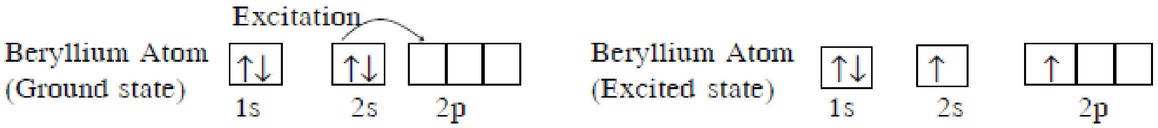


Fig. 5.1: *Formation of hydrogen molecule from overlapping of two hydrogen atoms*

This simple approach can be used to explain the bonding in simple diatomic molecules like HF, F_2 etc. However, to explain bonding in molecules containing more than two atoms some additional concepts like excitation and hybridization need to be used.

5.5.1.1 Hybridisation

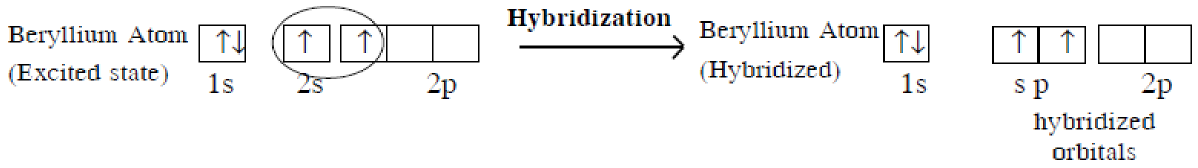
Let us take up the example of bonding in a diatomic molecule; say beryllium hydride (BeH_2) to understand the concept of hybridization of orbitals and the need for the same. The atomic number of beryllium is 4. Its electronic configuration is $1s^2\ 2s^2$. In order to form bonds with the *1s* electrons of the two hydrogen atoms the valence electrons ($2s^2$) of beryllium atom must overlap with the 1s electrons of the two hydrogen atoms. Since the valence shell of beryllium atom contains both the electrons in the same orbital (i.e.,*2s*) it cannot overlap with the *1s* orbital of hydrogen atoms containing one electron. [You know that an orbital can contain a maximum of two electrons with opposite spin]. Pauling got over this problem by suggesting that in the process of bond formation an electron from the *2s* orbital of beryllium atom gets momentarily excited to the empty *2p* orbital as shown below.



Now the two valence electrons are in two singly occupied orbitals which can overlap with the 1s orbitals of the two hydrogen atoms and form two bonds. The problem is still not over. The two bonds formed by these overlaps would be of different nature. One of these would involve overlapping of *2s* orbital of beryllium with 1s orbital of hydrogen while the other would involve overlapping of *2p* orbital of beryllium with 1s orbital of hydrogen. However, experimentally the two bonds are found to be equivalent.

This problem is solved with the help of a concept called hybridisation of orbitals. According to this two or more than two non equivalent orbitals (having different energies and shapes) of comparable energies mix or hybridize and give rise to an equal number of equivalent (same energies and shapes) hybrid orbitals.

In case of $BeCl_2$ the two singly occupied orbitals (*2s* and *2p*) hybridize to give two sp-hybrid orbitals. This is called **sp-hybridisation**. These hybrid orbitals lie along the z-direction and point in opposite directions.



These hybrid orbitals can now overlap with the 1s orbitals of hydrogen atoms to give the linear molecule of $BeCl_2$ as shown below, Fig.5.2.

The concept of hybridisation as illustrated above can be used to describe the bonding and shapes of different molecules by considering hybridization of suitable orbitals. Let us take up some more cases involving hybridization of *s* and *p* orbitals.

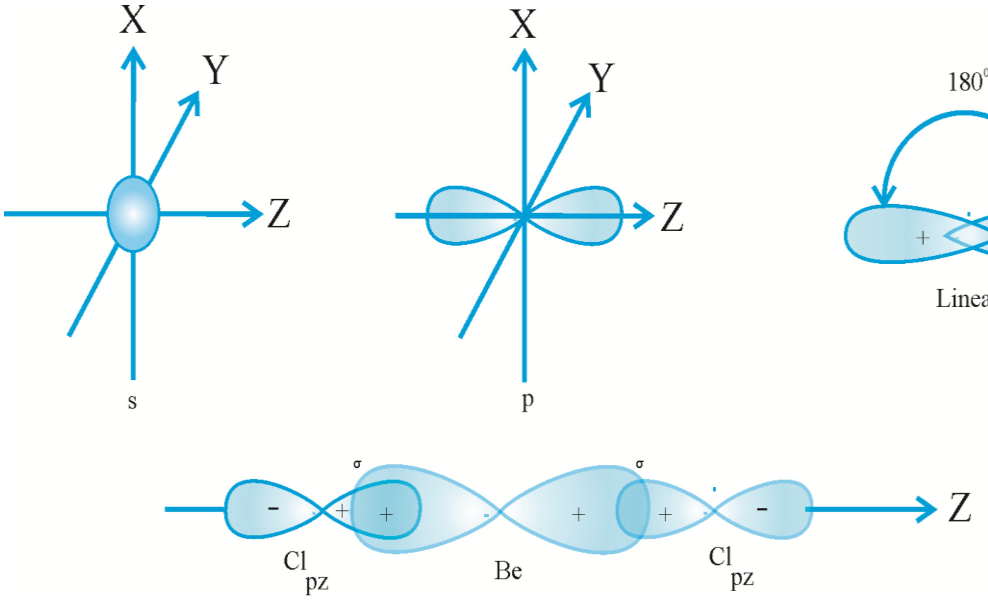
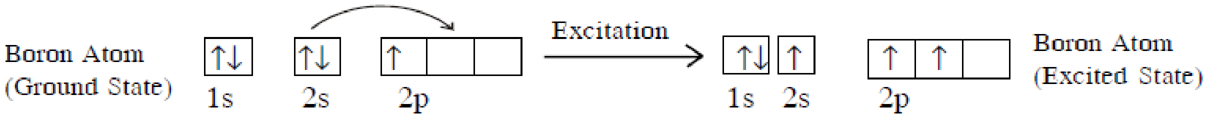
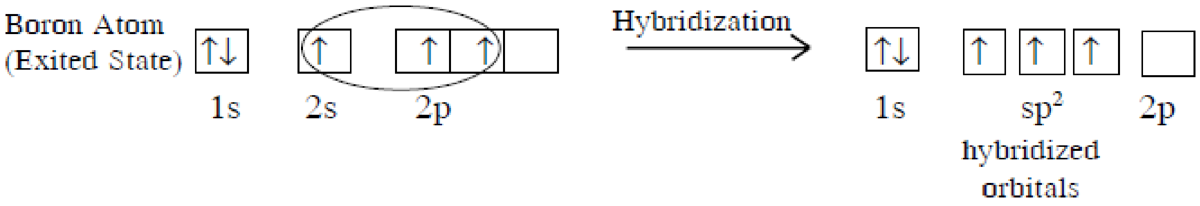


Fig. 5.2: *Formation of* $BeCl_2$*; sp hybridization*

Boron trichloride (*Sp*^{2} hybridisation) : In boron there are five electrons and the electronic configuration is *1s*^{2}, *2s*^{2}, *2p*^{1}. There are three electrons in the valence shell of boron atom. In order to form bonds with three chlorine atoms one of the electrons from the *2s* orbital of boron atom is excited to its *2p* orbital.



One 2s orbital and two 2p orbitals hybridise to give three sp2 hybridized orbitals. This is called **sp2 - hybridisation**.



The three hyrbidized orbitals are coplanar and directed towards the corners of an equilateral triangle. These **hybrid** orbitals then form bonds with the p-orbitals of chlorine atoms as shown below. fig. 5.3

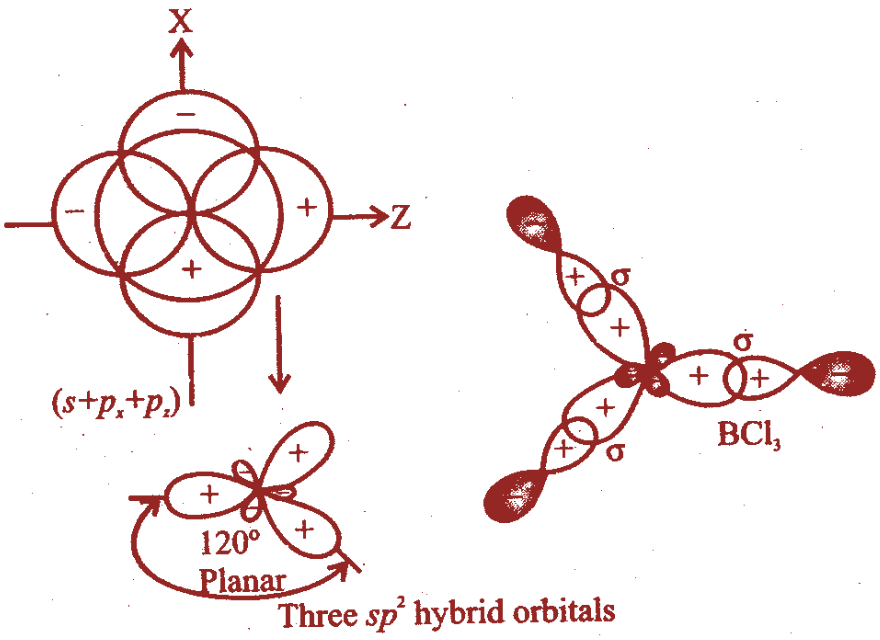
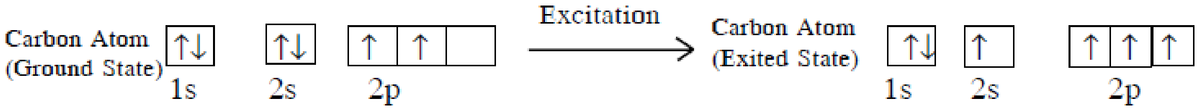
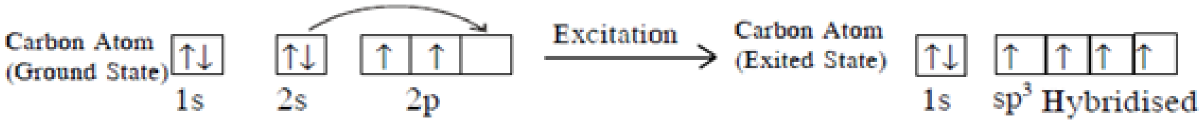


Fig. 5.3: *Formation of $BeCl_3$; sp^2 hybridisation*

Bonding in Methane (Sp^3 hybridisation): In case of methane the central atom, carbon, has an electronic configuration of $1s^2$, $2s^2$, $2p^2$. In order to form bonds with four hydrogen atoms one of the electrons from the *2s* orbital of carbon atom is excited to the *2p* orbital



One *2s* orbital and three *2p* orbitals of the carbon atom then hybridize to give four *sp3* hybridised orbitals. This is called **sp^3-hybridisation**.



These four sp^3 hybrid orbitals are directed towards the corners of a regular tetrahedron. These hybrid orbitals then form bonds with the 1s orbitals of hydrogen atoms to give a methane molecule as shown below, Fig. 5.4.

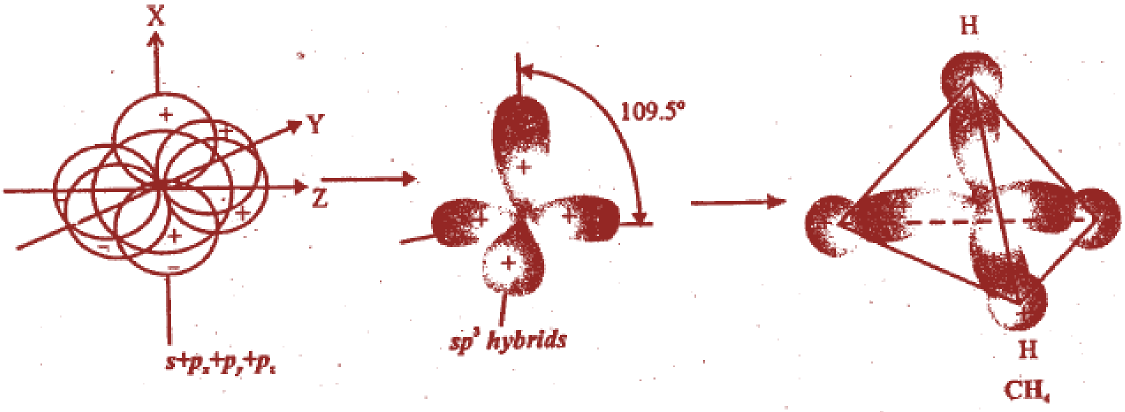
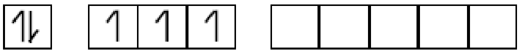


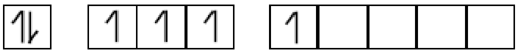
Fig. 5.4: *Formation of CH_4; sp^3 hybridisation*

Phosphorus pentachloride (sp^3d hybridisation):

P (ground state)



P (excited state)

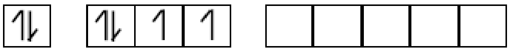


sp^3d hybridisation

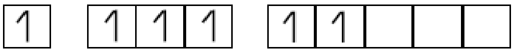
Five sp^3d hybrid orbitals are formed which are directed towards the corners of a trigonal bipyramidal (Fig. 5.5a). These orbitals overlap with singly filled *p*-orbitals of five chlorine atoms and five σ bonds are formed. Thus PCl_5 molecule has a trigonal bipyramidal geometry. Three P-Cl bonds (equatorial) make an angle of 120^0 with each other and lie in one plane. The other two P-Cl bonds (axial) are at 90^0 to the equatorial plane, one lying above and the other lying below the plane.

SF_6 (sp^3d^2 hybridisation) :

P (ground state)



P (excited state)



sp^3d^2 hybridisation

Six sp^3d^2 hybrid orbitals are formed which are directed towards the corners of a regular octahedron. These orbitals overlap with singly filled orbitals of six F atoms and form bonds giving a regular octahedral geometry (Fig. 5.5b).

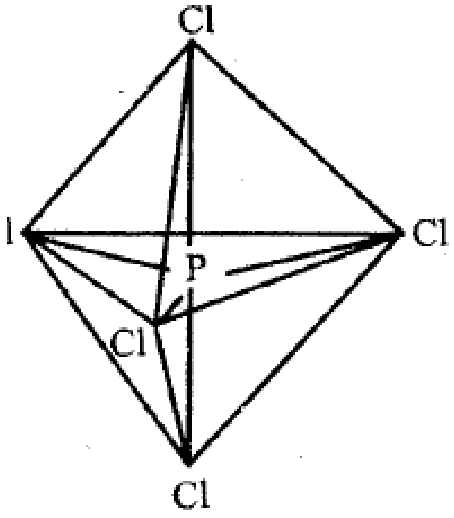


Fig. 5.5(a) : *Trigonal bipyramidal geometry of* PCl_5 *molecule*

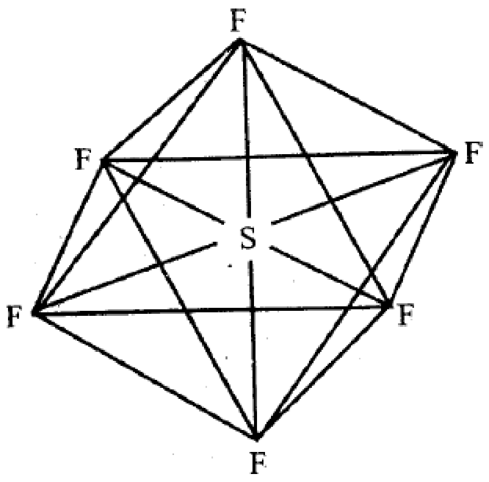


Fig. 5.5(b) : *Octahedral geometry of* SF_6 *molecule*

5.5.1.2 Hybridisation and Multiple Bonds

So far we have discussed the bonding in those molecules in which the orbitals on a single central atom are hybridized. Let us see how does the concept of hybridisation help us in understanding bonding between pairs of such atoms. In the case of bonding in ethane (C_2H_6), two carbon atoms are bonded to each other and each carbon atom is bonded to three hydrogen atoms. You would recall that in the case of methane the valence orbitals of carbon atom undergo sp^3 hybridisation. In ethane each carbon atom undergoes sp^3 hybridisation to give four sp^3 hybridized orbitals. The two carbon atoms form a carbon - carbon bond by sp^3 - sp^3 overlapping. The remaining six sp^3 hybridized orbitals overlap with *1s* orbitals of hydrogen atoms to give a molecule of ethane, C_2H_6 as shown in fig. 5.6 The C-C bond so formed is along the internuclear axis. Such a bond is called a **σ bond**.

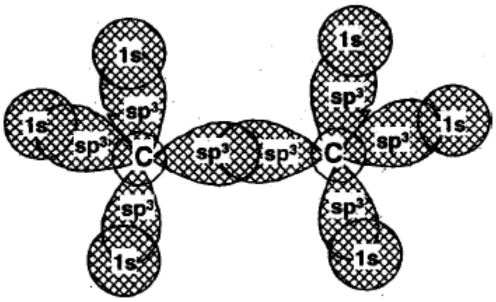


Fig. 5.6 : *Formation of ethane molecule*

Bonding in ethane: In case of ethene, the relevant orbitals of the carbon atoms undergo *sp*^{2} hybridisation. Here, only two of the three *p* orbitals of the carbon atoms hybridize with the *2s* orbital to form three *sp*^{2} hybrid orbitals each. The remaining *p*-orbitals (one on each carbon atom) do not take part in hybridization. A carbon - carbon bond is formed by overlapping of *sp*^{2} orbital on the two carbona atoms (Fig. 5.7(a)). The remaining four *sp*^{2} hybridized orbitals overlap with the *1s* orbitals of hydrogen atoms to give the basic skeleton of the molecule. This leaves an un-hybridized p orbital each on both the carbon atoms (Fig. 5.7(b)) . These are perpendicular to the molecular plane and undergo sideways overlap to give an electron cloud in the above and below the plane of the molecule (Fig. 5.7 (b and c)). This is called **Π-bond**. In ethene there are two bonds between the carbon atoms (one sigma and one pi bond).

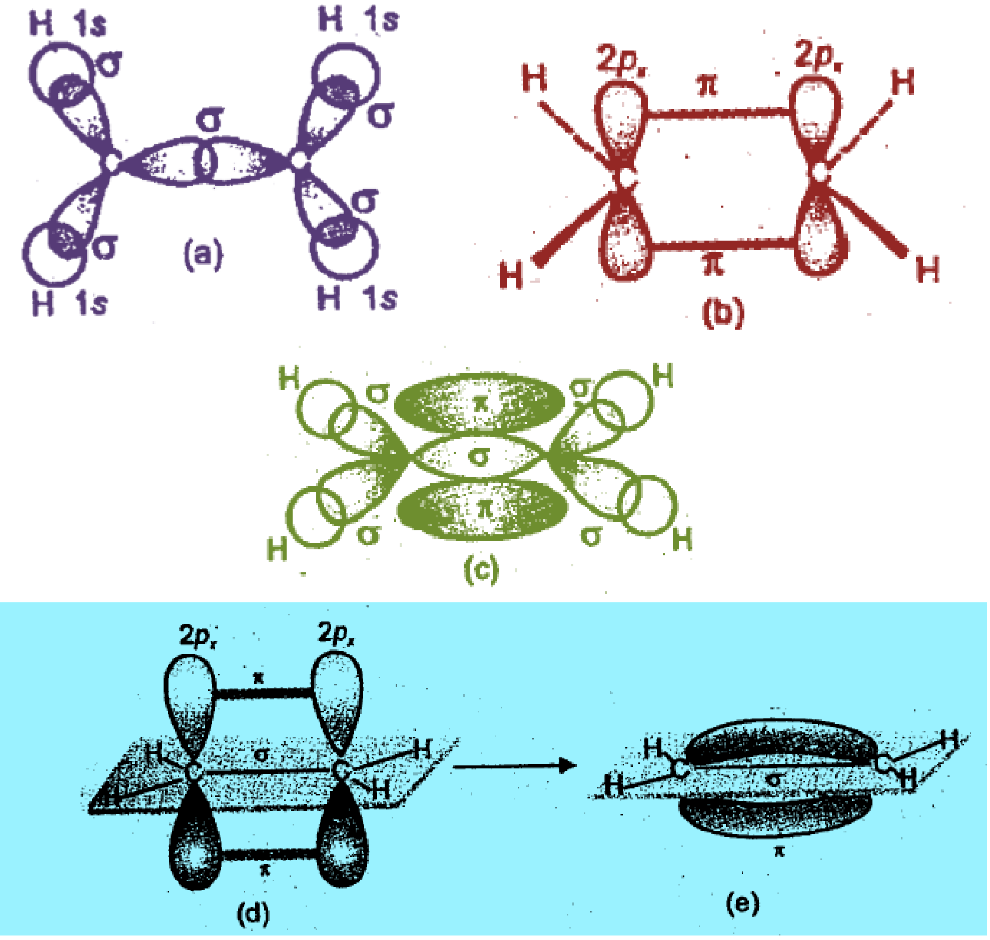


Fig. 5.7 : *Formation of ethylene molecule : a) formation of the basic skeleton of the*

molecule b) sideways overlapping of the un-hybridized p orbitals and c) a π−bond d) and (e) complete picture of ethylene molecule.

Bonding in ethyne (acetylene): In case of acetylene the bonding can be explained in terms of *sp*-hybridisation in carbon atoms. One *2s* and one *2p* orbitals hybridize to give two *sp*-hybridized orbitals. This leaves two mutually perpendicular unhybridized *p* orbitals each on both the carbon atoms. The carbon - carbon bond is formed by *sp* - *sp* overlapping with each other. The remaining *sp* orbital on each carbon overlaps with the *1s* orbital of hydrogen to give C-H bonds (Fig. 5.8). The unhybridised *p* orbitals each on both the carbon atoms overlap sideway to give two -bonds.

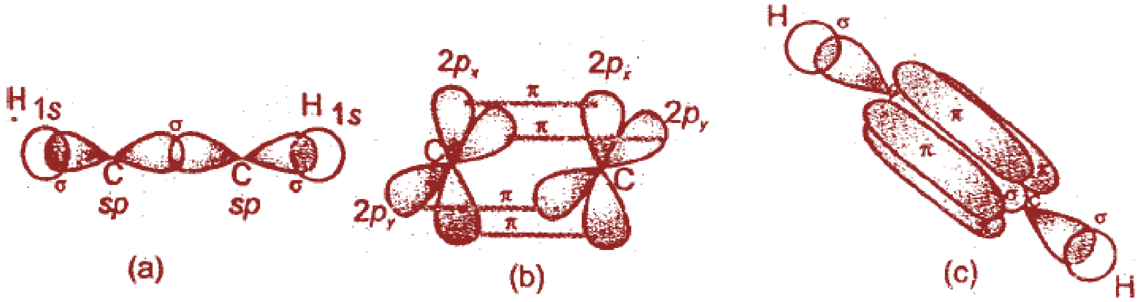


Fig. 5.8 : *Formation of acetylene molecule : a) formation of the basic skeleton of the molecule b) sideways overlapping of the un-hybridized p orbitals and c) two mutually perpendicular bond*

Intext Questions 5.3

1. What do you understand by the term “hybridisation”?

....

2. How would you explain the shape of ammonia molecule on the basis of hybridisation?

....

5.5.2 Molecular Orbitals Theory

You have just learnt about valence bond theory. It describes bond formation as result of overlapping of the atomic orbitals belonging to the constituent atoms. The overlapping region responsible for bonding is situated between the two atoms i.e., it is localised. Molecular orbital theory (MOT) developed by **F. Hund** and **R.S. Mulliken** in **1932**, is based on the wave mechanical model of atom. In contrast to the localized bonding in VBT, the molecular orbital theory visualises the bonding to be delocalised in nature i.e., spread over the whole molecule. According to MOT, in the process of bond formation

- **The atomic orbitals of the constituent atoms combine to generate new types of orbitals (called molecular orbitals)**. These are spread over the whole molecule i.e., they are delocalised. In other words these new orbitals, do not “belong” to any one atom but extend over the entire region of the bonded atoms.
- These molecular orbitals are created by Linear Combination of Atomic Orbitals (LCAO) approach in which, **the atomic orbitals of comparable energies and of suitable symmetry combine to give rise to an equal number of molecular orbitals.**

- The available **electrons then fill these orbitals in the order of increasing energy as in the Aufbau principle** used in the electron configurations of atoms.

Let us take the example of hydrogen molecule to understand the molecular orbital approach to chemical bonding. The two hydrogen atoms have an electron each in their respective *1s* orbitals. In the process of bond formation the atomic orbitals of two hydrogen atoms can combine in two possible ways. In one, the MO wave function is obtained by addition of the two atomic wave functions whereas in the other MO is obtained by substration of the atomic orbitals. The combination of the *1s* orbitals on the two hydrogen atoms are shown in fig. 5.9

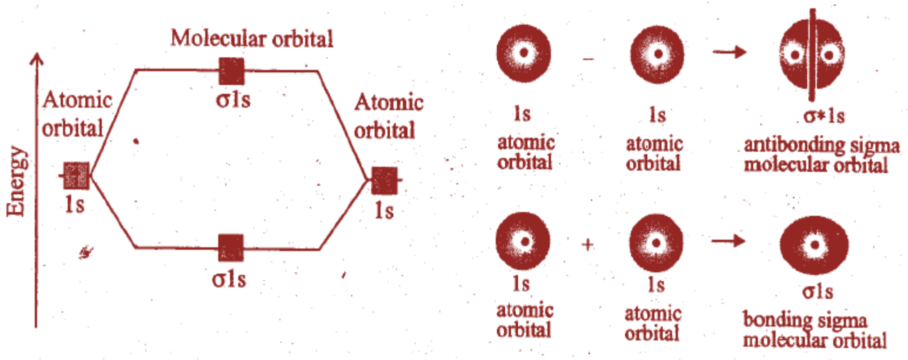
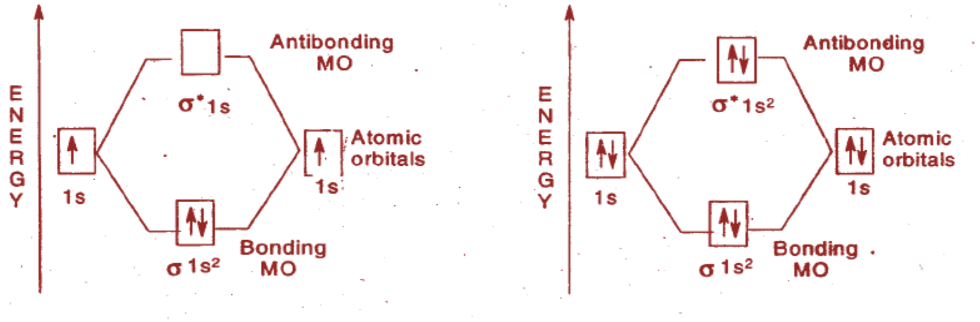


Fig. 5.9 : *Formation of bonding (σ) and anti bonding (σ*) molecular orbitals*

The molecular orbital obained by the addition of atomic orbitals is of lower energy than that of the atomic orbitals and is called a **bonding orbital**. On the other hand, the orbital obtained by substraction of atomic orbitals is of higher energy and is called an **anti-bonding orbital**. You can note here that the molecular orbitals obtained here are symmetric around the bond axis (the line joining the two nuclei). Such molecular orbitals are called **sigma** (σ) molecular orbitals. The bonding orbital obtained above is denoted as σ1s while the anti-bonding orbital is denoted as σ*1s. Here σ indicates the type of molecular orbital; 1s tell about the atomic orbital involved and * is indicative of the anti-bonding nature of the MO. There are a total of 2 electrons in a hydrogen molecule, according to Aufbau principle these are filled into σ1s orbital. Since the σ1s orbital is a bonding orbital, it's getting filled leads to stability or the bond formation.

Like electronic configuration of atoms we write MO electronic configuration for molecules. The MO configuration of hydrogen molecule is given as $(\sigma 1s)^2$. The molecular orbital energy level diagram are given in Fig. 5.10 (a and b).



(a) (b)

Fig. 5.10 : *Molecular orbital energy level diagram for a) H_2 and b) He_2 molecules*

Bond Order : we may define a new parameter called bond order as

Bond order = (b.o.) = 1/2 (n_b - n_a)

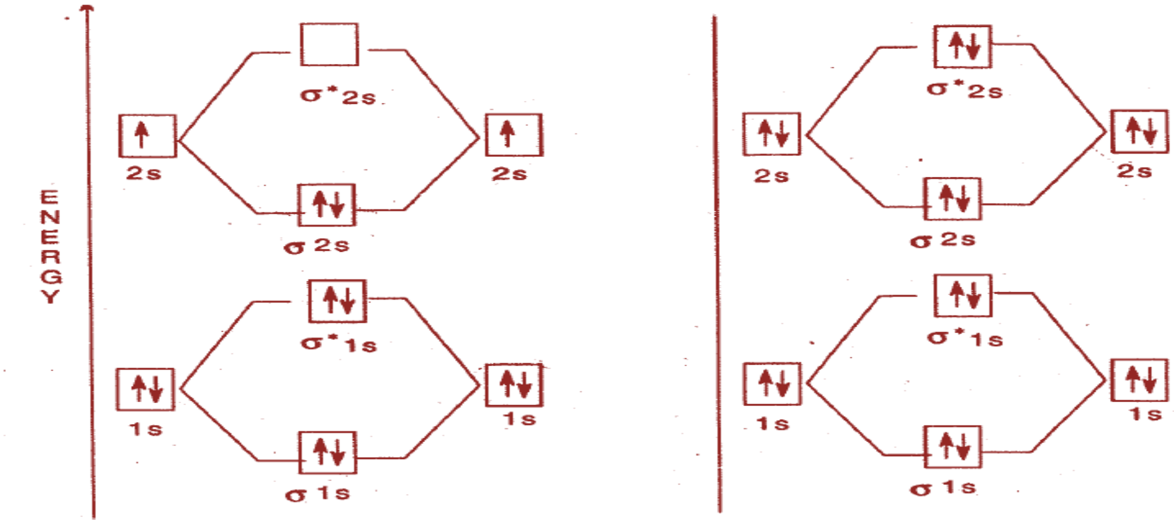
Where, n_b and n_a refer to the number of electrons present in bonding and antibonding molecular orbitals respectively. For hydrogen molecule the bond order will be $\frac{1}{2}$(2 - 0) = 1, i.e., there is a single bond between two hydrogen atoms.

Helium (He_2) molecule

In case of He_2, also there will be linear combination of 1s orbitals leading to the formation of σ 1s and σ* 1s orbitals. The four electrons would be distributed as per the MO electronic configuration : (σ 1s)2 (σ* 1s)2. The molecular orbital energy level diagram is given in fig. 3.10 (b). This is gives a bond order of $\frac{1}{2}$ (2 - 2) = 0, that is there is no bond between two helium atoms. In other words He2 molecule does not exist.

Li_2 and Be_2 molecules

The bonding in Li_2 and Be_2 can be explained by combining the *1s* and *2s* orbitals to give appropriate MO's. the molecular orbital diagrams for Li_2 and Be_2 are given in Fig. 5.11



(a) **(b)**

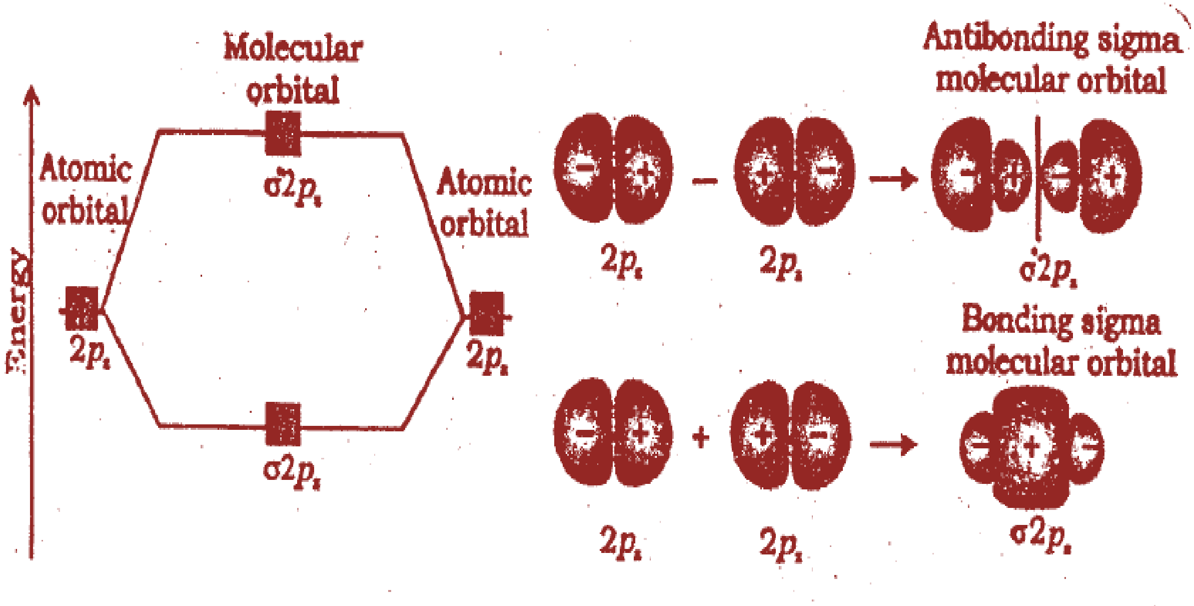
Fig. 5.11 : *Molecular orbital energy level diagram for a) Li_2 and b) Be_2 molecules*

5.5.2.1 Moelcular Orbital Bonding in Diatomic Molecules of Second Period

So far we have talked about bonding in the elements in which the MO's were obtained from the linear combination of *s* orbitals. In case of the atoms of second period (beyond Be) elements both *s* and *p* orbitals are involved in the formation of molecular orbitals. In such a case a number of different molecular orbitals are obtained depending on the type and symmetry of the atomic orbitals involved in the process. Let us try to understand the nature of MO's obtained in this case.

Here also the *1s* and *2s* orbitals of the two would combine to give corresponding bonding and anti-bonding molecular orbitals as shown in Fig. 5.11 (b). Let us learn about the formation of MO's from the combination of *p*-orbitals.

As mentioned above, in LCAO, the atomic orbitals of **comparable energies** and of **suitable symmetry** combine to give molecular orbitals. A suitable symmetry means that the combining orbitals should have same symmetry about the molecular axis. It is normally assumed that the bond formation takes place along the z-direction. You have learnt in the first unit that the three *p* orbitals are directed towards three mutually perpendicular direction namely the x, y and z directions. Therefore the P_z orbitals of the two atoms would combine along the bond axis to give two molecular orbitals as shown below fig. 5.12 Since these molecular orbitals are symmetric around the molecular axis these are called σ orbitals. The designation of the orbitals would be σ_{2pz} and σ^*_{2pz}.



(a) (b)

Fig. 5.12 : *Overlapping of two* $2P_z$ *orbitals to give molecular orbitals*

Combination of a P_z-orbital with either a P_x or P_y orbital would not lead to any bonding. On ther other hand a P_x orbital will combine with a P_x and the P_y with a P_y as shown in Fig. 5.13

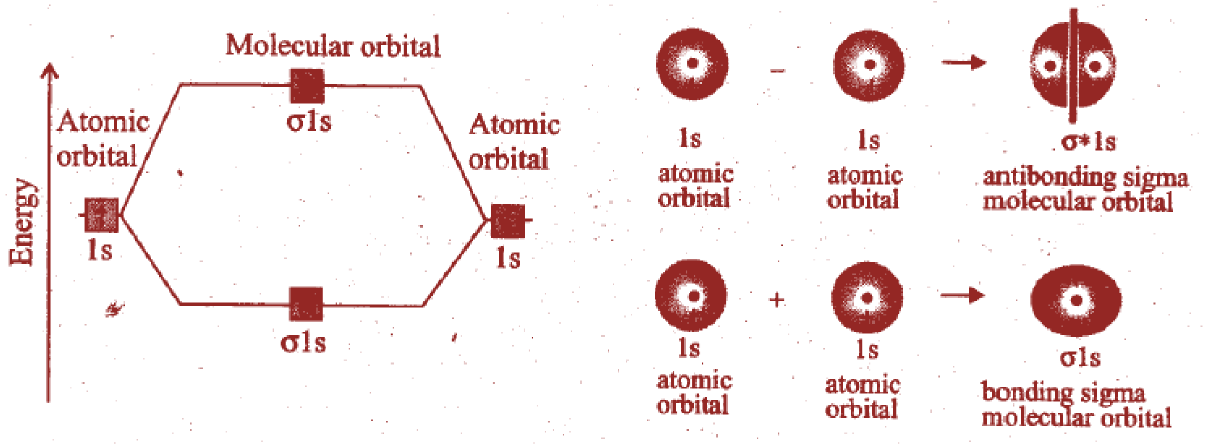


Fig. 5.13 : *Formation of molecular orbitals from two* $2P_x$ *atomic orbitals*

You may note here that these orbitals combine in a lateral fashion and the resulting molecular orbitals are not symmetric around the bond axis. These MO's are called π-molecular orbitals. These have large electron density above and below the internuclear axis. The anti-bonding π orbital, $\pi^*\ 2P_x$ (or $\pi^*\ 2P_y$) have a node (a region of zero electron density) between the nuclei.

The molecular orbitlas obtained as a result of combination of respective AO's of two atoms can be represented in the form of following energy level diagram, Fig 5.14 (a). The MO's obtained from the combination of 1s orbitals are not shown. (these beong to the inner core and are completely filled). The electrons in these molecular orbitals are filled in accordance with Aufbau principle and Hund's rule.

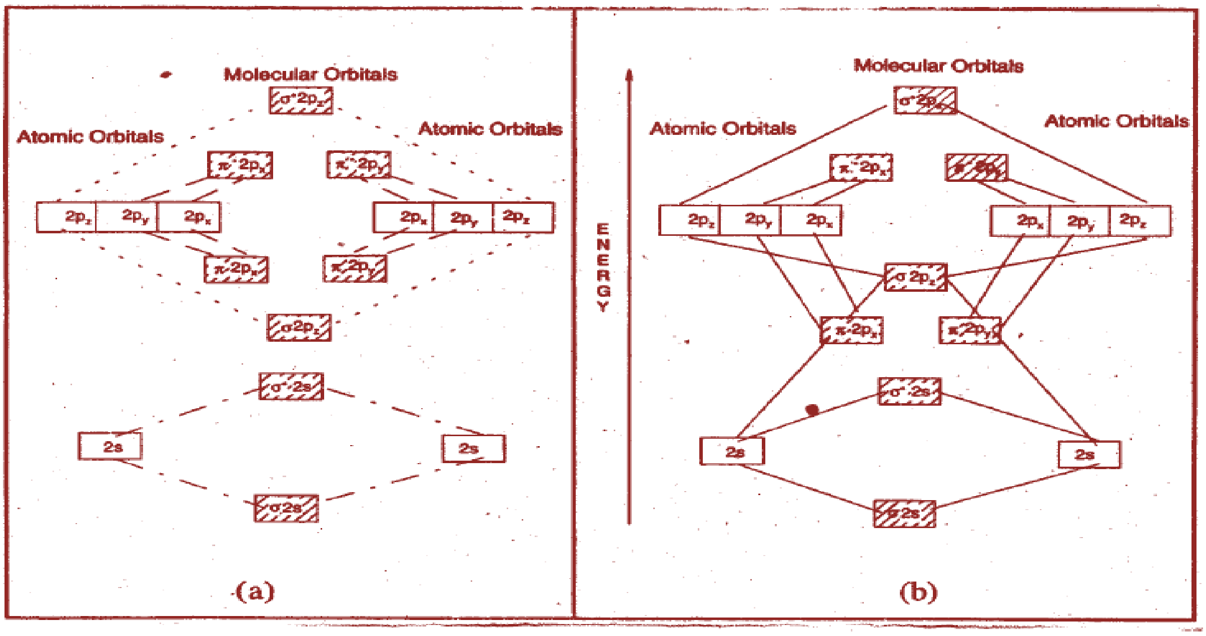


Fig. 5.14 : *Molecular orbital energy level diagams (a) for O_2 and F_2 and (b) for diatomic orbitals of lighter elements Li, Be, B, C and N*

However, this energy level diagram is valid for the diatomic molecules O_2 and F_2 only; For the diatomic molecules of the lighter elements like, B, C and N this energy level diagram is somewhat modified. It is so because in case of lighter elements the difference in the energy of *2s* and *2p* orbitals is very low and *s* and *p* orbitals on the two atoms get mixed up. In place of normal pure *2s-2s* or *2p-2p* combinations we may have *s-p* combinations; for example *2s* orbital of first atom can have a reasonable overlapping with $2P_z$, orbital of the second atom and vice versa. The modified level diagram is given in Fig 5.14 (b).

5.5.2.2 Electronic Configuration and Properties of the Molecule

The MO energy level diagram discussed above can be used to find out the MO electronic configuration of the molecule. This in turn provides the information about some properties of the molecule. Let us take the example of nitrogen molecule. An atom of nitrogen has five valence electrons; since there are two atoms, we have a total of ten valence electrons that need to be filled in the MO's Using Fig. 5.14, the MO electronic configuration can be written as $\sigma 2s^2$, $\sigma^* 2s^2$, $\pi 2p_x^2$, $\pi 2p_y^2$, $\sigma 2s_z^2$,

Bond order : $\frac{1}{2}[n_b\text{-}n_a] = \frac{1}{2}[8\text{-}2] = \frac{1}{2}[6] = 3$; this means that in nitrogen molecule, a triple bond exists between the two nitrogen atoms.

Megnetic nature: molecules show magnetic behaviour depending on their MO electronic configuration. If all MO's are **doubly occupied** the substance shows **diamagnetic** behaviour. In case one or more MO's are **singly occupied,** the substance shows **paramagnetic** behaviour. The MO electronic configuration of O_2 (with 12 valence electrons) is $\sigma 2s^2$, $\sigma^* 2s^2$, $\pi 2s_z^2$, $\pi 2p^2$, $\pi 2p_y^2$, $\pi 2p_y^2$, $\pi^* 2p_x^1$, $\pi^* 2p_y^1$; Since it contains unpaired electrons, oxygen shows paramagnetic behaviour. This has been found to be so experimentally also. In fact, the explanation of the paramagnetic behaviour of oxygen is an achievement of MOT.

The bond order and the magnetic behaviour of the molecular cations and anions can also be obtained in the same way. In such cases we add one electron for every negative charge and for every +*ve* charge we subtract an electron. For example O_2^{2-} (oxygen molecule dianion) would have a total of 14 valence electrons (12+2) while oxygen molecule cation O_2^+ would have 12-1 = 11 valence electrons.

Intext Questions 5.4

1. What is the basic difference between the valence bond and molecular orbital theories ?

....

2. Calculate the bond orders for Li_2 and Be_2 molecules using the molecular orbital diagrams given in Fig. 5.12

....

3. Predict the magnetic behaviour of O_2.

....

What You Have Learnt

- A chemical bond may be visualised as an effect that leads to the decrease in the energy of the combination of two atoms when they come closer.
- The atoms combine in such a way so as to attain stable electronic configuration of noble gases.
- According to Kossel, transfer of an electron from one atom to the other achieves the stable configuration. This leads to formation of ions, which are held together by electrostatic interactions called ionic bond.
- According to Lewis, the stable configuration is achieved by sharing of electron pairs between the bonding atoms. This leads to the formation of a covalent bond.
- Bonding in simple molecules can be conveniently represented in terms of Lewis electron-dot structures.
- In some covalently bound atoms the shared pair of electron is more towards the atom with greater electronegativity and leads to partial ionic character in the molecule.
- Valence shell electron pair repulsion (VSEPR) theory is very helpful in predicting the shapes of simple molecules. It is based on the interactions between the electron pairs around the central atom in the molecule.
- Valence bond theory (VBT) and Molecular orbital theory (MOT) are two modern theories of chemical bonding. These are based on the wave mechanical model of atom.
- According to the valence bond theory the process of chemical bond formation can be visualised as the overlapping of atomic orbitals of the two atoms as they approach each other. The overlap increases the electron charge density in the inter-nuclear region.
- In order to explain bonding in molecules containing more than two atoms, Pauling proposed the concept of hybridisation. In hybridisation, the atomic orbitals of the valence

shell of the central atom ‘hybridise’ or merge and given never orbitals with proper orientations, which explain the shape of the molecule.

- According to the Molecular orbital theory the atomic orbitals of comparable energies and of suitable symmetry combine to give rise to an equal number of molecular orbitals. These molecular orbitals extend over the entire region of the molecule i.e. these are delocalised over the whole molecule.
- When two atomic orbitals combine it gives a pair of molecular orbitals; one is called bonding molecular orbital of lower energy and the other of higher energy is called anti-bonding orbital.
- The electrons present in the molecule are filled in these orbitals in the order of increasing energy (Aufbau principle) to give the MO electronic configuration.
- The number of bonds between the two atoms is called bond order and is defined as Bond order = b.o. = $\frac{1}{2}(n_b = n_a)$.
- The MO electronic configuration can be used to predict the magnetic nature of the molecule. If all the MO’s are doubly occupied the substance shows diamagnetic behaviour and if one or more MO’s are singly occupied the substance shows paramagnetic behaviour.
- The favourable conditions for the formation of ionic bond and properties of ionic compounds
- Valence bond theory is discussed.
- The consequences of hydrogen bond.

Terminal Exercise

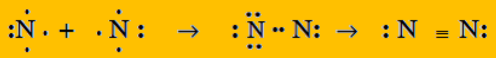
1. What do you understand by a chemical bond ?
2. Explain the process of bond formation as a decrease in energy.
3. What do you understand by the term, ‘bond length’ ?
4. Describe the two possible ways in which the noble gas electronic configuration is achieved in the process of bond formation.
5. What are Lewis electron-dot symbols ? Show the formation of $MgCl_2$ in terms of Lewis symbols.
6. Define a coordinate bond and give some examples.
7. What is VSEPR theory? predict the shape of SF_6 molecule using this theory.
8. Why do we need the concept of hybridisation? How does it help in explaining the shape of methane?
9. Give the salient features of molecular orbital theory.
10. Be_2 molecule does not exist. Explain on the basis of molecular orbital theory.
11. Write down the molecular orbital electronic configuration of the following species and compute their bond orders.

$$O_2 \; : \; O_2^{+} \; : \; O_2^{-} \; : \; O_2^{2-}$$

Answers to Intext

5.1

1. An electrovalent bond is formed when one or more electrons are transferred from one atom to another atom or atoms.

2. 

3. In a covalnet bond the shared pair of electrons is closer to the more electronegative atom. This leads to charge separation in the molecule and the bond becomes polar

4. A bond in which both the bonding electrons are contributed by one atom only

5. i) Low iozation energy ii) Low charge on the ion iii) Large atomic size

6. As ionic bond is non directional hence ionic compounds does not show isomerison.

5.2

1. The two postulates of VSEPR theory are

i. The electron pairs (both bonding and non-bonding) around the central atom in a molecule arrange themselves in space in such a way that they minimize their mutual repulsion.

ii. The repulsion of a lone pair of electrons for another lone pair is greater than that between a bond pair and a lone pair which in turn is stronger than that between two bond pairs. The order of repulsive force between different possibilities is as under.

lone pair - lone pair > lone pair - bond pair > bond pair - bond pair

2. In methane the central carbon atom would have four pairs of electrons in its valence shell. According to VSEPR theory these would be placed tetrahedrally around the carbon atom. Hence the methane molecule would have a tetrahedral shape.

3. Boiling point increase due to H-bonding.

5.3

1. Hybridisation is a concept which is quite useful in explaining the shapes of molecules. According to this two or more than two non equivalent orbitals with comparable energies and different shapes mix and give rise to an equal number of equivalent hybrid orbitals. The hybrid ortbitals have identical energies and shapes.

2. In ammonia the 2s and three 2p orbitals hybridize to give four sp^3 hybridized orbitals. Three of these overlap with the 1s orbitals of hydrogen and one remains nonbonding containing a lone pair. The sp3 hybridized orbitals are directed towards the corners of a regular tetrahedron. But due to the pair the ammonia molecule has a distorted tetrahedral shape which is somewhat like a trigonal pyramid.

1. Valance bond theory visualises the bond formation to be localized whereas according to MOT it is delocalised.

2. Bond order = b.o. = $\frac{1}{2}(n_b - n_a)$

for Li_2 ; Bond order = $\frac{1}{2}[4-2] = \frac{1}{2}[2] = 1$

for Be_2 : Bond order = $\frac{1}{2}[4-4] = \frac{1}{2}[0] = 0$

3. MO configuration of O_2 is $\sigma 2s^2$, $\sigma^* 2s^2$, $\sigma 2pz^2$, $\pi 2px^2 = \pi 2py^2$. $\pi^* 2p^1_x = \pi^* 2p^1_y$

Due to 2 unpaired electrons O2 molecule is paramagnetic.

Module - III

State of Matter

06. The Gaseous state

07. The Liquid State

08. The Solid State

09. Solutions

10. Colloids

Chapter 06

THE GASEOUS STATE

We know that matter exist in three different states namely solid, liquid and gas. The most familiar example to show these different states of matter is water. Water exists as a solid (ice), a liquid (water) and a gas (steam) under different conditions of temperature and pressure. The difference between these three states of matter is due to the difference in their intermolecular distance and intermolecular forces. In addition to these, temperature and pressure also play an important role in deciding the states of matter. Apart from these three states a fourth phase of plasma also exist

In this lesson we shall first discuss the differences in properties of the solid, liquid and gaseous state and the factors due to which these differences arise. We shall also study the effect of pressure and temperature on the volume of the given amount of gas. These are governed by the gas laws namely Boyle's law, Charles' law and Avogadro's law.

Objectives

After reading this lesson you will be able to:

- Differentiate between the three states of matter - solid, liquid and gas;
- List the characteristic properties of gases;
- State the gas laws (Boyle's law, Charles's law and Avogadro's law) and express them mathematically.
- Draw the p – V, p – 1/V, p – pV and V – T graphs.
- Interpret the effect of temperature and pressure on the volume of a gas from the graph;
- Derive the ideal gas equation from the gas laws;
- State the Dalton's law of partial pressure and explain its significance;
- State Graham's law of diffusion;
- State the postulates of Kinetic Molecular Theory of gases;
- Explain the Maxwell's distribution of velocities.
- Differentiate between u_{rms}, u_{mp} and u_{av}
- Explain the deviation of real gases from ideal behavior in term of compressibility factor
- State the Van der Waals equation and explain the significance of van der Waals constants and explain the liquifaction of gases with the help of Andrews curves

6.1 The Three States of Matter

At any given conditions of temperature and pressure matter exists in one of the three states namely solid, liquid and gas. The characteristic properties of solid, liquid and gaseous state are listed in Table 6.1.

Table 6.1: Properties of different states of matter

Property	Solid	Liquid	Gas
Shape	Definite	Indefinite; Takes up the shape of the vessel.	Indefinite
Volume	Definite	Definite	Indefinite (fills the container completely)
Density	High	Less than solids but much higher than gases.	Low
Compressibility	Incompressible	Largely incompressible	Highly compressible

In solid state, the particles are held close together in a regular pattern by strong intermolecular forces. In liquid state, intermolecular forces are weak as compared to solid state hence the particles are less tightly held and allow them to move away from each other. In the gaseous state, the molecules are farthest apart as compared to solid and liquid states and the intermolecular forces are negligible so the particles move randomly. A simplified picture of particles in solid, liquid and gaseous state is represented in Fig. 6.1.

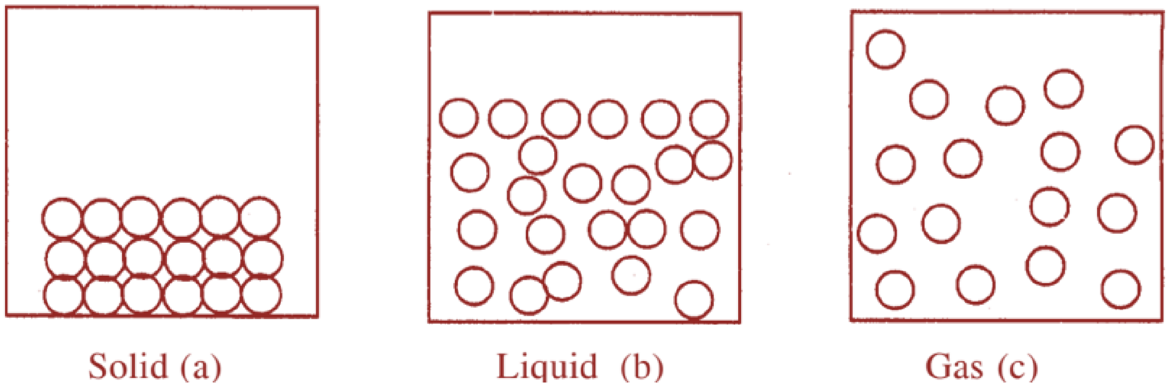


Fig. 6.1: A simplified picture of particles in solid, liquid and gaseous state

6.2 General behaviour of Gases: The Gas Laws

The volume of a given mass of gas depends upon the temperature and pressure under which the gas exists. It is, therefore, possible to describe the behaviour of gases in terms of the four variables: temperature, T; pressure p; volume V and amount (number of moles, n). For a given amount of gas the volume of gas changes with change in variables such as temperature and pressure. The relationship between any two of the variables is studied, keeping the other variable constant by various laws which are described below.

6.2.1 Effect of Pressure on the Volume of the Gas (Boyle's law)

The effects of pressure on the volume of gas for a given amount of gas at constant temperature was studied by Robert Boyle in 1662 for different gases. He observed that if the volume of gas is doubled the pressure is halved and vice versa. Boyle's law states that at constant temperature, the volume of a given amount of a gas is inversely proportional to its pressure. Mathematically Boyle's law is expressed as shown below

$$V \propto {}^{1}/_{p} \quad \text{or} \quad p_1 V_1 = p_2 V_2 \qquad \text{(at constant T and n)}$$

when the pressure of the gas, p is plotted against volume of the gas V, the exponential curve is obtained (Fig.6.2). However, when the pressure, *p* of the gas is plotted against 1/V a straight line is obtained (Fig. 6.2). If the product of pressure and volume (*pV*) is plotted against pressure (*p*) a straight line parallel to x-axis (pressure is axis) is obtained (Fig. 6.4)

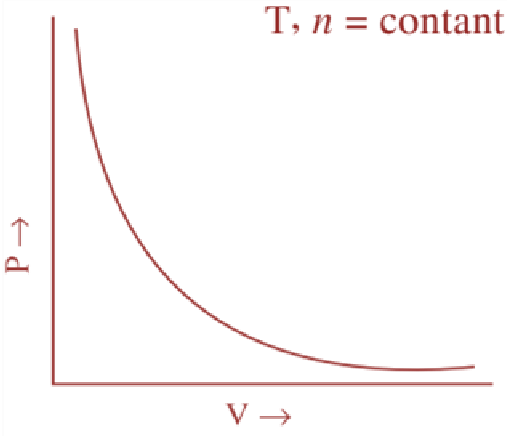


Fig. 6.2 : *A graph of p versues V*

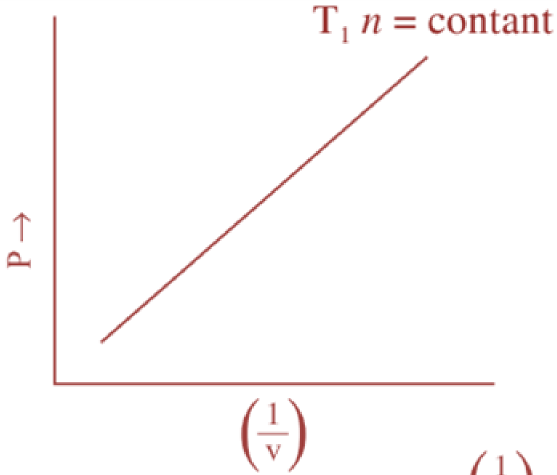


Fig. 6.3 : *A graph of p versues* $\left(\frac{1}{V}\right)$

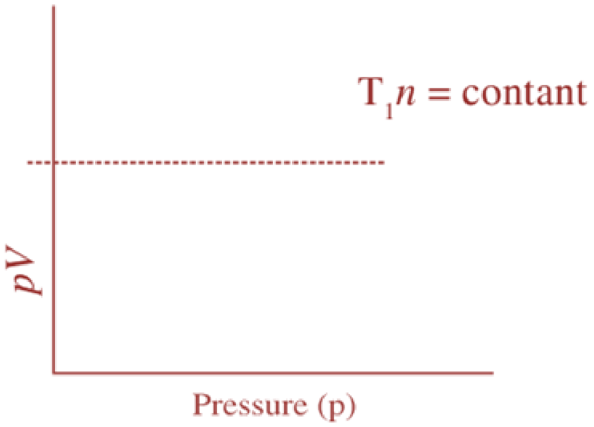


Fig. 6.4 : *A graph of p V versues p*

Example 6.1: The volume occupied by a given mass of a gas at 298K is 24 mL at 1 atmospheric pressure. Calculate the volume of the gas if the pressure is increased to 1.25 atmosphere keeping temperature constant.

Solution: Given that

V = 25 mL p1 = 1 atm
V2 =? p2 = 1.25 atm

According to Boyle's Law, $p_1 V_1 = p_2 V_2$

Substituting the value of p_1, V_1 and p_2 in the above expression we get

$$V_2 = \frac{p_1 V1}{p_2} = \frac{(1\ \text{atm})\ (25\text{mL})}{(1.25\ \text{atm})} = 20\ \text{mL}$$

The volume occupied by the gas is 20 mL at 298 K and 1.25 atm pressure.

Example 6.2: The volume of a certain amount of a gas is decreased to one fifth of its initial volume at a constant temperature. What is the final pressure?

Solution: Let

Initial volume $= V_1$ Initial pressure $= p_1$
Final volume $V_2 = V_1/5$ Final pressure $= p_2$

By Boyle's law, we know that at constant temperature

$$p_1 V_1 = p_2 V_2$$

$$p_2 = \frac{p_1 V_1}{p_2} = \frac{p_1 V_1}{\frac{V_1}{5}} = 5p_1$$

Thus, when volume is decreased to 1/5th of the initial volume, the pressure is increased by 5 times of the initial pressure

6.2.2 Effect of Temperature on the Volume of Gas (Charles' Law)

The effects of temperature on the volume of the gas were studied by Jacques Charles in 1787 and Gay Lussac in 1802 at constant pressure for different gases. Their conclusion can be given as Charles' law which states that at a constant pressure, the volume of a given amount of gas is directly proportional to the absolute temperature.

So, according to Charles' Law, the volume of a gas increases as its absolute temperature is being raised, if its absolute temperature is lowered, its volume will consequently decrease. Mathematically, Charle's Law is expressed as shown below:

$V \propto T$ (at constant p and n)
or $V = k.T$ (k is a constant)
Therefore $V_1/T_1=V_2/T_2$

Graphical representation of Charle's Law is a straight line pointing away from the origin of the graph as shown in Fig. 6.5

Here graph of the volume of a gas (V) plotted against its temperature at constant pressure and amount (in moles). Notice that the graph is a straight line with a positive gradient (slope).

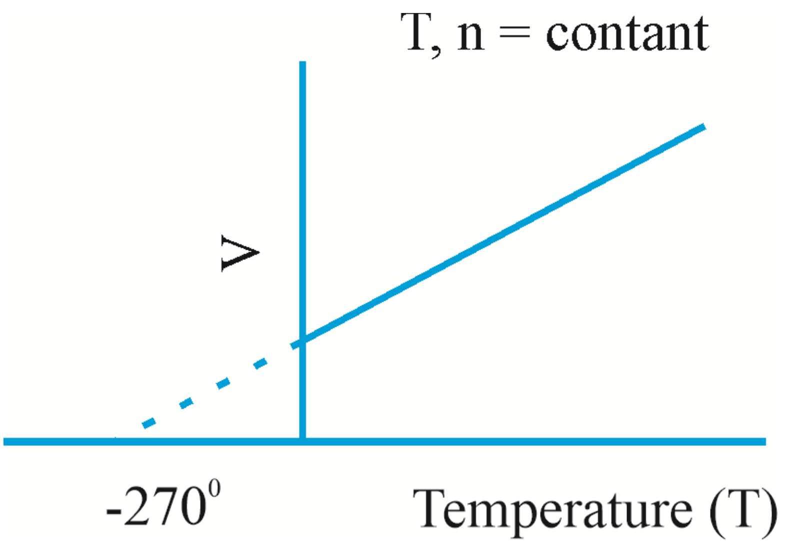


Fig 6.5: A graph of V versus T

Mathematically volume of a gas at temperature t is given as

$$v_t = v_o + \frac{v_0}{273} x t = v_0\left(1+\frac{t}{273}\right) = v_0\left(\frac{273+t}{273}\right)$$

Thus at $t = -273^0C$

$$v_t = v_o\left(\frac{273-273}{273}\right) = 0$$

This means that at -273°C, the volume of the gas is reduced to zero i.e., the gas ceases to exist. Thus this temperature (-273°C) at which the gas hypothetically ceases to exist is called Absolute zero. It is represented by zero K.

This is the theoretically lowest possible temperature. In actual practice, we cannot reduce the temperature of the gas to zero kelvin.

Kelvin Scale of Temperature

The scale of temperature which has -273°C as zero is called Kelvin scale. Degree Celsius is converted to Kelvin by adding 273. Thus

$$t/°C + 273 = T/K$$

where T= temperature in Kelvin t= temperature in Celsius

For example 15°C can be converted in K by adding 273 to 15.

6.2.3 Effect of Temperature on Pressure (Pressure-Temperature Law)

This law states that.

Pressure of given amount of gas at constant volume is directly proportional to its absolute temperature.

$$p \propto T$$

$$p = kT$$

Example 6.3: A given amount of a gas is maintained at constant pressure and occupies a volume of 2 liters at 1000°C. What would be volume if gas is cooled to 0°C keeping pressure constant.

Solution: Given that,

Initial volume V_1 = 2L $T_1 = 1000 + 273 = 1273$ K

Final volume V_2 = ? $T_2 = 0 + 273 = 273$ K

Now using Charle's Law $V_1 / T_1 = V_2 / T_2$ or $V_2 = (V_1 / T_1) \times T_2$

On substituting the values we get

$$V_2 = (V_1 / T_1) \times T_2 = (2L / 1273\ K) \times 273 = 0.4291\ L$$

6.2.4 Avogadro's Law

The Italian physicist Amadeo Avogadro was the first to propose, in 1811, a relationship between the volume of a gas and the number of molecules present in it. This, relationship is known as Avogadro's Law. It states that:

Equal volumes of all gases at the same temperature and pressure contain equal number of molecules.

Mathematically, Avogadro's law is expressed as:

$$V \propto N \qquad \text{(at constant temperature and pressure)}$$

Where V and N are volume and number of molecules respectively

At a given temperature and pressure, the number of molecules present in the gas is directly proportional to the number of moles.

therefore, $N \propto n$

Where n is the number of moles $\therefore V \propto n$

or V/n = constant

Also $V_1/n_1 = V_2/n_2$

He also found that the number of molecules present in 1 mole of any substance (22.4 litre of any gas at 273K temperature and 1 atmosphere pressure) is 6.022 x 10^{23} molecules. This number is known as **Avogadro's number**.

It is the number of molecules (6.022 x 10^{23}) of any gas present in a volume of 22.4 L (at 273 K and 1 atm) and it is the same for the lightest gas (hydrogen) as for a heavy gas such as carbon dioxide or bromine.

Example 6.4: 0.965 mol of a gas occupies a volume of 5.0L at 298 K/temperature and 1 atm pressure. What would be the volume of 1.80 mol of the gas at the same temperature and pressure?

Solution:

$$V_1 \; n_2 = V_2 \; n_1$$

$$\frac{V_2 \, n_2}{n_1} = \frac{(5.0L)(1.8mol)}{(0.965mol)}$$

$$V_2 = 9.33 \text{ L}$$

Example 6.5: Compare the volumes of 16g of oxygen and 14g nitrogen at the same temperature and pressure.

Solution:

Number of moles of O_2 = 16 g/32 g mol^{-1} = 0.5 mol

Number of moles of N_2 = 14 g/28 g mol^{-1} = 0.5 mol

Since the two gases are at the same temperature and pressure, and contain equal number of mole, hence according to the Avogadro's Law they should also occupy the same volume.

Intext Questions 6.1

1. The density of a gas is usually less than that of the liquid. Explain.

....

2. Calculate the pressure (atm) required to compress 500 mL of gas at 0.20 atm into a volume of 10mL.

....

3. Equal volumes of oxygen gas and an unknown gas weigh 2.00 and 1.75 g respectively under the same experimental conditions. What is the molar mass of the unknown gas?

....

6.3 The Ideal Gas Equation

Boyle's Law, Charle's Law and Avogadro's Law can be combined to give a single equation which represents the relation between the pressures, volume and kelvin temperature of a given amount of gas under different conditions. Thus

$V \propto 1/p$ at constant temperature (Boyle's Law)

$V \propto T$ at constant pressure (Charle's Law)

$V \propto n$ at constant temperature and pressure (Avogadro's Law)

All the three expressions can be combined into a single expression.

$V \propto nT/P$ or $pV \propto nT$ or $pV = \textit{constant} \times nT$

The constant in this equation is called "universal gas constant' or 'molar gas constant', represented by R. Thus, we can write for 1 mole of a gas.

$$pV = RT$$

Correspondingly, for n moles of a gas we have

$$pV = n\,RT$$

This is known as the ideal gas equation because it holds only when gases are behaving as 'ideal' gases.

Since for a given mass of gas we can write

pV/T = a constant, we have

$$p_1 V_1/T_1 = p_2 V_2/T_2$$

Where p_1 V_1T_1 refer to one set of conditions and p_2, V_2T_2 refer to a different set of conditions.

The numerical value of R can be found by substituting experimental quantities in the equation.

At STP, T = 273.15 K, p = 1 atm and for 1 mol of gas (n = 1), V = 22.414 L. Consequently

$$R = pV/nT = (1\text{ atm})(22.414\text{L}) / (1\text{ mol})(273.15\text{K})$$
$$= 0.082057\text{ L atm mol}^{-1}\text{ K}^{-1}$$

The value of R depends on the units adopted for the quantities in the equation pV = nRT. The various values are:

$R = 0.082057$ L atm K^{-1} mol^{-1} (for calculation purpose the value is taken as 0.0821 L atm K^{-1} mol^{-1})

$R = 8.314 \times 107$ erg K^{-1} mol^{-1}

$R = 8.314$ J K^{-1} mol^{-1}

$R = 1.987$ cal K^{-1} mol^{-1}

Example 6.6: At 273 K, 10 mol of gas is confined in container of volume 224 L. Calculate the pressure of the gas. R = 0.0821 L atm mol^{-1} K^{-1}.

Solution: The ideal gas equation pV = nRT will be used here

n = 10 mol, R = 0.0821 atm L K^{-1} mol^{-1}

V = 224 L T = 273 K p =?

On substituting these values in the above equation, we get

$$p = nRT/V = (10\text{ mol} \times 0.0821\text{ atm L mol}^{-1}\text{ K}^{-1} \times 273\text{ K}) / 224\text{L}$$
$$= 0.99998\text{ atm} = 1\text{ atm.}$$

6.4 Dalton's Law of Partial Pressure

The behaviour observed when two or more non-reacting gases are placed in the same container is given by Dalton's Law of partial pressures. Dalton's Law states that.

The total pressure exerted by a mixture of non-reacting gases is equal to the sum of the partial pressures of the various gases present in the mixture.

The partial pressure is defined as the pressure the gas would exert if it was alone in the container. Suppose a sample of hydrogen is pumped into a one litre box and its pressure is found to be 0.065 atm. suppose further a sample or argon is pumped into a second one litre box and its pressure is found to be 0.027 atm. If both samples are now transferred to a third one litre box, the pressure is observed to be 0.092 atm. For the general case, Dalton's Law can be written as

$$P_{total} = P_A + P_B + P_C + \ldots\ldots$$

Where $P_A P_B P_C$........ are the partial pressure of gases A, B, C respectively. This gas laws provide a simple way of calculating the partial pressure of each component, given the composition of the mixture and the total pressure. First, we introduce the mole fractions X_A and X_B. These are defined as

$$X_A = \frac{n_A}{n} \text{ and } X_B = \frac{n_B}{n}$$

Where n_A and n_B are the number of moles of gas A and B respectively and $n = n_A + n_B$. Since $P_A = n_A\, RT/V$, $P_B = n_B\, RT/V$, and $p = n\, RT/V$,

it follows that $P_A = X_A\, p$ and $p_B = X_B p$

This is an exceptionally useful (and simple) way of calculating at partial pressures when the composition and total (measured) pressure of a mixture of gas is known.

Example 6.7: Atmosphere is often considered mainly as a mixture of nitrogen and oxygen: 76.8% by mass of nitrogen and 23.2% by mass of oxygen. Calculate the partial pressure of each gas when the total pressure is 1 atm.

Solution: The number of moles of each component is

$$P_{N_2} = 76.8 \text{ g} / 28 \text{ g mol}^{-1} = 2.74 \text{ mol}$$

$$P_{O_2} = 23.2 \text{ g} / 32 \text{ g mol}^{-1} = 0.725 \text{ mol}$$

The mole fractions of the components are therefore

$$X_{N_2} = \frac{2.74}{2.74 + 0.725} = 0.791\ ; \qquad X_{O_2} = \frac{0.725}{2.74 + 0.725} = 0.209$$

The partial pressures are therefore given by

$$P_{N_2} = 0.791 \text{ x } 1 \text{ atm} = 0.791 \text{ atm}$$

$$P_{O_2} = 0.209 \text{ x } 1 \text{ atm} = 0.209 \text{ atm}$$

6.5 Graham's Law of Diffusion

If we open a bottle of perfume in one corner of a room or burn an incense stick, we can feel the smell of the perfume or the incense stick all over the room also. The smell of perfume or incense stick spreads from one point of the room to the other by mixing with air. This free intermingling of gases when placed in contact with each other is known as **diffusion.**

Diffusion occurs in liquids as well as in gases. **Effusion** is the escape of a gas through a small hole, as in case of a puncture in a tyre.

The experimental observation of the rate of effusion of gases through a small hole led Graham (1829) to formulate the following law;

At constant temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its density. Graham's law is applicable to both diffusion and effusion.

If the time for a given volume of gas A to escape is t_A, while the time of the same volume of gas B to escape is t_B, it follows that

$$t_A/t_B = (\text{rate})_B / (\text{rate})_A = \sqrt{\rho_A / \rho_B}$$

Where ρ_A and ρ_B are the densities of gases A and B respectively. The ratio of the densities of the molecules is the same as the ratio of the molecular masses of the gases at the same temperature and pressure.

$$\text{hence, } t_A/t_B = (\text{rate})_B / (\text{rate})_A = \rho_A / \rho_B = \sqrt{M_A / M_B}$$

Where M_A and M_B are the molecular masses of gases A and B respectively

Intext Questions 6.2

1. What is the difference between diffusion and effusion?

....

2. Explain why Dalton's law is not applicable to a system of ammonia and hydrogen chloride gas.

....

3. The rates of diffusion of CO_2 and O_3 were found to be 0.29 and 0.271. What is the molecular mass of O_3 if the molecular mass of CO_2 is 44

....

4. Calculate the pressure exerted by 5.0 mol of carbon dioxide in a 1 litre flask at 470^0C using ideal gas equation.

....

6.6 Kinetic Molecular Theory of Gases (Accounting for the Gas Laws)

To explain the behaviour of the gases theoretically, Claussius, Maxwell and Boltzmann made the following assumptions:

1) Gases consist of large number of tiny particles called molecules.
2) The gas molecules are so small and so far apart that the total volume of the molecules is a negligible fraction of the total volume occupied by the gas.
3) The molecules are in state of constant, rapid and random motion colliding with one another and with the walls of the container.
4) There are no attractive or repulsive force between the molecules of the gas.

5) The collisions of the molecules among themselves and with the walls of the containing vessel are perfectly elastic, so that there is no loss of energy during collisions.
6) The pressure exerted by a gas is due to the bombardment of the molecules on the walls of the containing vessel.
7) The kinetic energy of a gas is directly proportional to the absolute temperature of the gas.

On the basis of this model, it is possible to derive the following expression for a gas:

$$pV = \frac{1}{3} mN\overline{C^2}$$

Where p is pressure, V denotes volume and m is the mass of a gas molecule. N is the total number of molecules and C is the root mean square velocity of the gas molecules.

6.6.1 Root Mean Square Velocity

Root mean square velocity is the square root of the average of the squares of all the molecular velocities. Mathematically

$$\text{RMS Velocity} = \sqrt{(C_1^2 + C_2^2 + ... + C_N^2)} / N$$

where C_1, C_2…..C_N the molecular velocities.

Kinetic gas equation - Deduction of gas law's from the kinetic gas equation

All the gas laws can be deduced from the kinetic gas equation.

$$\mathbf{PV= 1/3\ mnc^2}$$

a) Boyle's law: According to kinetic gas equation $PV = 1/3\ mnc^2$ Here, P is pressure of the gas molecules we can write

$\mathbf{PV= 2/3\ (1/2\ mnc^2)}$ the kinetic energy of 'm' mole's of the gas is $1/2\ mnc^2$.

According to kinetic molecular theory, kinetic energy is directly proportional to the temperature in Kelvin, or $1/2\ mnc^2 = KT$.

Where 'K' is constant on substituting this result in the above equation expression we have

$$\mathbf{PV = 2/3\ KT} \quad .... \quad (1)$$

At constant temperature (T) = **PV = constant**.

This is Boyle's law equation.

b) Charles law: From the equation (1) **PV = 2/3 KT**

Or $$V = \frac{2KT}{3\ P} \quad .... \quad (2)$$

At constant pressure (P), we have V = constant x T (or) v T (p and n are constants)

This is Charles law.

c) Avogadro's law: consider equal volumes of the two different gases at same temperature and pressure. As per the kinetic gas equation

$PV = 1/3\ m_1N_1c_1^2$ Kinetic gas equation for the first gas

$PV = 1/3\ m_2N_2c_2^2$ Kinetic gas equation for the second gas

Since $1/3\ m_1N_1c^2 = 1/3\ m_2N_2c^2$ ………… (3)

(Since on left side both equations have same Pv)

Since temperature (T) is the same for the two gases their average Kinetic energy per molecule will also be the same

$$\text{i.e.}\quad \frac{1}{2}\, m_1\, c_1^{\,2} = \frac{1}{2}\, m_2\, c_2^{\,2} \text{ .... } (4)$$

Dividing equation (3) by equation (4)

$$\therefore \frac{\frac{1}{3}m_1n_1c_1^{\,2}}{\frac{1}{2}m_1c_1^{\,2}} = \frac{\frac{1}{3}m_2n_2c_2^{\,2}}{\frac{1}{2}m_2c_2^{\,2}} (\text{or})n_1 = n_2$$

It means that equal volumes of any two gases at the same temperatures and pressures will have equal number of molecules. This is Avogadro's law.

d) Dalton's law of partial pressures: Consider a gas in a vessel of volume V. If 'n_1' is the number of molecules 'm_1' is the mass of a molecule and 'c_1'is the RMS velocity. According to Kinetic gas equation, pressure of the gas.

$$P_1 = \frac{\frac{1}{3}m_1n_1c_1^{\,2}}{V}$$

If the gas is replaced by another gas in the same vessel we will have

$$P_2 = \frac{\frac{1}{3}m_2n_2c_2^{\,2}}{V}$$

Where, P_2 is the pressure of the 2nd gas;

m_2, the mass of its molecules;

N_2 the number of its molecule;

C_2 the R.M.S. velocity of its molecule;

Suppose that the two gases are taken in the same vessel. Let the total pressures of the mixture be 'P'

$$PV = 1/3\ m_1\ n_1\ c_1^{\,2} + 1/3\ m_2\ n_2\ c_2^{\,2}$$

$$P = \frac{\frac{1}{3}m_1n_1c_1^{\,2}}{V} + \frac{\frac{1}{3}m_2n_2c_2^{\,2}}{V} \quad \text{or} \qquad P + P_1 + P_2$$

This is Dalton's law of particle pressures

6.7 Distribution of Molecular Speeds

According to Maxwell in a gas all the molecules are in a state of constant rapid random motion and they collide with one another and with the walls of the vessel. During collision the redistribution of the energy takes place. Their speed and kinetic energy changes as a result. Therefore, at any instant different molecules have different speed and hence different kinetic energy. At the given temperature even though the speed of the individual molecule continuously changes, the fraction of the molecules having the same speed remains constant and this is known as Maxwell-Boltzmann Distribution Law.

At the given temperature this fraction is denoted by **dN/N** where dN is number of molecules having the same velocity and N is the total number of the molecules present in the gas. At the given temperature this fraction of the molecule is plotted against the molecular speed as shown in figure 6.6.

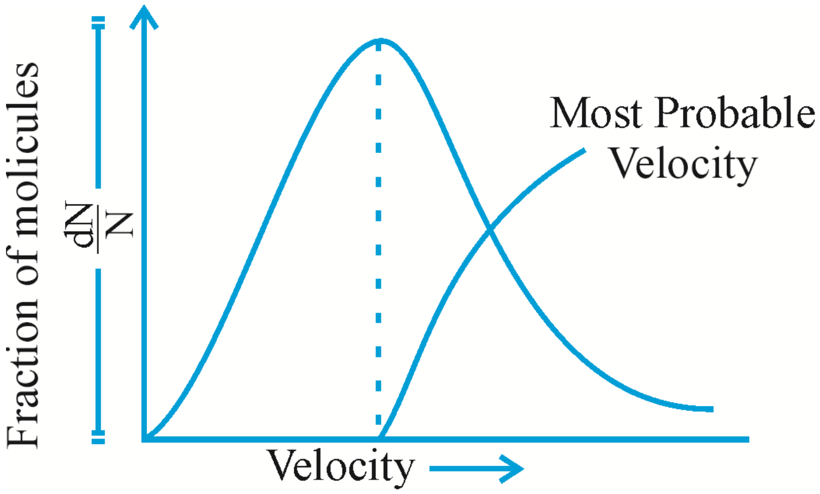


Fig. 6.6: Maxwells' distribution of velocities at constant temperature

In above Fig. 6.6 the maximum in the distribution curve corresponds to the speed possessed by the highest fraction of the molecule, this is known as most probable speed. It may be noted that if the temperature is increased the fraction of the molecule with higher speeds increase thus the most probable speed increases with increase of temperature. The temperature dependence of the distribution of the speed is as shown in Fig. 6.7.

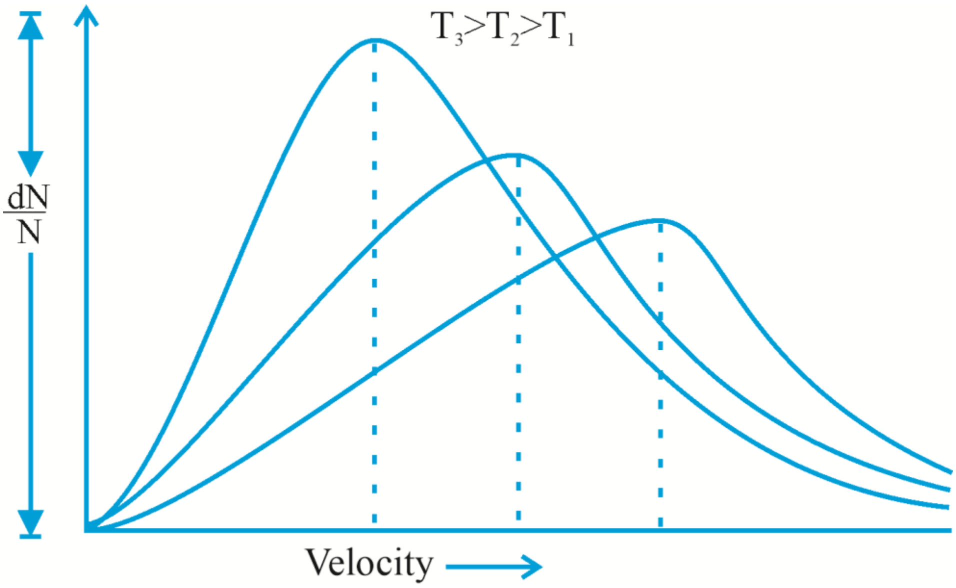


Fig. 6.7: Effect of temperature on distribution of velocities.

At the given temperature the most probable speed is given by the following expression.

$$U_{mp} = \sqrt{\frac{2RT}{M}}$$

The three speeds, root mean square speed, average speed and most probable speed are related by the following expressions

$$u_{rms} : u_{av} : u_{mp} :: \sqrt{3} : \sqrt{8/\pi} : \sqrt{2}$$

and also 1.224 : 1.128 : 1, so

$$u_{rms} > u_{av} > u_{mp}$$

The most probable velocity u_{mp} increases with the use in temperature of gas.

6.8 Deviation from Ideal Gas Behaviour

The gas laws mentioned above are strictly valid for an ideal gas under all conditions of temperature and pressure. Real gases show deviation from these laws at low temperature and high pressure. These deviations can be shown clearly by plotting **pV/nRT** as a function of pressure at constant temperature,

$$\frac{p\bar{V}}{nRT} = \frac{V_{observed}}{V_{ideal}} = Z \text{ (compressibility factor)}$$

Gases deviate from ideal behaviour due to the following faulty assumption of kinetic theory:

1. Volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.
2. There is no force of attraction between the molecules of a gas.

Contrary to assumption (1), the volume occupied by the molecules of a gas becomes significant at high pressures. If nb is the volume occupied by the molecules, the actual volume of the gas is (V-*nb*). Assumption (2) too doesn't hold well as at high pressures molecular interactions start operating. Molecules are dragged back by other molecules which affects the pressure exerted by them on the walls of the container.

$$P_{ideal} = P_{real} + \frac{an^2}{V^2}$$

(P_{real} is observed pressure and $an^2/V^2$is correction term)

In view of the corrections for pressure and volume, ideal gas equation can be rewritten as

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

This is known as van der Waals equation

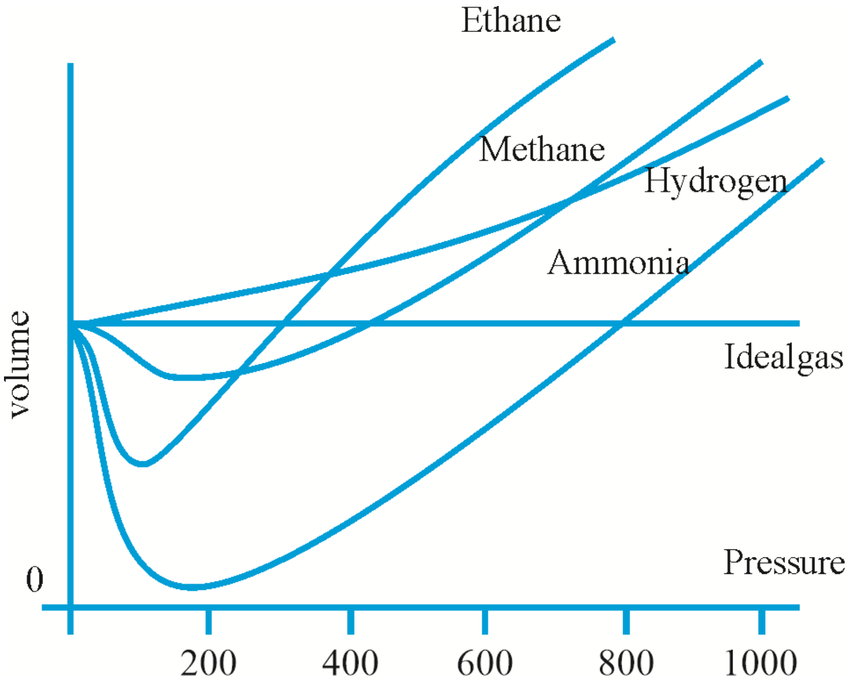


Fig. 6.8: The plot volume versus P for real gases

Behaviour of real gases, deviation from ideal behaviour, Compressibility factor Vs pressures diagrams of real gases.

6.9 Liquifaction of Gas

Any gas can be liquified at atmospheric pressure if it is cooled sufficiently. Many gases (but not all) can be liquefied at ordinary temperature by compressing them.

The conditions of temperature and pressure under which gases liquify were first investigated by Andrews in 1869.

Andrews subjected CO_2 to various pressures at different temperatures and plotted the effect of pressure on volume (Fig. 6.9). The curve obtained at a given temperature is called isotherm. As can be seen in the figure, at 321K the volume of the gas decreased with the increased pressure approximately in accordance with the Boyle's Law. At 294K, however, the volume first decreases in accordance with Boyle's Law until the pressure was increased. Boyle's Law until the pressure was increased to about 60 atm. At this pressure there was a sudden break in the curve and liquid carbon dioxide appeared. The pressure has been converted into liquid. Subsequent increase of pressure caused practically no change in volume. In accordance with the general rule, that extremely high pressures are required to compress the liquids appreciably.

Similar changes took place when the isotherms were constructed for temperatures below 294K, except that the pressure required to liquefy the gas became smaller as the temperature decreased. Andrews found that liquefaction could be brought about at all temperatures below 304.1K. But above this temperature no liquifaction occurred no matter how much pressure was increased. This temperature was therefore called the critical temperature for CO_2. The pressure required to liquify the gas at the critical temperature was called critical pressure, and the volume of 1 mole of the substance at the critical temperature and pressure, the critical volume.

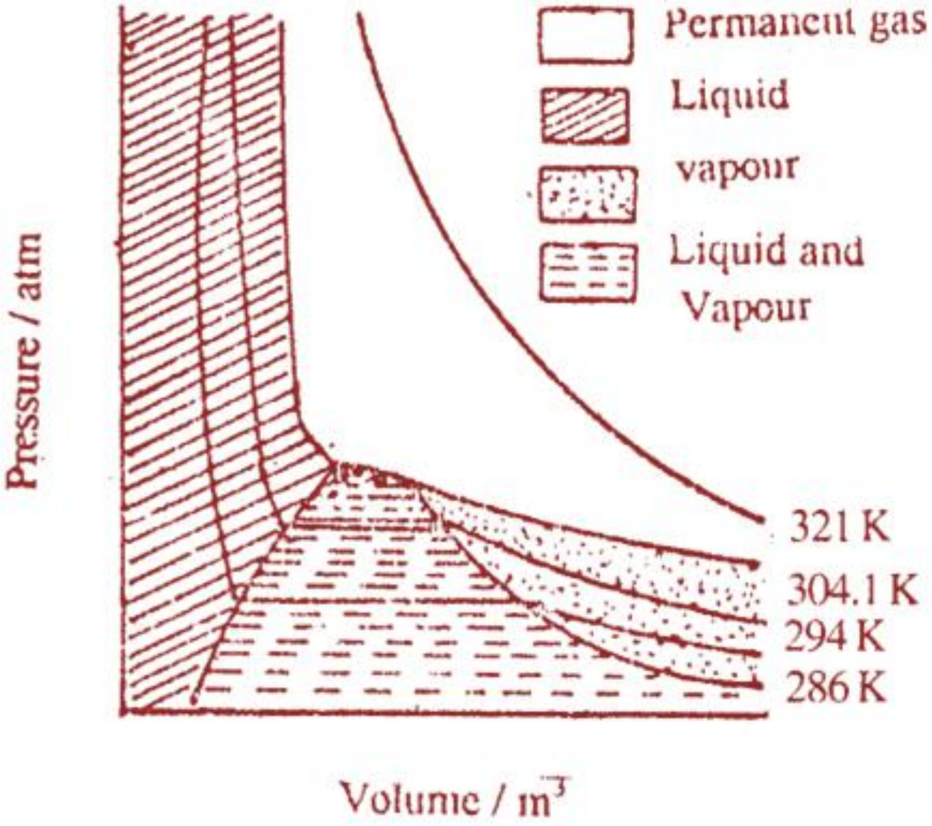


Fig. 6.9: Isotherms of carbon dioxide

The temperature above which, a gas cannot be liquified, however large the pressure may be is known as critical temperature.

Table 6.2 list values of the critical temperature and pressure critical volume for some common substances.

Table: 6.2 Critical temperatures and critical pressures

Substance	Critical Temperature (K)	Critical Pressure (atm)
Water, H_2O	647	217.7
Sulphurdioxide, SO_2	430	77.7
Ammonia, NH_3	406	112.5
Hydrogen Chloride, HCl	324	81.6
Carbondioxide, CO_2	304	73.0
Oxygen, O_2	154	49.7
Nitrogen, N_2	126	33.5
Hydrogen, H_2	33	12.8

Intext Questions 6.3

1. What are the conditions under which real gases behave as ideal gas?

....

2. Which term in Van der Waals equation accounts for the molecular volume?

....

3. Calculate the root mean square velocity of ozone kept in a closed vessel at 200 C and 1 atm pressure?

....

4. What is compressibility factor?

....

What You Have Learnt

- Matter exists in three states, namely, solid, liquid and gas.
- The three states of matter differ in the relative closeness of the molecules constituting them.
- There exists a definite relationship between the pressure, volume, temperature and number of moles of a gas and they are given by Boyle's law, Charle's law and Avogadro's law.
- The gases obeying gas laws are known as ideal gases.

- Dalton's law gives the relationship between partial pressures exerted by the non-reacting gases to the total pressure.
- Most of the gases deviate from the ideal behaviour. The deviations of gases from ideal behaviour are due to the wrong assumptions of kinetic molecular theory.
- Real gases can be liquified under appropriate conditions.

Terminal Exercise

1. Draw the graphs of the following:
    - *a)* p vs V at constant T and n.
    - b) 1/T vs p at constant T and n.
    - c) T vs V at constant p.
2. What is the volume occupied by one mole of a gas at STP?
3. The volume of a sample of gas is 500mL at a pressure of 1.5 atm. If the temperature is kept constant, what will be the volume of that gas at
    - i) 1 atm ii) 5.0 atm.
4. List the wrong assumptions of kinetic theory of gases which led to van der Waals equation.
5. What is the standard temperature and pressure?
6. What is the lowest possible temperature?
7. CO cannot be liquefied at 35°C, however large the pressure may be, why?
8. A sample of nitrogen gas weighing 9.3 g at pressure 0.99 atm occupies a volume of 12.4 litres when its temperature is 55K. What will be its volume when the temperature is 220 K? Assume pressure is kept constant.
9. Calculate the volume of one mole of oxygen at 27°C and 2 atm pressure, given that the volume of oxygen at STP is 22.4 litres.
10. What is the Maxwell-Boltzmann Law?

Answers to Intext Questions

6.1

1. Due to more intermolecular distances in gaseous molecule compared to liquid.
2. Boyle Law equation is

$$p_1V_1 = p_2V_2$$

$$(0.20 \text{ atm})\ (500 \text{ mL}) = p2\ (10 \text{ mL})$$

$$p2 = (0.20\text{atm})\ (500\text{ml}) / 10\text{mL}$$

$$p2 = 10 \text{ atm.}$$

3. By Avogadro's Law

$$\text{moles of } O_2 = \text{moles of unknown gas}$$

$$\frac{2.00\text{g}}{32\text{gmol}^{-1}} = \frac{1.75 \text{ g}}{\text{Molecular weight of unknown gas}}$$

$$\text{Molar mass of unknown gas} = \frac{1.75\text{x}32}{2.00} = 28 \text{ g mol-1}$$

6.2

1. Movement of gas molecules through another gas is called diffusion.
   When gas escapes from a container through a very small opening it is called effusion.
2. Ammonia and hydrogen chloride gases are reacting gases and Dalton's Law is applicable to mixture of non-reacting gases.
3.

$$\frac{rO_3}{rco_2} = \left(\frac{M_{co_2}}{M_{o_3}}\right)^{1/2}$$

$$\frac{0.271}{0.290} = \left(\frac{44}{M_{o_3}}\right)^{1/2}$$

Squaring both sides

$$\frac{(0.271)^2}{(0.290)^2} = \frac{44}{Mo_3}$$

$$Mo_3 = \frac{44x0.29x0.29}{0.271x0.271} = 50.4$$

Molecular mass of O_3 = 50.4

4. By ideal gas equation

$$pV = nRT$$

$$p \text{ x } 1.0 = (5.0\text{ mol})\ (0.0821\text{ L atm K}^{-1}\text{ mol}^{-1})\ 320\text{ K}$$

$$p = \frac{(5.0\text{ mol})\ (0.0821\text{ L atm K}^{-1}\text{ mol}^{-1})\ 320\text{ K}}{1.0\text{ L}}$$

$$p = 131.3\text{ atm.}$$

6.3

1. Low pressure and high temperature.
2. B
3. $U_{rms} = \sqrt{\frac{3RT}{M}}$

$$= \sqrt{\frac{3.(8.314Jk^{-1}mol^{-1})(293K)}{(0.048kgmol^{-1})}} = \sqrt{\frac{(8.314Kgm^2s^{-2}K^{-1}mol^{-1})(293K)}{0.048kgmol^{-1}}}$$

$$= 390.3\text{ ms}^{-1}$$

Chapter 07

THE LIQUID STATE

You are familiar with gases, liquids and solids in your daily life. You are aware that water can exist as a liquid, a solid (ice) or as a gas (vapour). These are called three states of matter. In lesson 6, you have learnt about the differences in properties of these three states of matter. The properties of gaseous state can be explained in terms of large separation of molecules and very weak intermolecular forces. In this lesson we shall study about the intermolecular forces in liquids and see how their properties can be explained in terms of these forces.

Objectives

After reading this lesson you will be able to:

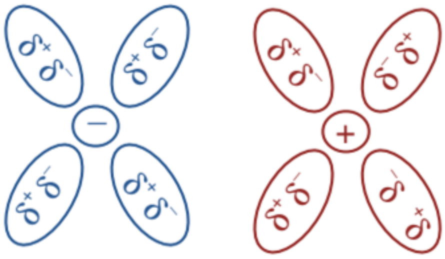
- Explain the properties of liquids in terms of their structure (molecular arrangement and intermolecular forces);
- Differentiate between evaporation and boiling;
- Define vapour pressure of a liquid and correlate it with its boiling point;
- Define surface tension and explain the effect of various factors on it;
- Explain the consequences of surface tension and
- Define viscosity of a liquid and correlate it with intermolecular forces.

7.1 Inter molecular forces:

We know about molecular polarities. They give rise to some of the forces that occur between the molecules. Take H_2O for example. H_2O molecule consists of two hydrogen atoms and one oxygen atom joined together in a specific way by the intermolecular forces known as “Covalent bonds”. But water exists either as solid ice or liquid water or gaseous steam, depending on its temperature. For this, there must be some intermolecular forces between molecules that hold them together at certain temperatures. These intermolecular forces are usually called *Van der Walls* forces after J. Van der Walls (1837-1923). These forces are of several different types like *ion* - *dipole, dipole* - *dipole*, *dipole* - *induced dipole* and *induced dipole* - *induced dipole* (London dispersion) forces - Hydrogen bond is specific intermolecular force limited to certain kinds of molecules. All these intermolecular forces are electrical. They result from the mutual attractions of unlike charges or repulsions of like charges. If the species are ions full charges are present and ion- ion interactions are very strong (500-1000 kJ. mol-1). They give rise to the so-called ionic bonds. If the molecules are neutral, then partial charges are possible to give substantial attractive forces.

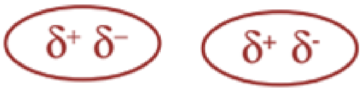
Ion - Dipole force:

Water molecules are polar and in them hydrogen atoms possess partial positive charges and oxygen atoms possess partial negative charges due to electro negativity different between hydrogen and oxygen atoms. When ionic compounds like NaCl dissolve in water, they dissociate into its components. Negative and positive charges are possible to give substantial attractive forces, they dissociate into component ions like. Na^+ and Cl^-. Now the water molecules orient in the presence of ion's in such a way that the positive end of the dipole is near an anion and the negative end of the dipole is near a cation. The magnitude of interaction energy depends on its charge 'z', molecule's dipole moment 'μ' and on the inverse square of the distance 'r' between the ion and the dipole $E = z\mu/r^2$. Ion dipole forces are mainly important in aqueous solutions of ionic substance. Such as NaCl in which dipolar water molecules surround the ions.



Dipole - Dipole forces:

Neutral but polar molecules experience dipole-dipole forces. These are due to the electrical interaction's among dipoles on neighbouring molecules. These forces are again attractive between unlike poles and repulsive between like poles and depend on the orientation of the molecules. The net forces in a large collection of molecules results from many individual interactions of both types. The forces are generally weak (energies of the order of 3-4 kJ mol^{-1}) and are significant only when the molecules are in close contact. The strength of a given dipole - dipole interaction depends on the sizes of the dipole moments involved. The more polar the molecules or the higher the dipole moment the greater is the strength of interactions and higher is the boiling points of those substances. Dipole-Dipole interaction energy between stationary polar molecules as in solid's is proportional to $1/r^3$ and that between rotating molecules is proportional to $1/r^6$ 'r' is the distance between the polar molecules.



Dipole - induced Dipole forces:

These forces are between polar molecules with permanent dipole moments and the molecules with no permanent dipole-moment. Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electronic cloud. Here also the interaction range is proportional to $1/r^2$ where 'r' is the distance between the molecules. The magnitude of induced of dipole moment also depends on the magnitude of dipole moment of permanent-dipole and polarizability of neutral molecule. Large molecules are easily polarized. Here also cumulative effect of dispersion forces and dipole-induced dipole interactions exist. There are repulsive forces between the particles (atoms, molecules or ions) due to electron- electron repulsions or (Nucleus-Nucleus) repulsions.

Thermal energy:

It is due to the motion of the atoms or molecules of the substance. This energy is directly proportional to the absolute temperature of the substances. It is a measure of average kinetic energy of the molecules of the substance. The movement of particles is called thermal motion.

Intermolecular forces Vs thermal energy:

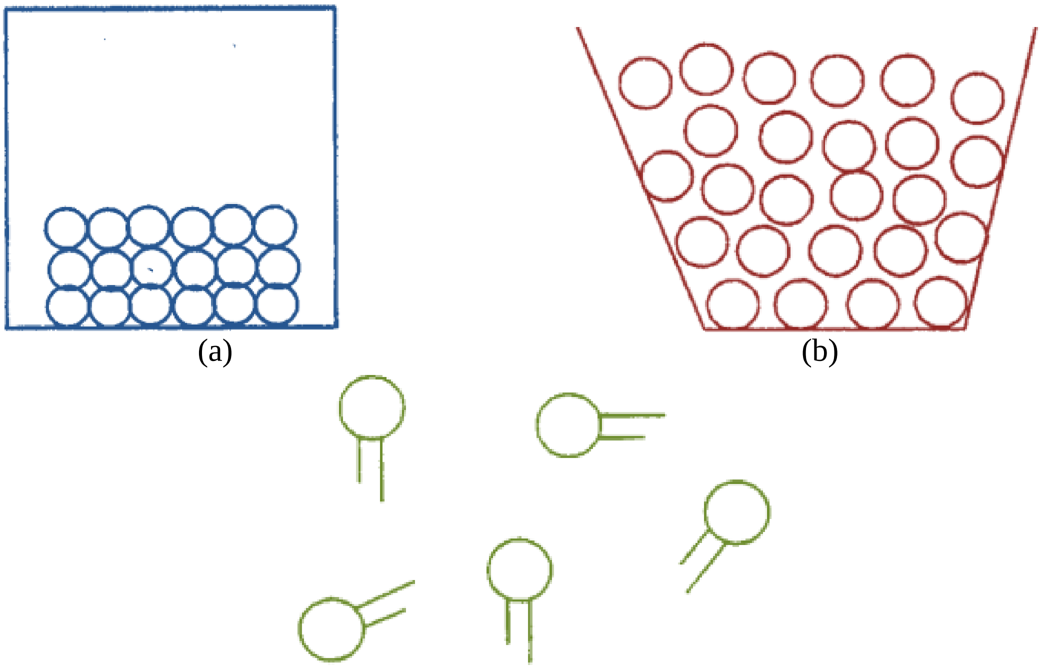
Intermolecular forces tend to keep the molecules together but thermal energy tends to keep them apart. If thermal energy predominates over inter molecular forces the substances would change from.

Solid → Liquid → Gas

And if intermolecular forces predominate, then the substances change from

Gas → Liquid → Solid

7.2 Nature of Liquids



(a) (b)

(c)

Fig 7.1 Arrangement of molecules in (a) Solid, (b) Liquid and (c) Gas

Look at Figure 7.1 in which the molecular arrangement has been shown in the three states of matter. What do you notice? In figure 7.1a, you would find that the molecules are far apart, a gaseous state can be represented by this arrangement. In liquid state (figure 7.1b), molecules are closer as compared to gaseous state. You would notice that they have very little spaces between them. However, there is no order in arrangement of molecules. Further we say that, these molecules can move about, but with lesser speeds than those in gases. They can still collide with one another as in the gaseous state. You would recall that the molecules in gases have very little attraction between them. But in liquid state the attraction between the molecules is comparatively much stronger as compared to that in the gaseous state. The attractions are strong enough to keep the molecules in aggregation. Contrary to this, in solids (Fig 7.1a) you notice that the molecules are arranged at the closest possible distance. Solid state is a well-ordered state and has very strong intermolecular forces. You would learn more about solids in lesson 8.

We would say, in a gas there is complete chaos due to very weaker molecular forces, whereas in solids there is a complete order due to strong forces. Liquid falls between gases and solid state. Liquid molecules have some freedom of gases state and some order of solid state. Intermolecular forces in liquids are strong enough to keep the molecules close to one another but not strong enough to keep them in perfect order. In this section you would learn how the properties of liquids can be explained in terms of molecular arrangement and intermolecular forces. Let us consider a few properties of liquids as examples.

7.2.1 Volume and Shape

You would recall that the liquids (for example water) take the shape of the container in which they are kept. However, they have a definite volume. How can you explain the properties of definite volume and variable shape? In liquids, the attractive forces are strong enough to keep the molecules moving within a definite boundary. Thus, they maintain a definite volume. These intermolecular forces are not strong enough to keep them in definite positions. The molecules can, therefore, move around and take the shape of the container in which they are kept.

7.2.2 Compressibility

Compressibility of a substance is its ability to be squeezed when a force is applied on it. Let us study the compressibility of liquids with the help of the following activity.

Activity 7.1

Aim: To study the compressibility of water.

What is required?

A 5 mL syringe and water

What to do?

i) Take the syringe and fill it with water by pulling out the plunger.
ii) Note the volume of water.
iii) Press the plunger while blocking the nozzle of the syringe with a finger.

What to observe?

- Observe the volume of water in the syringe while pressing the plunger. Does the volume of water change by pressing the plunger? You would observe that it does not change.
- The above activity clearly shows that liquids are largely incompressible. It is because there is very little empty space between the molecules. In contrast, the gases are highly compressible because of large empty spaces between their molecules.
- The large difference in the free space in gaseous and liquid states becomes evident from the fact that the volume occupied by a given amount of a substance in liquid state is 100-1000 times less than that in the gaseous state.

7.2.3 Diffusion

Diffusion is the process of spreading of a substance from a region of higher concentration to a region of lower concentration. Let us study the phenomenon of diffusion in liquids with the help of the following activity.

Activity 7.2

Aim: To study the phenomenon of diffusion through water.

What is required?

A glass, water, blue ink and a dropper

What to do?

i) Take some water in the glass.
ii) Add a few drops of blue ink into water with the help of a dropper.

What to observe?

- Observe the water and ink in the beaker. Initially the ink does not mix with water. After some time it starts spreading slowly. After a few hours the whole of water in the glass becomes coloured due to diffusion of ink through water.
- The above activity demonstrates that diffusion occurs in liquids. Why does it happen? Because the molecules of both the liquids are moving and help in the diffusion process.

7.2.4 Evaporation

You know that water left in an open pan evaporates slowly until the pan becomes dry. Evaporation is the process by which a liquid change into vapour. It occurs at all temperatures from freezing point to boiling point of the liquid.

In a liquid, at any temperature, a small fraction of the molecules is moving with relatively high velocity. Such molecules have high kinetic energy. These can overcome the intermolecular attractive forces and escape through the surface of the liquid.

Rate of evaporation of a liquid depends on a number of factors. For example, more is the surface area, faster will be the evaporation. For faster dying, we increase the surface area by spreading the wet clothes. If we supply heat to the liquid, evaporation is faster. The wet clothes dry faster in the sun. The increase in temperature increases the kinetic energy of the molecules of the liquid and the liquid evaporates at a faster rate. We feel cool after the bath. Why do we feel so? It is because during evaporation water takes the heat from our body and we feel cold.

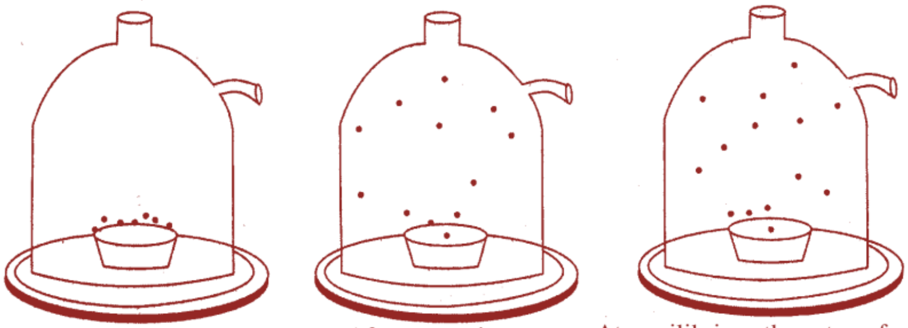
Now let us compare the rate of evaporation of two liquids, for example, water and alcohol. Which of these two liquids evaporates faster? You mut have experience that alcohol evaporates faster. Why does this happen? The number of molecules escaping from a liquid depends upon the attractive forces. When these forces are stronger, fewer molecule escape. In alcohol, these attractive forces are weaker than those in the water. Hence, alcohol evaporates faster than water.

7.3 Vapour Pressure and Boiling Point

In the previous section you have learnt that liquids evaporate when kept in an open vessel. Different liquids evaporate to different extent under similar conditions. The extent of evaporation of a liquid is measured with the help of vapour pressure of a liquid. In this section, you will study about it and also about the boiling point of a liquid.

7.3.1 Vapour Pressure of a liquid

You know that a liquid placed in an open vessel evaporates completely. If, however, the liquid is allowed to evaporate in a closed vessel say in stoppered bottle or a bell jar, evaporation occurs, but after sometime the level of the liquid does not change any further and become constant. Let us understand how it happens. In the closed vessel, the molecules evaporating from the liquid surface are confined to a limited space. These molecules may collide among themselves or with the molecules of air and some of them may start moving towards the surface of the liquid and enter into it. This is known as condensation. In the beginning, rate of evaporation is greater than the rate of condensation. But as more and more molecules accumulate in the space above the liquid, rate of condensation gradually increases. After some time, rate of evaporation becomes equal to the rate of condensation and an equilibrium state is reached (Fig. 7.2).



Initially molecules evaporate

After some time condensation begins

At equilibrium the rates of evaporation and condensation become equal

Fig. 7.2: Establishing (vapour liquid) equilibirum under a evacuated jar

The number of molecules in the vapour above the liquid becomes constant. These molecules exert certain pressure over the surface of the liquid. This pressure in known as equilibrium vapour pressure, saturated vapour pressure or simply as vapour pressure. The vapour pressure of a liquid has a characteristic value at a given temperature. For example, vapour pressure of water is 17.5 torr and that of benzene is 75.00 torr at 20°C. The vapour pressure of a liquid increases with increase in temperature. It is so because at a higher temperature more molecules have sufficiently high energy to overcome the forces of attraction and escape to form vapour. A plot of vapour pressure as a function of temperature is called vapour pressure curve. Figure 7.3 depicts the vapour pressure curves of some liquids.

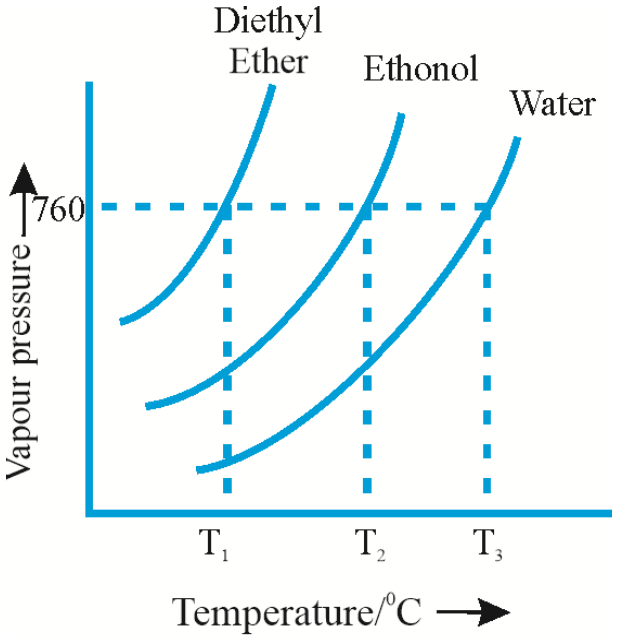


Fig. 7.3: Vapour pressure curves of some liquids

What would happen if we remove some of the vapour from the closed vessel. Would the vapour pressure of the liquid increase, decrease or remain constant? Vapour pressure of the liquid would remain constant at that temperature. In the beginning, the vapour pressure would decrease after the removal of the vapour, but soon more liquid would evaporate to maintain the equilibrium and the original vapour pressure would be restored. So the vapour pressure of a liquid has a definite value at a particular temperature.

7.3.2 Boiling

You must have seen the formation of bubbles at the base of a vessel, in which a liquid is heated. The rate of formation of bubbles increases with increase in heat supplied. What are the bubbles made up of? The first bubbles that you see are of the air, which is driven out of the liquid by increase in temperature. After some time, bubbles of the liquid are formed throughout it. These bubbles rise to the surface and break. When this happens, we say that the liquid is boiling. The bubbles of the liquid would form only if its vapour pressure is equal to the atmospheric pressure. The temperature at which boiling occurs is called the boiling point of the liquid. At this temperature the vapour pressure of the liquid is equal to the atmospheric pressure. The boiling point, therefore, depends upon the atmospheric pressure. For example, water boils at 100°C at 760 torr and at 97.7°C at 700 torr.

The normal boiling point of a liquid is defined as the temperature at which the vapour pressure of a liquid is equal to one atmosphere or 760 torr.

The boiling point of a liquid depends upon its nature. A more volatile liquid would boil at a lower temperature than a less volatile liquid. You can refer to figure 7.3 and note that diethyl ether boils at a much lower temperature than water, because it is highly volatile liquid. The boiling point of ethanol lies in between those of diethyl ether and water. Vapour pressures or boiling points of liquids give us an idea of the strength of attractive forces between molecules in liquids. Liquids having lower boiling points have weaker attractive forces in comparison to those having higher boiling points. You can make a liquid boil at temperature other than normal boiling point. How? Simply alter the pressure above the liquid. If you increase this pressure, you can increase the boiling point and if you can decrease this pressure, you decrease the boiling point. On the mountains, the atmospheric pressured decrease and therefore boiling point of water also decreases. People living on hills face problem in cooking their meals. They, therefore, use pressure cooker. How food is cooked faster in it? The lid of pressure cooker does not allow water vapour to escape out. On heating the water vapour accumulate and the inside pressure increases. This makes the water boil at a higher temperature and the food is cooked faster.

7.3.3 Evaporation and Boiling

Evaporation and boiling, both involve conversation of a liquid into vapour and appear to be similar. However, they differ from each other in some aspects. Evaporation occurs at all temperatures from freezing point of a liquid to its boiling point, while boiling occurs at a definite temperature only i.e., it is boiling point. Evaporation occurs slowly while boiling is a fast process. Evaporation of a liquid occurs at its surface alone while boiling occurs throughout the liquid. These differences between evaporation and boiling have been summarized in Table 7.1.

Table 7.1: Differences between evaporation and boiling

S.No.	Evaporation	Boiling
1.	It takes place at all temperatures.	It takes place at a definite temperature.
2.	It is a slow process.	It is a fast process
3.	It occurs only at the surface of the liquid.	It occurs throughout the liquid.

Intext Questions 7.1

1. Match the following.

Column I		Column II
i) liquids have a definite volume.	a)	The molecules in a liquid can move about
ii) Liquids acquire the shape of their container.	b)	The molecules in liquids are close and have very little free space.
iii) Liquid are largely incompressible.	c)	The inter molecular forces liquid strong enough to keep the molecules moving with in a definite space.

2. When a liquid is heated till it starts boiling.

i) What are the small bubbles that appears initially at the bottom and sides of the vessel made up of?

…………………..
...

ii) What are the large bubbles that form in the boiling liquid made up of?

…………………..
...

3. Liquids A, B and C boil at 65^0C, 120^0C and 90^0C respectively. Arrange them in the decreasing order of the strength of intermolecular forces

…………………..
......

7.4 Surface Tension

Liquids show the effects of inter molecular forces most dramatically in another property, namely, surface tension. Any molecule in the interior of liquid is equally attracted by neighbour molecules from all sides and it does not experience any 'net' force. On the other hand, any molecule at the surface of a liquid is attracted by other molecules at the surface of the liquid or below it. Due to the imbalance of forces, any molecule at the surface experiences a net inward pull (Figure 7.4). As a result, the surface is under tension as if the liquid were covered with a tight skin (or stretched membrane). The phenomenon is called surface tension, Quantitively, the surface tension is defined as the force acting on an imaginary line of unit length drawn on the surface of the liquid and acting perpendicular to it towards the liquid side as shown in Figure 7.5 It is represented by the Greek letter gamma, γ. Its SI unit is newton per meter (N m^{-1}) and CGS unit is dyne per centimetre (dyne cm^{-1}). The two units are related as: 1 Nm^{-1} = 103 dyne cm^{-1}.

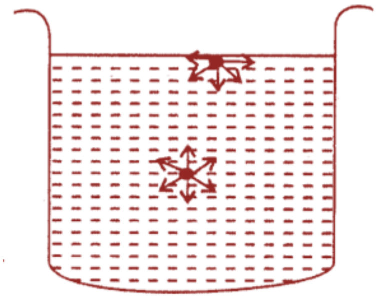


Fig. 7.4: Forces acting one molecules, at the surface and in bulk of liquids

Surface molecules of a liquid experience a constant inward force. Therefore, they have a higher energy than the molecules in the bulk of the liquid. Due to this reason liquids tend to have minimum number of molecules at their surface. This is achieved by minimising the surface area. In order to increase the surface area more molecules must come to the surface. This can happen only if some energy is supplied or work is done. The energy supplied (or work done) for increasing the surface area of a liquid by a unit amount is known as its surface energy. Its units are joule per square meter Jm^{-2} or Nm^{-1} (since 1J = 1Nm). Thus dimensionally, the surface tension and surface energy are similar quantities and they have the same numerical value.

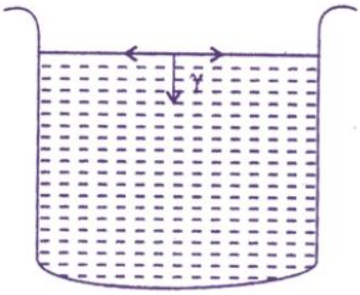


Fig. 7.5: Surface tension force acting on the surface of a liquid.

Effect of Temperature

One raising the temperature surface tension of a liquid decreases. It completely vanishes at the critical temperature. This happens due to the following two factors:

i) On heating, the liquids expand. This increases the intermolecular distances.

ii) On heating, the average kinetic energy of molecules and hence their chaotic motion increases.

Due to both of these factors, the intermolecular forces become weak and the surface tension decreases.

Effect of adding Surface Active Solutes

The solutes which get more concentrated on the surface of the liquid than in the bulk called surface active solutes or surfactants. Alcohols are examples of such substances. Their addition to a liquid lowers its surface tension. The cleaning action of soaps and detergents is based on this fact.

Some Effects Surface Tension

Surface tension results in many interesting and important properties of liquids. Let us now study some of them.

i) Spherical Shape of liquid drops

You have already learnt that liquids tend to have a minimum surface area. For a given volume, the geometrical shape having minimum surface area is a sphere. Hence, liquids have a natural tendency to form spherical drops, when no external force acts on them. Rain drops are distorted and the distortion is due to the friction of air.

ii) Wetting and Non- wetting properties

When a drop of liquid is placed on solid surface, the force of gravity should cause it to spread out and form a thin layer (Fig. 76). Such a liquid is called a wetting liquid. This happens in case of most of the liquids. For example, drops of water or alcohol spread-out on the surface of glass. Some liquids behave differently. When a drop of mercury is placed on the surface of glass, it does not spread out (Fig. 7.6). Solid liquids are called non-wetting liquids.

Wetting or non-etting nature of a liquid depends upon two types of forces. The intermolecular attractive forces between molecules of a liquid are called **cohesive force** while those between the molecules of the liquid and the solid (whose surface is in contact with the liquid) are called **adhesive forces**. If adhesive forces are stronger than cohesive forces, the liquid would be wetting in nature and when cohesive forces are stronger than adhesive forces it would be non-wetting in nature on the surface of a particular solid.

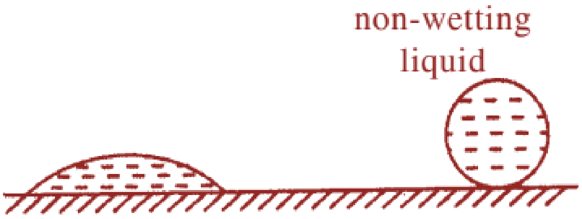


Fig. 7.6: Establishing (vapour liquid) equilibrium under a evacuated jar

iii) Capillary Action

Let us carry out the following activity.

Activity 7.3

Aim: To study the capillary action.

What is required?

Glass capillary tubes, water, mercury and two petri dishes

What to do?

i) Take some water in a petri dish.
ii) Dip one end of a 3-4 cm long capillary in it.
iii) Take some mercury in another petri dish.
iv) Dip one end of another 3-4 cm long capillary in it.

What to observe?

Observe the levels of water and mercury in the capillaries. Is it below or above the levels of the liquid in petridishes.

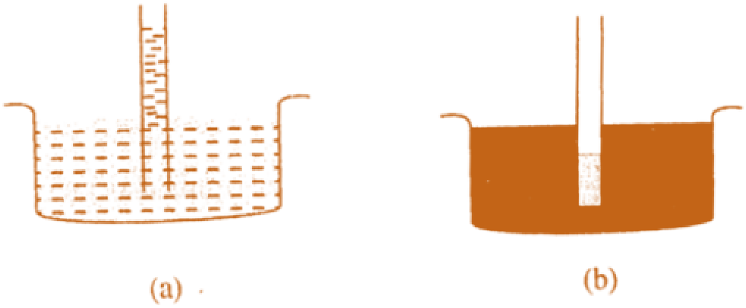


Fig. 7.7: Capillary Action

You would observe that when end of a capillary tube is dipped in water, it rises in the capillary as shown in Fig. 7.7(a). On the other hand when one end of a capillary tube is dipped in mercury, its level falls in the capillary as in Fig .7.7 (b).

The phenomenon of rise or fall of a liquid in a capillary is known as **capillary action**. The rise of water in the glass capillary is due to its wetting nature as the adhesive forces are stronger than cohesive forces. Water tends to increase the area of contact with glass wall of the capillary by rising in it. Mercury being non-wetting with respect of glass (its cohesive forces are stronger than adhesive forces) tends to minimise the area of contact by depressing inside the capillary.

iv) Curved menisus

When a wetting liquid such as water is taken in a glass tube, the liquid tends to rise lightly along the walls of the tube for increasing its area of contact with glass. The surface of the liquid (meniscus) becomes curved. It is concave in shape (Fig. 7.8 (a)]. When a non-wetting liquid like mercury is taken a glass tube, it tends to decrease its area of contact and depresses along the walls of the glass tube. The meniscus is convex in shape in this case (Fig. 7.8)(b)].

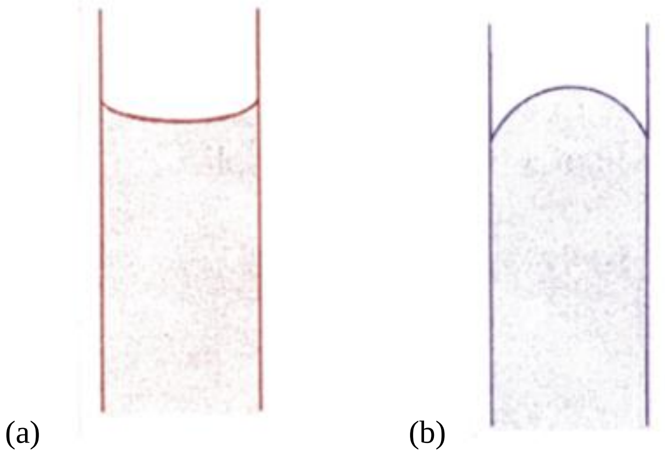


Fig. 7.8: Curved meniscus of liquids (a) Concave meniscus (b) Convex meniscus

7.5 Viscosity

Every liquid has the ability to flow. It is due to the fact that molecules in a liquid move freely, although within a limited space. Water flows down a hill under gravitational force or through pipes when forced by a pump. Some external force is always required for a liquid to flow. Some liquids like glycerol or honey flow slowly while others like water and alcohol flow rapidly. This difference is due to the internal resistance to flow which is called viscosity. The liquids with higher viscosity flow slowly and are more viscous in nature like glycerol or honey. Water and alcohol have lower viscosity and are less viscous in nature. They flow more rapidly.

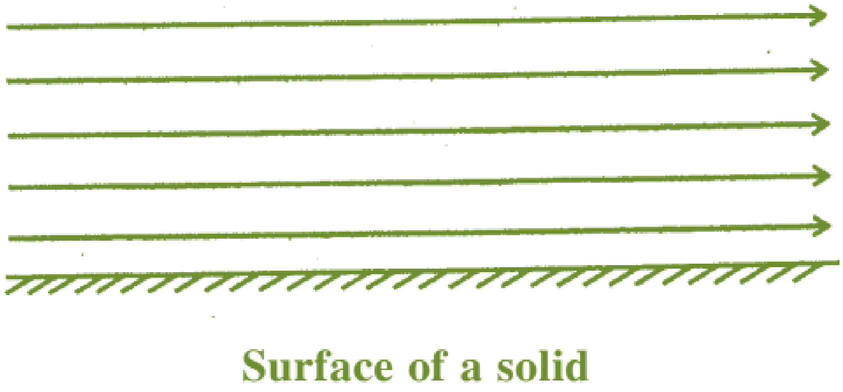


Fig. 7.9: Flow of different layers of a liquid

The viscosity is related to the intermolecular forces. Stronger the intermolecular forces more viscous are the liquids. Let us understand this with the help of Figure 7.9. When a liquid flows steadily, it flows in different layers with one layer sliding over the other. Such a flow is known as **laminar flow**. Consider a liquid flowing steadily on a plane surface. The layer closest to it is almost stationary due to adhesive forces. As the distance of the layer from the surface increases, is velocity increases. Thus, different layers move with different velocities. Due to intermolecular forces (cohesive forces) each layer experiences a force of friction from its adjacent layers. This force of friction, f between two layers depends upon:

i) area of contact between them A.
ii) distance between the layers, *dx*.
iii) difference in velocity between the layers, *du*. These quantities are related as

$$f = \eta A \frac{du}{dx}$$

Hence η(Greek letter ‘eeta’) is called the coefficient of viscosity and du/dx velocity gradient between the layers.

If $A = 1\ \text{cm}^2$, $du = 1\ \text{cm s}^{-1}$ and $dx = 1$ cm, then

$$f = \eta$$

Thus, coefficient of viscosity is the force of friction between two parallel layer of the liquid which have $1\ \text{cm}^2$ area of contact, are separated by 1 cm and have a velocity difference of 1cm s^{-1}. It may be noted that f is also equal to the **external force** which is required to overcome the force of friction and maintain the steady flow between two parallel layers having an area of contact, and which are *dx* distance apart and moving with a velocity difference of *du*.

Units

CGS unit of viscosity is dyne cm^{-2} s. This unit is also known as poise(P). The SI unit of viscosity is N m^{-2}s or Pas.

The two units are related as: 1 pas = 10 P

The unit poise is found to be too large and its submultiples centipoise (1 cP = 10^{-2} P) and milli poise (1 mP = 10^{-3} P) are used for liquids and micropoise (P = 10^{-6} P) is used for gases.

Effect of Temperature

Viscosity of a liquid decreases on raising the temperature. It is due to decrease in intermolecular forces on heating as discussed in previous section (Section 7.4).

Intext Questions 7.2

1\.

i) A molecule at the surface of a liquid has energy than the one within the liquid.

ii) Surface tension of liquid on cooling.

iii) Meniscus of a non-wetting liquid is in shape while that of a wetting liquid is in shape.

iv) When one end of a glass capillary tube was dipped in a liquid, the level of liquid inside the capillary was observed to fall. The adhesive forces in this liquid are .... than the cohesive forces between the liquid and glass.

v) Liquid X is more viscous than liquid Y. The intermolecular forces in Y are................... than in X.

2\. What are the SI units of

i) Surface tension. ....

ii) Coefficient of viscosity. ....

3\. Why do liquids have a tendency to acquire minimum surface area?

………………...

What You Have Learnt

- In liquids the intermolecular force are quite strong as compared to gases but weak enough to allow the molecules to move within a limited space and the intermolecular distance is short.
- Liquids have definite volume but no definite shape, are almost incompressible and can diffuse.
- Liquids evaporate and exert a definite vapour pressure at specified temperature.
- Boiling point is the temperature at which the vapour pressure of the liquid becomes equal to the external pressure.
- Surface tension is the force acting on an imaginary line of unit length drawn on the surface of the liquid and acting perpendicular to it towards the liquid side.
- Due to surface tension, liquids tend to have minimum surface area and show the phenomena of capillary rise or fall and curved meniscus Viscosity is the internal force of friction to the flow of liquid.

Terminal Exercise

1\. Explain the following properties of liquids on in basis of their structure.

i) Volume ii) Shape iii) Compressibility iv) Ability to flow

2\. Why diffusion can occur in liquids. Explain.

3. Define i) vapour pressure ii) boiling point

4. Differentiate between evaporation and boiling.

5. Explain the effect of temperature on vapour pressure of a liquid.

6. Define surface tension and give its CGS and SI units.

7. What is surface energy?

8. Why is energy required to increase the surface area of a liquid?

9. What is the effect of addition of a surface-active substance on the surface tension of a liquid.

10. Why are liquid drops spherical in shape?

11. What are wetting and non-wetting liquids?

12. The cohesive forces acting in liquids A and B are C1 and C2 respectively C1 > C2 which of them would have higher surface tension.

13. Liquid A rises in glass capillary tube. If one drop of it is put on a plane glass surface, would it spread out or not. Explain.

14. A liquid form a convex meniscus in glass tube. Comment on its nature.

15. Define viscosity.

16. What is coefficient of viscosity?

17. Give CGS and SI units of coefficient of viscosity.

18. What is the effect of temperature on (i) vapour pressure (ii) surface tension and (iii) viscosity of a liquid?

Answers to Intext Questions

7.1

1. i) C; ii) A; iii) B
2. i) Air ii) Liquid
3. B > C > A

7.2

1. i) more ii) increases iii) convex; concave iv) Stronger v) weaker
2. i) N m^{-1}; ii) $Nm^{-2}s$
3. Molecules in the surface of a liquid have higher energy due to an inward force on them. Therefore, liquids tend to have minimum number of molecules in the surface or have minimum surface area.

Chapter 08

SOLID STATE

You are aware that the matter exists in three different states viz., solid liquid and gas. In these, the constituent particles (atoms, molecules or ions) are held together by different forces of attraction between them. However, the nature and magnitude of the forces varies. In the first two lessons of this module, you have learnt about the gaseous and the liquid states of matter. In this lesson you would learn about solid state- a compact state of matter. The solids are distinguished from a liquid or gas in terms of their rigidity which makes them occupy definite volume and have a well-defined shape. In solid state, the constituent particles are in close contact and have strong forces of attraction between them. Here, you would learn about structure, classification and properties of solids.

Objectives

After reading this lesson, you should be able to:

- explain the nature of solid state;
- explain the properties of solids in terms of packing of particles and intermolecular attractions;
- explain the melting point of a solid;
- differentiate between crystalline and amorphous solids;
- classify the crystalline solids according to the forces operating between the constituent particles;
- explain different types of packing in the solids;
- define coordination number;
- explain different types of unit cells;
- calculate the number of particles in simple cubic, face-centred cubic and body centred cubic unit cells;
- define radius ratio;
- correlate the radius ratio with the structure of solids;
- explain the structure of simple ionic compounds and
- explain Frenkel and Schottky defects.

8.1 Nature of Solid State

You have learnt in lesson 6 that according to Kinetic Molecular Theory, the gases consist of a large number of molecules, which are in constant random motion in all directions in the available space. These molecules have very weak or negligible forces of attraction between them. A sample of gas can be compressed, as there is a lot of free space between the molecules Fig.8.1 (a). In liquids Fig.8.1 (b) on the other hand the molecules are also in constant motion but this motion is relatively restricted. Since there is very little free space available between the molecules the liquids are relatively incompressible.

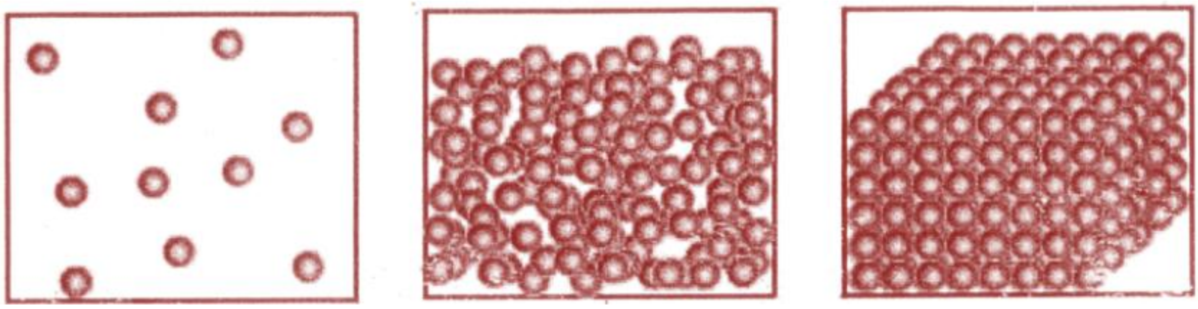

(a) (b) (c)

Fig. 8.1: A pictorial representation of the three states of matter:
(a) gas (b) liquid and (c) solid state.

In solid state the constituent particles are arranged in a closely packed ordered arrangement Fig.8.1 (c) with almost no free space. They can just vibrate about their fixed positions. These are in close contact and cannot move around like the molecules of a gas or a liquid. As a consequence, the solids are incompressible, rigid and have a definite shape. Like liquids, the volume of a solid is independent of the size or the shape of the container in which it is kept.

8.2 Classification of Solids

On the basis of nature of arrangements of the constituent particles the solids are classified into amorphous and crystalline solids.

8.2.1 Amorphous and Crystalline Solids

In crystalline solids the constituent particles are arranged in a regular and periodic pattern and give a well-defined shape to it. The term ‘crystal’ comes from the Greek word, *krustallos* meaning ice. The regular pattern extends throughout the solid and such solids are said to have **long range order**. On the other hand, some solids have only a short range of order. This means that the particles are arranged regularly in only some regions of the solid and are relatively disordered in other regions. Such solids are called **amorphous solids**. In Greek, a means *without* and *morph* means *form*. Thus, the word amorphous means without form. Sodium chloride and sucrose are common examples of crystalline solids while glass, fused silica, rubber and high molecular mass polymers are some examples of amorphous solids.

An important difference between the amorphous and crystalline solids is that while amorphous solids are isotropic in nature (i.e., these exhibit same value of some physical properties in all directions) the crystalline solids are **anisotropic** (i.e., the values of some physical properties are different in different directions). Refractive index and coefficient of thermal expansion are typical physical properties, Which have different values between amorphous and crystalline solids is that while crystalline solids have a sharp or definite melting point, whereas the amorphous solids do not have definite melting point, these melt over a range of temperature.

The crystalline solids can be further classified on the basis of nature of interaction between the constituent particles as discussed below.

8.2.2 Classification of Crystalline Solids

In crystalline solids the constituent particles are arranged in an ordered arrangement and are held together by different types of attractive forces. These forces could be coulombic or electrostatic, covalent, metallic bonding or weak intermolecular in nature. The differences in the observed properties of the solids are due to the differences in the type of forces between the constituting particles. The types of forces binding the constituent particles can be used as a basis for classification of crystalline solids. On this basis, the crystalline solids can be classified into four different types –ionic –molecular, covalent and metallic solids. The characteristics and the properties of different types of solids are compiled in Table 8.1.

Table 8.1: Characteristics and properties of different types of solids

Type of Solid	**Constituent Particles**	**Nature of interaction between the particles**	**Appearance**	**Melting Point**	**Examples**
Ionic	Ions	Coulombic	Hard and brittle	High	Sodium chloride zinc sulphide, etc
Molecular Non polar Polar	Molecules	van der Walls Dipole-dipole	Soft and brittle	low	Water, carbon dioxide, iodine etc
Covalent	Atoms	Covalent bonding	Hard	Very high	Diamond, graphite silica, etc.
Metallic	Atoms	Metallic bonding	Hard and malleable	Variable	Copper, silver, etc.

Sodium chloride is an example of an ionic solid because in this case the sodium ions and chloride ions are attracted to each other by electrostatic interactions. Iodine on the other hand is an example of a molecular solid because in this the molecules are held together by weak vander Waals forces. Diamond, with strong covalent between the constituent carbon atoms is an example of covalent solids while in metals a large number of positive cores of the atoms are held together by a sea of electrons.

8.3 Properties of Crystalline Solids

You are familiar with the following properties of solids on the basis of handling solids in day-to-day work.

- Solids are rigid in nature and have well defined shapes
- Solids have a definite volume irrespective of the size and shape of the container in which they are placed.
- Solids are almost incompressible.

You are familiar with a number of crystalline solids like sugar, rock salt, alum, gem stones, etc. You must have noticed that such solids have smooth surfaces. These are called ‘faces’ of the crystal. These faces are developed in the process of crystal formation by ordered arrangement of the constituent particles. It is generally observed that the faces of crystals are developed unequally. The internal angle between a pair of faces is called **interfacial angle** and is defined as the angle between the normals to the intersecting faces. An important characteristic of crystalline solids is that irrespective of the size and shape of the crystal of a given substance, the interfacial angle between a pair of faces is always the same. This fact was stated by Steno as *the law of constancy of interfacial angles* (Fig. 8.2).

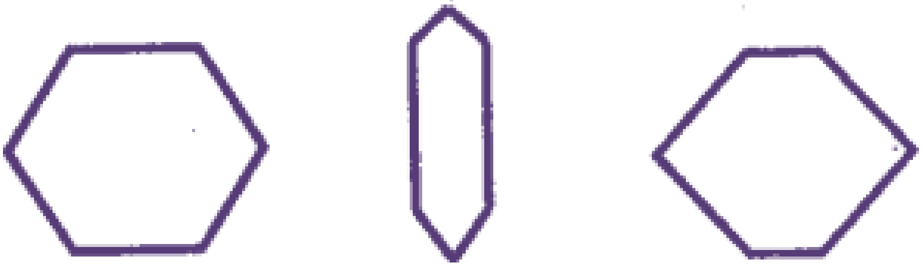


Fig. 8.2: The constancy of interfacial angles

8.3.1 Melting Point of a Solid

What is the effect of heat on a solid? You would have observed that when a solid is heated it becomes hot and eventually gets converted into a liquid. This process of conversion of a solid to a liquid on heating is called **melting**. You would also have observed that different solids need to be heated to different extents to convert them to liquids. The temperature at which a solid melt to give a liquid is called its **melting point**. Every solid is characterized by a definite melting point. This in fact is a test of the purity of the solid. The melting point of a solid gives us an idea about the nature of binding forces between constituent particles of the solid. Solids like sodium chloride (m.p = 1077 K) have very high melting points due to strong coulombic forces between the ions constituting it. On the other hand molecular solids like naphthalene (m.P. 353 K) have low metling points.

The effect of heat on a solid can be understood in terms of energy and motion of the constituent particles. You are aware that in a solid the constituent particles just vibrate about their mean position. As the heat is supplied to the solid, the constituent particles gain energy and start vibrating more vigorously about their equilibrium positions. As more and more heat is supplied, the energy keeps on increasing and eventually it becomes greater than the binding forces between them. As a consequence, the solid is converted into a liquid.

Intext Questions 8.1

1. Differentiate between solid, liquid and gaseous state?

....

2. How are solids classified on the basis of the intermolecular forces?

....

3. What is Steno’s law of constancy of interfacial angels?

....

8.4 Close Packed Structures of Solids

In the process of the formation of crystal the constituent particles get packed quite closely. The crystal structures of the solids can be described in terms of a close packing of identical spheres as shown in Fig. 8.3 These are held together by forces of attraction. Let us learn about the possible close packed structures of solids and their significance.

Fig. 8.3: Arrangement of identical spheres in one dimension

A linear horizontal arrangement of identical spheres in one dimension forms a row (Fig. 8.3). A two-dimensional close packed structure can be obtained by arranging a number of such rows to form a layer. This can be done in two possible ways. In one of these, we can place these rows in such a way that these are aligned as shown in (Fig. 8.4 (a)). In such an arrangement each sphere is in contact with four other spheres. This arrangement in two dimensions is called square close packing.

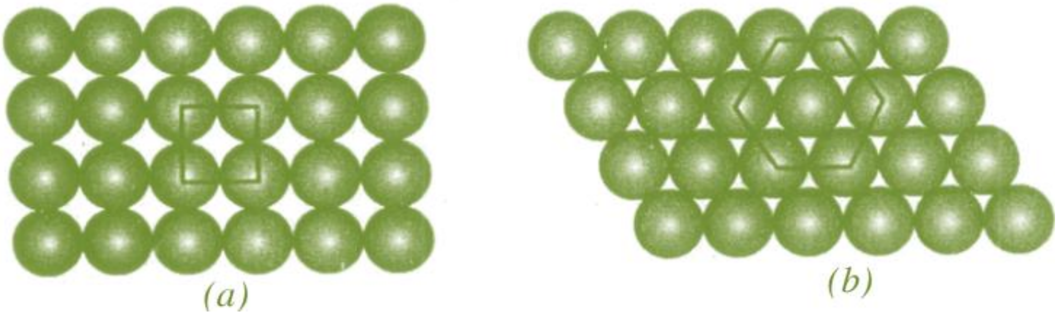


Fig. 8.4: (a) Square close packing and (b) hexagonal close packing of identical spheres in two dimensions

In the other way we can place the spheres of the second row in the depressions of the first row and so on so forth (Fig. 8.4 (b)). You may notice that in such an arrangement each sphere is in contact with six other spheres. Such an arrangement in two dimensions is called hexagonal **close packing**. In such a packing, the spheres of the third row are aligned with the first row. You may also have noticed that in the hexagonal close packing the spheres are more effectively packed. In Fig. 8.4 an equal number of identical spheres are arranged in two different types of packing.

A three-dimensional structure can be generated by placing such two-dimensional layers on top of each other. Before we move on to the three-dimensional packing let us look at the hexagonal close packed layer somewhat more closely (Fig. 8.5).

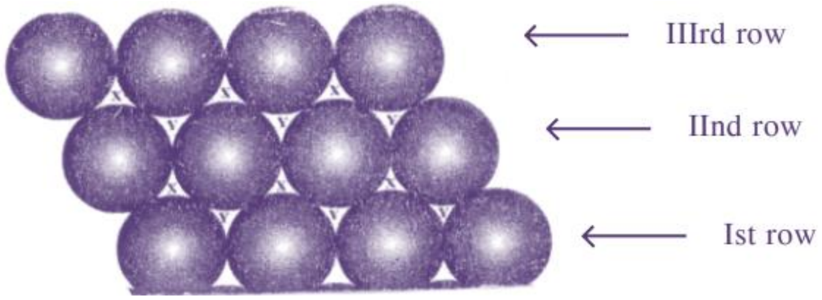


Fig. 8.5: A hexagonal close packed layer showing two types of triangular voids.

You may note from Fig. 8.5 that in a hexagonal close packed layer there are some unoccupied spaces or voids. These are triangular in shape and are called **trigonal voids**. You can further note that there are two types of triangular voids, one with the apex pointing upwards and the other with the apex pointing downwards. Let us call these as X type and Y type voids respectively as marked in the Fig. 8.5

Close Packed Structures in three dimensions

Let us take a hexagonal close packed layer and call it A layer and place another hexagonal close-packed layer (called the B layer) on it. There are two possibilities.

1. In one, we can place the second layer in such a way that the spheres of the second layer come exactly on top of the first layer.
2. In other, the spheres of the second layer are in such a way that these are on the depressions of the first layer. The first possibility is similar to square close packing discussed above and is accompanied by wastage of space. In the second possibility when we place the second layer into the voids of the first layer, the spheres of the second layer can occupy either the X or Y types trigonal voids but not both. You may verify this by using coins of same denomination. You would observe that when you place a coin on the trigonal void of a given type, the other type of void becomes unavailable for placing the next coin (Fig. 8.6).

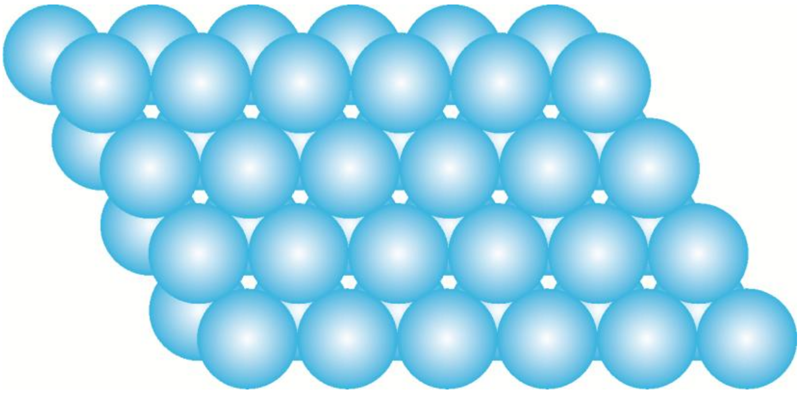
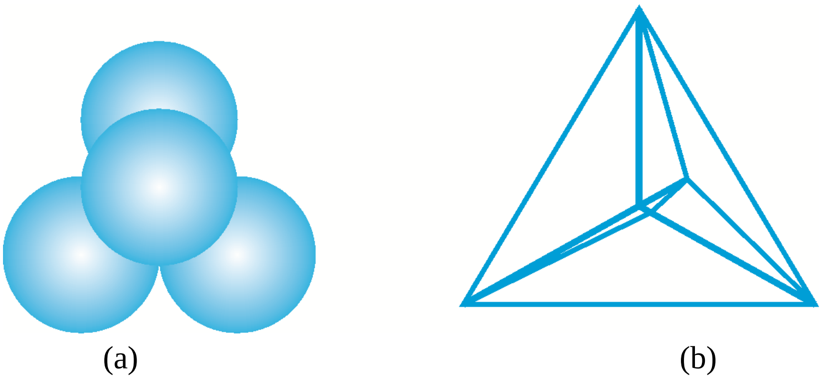


Fig. 8.6: Two layers of close packed spheres, the second layer occupies only one type (either X or Y) of triangular voids in the first layer.

In this process, the sphere of second layer covers the trigonal voids of the first layer. It results into voids with four spheres around it, as shown in Fig. 8.7 (a). Such a void is called a tetrahedral void since the four spheres surrounding it are arranged on the corners of a regular tetrahedron, Fig. 8.7 (b). Similarly, the trigonal voids of the second layers will be placed over the spheres of the first layer and give rise to tetrahedral voids.



(a) (b)

Fig. 8.7: A tetrahedral void

In a yet another possibility, the trigonal voids of the first layer have another trigonal void of the opposite type (B type over C and C type over B type) from the second layer over it. This generates a void which is surrounded by six spheres, Fig. 8.9 (a). Such a void is called an octahedral void because the six spheres surrounding the void lie at the corners of regular octahedron, Fig. 8.8 (b).

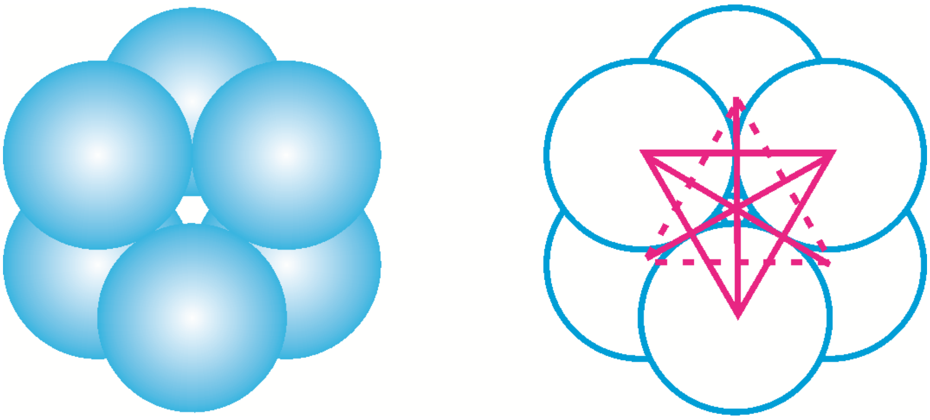

(a) (b)

Fig. 8.8: An octahedral void

A closer look at the second layer reveals that it has a series of regularly placed tetrahedral and octahedral voids marked as ‘t’ and ‘o’ respectively in Fig. 8.9

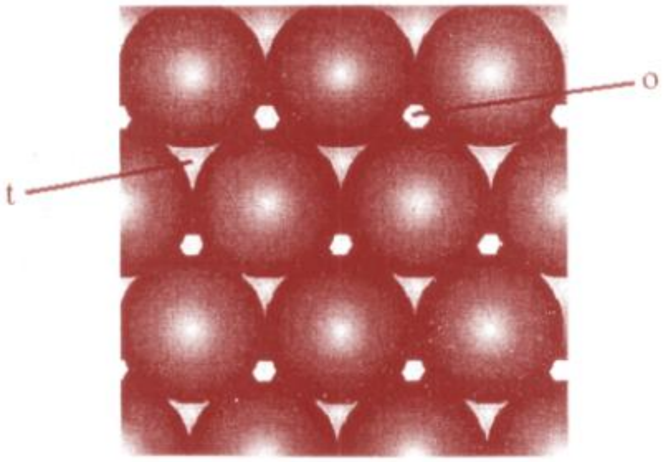


Fig. 8.9: The top view of the second layer showing the tetrahedral and octahedral voids

Now when we place the third layer over the second layer, again there are two possibilities i.e., either the tetrahedral or the octahedral voids of the second layer are occupied. Let us take these two possibilities. If the tetrahedral voids of the second layer are occupied then the spheres in the third layer would be exactly on top (i.e., vertically aligned) of the first or A layer the next layer (4th layer) which is then placed would align with the B layer. In other words, every alternate layer will be vertically aligned. This is called AB AB……. pattern or AB AB…. repeat. On the other hand, if the octahedral voids of the second layer are occupied, the third layer is different from both the first as well as the second layer. It is called the C layer. In this case the next layer, i.e., the fourth layer, howsoever it is placed will be aligned with the first layer. This is called ABC ABC... pattern or ABC ABC... repeat. In three dimensional set up the AB AB... pattern or repeat is called **hexagonal closed**

packing (hcp) (Fig. 8.10 (c)) while the ABC ABC…... pattern or repeat is called **cubic closed packing**(ccp) (Fig. 8.10 (a)).

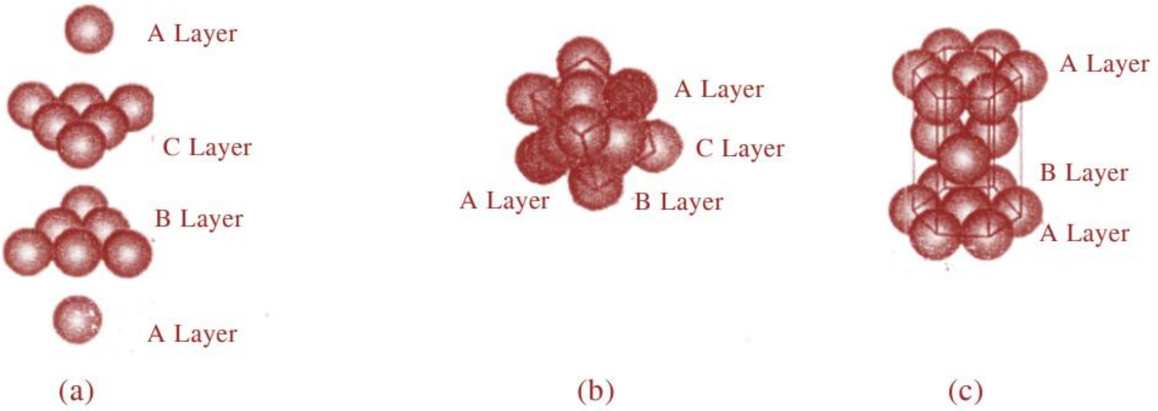


Fig. 8.10 : a) Cubic closed packing (ccp) as a result of ABC pattern of close packed spheres: b) the layers in a) tilted and brought closer to shows fcc arrangement c) hexagonal closed packing (hcp) as a result of ABAB pattern of close packed spheres.

This process continues to generate the overall three-dimensional packed structure. These three-dimensional structures contain a large number of tetrahedral and octahedral voids. In general there is one octahedral and two tetrahedral voids per atom in the close packed structure. These voids are also called as interstices. As mentioned earlier, the identical spheres represent the positions of only one kind of atoms or ions in a crystal structure. Other atoms or ions occupy these interstices or voids.

In the close packed structures (hcp and ccp) discussed above each sphere is in contact with six spheres in its own layer (as shown in Fig. 8.5) and is in contact with three spheres each of the layer immediately above and immediately below it. That is each sphere is in contact with a total of twelve spheres. This number of nearest neighbours is called its **coordination number**. The particles occupying the interstices or the voids will have a coordination number depending on the nature of the void. For example, an ion in a tetrahedral void will be in contact with four neighbours i.e., would have a coordination number of four. Similarly, the atom or ion in an octahedral void would have a coordination number of six.

Intext Questions 8.2

1. What is the difference between the square close packed and hexagonal close packed structures?

....

2. Which of the above two, is more efficient way of packing?

....

3. Clearly differentiate between, triagonal, tetrahedral and octahedral voids.

....

8.5 Crystal Lattices and Unit Cells

You know, the crystalline solids have long-range order and the closely packed constituent particles are arranged in an ordered three-dimensional pattern. The structure of the crystalline solids can be represented as an ordered three-dimensional arrangement of points. Here each point represented the location of a constituent particle and is known as lattice point and such an arrangement is called a crystal lattice or space lattice or simply a lattice.

To understand the meaning or the term lattice let us first take a repetitive pattern in two dimensions. In the crystal structure of sodium chloride in two dimensions the Na^+ and Cl^- ions are arranged in an ordered fashion as shown in Fig. 8.11 (a). If the position of each ion is represented as a point, then the same crystal can be represented as an array of such points in two dimensions (Fig. 8.11 (b)). It is called a two-dimensional lattice.

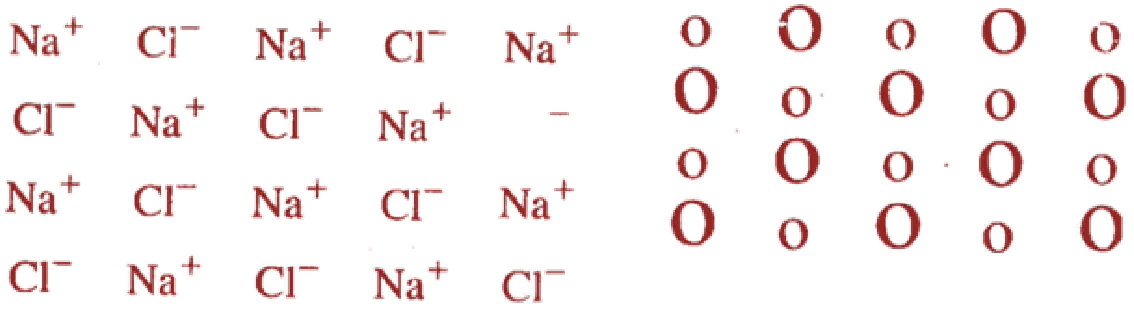


Fig. 8.11: a) A two dimensional arrangement of ions in sodium chloride (b)the lattice corresponding to the arrangement of ions in (a)

Similarly, in three dimensions, the crystal structure of a solid is represented as a three-dimensional array of lattice points. Remember that the lattice points represent the positions of the constituent particles of the solid (Fig. 8.12).

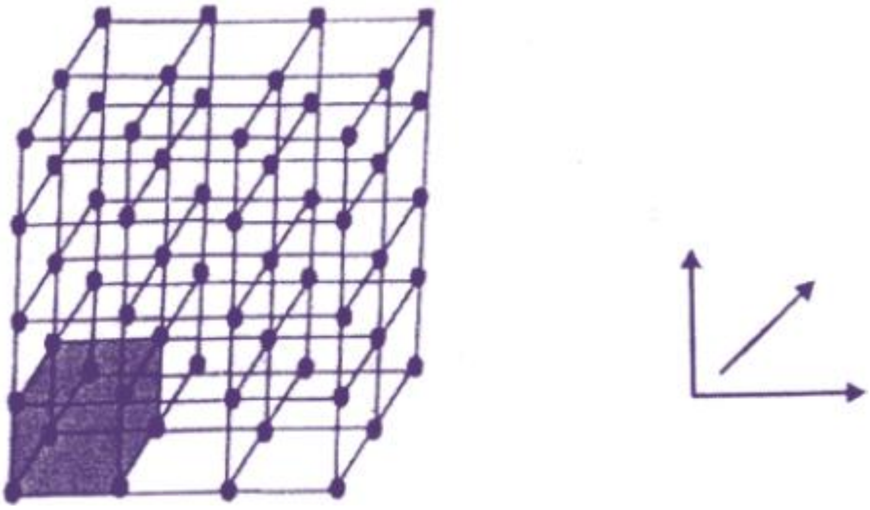


Fig. 8.12: Schematic representation of a three dimensional crystal lattice.

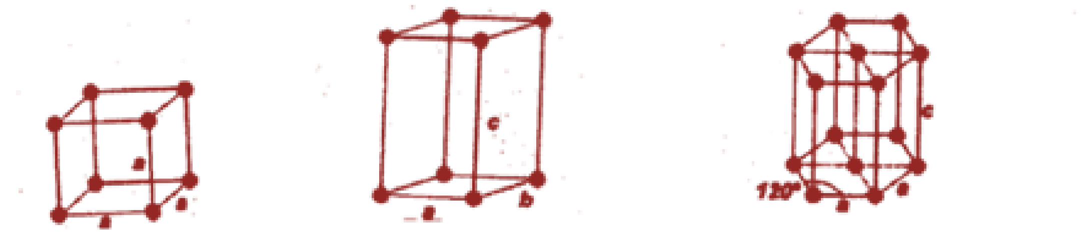
In a crystal lattice we can select a group of points which can be use to generate the whole lattice. Such a group is called repeat unit or the unit cell of the crystal lattice. The shadded region in the Fig. 8.12, represent a unit cell of the crystal lattice. The unit cell is characterized by three distances along the three edges of the lattice and the angles between them as shown in the figure. We can generate the whole crystal lattice by repeating the unit cell in the three directions. On the basis of the external appearance the known crystals can be classified into seven types. These are called crystal systems. In terms of the internal structure also the crystal lattices contain only seven types of unit cells. The seven crystal systems and the definition of their unit cells in terms of their unit distances and the angles are compiled in Table 8.2, the seven simple unit cells are given in Fig. 8.13

Table 8.2: The seven crystal systems and their possible lattice types

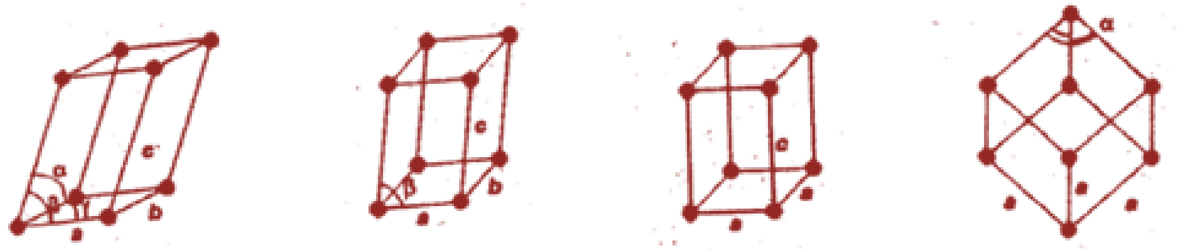
Systems	Axes	Angles	Possible lattice types
Cubic	$a = b = c$	$a = \beta = \gamma = 90^0$	P, F, I
Tetragonal	$a = b \neq c$	$a = \beta = \gamma = 90^0$	P, I
Orthorhombic	$a \neq b = c$	$a = \beta = \gamma = 90^0$	P, F, I, C
Rhombohedral	$a = b = c$	$a = \beta = \gamma \neq 90^0$	P
Hexagonal	$a = b \neq c$	$a = \beta = 90^0$; $\gamma = 120^0$	P
Monoclinic	$a \neq b = c$	$a = \gamma = 90^0$; $\beta \neq 90^0$	P, I
Triclinic	$a \neq b \neq c$	$a \neq \beta \neq \gamma \neq 90^0$	P

** P = primitive, I = body centered, F = face centered and C = side centered*

The unit cell shown in Fig. 8.12 and the ones given in Fig. 8.13 have the lattice points at the corners only.



Cubic Orthorhombic Hexagonal



Triclinic Monoclinic Tetragonal Rhombohedral

Fig. 8.12.a: The primitive unit cells; the relative dimensions of the three repeat distances (a, b and c) and the angles between them (α, β and γ) are given in Table 8.2

Such unit cells are called primitive (P) unit cells. Sometimes, the unit cell of crystal contains lattice point(s) in addition to the ones at the corners. A unit cell containing a lattice point each at the centers of its faces in addition to the lattice points at the corners is called a **face centered** (F) unit cell. On the other hand, a unit cell with lattice points at the center of the unit cell and at the corners is called a body centered unit cell (I). In some cases, in addition to the lattice points at the corners there are two lattice points located at the centers of any two opposite faces. These are called as **end centered** (C) unit cells. The possible lattice types in different crystal systems are also indicated in Table 8.2 The seven crystal systems when combined with these possibilities give rise to 14 lattice types. These are called **Bravais lattices.**

X-Ray diffraction of Crystals (X-rays and Crystal system)

The arrangement of particles in solid structures is determined by x-ray diffraction and to a lesser extent by electron diffraction. These processes are based on the fact that both x-rays and electrons have wave lengths which are of the same order as interatomic distances (10^{-10} m) and so crystals may be used as diffraction grating for them. The fundamentals of x-rays are discussed below.

X-ray diffraction

Bragg Method: The Bragg's or reflection method gives results which are easier to interpret. X-rays are produced when cathode rays fall on metals. The effect of atomic sized particles on metal is similar to the effect in a pond, a series of ripples (or water waves) are produced when the handful of pebbles thrown into a pond. In a pond, a series of ripples (or water waves) are produced and the crests of some of them will meet and reinforce each other. While some crests will meet through and cancel each other and cause interference. In the same way, two x-ray waves that are in same phase reinforce each other and produce a wave that is stronger than either of the original waves. The resultant wave has greater amplitude than either of the primary waves, but the wave length, **λ**, remains the same. Two x-rays waves that are completely out of phase cancel each other; the resultant has negligible intensity.

In crystals there are regular layers of atoms or ions and it is possible to calculate the conditions under which reinforcement will occur if a beam of x-ray strikes them. When x-rays are diffracted by the layers they behave as if they are being reflected.

Fig. 8.5a illustrates the determination of crystal spacing's by the use of x-rays of a single wave length. The rays impinge upon parallel planes of the crystal at an angle θ, an angle of reflection equals the angle of incidence. Some of the rays are reflected from the upper plane, some from the second plane, and some from the lower planes. A strong reflected beam will result only if the rays are in phase. In the illustration, the ray DFH travels further the ray ABC by an amount equal to EF + FG. These rays will be in phase at CH only if this difference equals a whole number of wave length. Thus EF + FG = nλ.
When 'n' is a single integer.

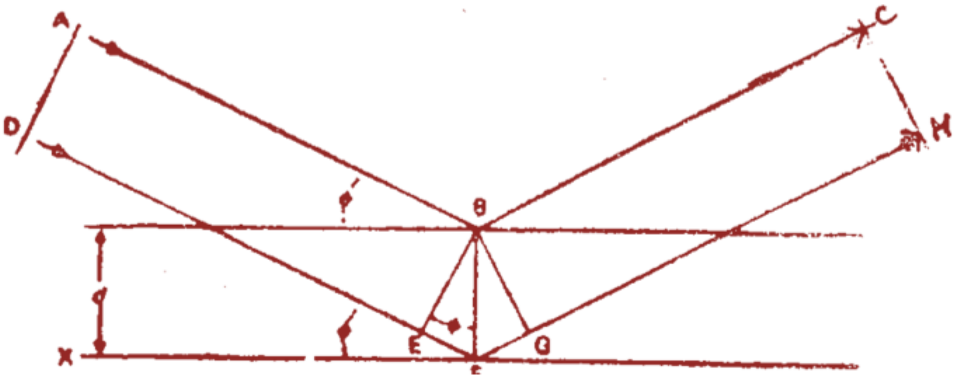


Fig. 8.13: Bragg's method

The line BE is drawn perpendicular to DF. Angle BEF, therefore equals 90°, since the sum of the angles of any triangle equals 180°, the sum of other two angles (EBF and EFB) of the triangle BEF must also equal 90°.
That is:

$$\angle EBF + \angle EFB = 90°$$

Angle XFB is a right angle, and angle XFE is θ, therefore angle EFB is equal to 90°, minus θ, consequently.

$$\angle EBF + (90° - \theta) = 90°$$

and angle EBF equals θ.

The sine of this angle, θ, is equal EF/BF, and since BF is equal to d (the distance between the planes of the crystal).

$\sin\theta = EF/d$ or $EF = d\sin\theta$

Likewise,

$FG = d\sin\theta$

$EF + FG = 2d\sin\theta$ or $n\lambda = 2d\sin\theta$

This equation was derived by William Henry Bragg and his son William Lawrence Bragg. The Bragg equation be rearranged as **$\sin\theta = n\lambda/2d$**

Thus, with x-rays of a definite wave length, reflections of various angles will be observed for a given set of planes with spacing equal to d. These reflections correspond to n = 1, 2, 3 and so as, and are spoken of as first, second, third order and so on. With each successive order, the angle increases, and the intensity of reflected beam weakens.

Sample Problem:

The diffraction of a crystal of barium with x-ray of wave length 2.29 Å gives first order reflection at 27081. What is the distance between the diffracted planes?

Solution:

$n\lambda = 2d\sin\theta$ Bragg's relation

$d = n\lambda/2\sin\theta$

$= (1 \times 2.29 \times 10^{-8}\ \text{cm}) / 2 \times 0.456$ (Since $\sin 27°8` = 0.456$)

$= 2.51 \times 10^{-8}\ \text{cm}$ means $= 2.51$ Å

8.5.1 Cubic Unit Cells

Of the seven crystal systems, let us discuss unit cells belonging to the cubic crystal system in somewhat details. As you can see from Table 8.2 that in the cubic crystal system the three repeat distances are equal and all three angles are right angles. The unit cells of three possible lattice types viz., primitive or simple cubic, body centered cubic and the face centered cubic, belonging to cubic crystal system are shown in Figure 8.14.

(a) (b) (c)

Fig. 8.14: Bragg's method

Number of atoms per unit cell

As you know that in unit cells the atoms can be on the corners, in the body center and on face centers. All the atoms do not belong to a single unit cell. These are shared amongst different unit cells. It is important to know the number of atoms per unit cell. Let us learn how to compute these for different cubic unit cells.

Simple Cubic Unit Cell

The simple or primitive unit cell has the atoms at the corners of the cube (Fig. 8.14 (a)). A lattice point at the corner of the unit cell is shared by eight-unit cells as you can see from the encircled atom in the Fig. 8.15. Therefore, the contribution of an atom at the corner to the unit cell will be 1/8. The number of atoms per unit cell can be calculated as follows:

Number of corner atoms = 8.

Number of unit cells sharing atoms of the corner = 8.

The number of atoms in a simple cubic unit cell = 8 x 1/8 = 1.

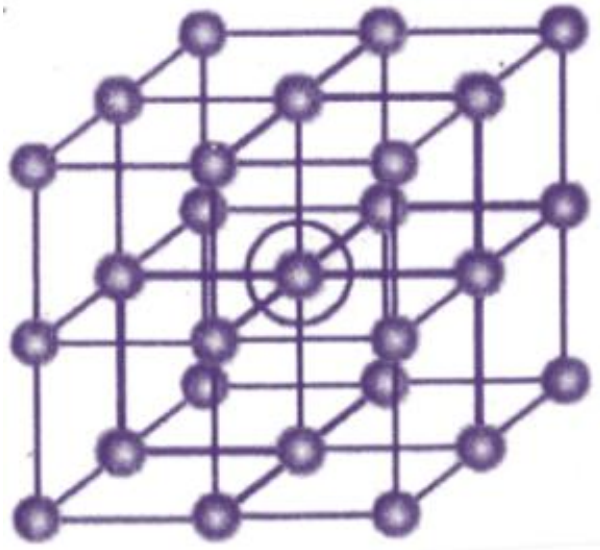


Fig. 8.15: A corner lattice point is shared by eight unit cells

Body Centered Cubic Unit Cell

A body centered cubic (bcc) unit cell has lattice points not only at the corners but also at the center of the cube (Fig. 8.14 (b)). The atom in the center of the cube belongs entirely to the unit cell, i.e., it is not shared by other unit cells. The corner atoms, on the other hand, as in the case of simple cubic unit cell, are shared by eight-unit cells. Thus, the number of atoms per unit cell can be calculated as

Number of corner atoms = 8.

Number of unit cells sharing atoms of the corner = 8.

Contribution to the unit cell = 8 x 1/8 = 1

Number of atoms at the center of the cube = 1.

Contribution to the unit cell = 1 (as it is not shared)

The number of atoms in a body centered cubic unit cell = 1 + 1 = 2

Face Centered Cubic Unit Cell

A face centered cubic (fcc) unit cell has atoms not only at the corners but also at the center of each face. Thus it has eight lattice points at the corners and six at the face centers (Fig. 8.14 (c)). A face centered lattice point is shared by two unit cells, Fig. 8.16. As before,

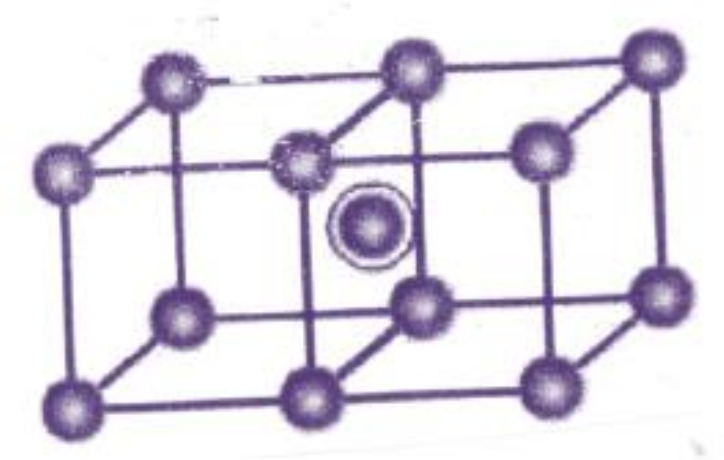


Fig. 8.16: A face centered lattice point is shared by two unit cells

Number of corner atoms = 8.
Number of unit cells sharing these = 8.
Contribution to the unit cell = 8 x 1/8 = 1
Number of atoms at the center = 1.
Number of unit cells sharing a face centered lattice point = 2
Contribution of the face centered atoms to the unit cell = 6 x 1/2 = 3
The number of atoms points in a face centered cubic unit cell = 1 + 3 = 4.

The number of atoms per unit cell in different types of cubic unit cells is given in Table 8.3

Table 8.3: Atoms per unit cell

Simple cubic	1
Body centered cubic	2
Face centered cubic	4

8.5.2 Structures of Ionic Solids

In case of ionic solids that consist of ions of different sizes, we need to specify the positions of both the cations as well as the anions in the crystal lattice. Therefore, structure adopted by an ionic solid depends on the relative sizes of the two ions. In fact, it depends on the ratios of their ratios of their radii called radius ratio. Here r + is the radius of the cation and r- is that of the anion. The radius ratios and the corresponding structures are compiled in Table 8.4.

Table 8.4: The radius ratios (r + / r-) and the corresponding structures

Radius ratio (r + /r-)	Coordination number	Structure adopted
0.225-0.414	4	Tetrahedral
0.414-0.732	6	Octahedral
0.732-0.91	8	Body centered cubic
> = 1.00	12	Close Packed structure

The common ionic compounds have the general formulae as MX, MX2 and MX3 where M represents the metal ion and X denotes the anion. We would discuss the structures of some ionic compounds of MX and MX2 types.

8.5.2.1 Structures of the Ionic Compounds of MX Type

For the MX type of ionic compounds three types of structures are commonly observed. These are sodium chloride, zinc sulphide and caesium chloride structures. Let us discuss these in some details.

Caesium Chloride Structure

In CsC1 the cation and the anions are of comparable sizes (the radius ratio = 0.93) and has a bcc structure in which each ion is surrounded by 8 ions of opposite type. The Cs^+ ions is in the body center position and eight Cl^- ions are located at the corners (fig. 8.17) of the cube. Thus, it has a coordination number of 8.

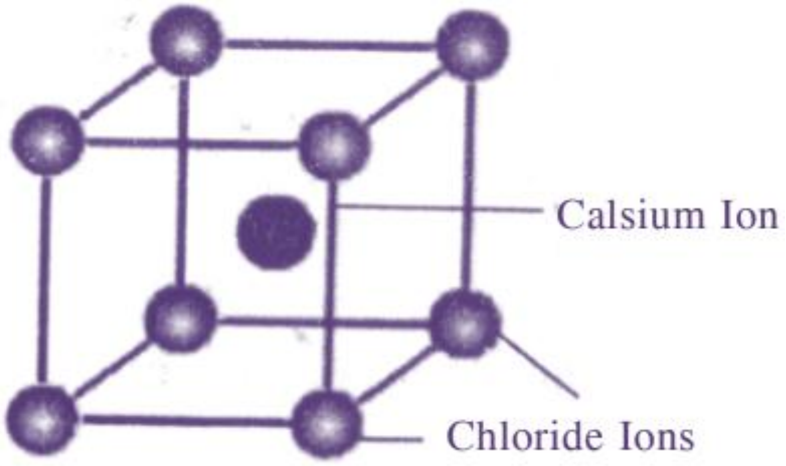


Fig. 8.17: Cesium chloride structure

Sodium Chloride Structure

In case of NaCl the anion (Cl^-) is much larger than the cation (Na^+). It has a radius ratio of 0.52. According to Table 3.3 it should have an octahedral arrangement. In sodium chloride the (Cl^-) form a ccp (or fcc) structure and the sodium ion occupy the octahedral voids. You may visualise the structure having chloride ions at the corners and the face centers and the sodium ions at the edge centers and in the middle of the cube (Fig. 8.18).

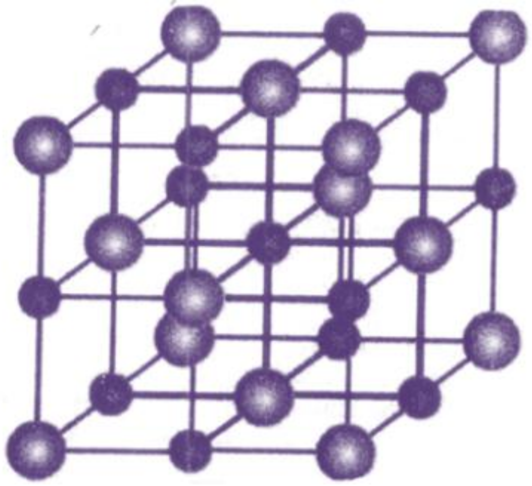


Fig. 8.18: Sodium Chloride structure

Zinc Sulphide Structure

In case of zinc sulphide, the radius ratio is just = 0.40. According to Table 3.3 it should have a tetrahedral arrangement. In Zinc sulphide structure, the sulphide ions are arranged in a ccp structure. The zinc ions are located at the corners of a tetrahedron, which lies inside the cube as shown in the Fi.g 8.19. These occupy alternate tetrahedral voids.

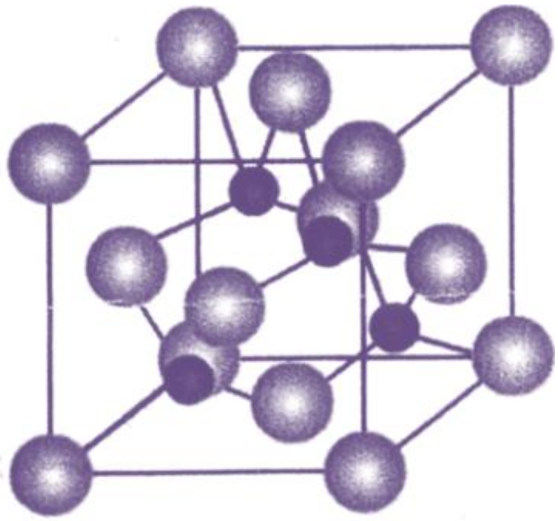


Fig. 8.19: Zinc Sulphide structure

Calcium flouoride or fluorite structure

In this structure the Ca^{2+} ions form a fcc arrangement and the fluoride ions are located in the tetrahedral voids (Fig. 8.20).

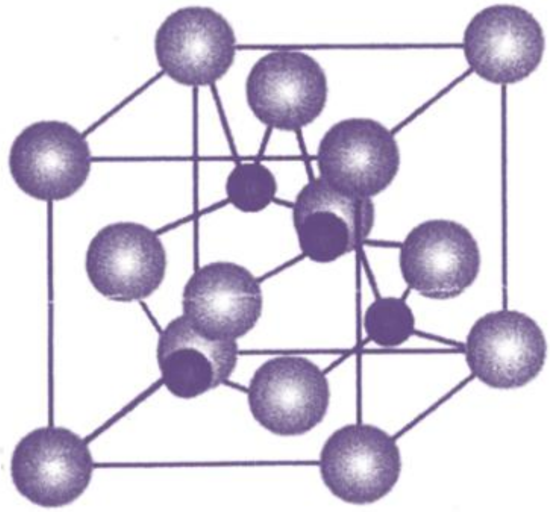


Fig. 8.20: Calcium fluoride or Fluorite structure; calcium ions occupy the corners of the cube and face centers the F^- ions are on the corners of the smaller cube.

Antifluorite Structure

Some of the ionic compounds like Na_2O have antifluorite structure. In this structure the positions of cations and the anions in fluorite structures are interchanged. That is why it is called anti fluorite structure. In Na_2O the oxide ions form the ccp and the sodium ions occupy the tetrahedral voids (Fig. 8.21).

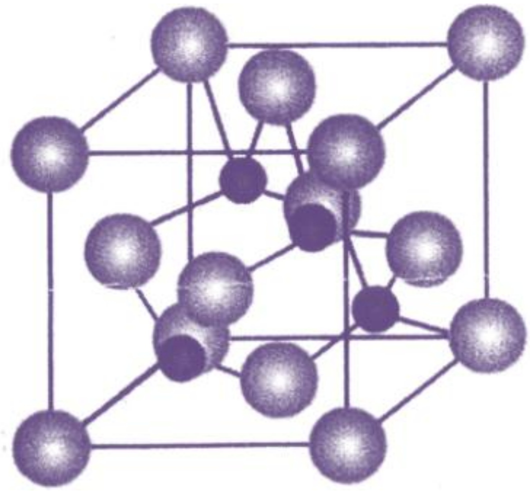


***Fig. 8.21:** Antifluorite structure adopted by Na_2O; The oxide ions occupy the corners of the cube and face centers and the Na+ ions (shown in black) are on the corners of the smaller cube.*

8.6 Defects in Ionic Crystals

You have learnt that in a crystalline solid the constituent particles are arranged in an ordered three-dimensional network. However, in actual crystals such a perfect order is not there. Every crystal has some deviations from the perfect order. These deviations are called imperfections or defects. These defects can be broadly grouped into two types. These are stoichiometric and non-stoichiometric defects depending on whether or not these disturb the stoichiometry of the crystalline material. Here, we would deal only with stoichiometric defects. In such compounds the number of positive and negative ions are in stoichiometry proportions. There are two kinds of stoichiometric defects, these are

- **Schottky defects**
- **Frenkel defects**

Schottky defects:

This type of defect is due to the absence of some positive and negative ions from their positions. These unoccupied lattice sites are called holes. Such defects are found in ionic compounds in which the positive and negative ions are of similar size e.g., NaCl and CsCl. the number of missing positive and negative ions is equal. The presence of Schottky defects decreases the density of the crystal (Fig. 8.22(a)).

Frenkel defects:

This type of defect arises when some ions move from their lattice positions and occupy interstitial sites. The interstitial sites refer to the positions in between the ions. When the ions leave its lattice site a hole is created there. ZnS and AgBr are examples of ionic compounds showing Frenkel defects. In these ionic compounds the positive and negative ions are of quite different sizes. Generally, the positive ions leave their lattice positions, as these are smaller and can accommodate themselves in the interstitial sites. The Frenkel defects do not change the density of the soilds (Fig. 8.22(b)).

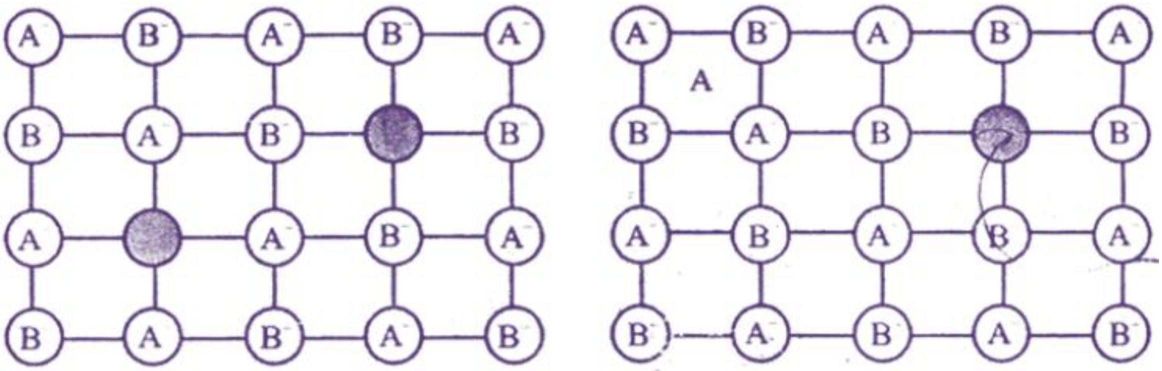


Fig. 8.22: Stoichiometric defects a) Schottky and b) Frenkel defects

These defects cause the crystal to conduct electricity to some extent. The conduction is due to the movement of ions into the holes. When an ion moves into a hole it creates a new hole, which in turn is occupied by another ion, and the process continues.

Intext Questions 8.3

1. What do you understand by crystal lattice?

....

2. What is a unit cell?

....

3. How many atoms are there in a fcc unit cell?

....

8.7 Treatment of metallic bond (elementary ideas)

The bonding in metals and their alloys is not completely understood. And therefore, structures are also not fully, realized. Any theory that is proposed for the bonding in metals must be capable of explaining the following.

- i) Bonding between atoms of the same element (identical atoms) and also between atoms of widely differing metals as well as bonding in alloys.
- ii) Should not involve directional bonding.
- iii) The properties as metals in solutions and in liquid states etc.
- iv) The mobility of electrons.

Various theories of bonding in metals have been suggested. The elementary ideas about these are given in the section that follows.

8.7.a Electron sea model :

This theory was initially proposed by Drude in 1900. This was further refined by Lorentz in 1923. This theory is also known as Drude - Lorentz theory.

According to this theory:

- i) A metal lattice comprises of rigid spheres of metal ions.
- ii) Each metal atom contributes its valence electrons to the sea.
- iii) These electrons move freely in the lattice spaces i.e., interstices.

iv) Cohesive forces result from electrostatic attractions between the positive metal ions and the electron cloud.

"The force that binds a metal ion to the mobile electrons within its sphere of influence is known as metallic bond."

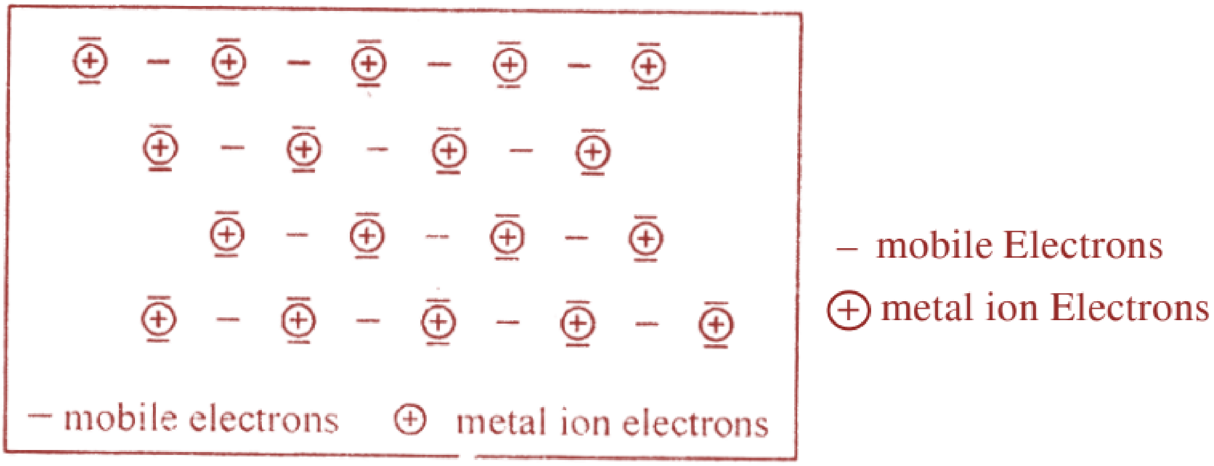


Fig. 8.23: Electron Sea model of a metal

Simply a metal was regarded as an assembly of positive ions immersed in a sea or pool of valence electrons. This theory explains qualitatively the model of a metal lattice but fails to explain quantitative calculations for lattice energies of ionic compounds.

8.7. b Valence bond theory of metals:

The theory was proposed by Linus Pauling 1937. This theory also referred to as Resonance theory. According to this theory the metallic bond, is essentially a polar or a non-polar covalent bond. This covalent bond involves resonance, between a number of structures, having one electron and electron pair bonds. As there is a possibility of insufficient valence electrons for the formation of electron pair bonds with each atom of the metal, it is assumed that resonance takes place throughout the solid metal. This resonance not only involves covalent bonds but also ionic linkages. The atoms undergo hybridization. For example, the resonance structure of sodium metal is represented taking four Na atoms only Fig 8.24

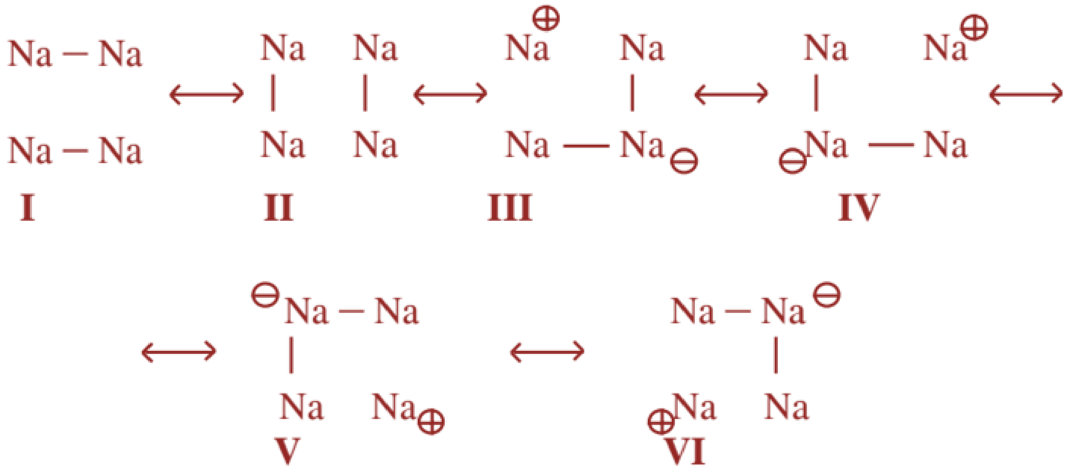


Fig. 8.24: Resonance structure of sodium metal

This theory does not explain the conduction of the heat in solids or their luster or the reflection of the metallic, properties either in the liquid state or in the solution.

What You Have Learnt

- In solid state the constituent particles are arranged in a closely packed ordered arrangement with almost no free space. These are held together by strong forces of attraction and vibrate about their fixed positions. Solids are incompressible and rigid and have definite shapes.
- Solids are classified into amorphous and crystalline solids. The crystalline solids have long range order while amorphous solids have only short-range order.
- The crystalline solids can be classified into four different types-ionic, molecular, covalent and metallic solids on the basis of nature of forces of attraction between the constituent particles.
- The temperature at which a solid melt to give a liquid is called its melting point.
- The crystal structure of the solids can be described in terms of a close-packing of identical spheres.
- In three dimensions there are two ways of packing identical spheres. These are hexagonal closed packing (hcp) and cubic closed packing (ccp). The hcp arrangement is obtained by ABAB repeat of the two-dimensional layers whereas the ccp arrangement is obtained by ABCABC repeat.
- The three-dimensional internal structure of a crystalline solid can be represented in terms of a crystal lattice in which the location of each constituent particle is indicated by a point.
- The whole crystal lattice can be generated by moving the unit cell in the three directions.
- On the basis of the external appearance the known crystals can be classified into seven types called crystal systems.
- The unit cells of cubic crystal system have three possible lattice types. These are simple cubic, body centered cubic and the face centered cubic.
- The atoms at the corner of a cubic unit cell are shared by eight-unit cells while a face centered atom is shared by two unit cells. The atom at the body center, on the other hand is exclusive to the unit cell as it is not shared.
- The number of atoms per unit cell for the simple cubic, bcc and fcc unit cells are 1.2 and 4 respectively.
- The structure adopted by an ionic solid depends on the ratios of their radii (r^+/r^-) called radius ratio.
- The structures of some simple ionic solids can be described in terms of ccp of one type of ions and the other ions occupying the voids.
- Actual crystals have some kind of imperfections in their internal structure. These are called defects.
- There are two types of defects called stoichiometric and non-stoichiometric defects depending on whether or not these disturb the stoichiometry of the crystalline material.
- There are two kinds of stoichiometric defects, these are called Schottky defects and Frenkel defects.

Terminal Exercise

1. Outline the differences between a crystalline and an amorphous solid.
2. How can you classify solids on the basis of the nature of the forces between the constituent particles?
3. What do you understand by the melting point of a solid? What information does it provide about the nature of interaction between the constituent particles of the solids?
4. What do you understand by coordination number? What would be an ion occupying a/n octahedral void?
5. Explain the following with the help of suitable examples.

a) Schottky defect
b) Frenkel defect

Answers to Intext Questions

8.1

1. Solids have definite shape and definite volume. Liquids have indefinite shape but define volume. gases have indefinite shape and indefinite volume.
2. Coulombic forces, dipole-dipole attractions, covalent bonding and metallic bonding.
3. Irrespective of the size and shape of the crystal of a substance, the interfacial angle between a pair of faces is always the same.

8.2

1. Refer to section 8.4
2. Hexagonal close packed
3. Refer to sections 8.4

8.3

1. Ordered three dimensional arrangements of points representing the location of constituent particles.
2. A select group of points which can be used generate the whole lattice. Unit cell is characterised by three edges of the lattice and angles between them.
3. Four.

Chapter 09

SOLUTIONS

You know that when sugar or salt is added to water, if dissolves. The resulting mixture is called a solution. Solutions play an important role in our life. In industry, solutions of various substances are used to carry out a large number of chemical reactions.

Study of solutions of various substances is very interesting.

In this lesson, let us learn about the various components of a solution and the ways in which concentration of solutions is expressed. We shall also learn about some properties of solutions which are dependent only on the number of solute particles. (You will learn about solute in this lesson).

Objectives

After reading this lesson, you will be able to:

- identify the components of different types of solution;
- express the concentration of solutions in different ways;
- list different types of solutions;
- state Henry's law;
- define vapour pressure;
- state and explain Raoult's law for solutions;
- define ideal solutions;
- give reasons for non-ideal behavior of solutions;
- state reasons of positive and negative deviations from ideal behavior;
- explain the significance of colligative properties;
- state reasons for the elevation of boiling point and depression in freezing point of solutions;
- explain the abnormal colligative properties;
- define osmosis and osmotic pressure;
- define Van't Hoff factor;
- correlate the degree of dissociation of solute and
- solve numerical problems.

9.1 Components of a Solution

When we put sugar into water, it dissolves to form a solution. We do not see any more sugar in it. Like sugar, a large number of other substances such as common salt, urea, potassium chloride etc dissolve in water forming solution. In all such solutions, water is the solvent and substances which dissolve are the solutes.

Thus, solute and solvent are the components of a solution. Whenever a solute mixes homogeneously with a solvent, a solution is formed.

solution + solvent → solution

A solution is a homogeneous mixture of two more substances.

Solvent is that component of a solution that has the same physical state as the solution itself.

Solute is substance that is dissolved in a solvent to form a solution.

9.1.1 The Concentration of a Solution

Some of the properties of solutions, *e.g.*. The sweetness of a sugar solution or the colour of a dye solution, depends on the amount of solute compared to that of the solvent in it. This is called the solution concentration. There are several ways for describing concentration of solution. They include molarity, molality, normality mole fraction and mass percentage.

Molarity: Molarity is defined as the number of moles of solute dissolved per litre of solution and is usually denoted by **M**. It is expressed as:

$$M = \frac{n}{v}$$

Where n is the number of moles of solute and V is the volume of the solution in litres. A 2.0 molar solution of sulphuric acid would be labeled as 2.0 M H_2SO_4. It is prepared by adding 2.0 mol of H_2SO_4 to water to make a litre of solution. Molarity of a solution changes with temperature because of expansion or contraction of the solution.

Molality: It is defined as the number of moles of solute dissolved per kilogram of solvent. It is designated by the symbol **m**. The label 2.0m H_2SO_4 is read "2 mole l sulphuric acid" and is prepared by adding 2.0 mol of H_2SO_4 to 1 kg of solvent.

Molality is expressed as: $$m = \frac{1000n_B}{W_A}$$

Where n_B is the number of moles of the solute and W_A is the mass in grams of solvent. The molality of a solution does not change with temperature.

Example 9.1: Find out the molarity of the solution which contains 32.0 g of methyl alcohol (CH_3OH) in 200 mL solution.

Solution: Molar mass of CH_3OH = 12 + 1 x 3 + 16 + 1 = 32 g mol^{-1}

$$\text{Number of moles of } CH_3OH = \frac{32}{32\text{ g mol}^{-1}} = 1\text{ mol}$$

Volume of the solution = 200 mL = 0.2 litre

$$\therefore \text{Molarity} = \frac{\textit{No. of moles of solute}}{\textit{Volume of solution in litres}} = \frac{1}{0.2} = 5\text{ M}$$

Example 9.2: What is the molality of a sulphiric acid solution of density 1.20 g/cm^3 containing 50% sulphuric acid by mass.

Solution: Mass of 1cm^3 of H_2SO_4 solution = 1.20 g
Mass of 1 litre (1000 cm^3) of H_2SO_4 solution = 1.20 x 1000 = 1200 g Mass of H_2SO_4 in 100 g solution of H_2SO_4 = 50 g

$$\text{Mass of } H_2SO_4 \text{ in 1200 g solution } H_2SO_4 = \frac{50}{100} \times 1200 = 600 \text{ g}$$

∴ Mass of water in the solution = 1200 - 600 = 600 g
Molar mass of H_2SO_4 = 98 g mol^{-1}

$$\text{No. of moles of } H_2SO_4 = \frac{\textit{Mass in grams}}{\textit{Molar mass}} = \frac{600 \text{ g}}{98 \text{ g mol}^{-1}}$$

$$\text{Molarity} = \frac{\textit{No. of moles of } H_2SO_4}{\textit{Mass of water in grams}} \times 1000$$

$$= \frac{600}{98} \times \frac{1}{600} \times 1000 = 6.8 \text{ m}$$

Normality: Normality is another concentration unit. It is defined as the number of gram equivalent weights of solute dissolved per litre of the solution.

The number of parts by weight of a substance (element of compound) that will combine with or displace, directly or indirectly 1.008 parts by weight of hydrogen, 8 parts by weight of oxygen and 35.5 parts by weight of chlorine is known as equivalent weight. Like atomic weight and molecular weight, equivalent weight is also a number and hence no units are used to express it. However, when equivalent weight is expressed in grams, it is known as gram equivalent weight of the substance.

$$\textbf{Equivalent weight} = \frac{\text{Atomic or molecular weight}}{\text{Valency}}$$

$$\textbf{Equivalent weight} \text{ of an acid} = \frac{\text{Molecular weight}}{\text{Basicity}}$$

$$\textbf{Equivalent weight} \text{ of a base} = \frac{\text{Molecular weight}}{\text{Acidity}}$$

$$\textbf{Equivalent weight} \text{ of salt} = \frac{\text{Molecular weight}}{\text{Total valency of the metal atom}}$$

Oxidising and reducing agents may have different equivalent weights if they react to give different products under different conditions. Thus, the equivalent weight of such substances can be calculated from the reactions in which they take part.
Normality is denoted by the symbol **N**.

$$\therefore \quad \text{Normality (N)} = \frac{\text{No. of gram equivalent weight of the solute}}{\text{volume of the solution in litres}}$$

$$= \frac{\text{Mass of the solute in grams}}{\text{Equivalent weight of the solute}} \times \frac{1}{\text{volume of the solution in litres}}$$

$$= \frac{\textit{Strength of solution in grams / litre}}{\textit{Equivalent weight of the solute}}$$

The label 0.5 N $KMnO_4$ is read "0.5 normal" and represents a solution which contains 0.5 gram equivalent of $KMnO_4$ per litre of solution.

Mole Fraction: The mole fraction of a component in a solution is the ratio of its number of moles to the total number of moles of all the components in the solution. If a solution contains 2 mol of alcohol and 3 mol of water, the mole fraction of alcohol is 2/5, and that of water 3/5. The sum of mole fractions of all the components of a solution is equal to one. The mole fraction (X_A) of a component A in solution with B is:

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

Where n_A and n_B are the number of the moles of A and B respectively.

Mass Percentage: Mass percentage is the mass of solute present in 100 g of solution. Thus 5% solution of $KMnO_4$ in water means that 5 g of $KMnO_4$ is present in 100g of the aqueous solution of $KMnO_4$.

Example 9.3: A solution contains 36.0 g water and 46.0 g ethyl alcohol (C_2H_5OH). Determine the mole fraction of each component in the solution.

Solution: Molar mass of water = 18 g mol^{-1}

$$\text{Number of moles of water} = \frac{36\ \text{g}}{18\ \text{g mol}^{-1}} = 2.0\ \text{mol}$$

$$\text{No. of moles of } C_2H_5OH = \frac{46\ \text{g}}{46\ \text{g mol}^{-1}} = 1.0\ \text{mol}$$

$$\text{Total number of moles in the solution} = 2.0 + 1.0 = 30$$

$$\text{Mole fraction of water} = \frac{\text{No. of moles of water}}{\text{Total no. of moles in the solution}} = \frac{2.0}{3.0} = 0.67$$

$$\text{Mole fraction of } C_2H_5OH = \frac{\text{No. of moles of } C_2H_5OH}{\text{Total no. of moles in the solution}} = \frac{1.0}{3.0} = 0.33$$

Example 9.4: Calculate the normality of a solution of NaOH if 0.4 g of NaOH is dissolved in 100 ml of the solution.

Solution: Mass of NaOH present in 100 mL of the solution = 0.4 g

$$\therefore \text{Mass of NaOH present in 1000 mL of the solution} = \frac{0.4}{100} \text{ x } 1000 = 4.0\text{g}$$

Mol. wat. of NaOH = 23 + 16 + 1 = 40amu

$$\text{Eq. wt. of NaOH} = \frac{\text{Mol. Wt.}}{\text{Acidity}} = \frac{40}{1} = 40$$

$$\therefore \text{Normality} = \frac{\text{Strength in g/litre}}{\text{Eq. wt.}} = \frac{4}{100} = \frac{1}{10}\text{N}$$

$$\text{Hence, the normality of the solution} = \frac{1}{10}\text{N or } 0.1\text{ N}$$

Intext Questions 9.1

1. List the various methods of expressing the concentration of a solution?

....
.....

2. Define the following?

i) Molarity ii) Molality iii) Normality

....
.....

9.2 Types of Solution

Solutions can be solid, liquid or gaseous. Depending upon the physical state of the solute and the solvent, there are nine possible types of solutions consisting of two components (binary solutions). Different types of solutions are given in Table 9.1.

Table 9.1 Different types of Solutions

Solute	Solvent	Solution
Gas	Gas	Air
Gas	Liquid	Soda Water
Gas	Solid	Hydrogen in palladium
Liquid	Gas	Humidity in air
Liquid	Liquid	Alcohol in water
Liquid	Solid	Mercury in gold
Solid	Gas	Camphor in air
Solid	Liquid	Sugar in water
Solid	Solid	Alloys such as brass (zinc in copper) and bronze (tin in copper)

Generally, we come across only the following three types of solutions:

(a) Liquids in Liquids: In the solution of liquids in liquids such as alcohol in water, the constituent present in smaller amounts is designated as solute and the constituent present in larger amounts is called the solvent. When two liquids are mixed, three different situations may arise:

i. Both the liquids are completely miscible, i.e., when, two liquids are mixed, they dissolve in each other in all proportions, e.g., alcohol and water, benzene and toluene.
ii. The liquids are partially miscible, i.e., they dissolve in each other only to a certain extent, e.g., water and phenol.
iii. The liquids are immiscible, i.e., they do not dissolve in each other, e.g., water and benzene, water and toluene.

The solubility of liquids in liquids generally increases with rise in temperature.

(b) Gases in Liquids: Gases are generally soluble in liquids. Oxygen is sufficiently soluble in water, which allows the survival of aquatic life in ponds, rivers and oceans. Gases like CO2 and NH_3 are highly soluble in water. The solubility of a gas in a liquid depends on the pressure, temperature and the nature of the gas and the solvent. These factors are discussed below in detail:

i. **Effect of Pressure:** The variation of solubility of a gas in a liquid with pressure is governed by Henry's law. Henry's law states that the mass or mole fraction, of a gas dissolved in a solvent is directly proportional to the partial pressure of the gas.

Henry's law is represented by

$$x = Kp$$

Where K is a constant, p is the partial pressure of the gas and x is the mole fraction of the gas in the solution. Let us now see what are the conditions for the validity of Henry's law.

(i) **Conditions for validity of Henry's law:** It is found that gases obey Henry's law under the following conditions.

  i. the pressure is not too high.
  ii. the temperature is not too low.
  iii. the gas does not dissociate, associate or enter into any chemical reaction with the solvent.

(ii) **Effect of temperature:** The solubility of gas in a liquid at constant pressure decreases with rise in temperature. For example, the solubility of CO_2 in **water** at 20^0C is 0.88 cm^3 per cm^3 of water, where as it is 0.53 cm^3 per cm^3 of water at 40^0C. This happens because on heating a solution, containing a dissolved gas, some gas is usually expelled from the solution.

(iii) **Effect of the nature of the gas and the solvent:** Gases like CO_2, HCl and, NH_3 are highly soluble in water where as H_2, O_2 and N_2, are sparingly soluble.

(c) Solids in liquids: When a solid is dissolved in a liquid, the solid is referred as the solute and the liquid as the solvent. For example, in a solution of sodium chloride in water, the solute is sodium chloride and water is the solvent. Different substances dissolve to different extent in the same solvent.

9.3 Vapour Pressure

If we keep an inverted beaker over a small beaker containing a pure liquid, it is found that the molecules of the liquid start evaporating in the form of vapours and fill the empty space above the beaker containing the liquid. A time comes when the number of molecules evaporating per unit time is equal to the number of molecules condensing during that time (Fig 9.1). Equilibrium is thus established between the vapour and the liquid phase. The pressure exerted by the vapour of the liquid in such a case is called the vapour pressure of the liquid.

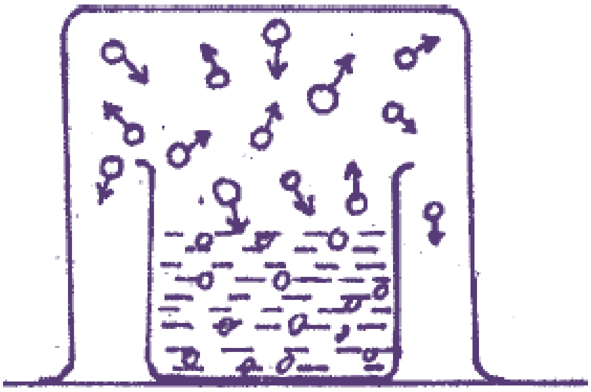


Fig. 9.1: *Vapour pressure of a liquid*

9.4 Raoult's Law for Solutions

Did you ever think that if you mix two miscible volatile liquids A and B, what would be the vapour pressure of the resulting solution? The relationship between vapour pressure of liquid and its mole fraction is given by Raoult's law.

Raoult's law states that for a solution of volatile liquids, the partial vapour pressure of each liquid in the solution is directly proportional to its mole fraction.

Raoult's law is applicable only if the liquids are miscible. The vapour phase now consists of vapour of both the liquids A and B. The partial vapour pressure of each liquid will depend upon its mole fraction in the solution. Let the mole fractions of the liquids A and B be X_A and X_B respectively. Aslo, if P_A and P_B are the partial vapour pressures of A and B respectively, then

$$P_A \propto X_A \quad or \quad P_A = P^O_A \; X_A$$

Similarly, $$P_B = P^O_B \; X_B$$

where P^O_A and P^O_B represent the vapour pressures of pure liquids A and B respectively.

If the values of P_A and P_B are plotted against the values of X_A and X_B for a solution, two straight lines are obtained as shown in Fig. 9.2 the total vapour pressure P of the solution is given by the sum of partial vapour pressures P_A and P_B.

Thus, $$P = P_A + P_B$$

or $$P = P^O_A X_A + P^O_B X_B$$

The total vapour pressure (P) of a solution is represented by the line joining P^O_A and P^O_B. The solutions which obey Raoult's law are known as **ideal solutions**.

A solution which obeys Raoult's law over the entire range of concentration at all temperatures is called an ***ideal solution***.

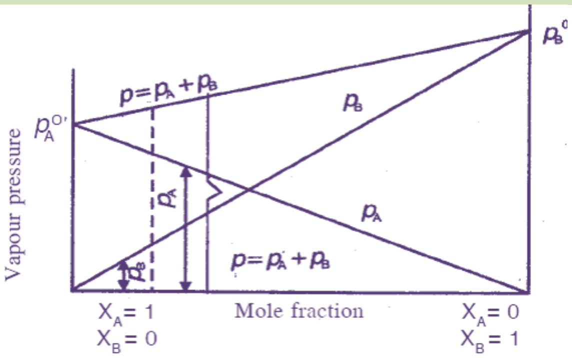


Fig. 9.2: *Relationship between vapour pressure and mole fraction in a solution*

Intext Questions 9.2

1. State Raoult's law.

....
.....

2. State Henry's law and list the conditions necessary for the validity of Henry's law.

....
.....

9.5 Raoult's Law for Solution Containing Non-Volatile Solute

If we have an aqueous solution containing a non-volatile solute, such as sugar or salt, what do you think about the vapour pressure exerted by such a solution? The vapour phase of such a solution consists of vapours of solvent (A) only because the solute is non-volatile. Since the mole fraction of the solvent in solution is less than one, therefore according to Raoult's law, the vapour pressure of the solution will be less than the vapour pressure of the pure solvent. If the total vapour pressure of the solution is p, then

$$P_A = P^O{}_A X_A \qquad (9.1)$$

for a binary mixture

therefore, $X_A + X_B = 1$

$$X_A = 1 - X_B$$

Substituting the value of X_A in equation (9.1) we get

$$P_A = P^O{}_A (1 - X_B)$$

$$\frac{P_A}{P_A^O} = 1 - X_B$$

Therefore $$\frac{P_A^O - P_A}{P_A^O} = X_B$$

In the above equation, $(P^O{}_A - P_A)$ represents the lowering of the vapour pressure and $\frac{P_A^O - P_A}{P_A^O}$ is called the relative lowering of the vapour pressure of the solution.

An alternative statement of Raoult's law for solutions of non-volatile solute is:

The relative lowering of vapour pressure for a solution is equal to the mole fraction of the solute, when only the solvent is volatile.

9.6 Ideal and Non-Ideal Solutions

Ideal solutions *obey Raoult's Law and during their formation there is no change in heat and volume.*

Non-ideal solutions *are those solutions which do not obey Raoult's law and whose formation is accompanied by changes of heat and volume.*

Most of the real solutions are non-ideal. They show considerable deviation from the ideal behaviour. Generally deviations are of two types:

i) Positive deviation: Positive deviations are shown by liquid pairs for which the A-B molecular interactions are weaker than the A-A and or B-B molecular interactions. The total vapour pressure for such solutions is greater than predicted by Raoults law. The total vapour pressure for such a solution will be maximum for a particular intermediate composition (Fig. 9.3). Examples of non-ideal solutions showing positive deviation from the ideal behaviour are mixtures of liquids such as water-propanol, ethanol-chloroform, acetone-carbon disulfide, ethanol-cyclohexane etc.

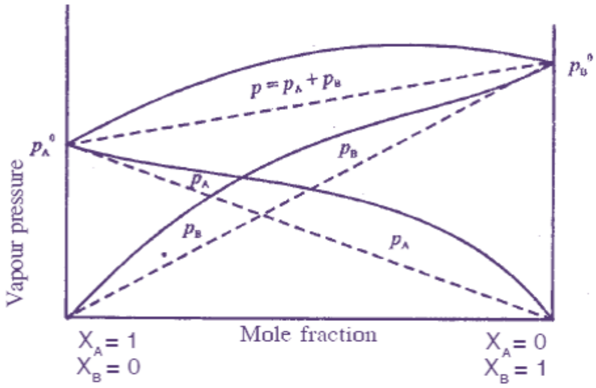


Fig. 9.3: *Positive deviation for a liquid pair*

ii) **Negative Deviation:** Negative deviations are shown by liquid pairs for which the A-B molecular interactions - are stronger than A-A or B-B molecular interactions. The total vapour pressure for such solutions is less than that predicted by Raoult's law. For a particular intermediate composition, the total vapour pressure of such a solution will be minimum (Fig. 9.4). Examples of such liquid pairs are chloroform acetone, water-sulphuric acid, phenol-aniline, water-HCI etc.

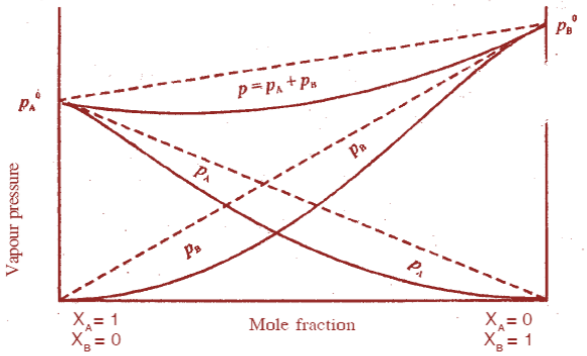


Fig. 9.4: *Negative deviation for a liquid pair*

9.7 Colligative Properties

Do you know that there are certain properties of dilute solutions which depend only on the number of particles of solute and not on the nature of the solvent and the solute? Such properties are called colligative properties. There are four colligative properties: relative lowering of vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure.

We shall discuss these colligative properties in detail in the following sections.

9.7.1 Relative Lowering of Vapour Pressure

According to Raoult's law for solutions containing non-volatile solute

$$\frac{P_A^0 - P_A}{P_A^0} = X_B \qquad \text{(see section 9.5)} \qquad \text{(i)}$$

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

In a dilute solution $n_B << n_A$ Therefore the term n_B can be neglected in the denominator.

Hence, $$X_B = \frac{n_B}{n_A} = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A}} = \frac{W_B.M_A}{W_A.W_B}$$

Therefore equation (i) can be written as

$$\frac{P^0{}_A - P_A}{P^0{}_A} = X_B = \frac{W_B \,.\, M_A}{W_A \,.\, M_B}$$

The above expression can be used to determine the molecular mass of the solute B, provided the relative lowering of vapour pressure of a solution of known concentration and molecular mass of the solvent are known. However, the determination of molecular mass by this method is often difficult because the accurate determination of lowering of vapour pressure is difficult.

Example 9.5: The relative lowering of vapour pressure produced by dissolving 7.2 g of a substance in 100g water is 0.00715. What is the molecular mass of the substance?

Solution: We know that

$$\frac{P^O{}_A - P_A}{P^O{}_A} = \frac{W_B}{M_B} \text{ x } \frac{M_A}{W_A}$$

Substituting the values we get

$$0.00715 = \frac{7.2 \text{ x } 18}{M_B \text{ x } 100} \quad \text{or } M_B = \frac{7.2 \text{ x } 18}{0.00715 \text{ x } 100}$$

∴ Molecular mass of the substance = 181.26 amu

9.7.2 Elevation of Boiling Point

Boiling point of a liquid is the temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure.

As you know, the vapour pressure of a pure solvent is always higher than that of its solution. So, the boiling point of the solution is always higher than that of the pure solvent. If you see the vapour pressure curves for the solvent and the solution (Fig. 9.5), you will find that there is an elevation in the boiling point of the solution.

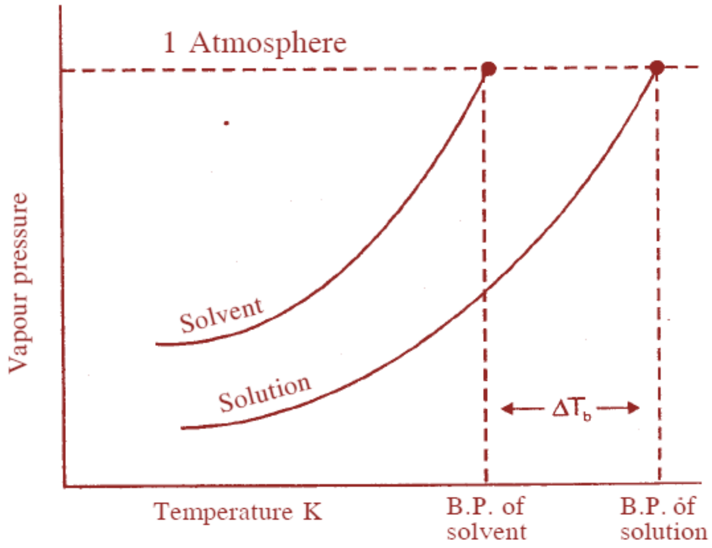


Fig. 9.5: *Vapour pressure curves for solvent and solution*

Now let ΔTb be the elevation in boiling point and □p be the lowering in vapour pressure. Then,

$$\Delta T_b \propto \Delta p \propto X_B \quad \text{or } \Delta T_b = K X_B$$

K is the proportionality constant

As you know $X_B = \frac{n_B}{n_A + n_B}$

In a dilute solution, $n_B << n_A$ and thus the term n_B is neglected in the denominator.

$$\text{Thus, } X_B = \frac{n_B}{n_A} = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A}} = \frac{W_B}{M_3} \text{ x } \frac{M_A}{W_A} = n_B \text{ x } \frac{M_A}{W_A}$$

Substituting the value of X_B in the equation (i) we get

$$\Delta T_b = K \text{ x } n_B \text{ x } \frac{M_A}{W_A}$$

If we take the mass of the solvent WA in kilograms the term $\frac{n_B}{W_A}$ is molality *m*. Thus

$$\Delta T_b = K\, M_A \,.\, m = K_B\, m$$

The constant K_b is called the **molal elevation constant** for the solvent. K_b may be defined as **the elevation in boiling point when one mole of a solute is dissolved in one kilogram of the solvent. K_b is expressed in degree per molality.**

9.7.3 Depression in Freezing Point

Freezing point is the temperature at which the solid and the liquid forms have the same vapour pressure

The freezing point of the solution is always less than that of the pure solvent. Thus, there is a depression in the freezing point of the solution. This is because the vapour pressure of the solution is always less than that of the pure solvent.

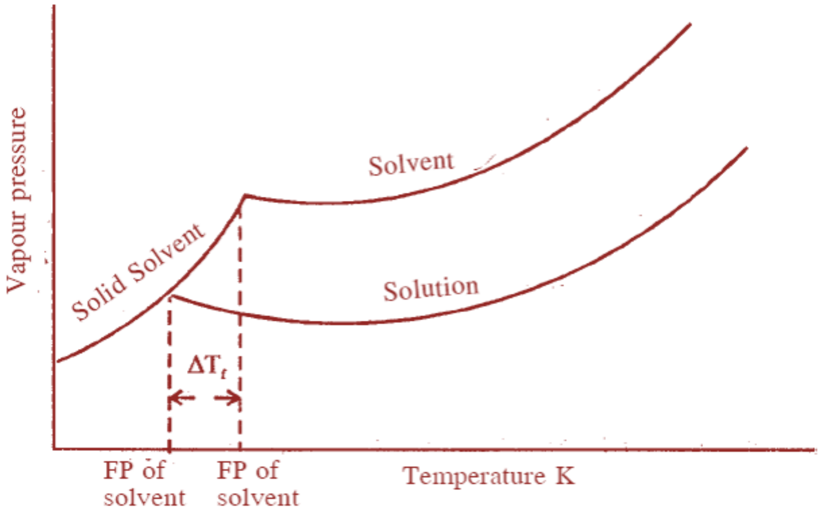


Fig. 9.6: *Vapour pressure curves for solid, solvent and solution*

Let ΔT_f be the depression in freezing point. Then:

$$\Delta T_f \;\alpha\; \Delta X_B$$

or $$\Delta T_f = KX_B \qquad \text{(ii)}$$

Where K the proportionality constant

You know that $X_B = \dfrac{n_B}{n_A + n_B}$

In dilute solution $n_B << n_A$

Therefore, the term *nB* can be neglected from the denominator. Thus,

$$X_B = \frac{n_B}{n_A} = \frac{W_B / M_B}{W_A / M_A} = \frac{W_B}{M_3} \text{x} \frac{M_A}{W_A} = n_B \text{ x } \frac{M_A}{W_A}$$

$$\left(\text{since } n_B = \frac{W_B}{M_B}\right)$$

Substituting the value of X_B in equation (ii) we get

$$\Delta T_f \;\; K \text{ x } n_B \text{ x } \frac{M}{W_A}$$

If the mass of the solvent W_A is taken in kg, then the term $\frac{n_B}{W_A}$ becomes molality *m*.

Thus, $\Delta T_f = K\, M_A .\, m = K_f .\, m$

The constant (K_f) for a solution is known as **molal depression constant or molal cryoscopic constant** for the solvent. K_f may be **defined as the depression in freezing point of a solution when one mole of a solute is dissolved in 1 kilogram of the solvent.**

Example 9.6: Find the (i) boiling point and (ii) freezing point of a solution containing 0.520 g glucose ($C_6H_{12}O_6$) dissolved in 80.2g of water. (K_f = 1.86 K/m, K_b = 0.52 k/m).

Solution: Molality of glucose =

$$= \frac{\text{Wt. of glucose}}{\text{mol. wt.}} \times \frac{1000}{\text{Wt. of solvent}}$$

$$= \frac{0.52}{180} = \frac{1000}{80.2} = 0.036$$

$\Delta T_b = K_b m = 0.52 \times 0.036 = 0.018\ K$

$\therefore$ Boiling point = 373 + 0.018 = 373.018 = 373.02 K

(ii) $K_f = 1.86$ K/m

$$m = \frac{0.52}{180} = \frac{1000}{80.2} = 0.036$$

$\therefore\ \Delta T_f = 1.86 \times 0.036 = 0.66$ K

$\therefore$ Freezing point = 273 - 0.66 = 272.34 K

9.7.4 Osmosis and Osmotic Pressure

You must have observed that if raisins are soaked in water for some time, they swell. This is due to the flow of water into the raisins through its skin which acts as a semi permeable membrane (permeable only to the solvent molecules). This phenomenon is also observed when two solutions of different concentrations in the same solvent are separated by a semi permeable membrane. In this case the solvent flows from a solution of lower concentration to a solution of higher concentration. The process continues till the concentrations of the solutions on both sides of the membrane become equal.

The spontaneous flow of the solvent from a solution of lower concentration (or pure solvent) to a solution of higher concentration when the two are separated by a semi permeable membrane is known as osmosis.

The flow of solvent into the solution of higher concentration from a solution of lower concentration (on pure solvent) can be stopped if some extra pressure is applied to that side of the solution which has a higher concentration. The pressure that just stops the flow of the solvent is called **osmotic pressure**.

Thus, *ostmic pressure may be defined as the excess pressure that must be applied to the solution side to just prevent the passage of pure solvent into it when the two are separated by a perfect semipermeable membrane.* This is illustrated in Fig. 9.7

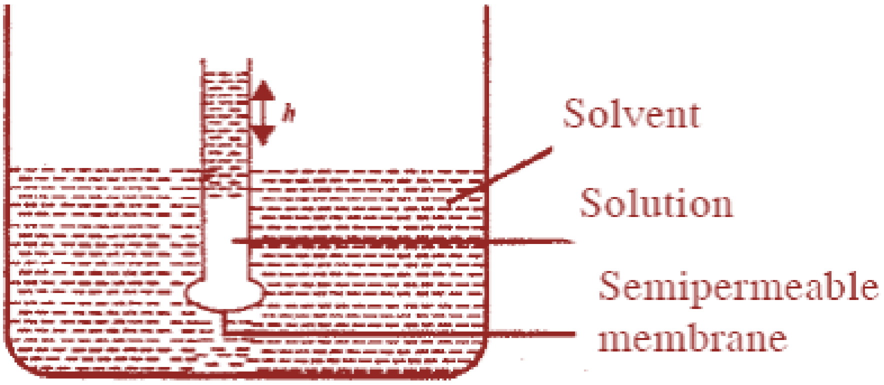


Fig. 9.7: *Osmosis*

The pressure that must be applied to the solution side to prevent it from rising in the tube is the osmotic pressure. It is also equal to the hydrostatic pressure of the liquid column of height.

If the two solutions have the same osmotic pressure, they are known as **isotonic** solutions. The osmotic pressure is a colligative property. It depends on the number of particles of solute present in the solution and not on their nature. At a given temperature T, the osmotic pressure (π) of a dilute solution is experimentally found to be proportional to the concentration of the solution in moles per litre.

Mathematically, $\pi = CRT$

where π is the osmotic pressure and R is the gas constant

or $$\pi = \frac{n_B}{V} RT$$

where n_B is the number of moles of solute present in V litres of the solution

or $$\pi V = \frac{W}{M_{solute}} RT$$

where w in the mass of solute dissolved in V litres of the solution and M_{solute} is the molar mass of the solute. Thus, knowing, π, v and w, the molar mass of the solute can be calculated.

Thus, the molar masses of the solutes can be determined by measuring the osmotic pressure of their solutions. This method has been widely used to determine the molar masses of macromolecules, proteins, etc., which have large molar masses and limited solubility. Therefore their solutions have very low concentrations and the magnitudes of their other colligative properties are too small to measure. Yet their osmotic pressures are large enough for measurements. As the osmotic pressure measurements are done at around room temperature, this method is particularly useful for determining the molar masses of biomolecules as they are generally not stable at higher temperature.

Example 9.7: The osmotic pressure of an aqueous solution of a protein containing 0.63 g of a protein in 100 g of water at 300 K was found to be 2.60 x 10^{-3} atm. Calculate the molar mass of the protein. R = 0.082 L atm K^{-1} mol^{-1}.

we know that osmotic pressure of a solution is given by the expression

$$\pi V = \frac{W}{M_{solute}} RT$$

or $$M_{solute} = \frac{W}{\pi V} RT$$

Substituting the values, we get

$$\text{Msolute} = \frac{(0.63\,\text{g})\,\text{x}\,(0.082\,\text{L} - \text{atm}\,\text{K}^{-1}\,\text{mol}^{-1})\,\text{x}\,(300\,\text{K})}{(2.60\,\text{x}\,10^{-3}\ \text{atm})\,\text{x}\,(0.100\,\text{L})}$$

$$= 61022\ \text{g mol}^{-1}$$

Thus, molar mass of the protein is 61022 g mol^{-1}

Reverse Osmosis and Water Purification

If a pressure higher than the osmotic pressure is applied to the solution side, the direction of flow of the solvent can be reversed. As a result, the pure solvent flows out of the solution through the semi permeable membrane. This process is called reverse osmosis. It is of great practical application as it is used for desalination of sea water to obtain pure water.

9.7.4.a Determination of Relative Lowering of Vapour pressure by Walker and Ostwald's dynamic method.

This method is very simple in which a slow current of dry air is drawn in succession through,

i. A series of two bulbs (A) containing the aqueous soltion (vapour pessure P).
ii. A similar series of two bulbs (B) containing the solvent (vapour pressure PO).
iii. A 'U' tube containing anhydrous $CaCl_2$ solid.

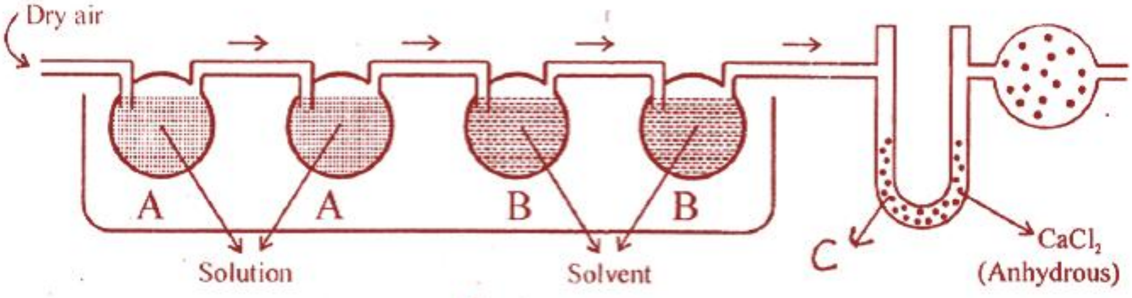


Fig. 9.8: *Ostwalds dynamic method*

Dry air is passed through the solution bulbs first. The air carries with it some solvent (water) in the form of vapour. Hence there will be loss of weight in the solution bulbs. This loss is proportional to the vapour pressure of solution (P).

Now the air containing the solvent (water) vapour is allowed to pass through the solvent bulbs. The vapour pressure of solvent (P_O) is higher than the vapour pressure of solution (P). Therefore the air containing the vapour already, takes some more vapour from the solvent bulbs. This loss is proportional to (P_O - P).

Now the air saturated with solvent vapour is passed through the 'U' tube, 'U' tube absorbs the solvent vapour. (Water vapour, since water is solvent). The weight of 'U' tube increase.

Calculations and Results:

Loss (x) in 'A' bulbs (solution bulbs) α P

Loss (y) in 'B' bulbs (solvent bulbs) α $P_O - P$

Total Loss = gain (z) in weight of 'U' tube (C)

$$x + y = P + (P_O - P) = PO$$

$$P_O - P = y$$

$$P_O = (x + y) = z$$

$$\therefore \quad \frac{P_O - P}{P_O} = \frac{y}{x+y} = X_s = \frac{n_s}{n_o}$$

$$\therefore \quad \frac{y}{x+y} = \frac{a}{M} \text{ X } \frac{W}{b}$$

$$M = \frac{aW}{b} = \frac{x+y}{y}$$

a = weight of solute; b = weight of solvent;

M = mol. Wt. of solute; W = mol. Wt. of solvent.

9.7.4.b Cottrell’s method of determining molecular weight of solute using elevation of Boiling point

This method, require (l) accurate determination of elevaiton of boiling point. Hence conventional thermometers are not useful.

So, Beckmann designed a thermometer which measures only the elevation in temperature

ΔT but not absolute values of B.P. This thermometer contains a reservoir of Hg at one end of the capillary and as usual a bulb at the other end. These are internally connected through the capillary. At any level of temperature (-60^{0}C to 3000^C) the elevation can be measured by adjusting the amount of Hg in the bulb unlike conventional thermometer temperature. This adjustment is done with the help of the reservoir.

(2) The second requirement is elimination of super heating during boiling.

For this, Cottrell used a special device (pumping device) which resembles an inverted funnel, whose stem is split into three symmetrically placed tubes as shown in the figure.

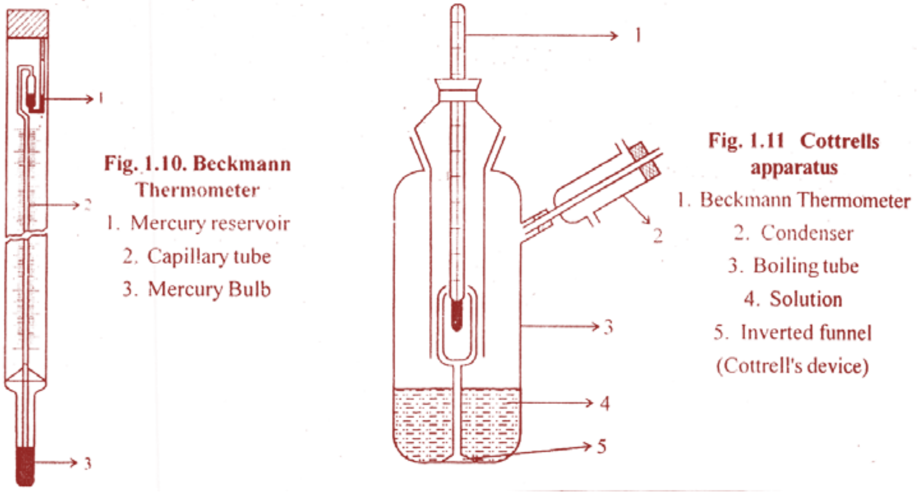


Fig. 1.10. Beckmann Thermometer

1. Mercury reservoir
2. Capillary tube
3. Mercury Bulb

Fig. 1.11 Cottrells apparatus

1. Beckmann Thermometer
2. Condenser
3. Boiling tube
4. Solution
5. Inverted funnel (Cottrell's device)

Fig. 9.9: *Cottrell’s method*

The apparatus consists of tube provided with a side tube. The tube contains another tube through which the thermometer is inserted. At the bottom of the outer tube a platinum wire is fused which is heated during boiling. The funnel like device is placed in the solution in the tube. This pumps the bubbles of the solution along with vapour on to the thermometer bulb. So, the liquid and the vapour will be in equilibrium on the surface of the bulb at the boiling point. This reduces super heating.

A known weight (b) of solvent (molecular weight - W) is taken in the Cottrell tube and the boiling point is determined (T_O). A known weight (‘a’ g) of the solute (molecular weight m) is introduced in the tube through the side tube in the form of a tablet. This dissolves completely and the boiling point of solution (T) is measured. Molar mass is calculated as follows.

Wt. of solvent = ‘b’ g
Wt. of solute = ‘a’ g
B.P. of solvent = T_O
B.P. of solution = T
Elevation in B.P. = $T - T_o = \Delta T$

$$\Delta T = K_b = \frac{a}{m} \times \frac{1000}{b}$$

where K_b = molal elevation constant of solvent.

Problem: The boiling point of $CHCl_3$ was raised 0.325K when 5.141 x 10^{-4} kg. of anthracene is dissolved in 3.5 x 10^{-4} kg of $CHCl_3$. Calculate the molar mass of anthracene. (K_b = 3.9 K.mol^{-1}).

Solution:

ΔT = 0.325 K

K_b = 3.9 Kg. mol^{-1}

A = 0.5141 g ; b = 3.5 g

$$\therefore M = \frac{K_b \times a \times 1000}{\Delta T_b \times b}$$

$$M = \frac{3.9 \times 5.141 \times 10^{-4} \times 1000}{0.325 \times 3.5 \times 10^{-3}}$$

$$= 0.1763 \text{ kg of } 176.3 \text{ g}$$

9.7.4.c Rast's Method :

This method was developed by Rast for Camphor as a solvent. This method is thus generally used for solid solutions i.e., solid solute and solid solvent.

A known weight of camphor (b) is taken and finely powdered in dry mortar. To this a known weight (a) of solid solute is added. The mixture is mixed thoroughly. The mixture is melted to form a homogeneous solution, cooled dried and powdered. The mixture is taken in a capillary tube whose one end is sealed. The melting point is determined carefully by the conventional melting point determination method. The melting point of the pure sample of camphor is determined separately using another capillary tube. The difference in the melting point gives ΔT_f .

From the values a, b & , ΔT_f M is calculated (K_f for camphor = 40 K.kg mol^{-1})

Wt. of camphor - b. g.

Wt. of solute - a. g.

Mol. wf. of solute - m

$$\Delta T_f = K_f \times \frac{a}{m} \times \frac{1000}{b}$$

$$\therefore M = \frac{K_f \times a \times 1000}{\Delta T_f \times b}$$

9.7.4.d Berkeley and Hartley's Method of determining osmotic Pressure :

It is method of applying pressure to the solution which was just sufficient to stop osmosis. A porous pot, open at both the ends and having a copper ferrocyanide membrane fused in its walls, is sealed into the outer bronze cylinder. The bronze cylinder contains the solution and is fitted with a piston upon which weights may be placed to exert external pressure on the solution.

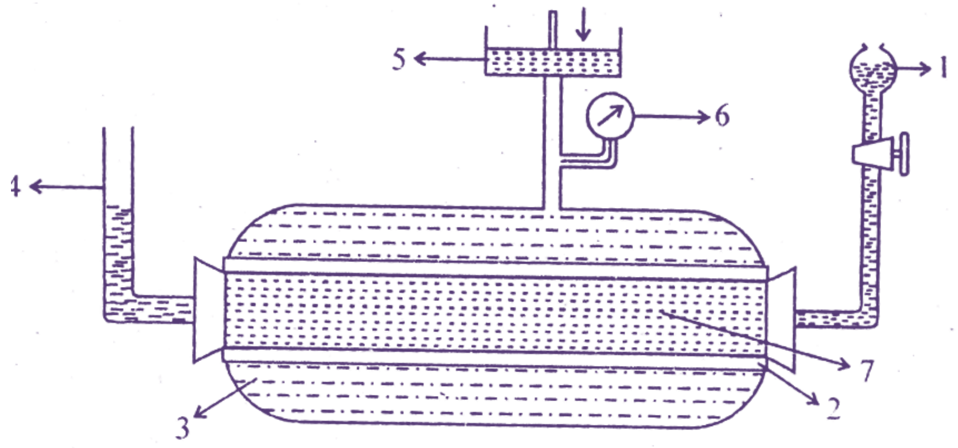


Fig. 9.10 : *Berkely - Hartley Method*
1. Solvent Reservoir 2. Semipermeable membrane
3. solution 4. Capillary tube 5. Piston 6. Pressure guage 7. Solvent

This porous pot is connected with a side tube (capillary tube) one end and a reservior containing water at the other end. The flow of water through the pot into the solution is indicated by the downward motion of the water meniscus in the side tube. This flow of osmosis of water into the solution can be stopped the application of external pressure on the solution with the help of the piston and this would be indicated when the water meniscus in the side tube becomes stationary. The pressure so applied on the piston is equal to the osmotic pressure of the solution. Thus substituting the values of osmotic pressure (π) molarity of the solution (C) and the temperature of the solution in Kelvin scale (T), in the equation

$$\pi = CRT \ (C = \frac{n}{V})$$

R = Gas Constant

The molecular weight of the solute can be calculated.

Problem:

What is the osmotic pressure of a solution containing 0.1 mole of non-volatile solute in 100 cm^3 of solution at 27^0C.

Solution:

$$\pi = \frac{n}{v} RT \qquad R = 0.82 l.atm.K^{-1}\ mol^{-1}$$

$$\pi = \frac{0.1}{0.1} \times 0.0082 \times 300 \qquad V = 100\ cm^3 = 0.1 l$$

$$\pi = 24.63\ atm \qquad V = 27^0C = 300\ K$$

Intext Questions 9.3

1. Define colligative property. List two colligative properties.

....

2. What type of liquid pairs show (i) positive deviations (ii) negative deviations?

....

3. Why is the determination of osmotic pressure a better method as compared to other colligative properties of determining the molar masses of biomolecules.

……

9.8 Abnormal Colligative Properties

The colligative properties of the solutions depend only upon the number of solute particles present in the solution and not on their nature. But sometimes while measuring colligative properties abnormal results are obtained due to the following reasons:

i) If the solution is very concentrated, the particles of the solute start interacting with each other. Therefore, the solution should not be concentrated.

ii) In case of association two or more solute molecules associate to form a bigger molecule. The number of effective molecules in the solution therefore decreases. Consequently the value of the colligative property (relative lowering of vapour pressure, elevation of boiling point, depression of freezing point, osmotic pressure) is observed to be less than that calculated on the basis of unassociated molecules. Since, the colligative property is inversely proportional to the molar mass, the molar mass of such solutes calculated on the basis of colligative property will be greater than the true molar mass of the solute.

iii) In case of dissociation of the solute in the solution, the number of effective solute particles increases. In such cases the value of the observed colligative property will be greater than that calculated on the basis of undissociated solute particles. The molar mass of the solute calculated from the measurement of colligative property will be lower than the true molar mass of the solute.

Van’t Hoff factor

In order to account for extent of association or dissociation Van’t Hoff introduced a factor ‘*i*’.

$$i = \frac{\text{Observed colligative property}}{\text{Normal (calculated or expected) colligative property}}$$

Since the colligative property is proportional to the number of solute particles or the number of moles of solute

$$i = \frac{\text{Total number of moles of solute in the solution}}{\text{Expected (calculated) number of moles of solute}}$$

Also, since colligative properties vary inversely as the molar mass of the solute, it follows that

$$i = \frac{\text{Normal (calculated or expected) molar mass}}{\text{Observed molar mass}}$$

Here the observed molar mass is the experimentally determined molar mass whereas the normal molar mass is the molar mass calculated on the basis of chemical formula of the solute. In case of association the value of Van’t Hoff factor, i, is less than unity while for dissociation it is greater than unity. For example, benzoic acid association in benzene to form a dimer. The value of '*i*' is, therefore, close to 1/2. The value of i for aqueous NaCl is close to 2.0 because NaCl dissociates in water to form Na^+ and Cl^- ions.

The inclusion of Van't Hoff factor, *i*, modifies the equations for the colligative properties as follows:

$$\frac{P^O_A - P_A}{P^O_A} = i\, X_B$$

$$\Delta T_b = i\, K_b\, m$$

$$\Delta T_f = i\, K_f\, m$$

$$\pi V = i\, CRT$$

Degree of Association

Degree of association may be defined as the fraction of the total number of molecules which associate to form a bigger molecule. Let us consider the association of benzioc acid in benzene. In benzene, two molecules of benzoic acid associate to form a dimer. It can be represented as

$$2C_6H_5COOH \longrightarrow (C_6H_5COOH)_2$$

If x represents the degree of association of benzoic acid in benzene (*i.e.* out of one molecule of benzoic acid, x molecules associate to form a dimer), then at equilibrium.

No. of moles of unassociated benzoic acid = $1 - x$

No. of moles of associated benzoic acid = $\frac{x}{2}$

Total number of effective moles of benzoic acid = $1 - x + \frac{x}{2} = 1 - \frac{x}{2}$

According to definition, Van't Hoff factor is given by

$$i = \frac{\text{Total number of moles of solute in the solution}}{\text{Expected (calculated) number of moles of solute}} = \frac{1 - \frac{x}{2}}{1}$$

Example 9.8: Acetic acid (CH_3COOH) associates in benzene to form double molecules 1.60g of acetic acid when dissolved in 100g of benzene (C_6H_6) raised the boiling point by 273.35 K. Calculated the Van't Hoff factor and the degree of association of benzoic acid. Kb for C_6H_6 = 2.57 K kg mol^{-1}.

Solution:

$$\Delta T_b = i\, K_b\, m = \frac{1000 i\, K_b\, W_B}{W_A M_B}$$

Normal molar mass (M_B) of CH_3COOH = 60 g mol^{-1}

$$\text{Van't Hoff factor, } i \text{, is} = \frac{\Delta T_b \text{ x } W_A \text{ x } W_B}{1000 \text{ x } K_b \text{ x } W_B}$$

$$= \frac{0.35 \text{ x } 100 \text{ x } 60}{1000 \text{ x } 2.57 \text{ x } 1.60}$$

$$= 0.51$$

Since, acetic acid associates in benzene to form double molecules, the following equilibrium exists in the solution.

$$2CH_3COOH \longrightarrow (CH_3COOH)_2$$

If x represents the degree of association of the solute, then we would have $(1\text{-}x)$ mol of acetic acid left unassociated and x/2 moles of acetic acid at equilibrium.

Therefore, total number of particles at equilibrium = $1 - x + \frac{x}{2}$

$$= 1 - \frac{x}{2}$$

The total number of particles at equilibirum equal Van't Hoff factor. But Van't Hoff factor (i) is equal to 0.51.

$\therefore 1 - \frac{x}{2} = 0.51$ or $\frac{x}{2} = 1 - 0.51 = 0.49$

$$x = 0.49 \times 2 = 0.98$$

Therefore, degree of association of acetic acid in benzene is 98%.

Degree of dissociation

Degree of dissociation may be defined as the fraction of the total number of particles that dissociate, *i.e.*, break into simpler ions. Consider a solution of KCl in water. When KCl is dissolved in water, it dissociates into K^+ and Cl^- ions.

$$KCl \longrightarrow K^+ + Cl^-$$

Let x be the degree of dissociation of KCl, then at equilibrium, number of moles of undissociated KCl = 1 - x.

According to the dissociation of KCl shown above, when x mol of KCl dissociates, x moles of K^+ ions and x mol of Cl^- ions are produces.

Thus, the total number of moles in the solution after dissociation = 1 - x + x + x = 1 + x

$$\text{Hence, } i - \frac{\text{Total number of moles of solute in the solution}}{\text{Expected (calculated) number of moles of solute}} = \frac{1+x}{1}$$

Example 9.9: A 0.5 percent aqueous solution of potassium chloride was found to freeze at 27.276K. Calculate the Van't Hoff factor and the degree of dissociation of the solute at this concentration. (K_f for H_2O = 1.86 K kg mol^{-1}).

Solution: Normal molecular weight of KCl = 39 + 35.5 = 74.5 g mol^{-1}

$$\text{van't Hoff factor (i)} = \frac{\text{Normal molecular weight}}{\text{Observed molecular weight}}$$

$$= \frac{74.5 \text{ g mol}^{-1}}{38.75 \text{ g mol}^{-1}} = 1.92$$

$$\text{van't Hoff factor (i)} = \frac{\text{Normal molecular weight}}{\text{Observed molecular weight}}$$

$$= \frac{74.5 \text{ g mol}^{-1}}{38.75 \text{ g mol}^{-1}} = 1.92$$

Potassium chloride in aqueous solution dissociates as follow.

$$KCl \longrightarrow K^+ + Cl^-$$

Let x be the degree of dissociation of KCl.

Thus at equilibrium.

No. of moles of KCl left undissociated = (1- x) mol

No. of moles of K^+ = x mol

No. of moles of Cl^- = x mol

Total number of moles at equilibrium = 1 - x + x + x = 1 + x.

$$\therefore \text{ Van't Hoff factor} = \frac{1+x}{1} = 1.92$$

or x = 1.92 - 1 = 0.92

∴ Degree of dissociation of KCl = 92%

What You Have Learnt

- Solution is a homogeneous mixture of two or more substances.
- Solvent is that component of a solution that has the same physical state as the solution itself.
- Solute is the substance that is dissolved in a solvent to form a solution
- Molarity is expressed as the number of moles of solute per litre of solution.
- Molality is expressed as the number of moles of solute per kilogram of solution.
- Normality is a concentration unit which tells the number of gram equivalents of solute per litre of solution.
- Mole fraction is the ratio of the number of moles of one component to the total number of moles in the solution.
- Solutions can be solid, liquid or gaseous.
- Henry's law states that mass or mole fraction of a gas dissolved in a solvent is directly proportional to the partial pressure of the gas.
- Raoult's law states that for a solution of volatile liquids, the partial pressure of each liquid in the solution is directly proportional to its mole fraction.
- A solution which obeys Raoult's law over the entire range of concentration at all temperatures is called an ideal solution.
- The relative lowering of vapour pressure for a solution is equal to the mole fraction of the solute, when only the solvent is volatile.
- Those properties of dilute solutions which depend only on the number of particles of solute and not on their nature are known as colligative properties.
- Molal elevation constant is the elevation in boiling point when one mole of solute is dissolved in one kilogram of the solvent.

- Boiling point of a liquid is the temperatures at which the vapour pressure of the liquid becomes equal to the atmospheric pressure.
- Freezing point is the temperature at which the solid and the liquid forms of the substance have the same vapour pressure.
- Abnormal result is obtained when the solute associates or dissociates in the solution.
- Van't Hoff factor is defined as the ratio of normal molar mass to experimentally determined molar mass.

Terminal Exercise

1. What do you understand by ideal and non-ideal solutions?
2. Define freezing point and boiling point.
3. Derive the relationship $\Delta T_b = K_b m$
4. A solution containing 7 g of a non-volatile solute in 250g of water boils at 373.26 K. Find the molecular mass of the solute.
5. 2g of a substance dissolved in 40g of water produced a depression of 274.5 K in the freezing point of water. Calculate the molecular mass of the substance. The molal depression constant for water is 274.85 K per molal.
6. Calculate the mole fraction of the solute in a solution obtained by dissolving 10g of urea (mol wt 60) in 100 g of water.
7. A solution containing 8.6g of urea (molar mass = 60 per dm^3) was found to be isotonic with a 5 per cent solution of an organic non-volatile solute. Calculate the molar mass of the non-volatile solute.
8. 2 g of benzoic acid (C_6H_5COOH) dissolved in 25g of benzene shows a depression in freezing point equal to 1.62 K. Molar depressions constant for benzene in 4.9 K kg mol^{-1}. What is the percentage association of C_6H_5COOH if it forms double molecules in solution?
9. The freezing point depression of 5.0×10^{-3} M solution of Na_2SO_4 in water was found to be 0.0265^0C. Calculate the degree of dissociation of the salt at this concentration. (K_f for H_2O is 1.86K kg mol^{-1})

Answers to Intext Questions

9.1

1. Molarity, Molality, Normality, Mole fraction, Mass percentage.

   Molarity is the number of moles of solute dissolved per litre of the soltion.

2. Molality is the number of moles of solute dissolved per kg of the solvent. Normality is the number of gram equivalents of solute dissolved per litre of solution

9.2

1. For a solution of volatile liquids the partial vapour pressure of each liquid is proportional to its mole fraction.
2. The mass of a gas dissolved in a solvent is directly proportional to its partial pressure. Pressure should not be too high temperature should not be too low. The gas should not associate or dissociate.

9.3

1. Properties that depend upon the number of particles of solute and not on the nature of solute. *e.g.* Elevation of boiling point, depression of freezing point.
2. For which A-B molecular interactions are :

i) Weaker than A-A and B-B interactions.

ii) Stronger than A-A and B-B interactions.

3. At low concentration the magnitude of osmotic pressure is large enough for measurement.

Chapter 10

COLLOIDS

You are familiar with solutions. They play an important role in our life. A large number of substances such as milk, butter, cheese, cream, coloured gems, boot polish, rubber, ink also play an important role in our daily life. They are also solutions of another kind. They are colloidal solutions. The term colloid has been derived from two terms: colla and oids. 'Kolla' means glue and 'Oids' means like i.e. glue-like. The size of the particles in colloidal solutions is bigger than the size of particles present in solutions of sugar or salt in water. In this lesson you will learn about the methods of preparation, properties and applications of colloidal solutions.

Objectives

After reading this lesson you will be able to:

- Explain the difference between true solution, colloidal solution and suspension;
- Identify phases of colloidal solution;
- Classify colloidal solution;
- Describe methods of preparation of colloids;
- Explain some properties of colloidal solutions;
- Recognize the difference between gel and emulsion and,
- Cite examples of the application of colloids in daily life.

10.1 Distinction between a True Solution, Colloidal Solution and Suspension.

You may recall that solution of sugar in water is homogeneous but milk is not. When you closely look at milk you can see oil droplets floating in it. Thus, although it appears to be homogenous it is actually heterogeneous in nature. The nature of the solution formed depends upon the size of the solute particles. If the size of the solute particles is less than 1 nm it will form true solution but when the size is between 1 to 100 nm then it will form colloidal solution. When the size of solute particles is greater than 100 nm it will form a suspension. Therefore we may conclude that colloidal solution is an intermediate state between true solution and suspension (Table 10.1).

Table 10.1: Some important properties of true solutions, colloids and suspensions

S. No.	Name of Property	True Solution	Colloids Solution	Suspension
1.	Size	Size of particles is less than 1 nm	Size of particles is between 1 nm and	Size of particles greater than 100nm
2.	Filterability	Pass through ordinary filter paper and also through animal membrane.	Pass through ordinary filter paper but not through animal membrane.	Do not pass through filter paper or animal membrane.
3.	Settling	Particles do not settle down on keeping	Particles do not settle down on their own but can be made to settle down by centrifugation.	Particles settle down on their own under gravity.
4.	Visibility	Particles are invisible to the naked eye as well as under a microscope	Particles are invisible to the naked eye but their scattering effect can be observed with the help of a microscope	Particles are visible to the naked eye.
5.	Separation	The solute and solvent cannot be separated by ordinary filteration or by ultra filteration.	The solute and solvent cannot be separated by ordinary filteration but can be separated by ultra-filteration.	The solute and solvent can be separated by ordinary filteration.
6.	Diffusion	Diffuse quickly	Diffuse slowly	Do not diffuse

10.2 Phases of Colloids Solution

Colloids solutions are heterogenous in nature and always consist of at least two phases: the dispersed phase and the dispersion medium.

Dispersed Phase: It is the substance present in small proportion and consists of particles of colloids size (1 to 100nm)

Dispersion Medium: It is the medium in which the colloids particles are dispersed.

For example in a colloidal solution of sulphur in water, sulphur particles constitute the 'dispersed phase' and water is the 'dispersion medium'.

Each of the two phases namely, dispersed phase and dispersion medium can be solid, liquid or gas. Thus, different types of colloidal solutions are possible depending upon the physical state of the two phases. Different types of colloidal solutions and their examples are shown in Table 10.2. You should note that gases cannot form a colloidal solution between themselves, because they form homogenous mixtures.

Table 10.2: Types of Colloidal Solutions

S. No	Dispersed Phase	Dispersion Medium	Type of Colloidal Solution	Examples
1.	Solid	Solid	Solid Solution	Gemstones,
2.	Solid	Liquid	Sol	Paints, muddy water, gold sol, starch sol, arsenious sulphide sol.
3.	Solid	Gas	Aerosol of solids	Smoke, dust in air
4.	Liquid	Solid	Gel	Jellies, Cheese
5.	Liquid	Liquid	Emulsion	Milk, Cream
6.	Liquid	Gas	Aerosol	Mist, fog, cloud
7.	Gas	Solid	Solid foam	Foam rubber,pumice stone
8.	Gas	Liquid	Foam	Froth, whipped cream

Out of the various types of colloidal solutions listed above, the most common are sols (solid in liquid type), gels (liquid in solid type) and emulsions (liquid in liquid type). If the dispersion medium is water then the 'sol' is called a hydrosol; and if the dispersion medium is alcohol then the 'sol' is called an alcosol.

Intext Questions 10.1

1. Classify the following into suspension, colloidal solution and true solution. Milk, sugar in water, clay in water, blood, boot polish, sand in water, face cream, jelly, foam.

....

2. Give one example each of (a) Sol (b) Gel (c) Aerosol (d) Emulsion

....

3. What is the difference between an alcohol and hydrosol?

....

4. 4. How does colloidal solution differ from true solution?

....

10.3 Classification of Colloids

Colloidal solutions can be classified in different ways:

(a) On the basis of interaction between the phases.

(b) On the basis of molecular size.

10.3.1 Classification Based Upon Interaction

Depending upon the interaction between dispersed phase and the dispersion medium colloidal solutions have been classified into two categories.

(a) Lyophilic Colloids: The word Lyophilic means solvent lover. Lyophilic colloidal solutions are those in which the dispersed phase has a great affinity (or love) for the dispersion medium. Substances like gum, gelatin, starch etc when mixed with suitable dispersion medium, directly pass into colloidal state and form colloidal solution. Therefore, such solutions are easily formed simply by bringing dispersed phase and dispersion medium in direct contact with each other. However these colloidal solutions have an important property i.e. they are reversible in nature. This means that once lyophilic colloidal solutions have been formed then dispersed phase and dispersion medium can be separated easily. Once separated, these can again be formed by remixing the two phases. These sols are quite stable. If water is used as dispersion medium then it is termed as hydrophilic colloid.

(b) Lyophobic Colloids: The word Lyophobic means solvent hating. Lyophobic colloidal solutions are those in which the dispersed phase has no affinity for the dispersion medium. Metals like Au, Ag and their hydroxides or sulphides etc., when simply mixed with dispersion medium do not pass directly into colloidal state. These sols have to be prepared by special methods. These sols can be readily precipitated and once precipitated they have little tendency to go back into the colloidal state. Thus these sols are irreversible in nature. Also they are not very stable and require a stability agent to remain in the colloidal form. In case water is used as dispersion medium it is called as hydrophobic sol.

10.3.2 Classification Based on Molecular Size

Depending upon the molecular size the colloids have been classified as

a) Macromolecular colloids - In this type of colloids the size of the particles of the dispersed phase are big enough to fall in the colloidal dimension as discussed earlier (*i.e.* -100 nm) Examples of naturally occurring macromolecular colloids are starch, cellulose, proteins etc.

b) Multi molecular colloids - Here individually the atoms are not colloidal size but they aggregate to join together forming a molecule of colloidal dimension. For example sulphur sol contains aggregates of S_8 molecules which fall in colloidal dimension.

c) Associated colloids - These are substances which behave as normal electrolyte at low concentration but get associated at higher concentration to form micelle and behave as colloidal solution. Soap is an example. Soap is sodium salt of long chain fatty acid RCOONa. When put in water, soap forms $RCOO^-$ and Na^+. These $RCOO^-$ ions associate themselves around dirt particles as shown below forming a micelle (Fig. 10.1)

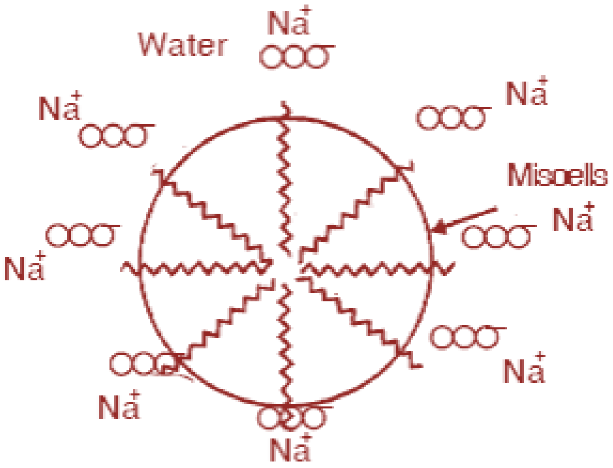


Fig. 10.1: Aggregating of RCCO ions to form a micelle.

10.4 Preparation of Colloidal Solutions

As discussed earlier, the lyophilic sols can be prepared directly by mixing the dispersed phase with the dispersion medium. For example, colloidal solutions of starch, gelatin, gum etc. are prepared by simply dissolving these substances in hot water. Similarly, a colloidal sol of cellulose nitrate is obtained by dissolving it in alcohol. The resulting solution is called Collodion.

However, lyophobic colloids cannot be prepared by direct method. Hence two types of methods are used for preparing lyophobic colloids. These are:

i) Physical methods ii) Chemical method

i) Physical methods

These methods are employed for obtaining colloidal solutions of metals like gold, silver, platinium etc. (Fig. 10.2)

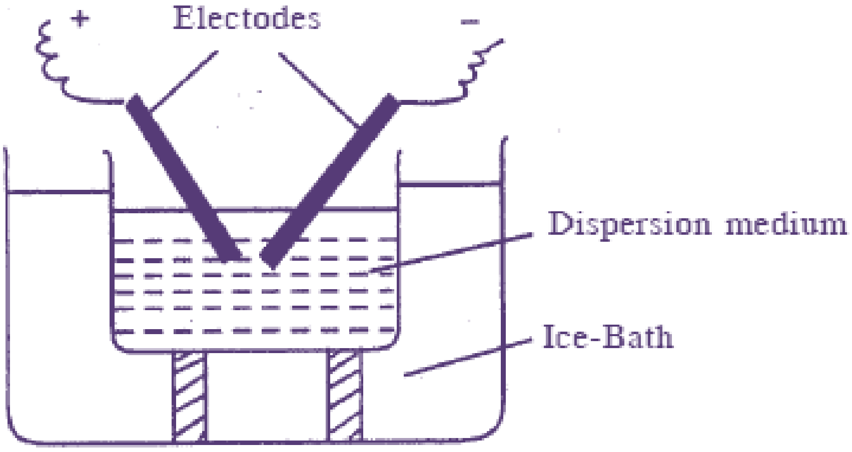


Fig. 10.2: Preparation of colloidal solution by Bredig's Arc Method

An electric arc is struck between the two metallic electrodes placed in a container of water. The intense heat of the arc converts the metal into vapours, which are condensed immediately in the cold water bath. This results in the formation of particles of colloidal size. We call it as gold so.

Peptisation: Peptisation is the process of converting a freshly prepared precipitate into colloidal form by the addition of a suitable electrolyte. The electrolyte is called peptising agent. For example when ferric chloride is added to a precipitate of ferric hydroxide, ferric hydroxide gets converted into reddish brown coloured colloidal solution. This is due to preferential adsorption of cations of the electrolyte by the precipitate. When $FeCl_3$ is added to $Fe(OH)_3$, Fe^{3+} ions from $FeCl_3$ are adsorbed by $Fe(OH)_3$ particles. Thus the $Fe(OH)_3$ particles acquire +ve charge and they start repelling each other forming a colloidal solution.

ii) Chemical Methods: By oxidation, Sulphur solution is obtained by bubbling H_2S gas through the solution of oxidizing agent like HNO_3 or Br_2 water, etc. according to the following equation:

$$Br_2 + H_2S \longrightarrow S + 2\,HBr$$

$$2\,HNO_3 + H_2S \longrightarrow 2\,H_2O + 2\,NO_2 + S$$

$Fe(OH)_3$ Sol, As_2S_3 sol can also be prepared by chemical methods

10.5 Purification of Colloidal Solution

When a colloidal solution is prepared it contains certain impurities. These impurities are mainly electrolytic in nature and they tend to destabilise the colloidal solutions. Therefore colloidal solutions are purified by the following methods:

i) Dialysis
ii) Electro dialysis

Dialysis: The process of dialysis is based on the fact that colloidal particles cannot pass through parchment or cello plane membrane while the ions of the electrolyte can. The colloidal solution is taken in a bag of cellophane which is suspended in a tub full of fresh water. The impurities diffuse out leaving pure colloidal solution in the bag (Fig. 10.3). This process of separating the particles of colloids from impurities by means of diffusion through a suitable membrane is called dialysis.

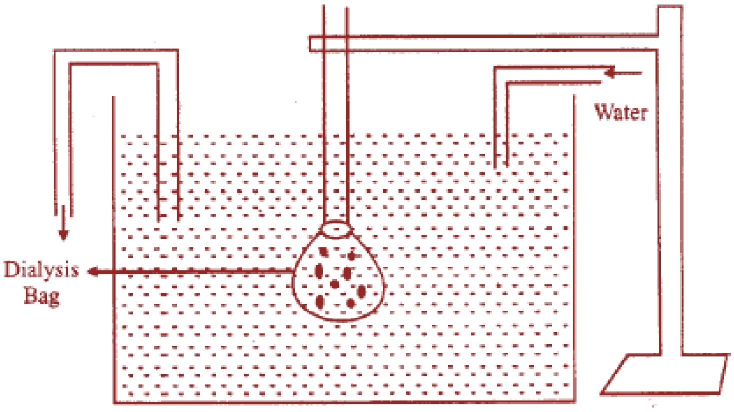


Fig. 10.3: A dialyser

Electro dialysis: The dialysis process is slow and to speed up its rate, it is carried out in the presence of an electrical field. When the electric field is applied through the electrodes, the ions of the electrolyte present as impurity diffuse towards oppositely charged electrodes at a fast rate. The dialysis carried out in the presence of electric field is known as electro dialysis (Fig. 10.4).

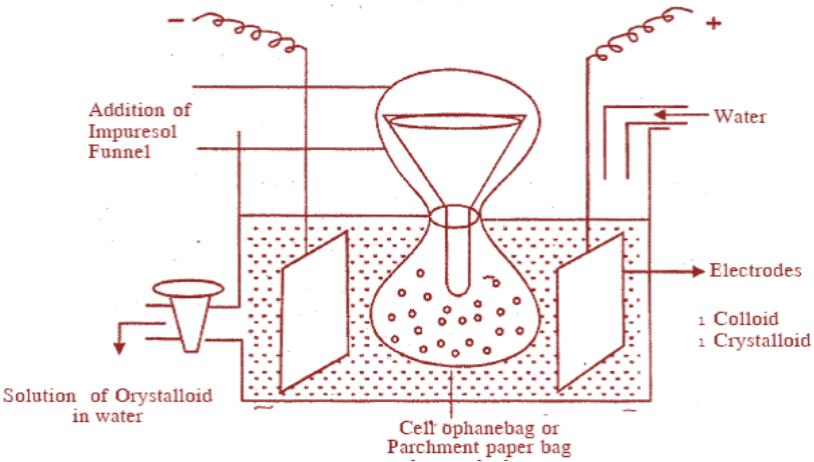


Fig. 10.4: Electro dialysis

The most important use of dialysis is the purification of blood in the artificial kidney machine. The dialysis membrane allows the small particles (ions etc.) to pass through, whereas large size particles like haemoglobin do not pass through the membrane.

Intext Questions 10.2

1. Name two colloids that can be prepared by Bredig's Arc method.

....

2. Name two colloids that can be prepared by chemical methods.

....

3. Differentiate between
   (a) Lyophilic and Lyophobic sol.
   (b) Macromolecular and multimolecular colloids.

....

4. Explain the formation of miscelle.

....

10.6 Properties of Colloids

The properties of colloids are discussed below:

a) Heterogeneous character: Colloidal particles remain within their own boundary surfaces which separate them from the dispersion medium. So a colloidal system is a heterogeneous mixture of two phases. The two phases are dispersed phase and dispersion medium.

b) Brownian movement: It is also termed as Brownian motion and is named after its discoverer Robert Brown (a Botanist).

Brownian motion is the zig-zag movement of colloidal particles in continuous random manner (Fi.g 10.5). Brownian motion arises because of the impact of the molecules of the dispersion medium on the particles of dispersed phase. The forces are unequal in different directions. Hence it causes the particles to move in a zig-zag way.

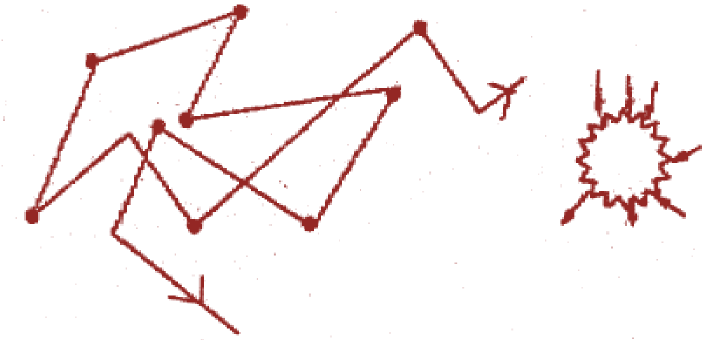


Fig. 10.5: Brownian movement

C) Tyndall Effect: Tyndall in 1869 observed that if a strong beam of light is passed through a colloidal solution then the path of light is illuminated. This phenomenon is called Tyndall Effect. This phenomenon is due to scattering of light by colloidal particles (fig. 10.6). The same effect is noticed when a beam of light enters a dark room through a slit and becomes visible. This happens due to the scattering of light by particles of dust in the air.

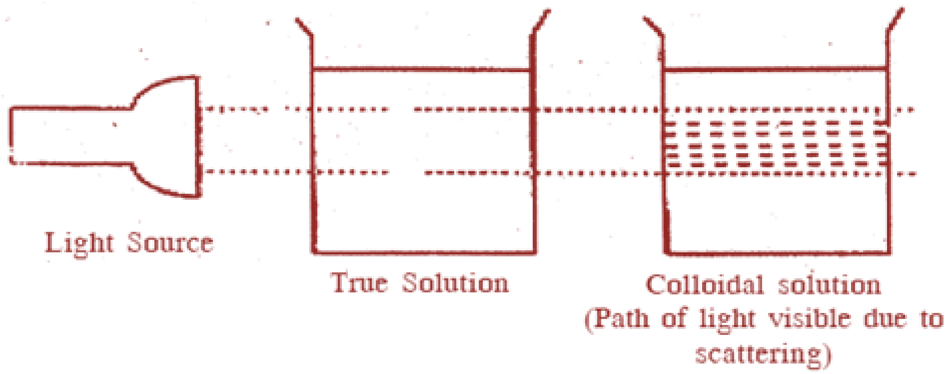


Fig. 10.6: The Tyndall Effect

d) Electrical Properties: The particles of a colloidal solution are electrically charged and carry the same type of charge, either negative or positive. The dispersion medium has an equal and opposite charge. The colloidal particles therefore repel each other and do not cluster together to settle down. For example, arsenious sulphide sol, gold sol, silver sol, etc. contain negatively charged colloidal particles whereas ferric hydroxide, aluminium hydroxide etc. contain positively charged colloidal particles. Origin of charge on colloidal particles is due to:

a) Preferential adsorption of cations or anions by colloidal particles.
b) Micelles carry a charge on them.
c) During the formation of colloids especially by Bredig arc method, colloidal particles capture electrons and get charged. The existence of charge on colloidal particles is shown by a process called electrophoresis.

Electrophoresis is a process with involves the movement of colloidal particles either towards cathode or anode under the influence of electrical field. The apparatus used is as shown in Fig. 10.7.

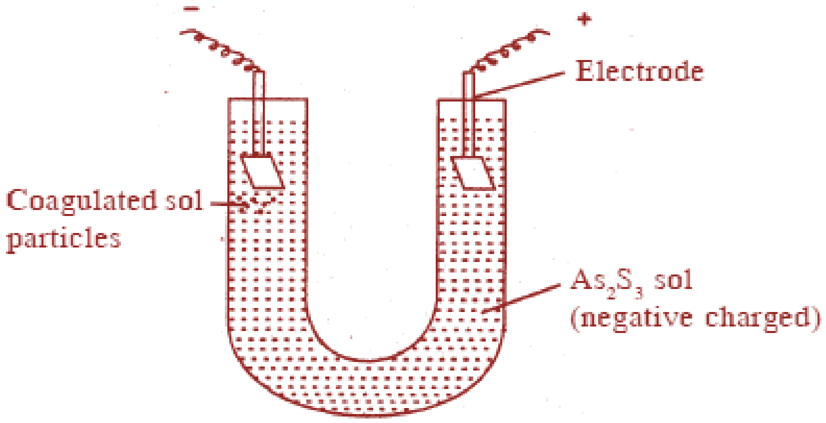


Fig. 10.7: A set up for Electrophoresis

10.7 Applications of Colloidal Solutions

Colloids play a very important role in our daily life. Some of these applications are discussed below:

i) Sewage disposal: Colloidal particles of dirt, etc. carry electric charge. When sewage is allowed to pass through metallic plates kept at a high potential, the colloidal particles move to the oppositely charged electrode and get precipitated there. Hence sewage water is purified.

ii) Purification of Water in Wells: When alum is added to muddy water, the negatively charged particles of the colloid are neutralized by Al^{3+} ions. Hence the mud particles settle down and the water can be filtered and used.

iii) Smoke Precipitation: Smoke particles are actually electrically charged colloidal particles of carbon in air. Precipitation of this carbon is done is a Cottrell's Precipitator. Smoke from chimneys is allowed to pass through a chamber having a number of metallic plates connected to a source of high potential as shown in Fig. 10.8 Charged particles of smoke get attracted to the appositively charged electrode and get precipitated and hot purified air passes out.

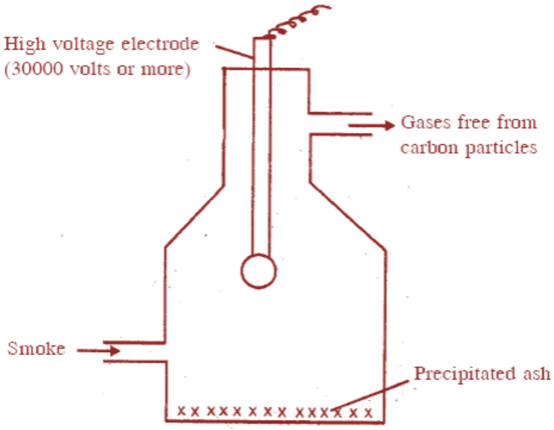


Fig. 10.8: Cottrell smoke precipitator

Other applications in day to day life are:

i) Photography: A colloidal solution of silver bromide in gelatin is applied on glass plates or celluloids films to form photo-sensitive plates in photography.

ii) Clotting of Blood: Blood is a colloidal solution and is negatively charged. On applying a solution of $FeCl_3$ bleeding stops and clotting of the colloidal particles of blood takes place.

iii) Rubber Plating: Latex is a colloidal solution of negatively charged rubber particles. The object to be rubber plated is made the anode in the rubber plating bath. The negatively charged rubber particles move towards the anode and get deposited on it.

iv) Blue Colour of Sky: Have you ever wondered why is the sky blue? It is because the colloidal dust particles floating about in the sky scatter blue light, that makes the sky appear blue. In the absence of these colloidal particles the sky would have appeared dark throughout.

10.8 Emulsion and Gel

Emulsions are colloidal solutions in which both the dispersed phase and dispersion medium are liquids. However, the two liquids are immiscible, as miscible liquids will form true solution.

Emulsion are of two kinds:

a) Oil-in-water emulsion: Here the dispersed phase is oil while the dispersion medium is water. Milk is an example of this kind as in milk liquid fats are dispersed in water. Vanishing cream is another example.

b) Water-in-oil emulsion: Here dispersed phase is water and dispersion medium is oil. Butter, cod-liver oil, cold creams are examples of this types.

The liquids forming emulsion i.e. oil and water will separate out on keeping as they are immiscible. Therefore an emulsifying agent or emulsifier is added to stabilise the emulsion. Soap is a common emulsifier. The preparation of emulsion in the presence of an emulsifier is called emulsification.

How does an emulsifier work? It is believed that an emulsifier gets concentrated at the interface between oil and water i.e. the surface at which oil and water come in contact with each other. It acts as a binder between oil and water.

Application of Emulsions - Emulsions play very important role in our daily life. Some of the common applications are given below:

1) The cleansing action of soap and synthetic detergents for washing clothes, bathing etc is based upon the formation of oil in water type emulsion.
2) Milk is an emulsion of fat in water. Milk cream and butter are also emulsions.
3) Various cold creams, vanishing creams, body lotions etc. are all emulsions.
4) Various oily drugs such as cod liver oil are administered in the form of emulsion for their better and faster absorption. Some ointments are also in the form of emulsions.
5) The digestion of fats in the intestine occurs by the process of emulsification.
6) Emulsions are used for concentrating the sulphide ores by forth flotation process. Finely powdered or is treated with an oil emulsion and the mixture is vigorously agitated by compressed air when the ore particles are carried to the surface and removed.

Gels - Gels are the types of colloids in which the dispersed phase is a liquid and the dispersion medium is a solid. Cheese, jelly, boot polish are common examples of gel. Most of the commonly used gels are hydrophilic colloidal solution in which a dilute solution, under suitable conditions set as elastic semi solid masses. For example 5% aqueous solution of gelatin in water on cooling forms the jelly block.

Gels may shrink on keeping by loosing some of the liquid held by them. This is known as syneresis or resetting on standing.

Gels are divided in two categories. Those are elastic gels and non elastic gels. Elastic gels are reversible. When partly dehydrated on loosing water, they change back into the original form on addition of water. The non elastic gels are not reversible. Gels are useful in many ways. Silica, cheese, jelly, boot polish, curd are commonly used gels. Solidified alcohol fuel is a gel of alcohol in calcium acetate.

What You Have Learnt

- Size of the particles in the colloidal state is intermediate between that of suspension and true solution.
- There are eight different types of colloidal systems.
- Sols are classified on the basis of (a) interaction between dispersed phase and dispersion medium (b) molecular size of dispersed phase.
- Colloidal solutions are prepared by physical and chemical methods. The zig-zag motion of colloidal particles is called Brownian motion.
- Colloidal size particles scatter light and so the path of light becomes visible in a semi darkened room due to dust particles.
- Colloidal particles may carry electric charge.

- A colloidal dispersion of a liquid in another liquid is called an emulsion. A colloidal solution of liquid dispersed in a solid medium is called a gel.
- Colloids are extremely useful to mankind both in daily life and in industry.

Terminal Exercise

1. List three differences between a true solution and colloidal solution.
2. Describe one method of preparation of
    a) lyophilic colloid   b) lyophobic colloid
3. What are associated colloids?
4. What is Brownian motion? How does it originate?
5. Why bleeding from a fresh cut stops on applying alum?
6. Two beakers A and B contain ferric hydroxide sol and NaCl solution respectively. When a beam of light is allowed to converge on them, (in a darkened room), beam of light is visible in beaker A but not in breaker B. Give the reason. What is this effect called?
7. Define the following terms and give two examples of each
    i) Gel   ii) Sol
8. Describe two important applications of colloidal solutions.
9. Give two examples of emulsions used in daily life.
10. Explain the role of emulsifier in an emulsion?

Answers to Intext Questions

10.1

1 Suspension - Clay in water, Sand in water
Colloidal - Milk, Blood, Boot polish, Face Cream, Jelly, Foam.
True Solution - Sugar in water
2 Sol - Starch in water
Gel - Silica gel
Aerosol - Fog
Emulsion - Milk
3 Alcosol - When alcohol is the dispersion medium.
Hydrosol - When water is the dispersion medium.

	True solution	**Colloidal solution**
4	i) size of solute in less than 1 nm	i) Particle size (1-100) nm.
	ii) Form transparent solution and allows light to pass through them.	ii) Path of light becomes visible.

10.2

1. Gol sol, Platinum sol
2. As_2S_3, $Fe(OH)_3$ (Arsenious sulphide sol, ferric hydroxide sol)
3. **a) Lyophilic sol :**
    1) Easy to prepare
    2) Affinity between dispersed phase and dispersion medium
    3) Reversible
    Lyophobic

1) Special method used for preparation
2) No affinity between the two phases.
3) Not reversible

b) Macromolecular - The size of the colloidal particles large enough to fall in the colloidal dimensions.

Multimolecular - Individually the particles are not of colloidal dimensions but they aggregate to join together to form molecules of colloidal side.

4. Refer to 10.3.2 (c)

Module - IV

Chemical Energetics

11.Chemical Thermodynamics

12. Spontaneity of Chemical reactions

Chapter 11

CHEMICAL THERMODYNAMICS

When a chemical reaction occurs, it is accompanied by an energy change which may take any of several different forms. For example, the energy change involved in the combustion of fuels like kerosene, coal, wood, natural gas, etc., takes the form of heat and light. Electrical energy is obtained from chemical reactions in batteries. The formation of glucose, $C_6H_{12}O_6$ by the process of photosynthesis requires the absorption of light energy from the sun. Thus, we see that the energy change that accompanies a chemical reaction can take different forms. In this lesson, you shall study the reactions in which heat is either evolved or absorbed.

Objectives

After reading this lesson you will be able to:

- define the commonly used terms in thermodynamics;
- differentiate between exothermic and endothermic reactions;
- explain the first law of thermodynamics;
- define enthalpy and enthalpy change;
- state the relationship between enthalpy change and internal energy change;
- define enthalpy of formation, enthalpy of neutralisation and enthalpy of combustion;
- state the relationship between enthalpy of reaction and enthalpies of formation of reactants and products;
- solve numerical problems based on the enthalpy changes;
- state Hess's law;
- calculate enthalpy of a reaction using Hess's law;
- define bond enthalpy and bond dissociation enthalpy and
- calculate enthalpy of a reaction using bond enthalpy data.

11.1 Some commonly used Terms

In this lesson you would come across some frequently used terms. Let us understand the meaning of these terms first.

11.1.1 System and Surrounding

If we are studying the reaction of two substances A and B kept in a beaker, the reaction mixture of A and B is a system and the beaker and the room where it is kept are surrounding as shown in figure 11.1

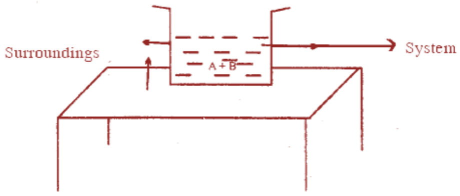


Fig. 11.1: System and surroundings

System is the part of the physical universe which is under study, while the rest of the universe is surroundings.

You know that hot tea/milk (let us call it a system) kept in a stoppered thermos flask remains hot for a couple of hours. If this flask is made of perfect insulating material, then there would be no exchange of matter or energy between the system and the surroundings. We call such a system as *isolated system*.

Isolated system is a system which can exchange neither matter nor energy with the surroundings.

If we keep hot tea/milk in a stoppered stainless steel flask, it will not remain hot after some time. Here energy is lot to the surroundings through the steel walls, but due to stopper, the matter will not be lost. We call this system a *closed system*.

Closed system is a system which can exchange energy but not matter with the surroundings.

If we keep stainless steel flask or thermos flask open, some matter will also be lost due to evaporation along with energy. We call such a system an open system. Plants, animals, human beings are all examples of open systems, because they continuously exchange matter (food, etc) and energy with the surroundings.

Open system is a system which can exchange both energy and matter with surroundings.

11.1.2 State of a System

We describe the state of a system by its measurable properties. For example, we can describe the state of a gas by specifying its pressure, volume, temperature etc. These variable properties are called state variables or state functions. Their values depend only on the initial and final state of the system and not on the path taken by the system during the change. When the state of a system changes, the change depends only on the initial and the final state of the system (Fig. 11.2).

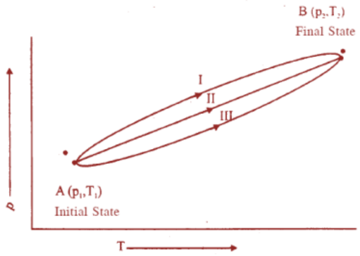


Fig. 11.2: *Change of state from initial state to final state through three paths I, II and III. The difference P_2 - P_1 and T_2 - T_1 are independent of the path since pressure and temperature are state functions.*

State functions are those functions which depend only on the state of the system.

Change in state of a system is defined by giving the initial and the final state of the system. We can understand it by considering another example. We travel from one point to another. The distance travelled depends on the path or the route we take. But the separation between these two points on the earth is fixed. Thus, separation is a state function, but not the distance travelled.

11.1.3 Properties of a System

As stated earlier, the measurable properties of a system are called state variable. They may be further divided into two main types.

i) Extensive property (variable) is one whose value depends upon the size of the system. For example, volume, weight, heat, etc.

ii) Intensive property (variable) is one whose value is independent of the size of the system. For example, temperature, pressure, refractive index, viscosity, density, surface tension, etc.

You may note that an extensive property can become an intensive property by specifying a unit amount of the substance concerned. For example, mass and volume are extensive properties, but density (mass per unit volume) and specific volume (volume per unit mass) are intensive properties.

11.1.4 Types of Processes

Let us first understand, what do we mean by a process. Suppose we want to raise the temperature of the system. We may do it by heating it. Here, heating is the process.

The method of bringing about a change in state is called process.

Process could be of different types. The different types of processes are explained below.

i) Isothermal Process: Ice melts at 273 K and 1 atm pressure. The temperature does not change as long as the process of melting goes on. Such processes are examples of isothermal process. We can define isothermal process as follows.

When the temperature of the system remains constant during various operations, then the process is said to be isothermal. This is attained either by removing heat from the system or by supplying heat to the system.

ii) Adiabatic Process: If an acid is mixed with a base in a closed thermos flask, the heat evolved is retained by the system. Such processes are known as adiabatic processes because the thermos flask does not allow exchange of heat between the system and the surroundings. Adiabatic process can be defined as follows:

In an adiabatic process there is no exchange of heat between the system and the surroundings. Thus, in adiabatic process there is always a change in temperature.

iii) Reversible Process: In a reversible process, the initial and the final states are connected through a succession of equilibrium states. All changes occurring in any part of the process are exactly reversed when it is carried out in the opposite direction. Thus both the systems and its surroundings must be restored exactly to their original state, when the process has been performed and then reversed.

Let us understand it by an example. Imagine a liquid in equilibrium with its vapour in a cylinder closed by a frictionless piston, and placed in a constant temperature bath as shown in figure. 11.3. If the external pressure on the piston is increased by an infinitesimally small amount, the vapours will condense, but the condensation will occur so slowly that the heat evolved will be taken up by the temperature bath. The temperature of the system will not rise, and the pressure above this liquid will remain constant. Although condensation of the vapor is taking place, the system at every instant is in the state of equilibrium. If the external pressure is made just smaller than the vapour pressure, the liquid will vaporize extremely slowly, and again temperature and pressure will remain constant.

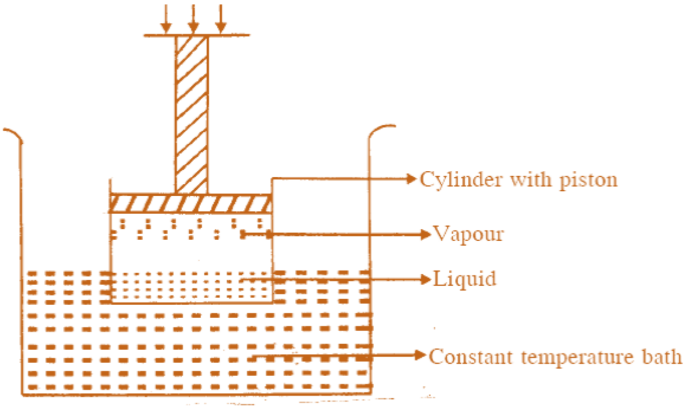


Fig. 11.3: Reversible Process

Reversible processes are those processes in which the changes are carried out so slowly that the system and surroundings are always in equilibrium.

iv) Irreversible Processes: In the above example rapid evaporation or condensation by the sudden decrease or increase of the external pressure, will lead to non-uniformity in temperature and pressure within the system and the equilibrium will be disturbed. Such processes are called as **irreversible processes**.

11.1.5 Standard States

You have seen that a system is described by the state variables. In order to compare the energies for different compounds, a standard set of conditions is chosen. This refers to the conditions of 1 bar pressure at any specified temperature, with a substance in its most stable form.

11.2 Exothermic and Endothermic Reactions

i) Add a few cm^3 of dilute hydrocholoric acid in a test tube containing a few pieces of granulated zinc and observe the evolution of a gas. Feel the test tube. It would be hot.

ii) You must have observed that when some water is added to quick lime to prepare white wash, a lot of heat is evolved.

iii) When a fuel like cooking gas or coal is burnt in air, heat is evolved besides light. Many chemical reactions lead to release of energy (heat) to the surrounding. We call these type of reactions as *exothermic reactions*.

Exothermic reactions are those reactions which proceed with the evolution of heat.

Let us now consider the following reactions:

i) Add a small amount of solid ammonium chloride in a test tube half-filled with water. Shake and feel the test tube. It will feel cold.

ii) Similarly repeat this experiment with potassium nitrate and feel the test tube, it will feel cold.

iii) Mix barium hydroxide with ammonium chloride in small quantities in water taken in a test tube. Feel the test tube. It will be cold.

In all the above processes we see that heat is absorbed by the system from the surroundings. Such reactions are called *endothermic reactions*.

Endothermic reactions are those reactions which proceed with the adsorption of heat from the surroundings.

11.3 Thermochemical Equations

You are familiar with equations for chemical reactions. Now we shall write the chemical equations which will specify heat energy changes and state of the reactants and products. These are called the thermochemical equations. For writing these equations, we follow the conventions listed below:

i) The heat evolved or absorbed in a reaction is affected by the physical state of the reacting substances. Therefore, gaseous, liquid and solid states are represented by putting symbols (g), (l), and (s) alongside the chemical formulae respectively.

For example, to represent burning of methane in oxygen, we write

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O + \text{heat}$$

In writing thermochemical reactions, we denote the amount of heat evolved or absorbed by a symbol ΔH. The amount of heat evolved or absorbed is written after the equation followed by semicolon. ΔH is negative for exothermic reactions and it is positive for endothermic reactions.

For example

An exothermic reaction is written as

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O\,(l)\ ;\ \Delta H = -891\ \text{kJ}$$

Whereas an endothermic reaction is written as

$$H_2(g) + I_2(g) \rightarrow 2HI\,(g);\ \Delta H = 52.2\ \text{kJ}$$

ii) In case of elements which exhibit allotropy, the name of allotropic modification is mentioned. For example, C (graphite), C (diamond), etc.

iii) The substances in aqueous solutions are specified using the symbol (aq). For example NaCl (aq) stands for any aqueous solution of sodium chloride.

iv) Thermochemical equations may be balanced even by using fractional coefficients, if so required. The coefficients of the substances of the chemical euqation indicate the number of moles of each substance involved in the reaction and the ΔH values given correspond to these quantities of substances.

v) In case the coefficients are multiplied or divided by a factor, ΔH value must also be multiplied or divided by the same factor. In such cases, the ΔH value will depend upon the coefficients. For example, in equation

$$H_2\,(g) + {}^1/_2\,O_2(g) \rightarrow H_2O\,(g)\ ;\ \Delta H = -\,242\ \text{kJ}$$

If coefficients are multiplied by 2, we would write the equation

$$2H_2(g) + O_2(g) \rightarrow 2H_2O\,(g)\ ;\ \Delta H = 2\,(-242) = -\,484\ \text{kJ}$$

11.4 The First law of Thermodynamics

You have learnt that chemical reactions are accompanied by energy changes. How do we determine these energy changes? You know that we cannot create or destroy energy. Energy only changes from one form to another. This is the observation made by many scientists over the years. This observation has taken the form of first law of thermodynamics.

It has been found valid for various situations. We state this law as follows:

Energy can neither be created nor destroyed. The total energy of the universe or an isolated system is constant.

Mathematically the first law of thermodynamics is stated as:

$$\Delta U = q + w \qquad (11.1)$$

Where ΔU = change in internal energy, q = heat absorbed by the system, and w = work done on the system. These terms are explained as:

11.4.1 Internal Energy (U)

Every system has a definite amount of energy. This amount is different for different susbstances. It includes translational, vibrational and rotational energies of molecules, energy of electrons and nuclei.

The internal energy may be defined as the sum of the energies of all the atoms, molecules or ions contained in the system.

It is a state variable. It is not possible to measure the absolute values of internal energy.

However, we can calculate the change in internal energy. If the internal energy of the system in the initial state is U_1 and that in the final state is U_2, then change in internal energy ΔU is independent of the path taken from the initial to the final state.

We can write this change as:

$$\Delta U = U_2 - U_1$$

The internal energy of the system can be changed in two ways:

i) either by allowing heat to flow into the system or out of the system; and

ii) by work done on the system or by the system

11.4.2 Heat (q) and Work (w)

Heat and work are not state functions. This is because the value of both q and w depend upon the way in which the change is carried out.

Since the law deals with the transfer of heat and work, we assign some signs to these quantities. Anything which increases the internal energy of a system is given a positive sign.

Heat given to the system (*q*) and work done on the system (*w*) are given positive signs. Let us illustrate this with an example.

If a certain change is accompanied by absorption of 50kJ of heat and expenditure of 30 kJ of work.

$$q = +\,50 \text{ kJ}$$

$$w = -\,30 \text{ kJ}$$

Change in internal energy ΔU = (+ 50kJ) + (-30 kJ) = + 20 kJ

Thus the system has undergone a net increase the internal energy of -20 kJ. Change in the internal energy of the surrounding will be 20 kJ.

11.4.3 Work of Expansion

Let us assume that pressure p is constant and the volume of the system changes from V_1 to V_2. The work done by a system is given as

$$w = -p\,(V_2 - V_1) = -p\ \Delta\ V \qquad (11.2)$$

(Here we have taken minus sign, because the work is done by the system). Let us substitutethe expression given for *w* in equation 11.1.

$$\Delta U = q - p\Delta V \tag{11.3}$$

If the process is carried off at constant volume, i.e. $\Delta V = 0$, then

$$\Delta U = q_V \tag{11.4}$$

The subscript V in q_V denotes that volume is constant.

The equation 11.4 shows that we can determine internal energy change if we measure the heat gained or lost by the system at constant volume. However, in chemistry, the chemical reactions are generally carried out at constant pressure (atmospheric pressure). What do we do then? Let us define another state function, called, enthalpy.

11.4.4 Enthalpy (H)

For meaning heat lost or gained at constant pressure, we define a new state function called enthalpy. It is denoted by the symbol H and is given by

$$H = U + pV \tag{11.5}$$

Enthalpy changes, ΔH, is given by

$$\Delta H = \Delta U + \Delta (pV) \tag{11.6}$$

or $\quad \Delta H = \Delta U + p\Delta V + V\Delta p$

If the change is carried out at constant pressure, then $\Delta p = 0$. The equation 11.6 will become

$$\Delta H = \Delta U + p\Delta V \text{ (at constant pressure)} \tag{11.7}$$

Substituting the value of ΔU from equation 11.3 in equation 11.7 we get

$$\Delta H = q - p\Delta V + p\Delta V$$

$= q$ (at constant pressure) we denote q at constant pressure by q_p hence

$$\Delta H = q_p \tag{11.8}$$

Equation 11.8 shows that by measuring heat lost or gained at constant pressure, we can measure enthalpy change for any process.

11.4.5 Reaction between ΔH and ΔU

For liquids and solids, the difference between ΔH and ΔU is not significant but for gasses, the difference is significant as we will see here.

Let V_A be the total volume of the gaseous reactants,

V_B the total volume of the gaseous products,

n_A the number of moles of gaseous reactants,

and n_B the number of moles of gaseous products, at constant pressure and temperature.

Then, using ideal gas law, we can write

$$p\,VA = nA\,RT \tag{11.9}$$

$$p\,VB = nB\,RT \tag{11.10}$$

Subtracting equation 11.9 from equation 11.10, we get

$$p\,VB = pVA = nB\,RT - nB\,RT = (nA - nB)\,RT$$

$$p\,(VB - VA) = p\Delta V = \Delta ng\,RT$$

At constant pressure

$$\Delta H = \Delta U + p\Delta V$$

Therefore $\quad \Delta H = \Delta U + \Delta ng\,RT$

Here Δn_g = (number of moles of gaseous products) - (number of moles of gaseous reactants)

Thus we can find the value of ΔH from ΔU or vice versa.

For solids and liquids ΔV is very small. We can neglect the term $p \Delta V$, hence ΔH is nearly the same as ΔU.

Intext Questions 11.1

1. Which of the following is false?

a) The reaction

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) + 185$ kJ

in endothermic.

b) Enthalpy change is a state function.

c) Standard state condition for a gaseous system is 1 bar pressure at a specified temperature.

………

2. For the reaction at 298 K,

$1/2\ N_2(g) + {}^3/2\ H_2(g) \rightarrow NH_2(g)$; $\Delta H = -46$ kJ

a) What is the value of Δn_g?

………

b) Calculate the value of ΔU at 298 K?

………

3. Which of the following will increase the internal energy of a system?

a) Heat given to the system

b) Work done by the system

………

11.5 Standard Enthalpy of Reactions

Let as denote total enthalpy of reactants as $H_{\text{reactants}}$ and total enthalpy of products as H_{products}. The difference between these enthalpies, Δ H, is the enthalpy of the reaction

$$\Delta_r H = H_{\text{products}} - H_{\text{reactants}}$$

When H_{products} is greater than $H_{\text{reactants}}$ then Δ H is positive and heat is absorbed in the reaction, and the reaction will be endothermic. For example,

$$H_2(g) + I_2(g) \rightarrow 2HI(g) ;\ \Delta_r H = 52.5 \text{ kJ}$$

When H_{products} is greater than $H_{\text{reactants}}$ then Δ H is negative and heat is evolved in the reaction, and the reaction will be exothermic, For example,

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) ;\ \Delta_r H = -890.4 \text{ kJ}$$

Enthalpy of a reaction changes with pressure and temperature. It is convenient to report enthalpies of the reactions in terms of standard state of substances as we have defined earlier. When substances are in their standard states, we call the enthalpy of reaction as *standard enthalpy of reaction*. It is defined as the enthalpy change for a reaction, when the reactants and the products are in their standard states. It is denoted by $\Delta_r H^0$.

11.5.1 Enthalpy of formation ($\Delta_f H^0$)

The enthalpy change when one mole of a pure compound is formed from its elements in their most stable states is called the enthalpy of formation and is denoted by $\Delta_f H^0$.

When the reacting elements and the products formed are all in their standard states, the enthalpy change accompanying the chemical reaction is called the standard enthalpy of formation and is denoted by $\Delta_f H^0$. By convention, we take the standard enthalpy of formation of an element in its most stable state as zero.

For example :

$$C(\text{Graphite}) + O_2(g) \rightarrow CO_2(g) \; ; \; \Delta_f H^0 = -393.5 \text{ kJ mol}^{-1}$$

This means that carbon dioxide is formed from its elements in their most stable states. Carbon in the form of graphite and at room temperature and gasesous O_2 and CO_2 being at 1 bar.

11.5.2 Enthalpy of Combustion ($\Delta_{comb} H^0$)

Enthalpy of combustion is the enthalpy change (heat evolved) accompanying the complete combustion of 1 mole of a substance in oxygen at a given temperature and 1 bar pressure.

For example:

$$C_2H_5OH\ (l) + 3O_2(g) \rightarrow 2CO_2\ (g) + 3H_2O\ (l) \; ; \; \Delta_{comb} H^0 = -1365.6 \text{ kJ}$$

Enthalpy of combustion of C_2H_5OH (l) is -1365.6 kJ mol^{-1}

11.5.3 Enthalpy of Neutralization ($\Delta_{neut} H^0$)

Enthalpy of neutralization is the enthalpy change (heat evolved) when one mole of hydrogen ions (H^+) is neutralized by one mole of hydroxyl ions (OH^-) in dilute aqueous medium to form water.

For example:

$$H^+\ (aq) + OH^-\ (aq) \rightarrow H_2O\ (l) \; ; \; \Delta_{neut} H^0 = -57 \text{ kJ/mol}$$

Enthalpy of neutralization of a strong acid with a strong base is always constant having a value of -57 kJ. However, enthalpy of neutralization of strong acid with a weak base or weak acid with a strong base will be different, because of varying degree of ionization of weak acids and bases.

11.6 Laws of Thermochemistry

There are two laws of thermochemistry:

- The Lavoisiter - Laplace law
- The Hess's Law of Constant Heat Summation.

Lavoisier - Laplace Law: When a chemical equation is reversed, the sign of $\Delta_r H$ is changed.

For example.

$$N_2\ (g) + O_2\ (g) \rightarrow 2NO\ (g) \; ; \qquad \Delta_r H = 180.5 \text{ kJ}$$

$$2NO\ (g) \rightarrow N_2\ (g) + O_2\ (g) \; ; \qquad \Delta_r H = 180.5 \text{ kJ}$$

Hess's Law of constant heat summation: Hess's law states that the enthalpy of reaction is independent of the number and the nature of the intermediate steps.

You have learnt that standard enthalpy change of the reaction

$$C\ (\text{graphite}) + O_2\ (g) \rightarrow CO_2\ (g)$$

is equal to - 393.5 kJ mol^{-1}. This value can be determined with the help of a calorimeter.

However, there are some reactions for which the direct measurement of enthalpy in the laboratory is not possible. For example the standard enthalpy change for the reactions.

$$C\ (graphite) + 1/2\ O_2\ (g) \rightarrow CO\ (g)$$

cannot be determined with the help of calorimeter because the combustion of carbon is incomplete unless an excess of oxygen is used. If excess of oxygen is used, some of the CO is oxidized to CO_2. How can then we determine the enthalpy change for such reactions when direct measurement is not possible?

Since Δ H is a state function, it is not dependent on the way the reactions are carried out. Let us carry out the reactions as follows.

1. First carry out the following reaction and let $\Delta_r H^0$ be the enthalpy change of the reaction.

   $$C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g)\ ;\ \Delta_r H_1^0 = -393.5\ kJ/mol.$$

2. Now let us write the reaction for which we have to determine the enthalpy change of the reaction and let it be $\Delta_r\ H_2^0$.

   $$C\ (graphite) + 1/2\ O_2\ (g) \rightarrow CO\ (g)\ ;\ \Delta_r H_2^0 = ?$$

3. Let us carry out the following reactions and let $\Delta_r H_3^0$ be the enthalpy change of the reaction.

   $$CO\ (g) + 1/2\ O_2\ (g) \rightarrow CO_2\ (g)\ ;\ \Delta_r H_3^0 = -283.0\ kJ$$

We have obtained the products CO_2 (g) from carbon and oxygen through two routes, namely first as in step (1) and second as in step (2) + (3). According to Hess's Law

$$\Delta_r\ H_1^0 = \Delta_r\ H_2^0 + \Delta_r\ H_3^0$$

or

$$\Delta_r\ H_2^0 = \Delta_r\ H_1^0 + \Delta_r\ H_3^0$$

Fig. 11.4 shows alternate paths for the conversion of carbon and oxygen to carbon dioxide.

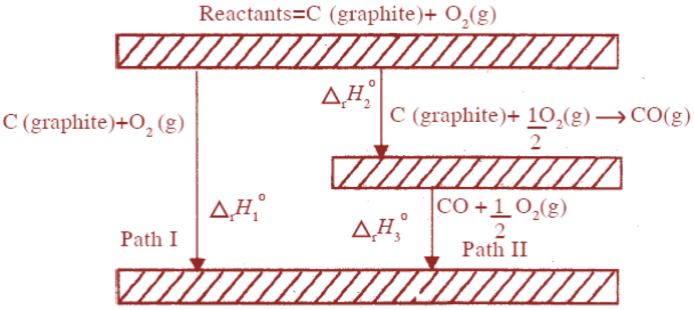


Fig. 11.4: *Alternate paths for the conversion of carbon and oxygen to carbon dioxide*

The result of Hess's law is that thermochemical equations can be added and subtracted just like algebraic equations to get the desired reaction. A useful practical application of this law is that we can calculate enthalpy changes for the reactions which cannot be studied directly as in the above case.

To obtain the enthalpy change for the reactions, we algebraically combine the known values of $\Delta_r\ H^0$ in the same way as the reactions themselves,

Thus, $C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g)\ ;$ $\Delta_r\ H_1^0 = -393.5\ kJ/mol.$
$-\ [CO\ (graphite) + 1/2\ O_2\ (g) \rightarrow CO_2\ (g)]\ ;$ $\Delta_r\ H_3^0 = -283.0\ kJ$
$C\ (graphite) + 1/2\ O_2\ (g) \rightarrow CO\ (g)\ ;$ $\Delta_r\ H_2^0 = [(-393.5) - (-283.0)]$
$= -110.5\ kJ/mol$

Example 11.1: The heat evolved in the combustion of glucose is shown in the following equation.

$$C_6H_{12}O_6\ (s) + 6O_2\ (g) \rightarrow 6CO_2\ (g) + 6H_2O(l);\quad \Delta_{comb}\ H = -2840\ kJ/mol$$

How much energy will be required for the production of 1.08 g of glucose?

Solution: Glucose will be prepared by the reverse reaction.

$$6CO_2\ (g) + 6HO_2\ (l) \rightarrow C_6H_{12}O_6\ (s) + 6CO_2\ (g);\quad \Delta\ H = 2840\ kJ$$

This equation refers to 1 mol of glucose (180g of glucose).

Production of 180g of glucose requires 2840 kJ of energy. Therefore, production of 1.08 g will require:

$$\frac{2840\ kJ}{180\ g}\ x\ 1.08\ g = 17.04\ kJ$$

Example 11.2: Calculate the standard enthalpy of formation of ethane, given that

$$C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g)\ ;\ \Delta_f\ H^0 = -394\ kJ/mol^{-1}$$

$$H_2\ (g) + {}^{1}/2\ O_2\ (g) \rightarrow H_2O\ (g)\ ;\ \Delta_f\ H^0 = -286\ kJ\ mol^{-1}$$

$$C_2H_6\ (g) + 7/2\ O_2\ (g) \rightarrow 2CO_2\ (g) + 3H_2O\ (l);\ \Delta_r\ H^0 = -1560\ kJ\ mol^{-1}$$

Solution : Given that

$$C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g)\ ;\ \Delta_r\ H_1^0 = -394\ kJ/mol \qquad (1)$$

$$H_2\ (g) + {}^{1}/2\ O_2\ (g) \rightarrow H_2O\ (1)\ ;\ \Delta_r\ H_2^0 = -286\ kJ/mol \qquad (2)$$

$$C_2H_6\ (g) + 7/2\ O_2\ (g) \rightarrow 2CO_2\ (g) + 3H_2O\ (l);\ \Delta_r\ H_3^0 = -1560\ kJ/mol \qquad (3)$$

The required equation is

$$2C\ (graphite) + 3H_2\ (g) \rightarrow C_2H_6\ (g)\ ;\ \Delta_f\ H^0 = ?$$

To obtain the above equation, multiply equations (1) by 2 and equation (2) by 3 and then add both the equations we get

$$2C(graphite) + 3H_2\ (g) + 7/2\ O_2\ (g) \rightarrow 2CO_2(g) + 3H_2O(l);\ \Delta_r\ H_5^0 = -1656\ kJ/mol\ (5)$$

(where $\Delta_r\ H_5^0 = 2\Delta_r\ H_1^0 + 3\Delta_r\ H_2^0 = 2 \times (-394) + 3 \times (-286) = -\ 1656\ kJ/mol$).

Substract equation (3) from equation (5) to get the equation (4)

$$2C(graphite) + 3H_2\ (g) \rightarrow C_2H_6\ ; \qquad (4)$$

where $\Delta_f\ H^0 = -\ 1656 - (-1560) = -96\ kJ/mol$

Thus, standard enthalpy of formation of ethane is -96 kJ/mol

Intext Questions 11.2

1) Which of the following is true?

a) Enthalpy of formation is the heat evolved or absorbed when one gram of a substance is formed from its elements in their most stable states.

b) When one mole of H^+ (aq) and 1 mole of OH^- (aq) react, 57.1 kJ of energy is absorbed.

c) In the thermochemical equation.

$$C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g)\ ;\ \Delta_f\ H^0 = -394\ kJ/mol^{-1}$$

$\Delta_f\ H^0$ is known as enthalpy of formation of CO_2 (g)

2. Calculate the enthalpy change for complete combustion of 29.0 g of butane, if

$$C_4H_{10}\ (g) + 3/2\ O_2\ (g) \rightarrow 4CO_2\ (g) + 5H_2O\ (l);\ \Delta_{comb}\ H^0 = -2658\ kJ$$

3. Calculate the standard enthalpy of the reaction

$$2H_2S(g) + SO_2\ (g) \rightarrow 3S\ (s) + 2H_2O\ (l)$$

given that

$\Delta_f H^0 (H_2S) = - 20.6$ kJ mol-1
$\Delta_f H^0 (SO_2) = - 296.9$ kJ mol-1
$\Delta_f H^0 (H_2O) = - 289.9$ kJ mol-1

11.7 Bond Enthalpies

In a chemical reaction, you have seen that energy is either absorbed or evolved. Do you know the origin of this change in energy? You know that bonds are broken and new bonds are formed in chemical reactions. Energy changes take place in breaking some bonds of the reactants and in forming new bonds of the products. So the energy changes in a chemical reaction are a result of energy changes in breaking and forming of bonds. Let us consider the gaseous reactions, because in these, we encounter the energy changes due to breaking and forming of bonds only.

At high temperature, hydrogen molecules dissociate into atoms as

$$H_2 (g) \rightarrow H (g) + H (g) ; \Delta_r H = 435 \text{ kJ/mol}$$

The heat absorbed in this reaction is used to break the chemical bonds holding the hydrogen atoms together in the H_2 molecules. For a diatomic molecule like H_2 (g), we define **bond dissociation energy as the enthalpy change of the reaction in which one mole of the gaseous molecules are dissociated into gaseous atoms.**

Now, let us consider a polyatomic molecule like H_2O (g). The dissociation may involve fragmenting the molecules into an atom and a group of atoms, called a radical, as in

$$H_2O (g) \rightarrow H (g) + OH (g) ; \qquad \Delta_r H^0 = 502 \text{ kJ/mol}$$
$$OH (g) \rightarrow O (g) + H (g) ; \qquad \Delta_r H^0 = 472 \text{ kJ/mol}$$

In the first reaction, one of the two OH bonds in H_2O (g) dissociates with an enthalpy change of 502 KJ/mol and in the second reaction, second OH bond dissociates with an enthalpy change of 427 KJ/mol. It is clear that the dissociation energy of the O - H bond is sensitive to its environment. However, the difference is not very large. We take the average value (464.5 kJ/mol in this case) in case of polyatomic molecules and call it bond enthalpy.

Bond enthalpy is defined as the average amount of enthalpy change involved in the dissociation of one mole of bonds present in different gaseous compounds.

Now you know the distinction between bond dissociation enthalpy and bond enthalpy. Bond dissociation enthalpy refers to breaking a particular bond in a particular molecule where as bond enthalpy is the average value of bond dissociation energies for a given type of bond. The bond enthalpies of some bonds are listed in table 11.1.

By using bond enthalpies (B.E) it is possible to estimate the energy released when a gaseous molecule is formed from its gaseous atoms. For example, the energy released at constant pressure for the reaction ($\Delta_r H$).

$$3H (g) + C (g) + Cl (g) \rightarrow CH_3Cl (g)$$

is the sum of the energies of three C - H bond, and one C - Cl bond, all taken with a negative sign, because energy is released. Using the values of bond enthalpies (B.E.) from table 11.1 we get,

$$\begin{aligned} \Delta_r H &= - 3 \times \text{B.E (C - H)} - \text{B.E. (C - Cl)} \\ &= (- 3 \times 145 - 335) \text{ kJ mol}^{-1} \\ &= (- 1245 - 335) \text{ kJ mol}^{-1} \\ &= - 1574 \text{ kJ mol}^{-1} \end{aligned}$$

We will now show you how to use bond enthalpy data to estimate the enthalpy of a reaction, when direct calorimetric data are not available. Note that in section 11.7 we used enthalpy of formation data to estimate enthalpy of a reaction. In principle, bond enthalpy data can be used to calculate Δ_r H for a chemical reaction occurring in gaseous state by making use of difference in energy absorbed in breaking the bonds in reactants and energy released in formation of bonds in products.

$$\Delta_r H = \Sigma \text{ B.E. (reactants)} - \Sigma \text{ B.E. (products)} \qquad (11.10)$$

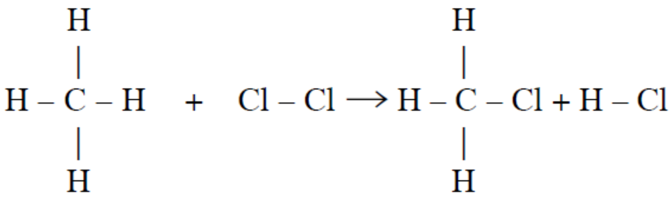
Table 11.1: Average Bond enthalpies

Bond	BOND Enthalpy / (kJ mol^{-1})
H - H	**435**
C - H	**415**
C - Br	**284**
C - C	**356**
C = C	**598**
Br - Br	**193**
Cl - Cl	**242**
C - Cl	**339**
F - F	**155**
H -Cl	**431**
H - O	**462**
H - N	**390**
H - F	**563**
H - Br	**366**
H - I	**296**
C - O	**355**
C = O	**723**
C - N	**391**
C = N	**619**
C ≡ N	**878**
C ≡ C	**832**

Example 11.3: Use bond enthalpy data given in table 11.1 to calculate the enthalpy of the reaction.

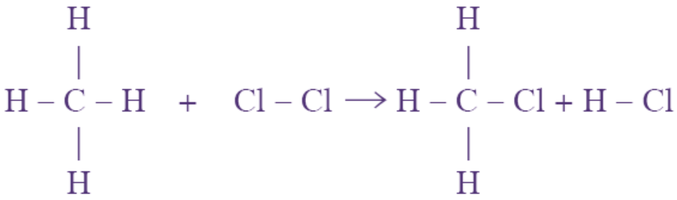
$$CH_3 \text{ (g)} + Cl_2 \text{ (g)} \rightarrow CH_3Cl \text{ (g)} + HCl \text{ (g)}$$

Solution: 1. Write the equation using structural formula



$$\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H-C-H}\\ |\\ \mathrm{H}\end{array} + \mathrm{Cl-Cl} \longrightarrow \begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H-C-Cl}\\ |\\ \mathrm{H}\end{array} + \mathrm{H-Cl}$$

2. List the bonds broken and bonds formed under the equation as shown



$$\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H-C-H}\\ |\\ \mathrm{H}\end{array} + \mathrm{Cl-Cl} \longrightarrow \begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H-C-Cl}\\ |\\ \mathrm{H}\end{array} + \mathrm{H-Cl}$$

Number of bonds broken	**Number of bonds formed**
C - H = 4	C - Cl = 1
Cl - Cl = 1	H - Cl = 1
	C - H = 3

3. Look up the values of bond enthalpies for the bonds in the reactants and products and list them as shown

Reactants	**Products**
B.E. (C - H) = 435 kJ mol^{-1}	B.E. (Cl - C) = 339 kJ mol^{-1}
B.E. (C - Cl) = 242 kJ mol^{-1}	B.E. (H - Cl) = 431 kJ mol^{-1}
	B.E. (C - H) = 435 kJ/mol^{-1}

4. Use equation 11.10,

Enthalpy of the reaction $\Delta_r H = \Sigma$ B.E. (reactants) - Σ B.E. (products)

= 4 (B.E. (C - H) + (B.E. (C - Cl) - [B.E. (C - Cl) + B.E. (H - Cl) + 3 B.E. (C - H)]

= [4 x 435 + 242] - [339 + 431 + 3 x 435] = - 93 kJ

Now let us take one example in which we calculate enthalpy of a reaction using

i) Enthalpy of formation data

ii) Bond enthalpy data.

Example 11.4: Calculate $\Delta_r H^0$ for the reaction

Cl_2 (g) + 2HF (g) → 2HCl (g) + F_2 (g)

a) Using enthalpy of formation data

$\Delta_r H^0$ (HCl) = - 92.5 kJ

$\Delta_f H^0$ (HF) = - 269 kJ

b) Using bond enthalpy data

B.E. (H - Cl) = 431 kJ mol^{-1}

B.E. (F - F) = 155 kJ mol^{-1}

B.E. (H - F) = 563 kJ mol^{-1}

B.E. (Cl - Cl) = 242 kJ mol^{-1}

Solution: a) Using enthalpy of formation of compounds,

$\Delta_r H = [2\Delta_f H^0 (HCl) + \Delta_f H (F_2)] - [2\Delta_f H^0 (HF) + \Delta_f H^0 (Cl_2)]$

f = [2 x (-92.5) + 0] - [2 x - (269)+ 0] kJ

= - 185 kJ + 538 kJ

= + 353 kJ

b) Using bond enthalpies

$\Delta_r H^0 = \Sigma$ B.E. (reactants bonds) - Σ B.E. (products bonds)

= [B.E. (Cl - Cl) + 2 B.E. (H - F)] - (2B.E. (H - Cl) + B.E. (F - F)]

= [242 + 2 (563)] kJ - [2 x 431 + 155] kJ

= 1368 kJ - 1017 kJ

$\Delta_r H^0$ = 351 kJ

$\Delta_r H^0$ calculated by these two different methods are nearly the same.

11.8 The Third Law of Thermodynamics

In 1910M. Planck suggested that "***The entropy of a pure and perfectly crystalline substance is zero at the absolute zero of temperature***" (-273^{0}C)

$$S_{\lim T\rightarrow 0} = 0$$

This is known as the third law of thermodynamics.

Unlike the first and the second laws, the third law does not lead to any new concept of thermodynamics. It only imposes a limitation on the value of entropy.

$$S_T = \int_0^T \frac{C_p}{T} dT$$

Thus entropy (S) of a substance at any temperature is calculated if the temperature dependence of C_p known in evaluating the absolute value of entropy of any substance.

Contribution to entropy due to phase transformations such as melting, vaporization, sublimation, transition from one allotropic from to the other allotropic form must be taken into account. Accurate determination of entropy (S_T) requires that the heat capacity at constant pressure (C_P) must be determined accurately. But C_P cannot be measured at absolute zero (-273^{0}C) or around absolute zero.

For this heat capacity at constant volume (C_V) measurements at various temperatures are made up to as low temperature as possible. C_V Value at absolute zero is obtained by using the extrapolating technique and the Debye equation.

$C_V = aT^3$; a = constant for a substance

At the temperature in the vicinity of absolute zero (C_p - C_V) is negligible. Hence C_p= C_V. Hence absolute entropy S^0 is calculated using C_v Value.

Intext Questions 11.3

1. Write True or False

a) Enthalpy of a reaction is equal to the sum of the enthalpy of formation of products minus the sum of the enthalpy of formation of the reactants.

b) Enthalpy of formation of any elementary substance is equal to zero.

c) If a reaction can be carried out in several steps, the enthalpy change for the overall reaction is equal to enthalpy change in the last step.

d) Bond enthalpy and bond dissociation energy are same for polyatomic molecules.

2. Calculate the bond enthalpy N - H in NH_3 (g), given

$1/2\ N_2 (g) + 3/2\ H_2 (g) \rightarrow NH3 (g)$; $\Delta_r H^0$ = - 46 kJ mol^{-1}

$1/2\ H_2 (g) \rightarrow H_2 (g)$; $\Delta_f H^0$ = 218 kJ mol^{-1}

$1/2\ N_2 (g) + N_2 (g)$; $\Delta_r H^0$ = 973 kJ mol^{-1}

3. Calculate the enthalpy of the reaction.

$H_2\ (g) + Cl_2\ (g) \rightarrow 2HCl\ (g)$

given,

Bond enthalpy (H - H) = 435 kJ mol^{-1}
Bond enthalpy (Cl - Cl) = 242 kJ mol^{-1}
Bond enthalpy (H - Cl) = 431 kJ mol^{-1}

What You Have Learnt

- System is the part of the physical universe which is under study, while the rest of the universe is surrounding.
- Isolated system is a system which can exchange neither matter nor energy with the surrounding.
- Closed system is a system which can exchange energy but not the matter with the surrounding.
- Open system is a system which can exchange both energy and matter with the surroundings.
- State functions are those functions which depend only on the state of the system.
- Extensive properties depend upon the size of the system whereas intensive properties do not depend upon the size of the system.
- When the temperature of the system is kept constant during various operations then the process is said to be isothermal.
- In an adiabatic process there is no exchange of heat between the system and the surroundings.
- Reversible processes are those processes in which the changes are carried out so slowly that the system and surrounding are always in equilibrium.
- Exothermic reactions are those reactions which proceed with the evolution of heat.
- Endothermic reactions are those which proceed with absorption of heat from the surroundings.
- First law of Thermodynamics states that energy can neither be created nor destroyed.
- Internal energy is the sum of the energies of all the atoms, molecules or ions contained in the system.
- The state function enthalpy (H) is given by the relation $H = U + PV$.
- When a chemical equation is reversed, the sign of Δ H is also reversed.
- The enthalpy of reaction is dependent on the number and nature of the intermediate steps.
- Bond enthalpy is the average amount of bond dissociation enthalpies for a given type of bond present in different gaseous compounds, when one mole of bonds is broken in the gaseous state.

Terminal Exercise

1. Enthalpy of combustion of ethyl alcohol, C_2H_5OH, is -950 kJ mol^{-1}. How much heat is evolved when one gram of ethyl alcohol burns?

2. Given:

$C_2H_2\ (g) + 5/2\ O_2\ (g) \rightarrow 2CO_2\ (g) + H_2O\ (l);\ \Delta_{comb}\ H = -1299\ kJ\ mol^{-1}$

C (graphite) + O_2 (g) ⟶ CO_2 (g) ; Δ_f H = -393 kJ mol^{-1}

H_2 (g) + 1/2 O_2 (g) ⟶ H_2O (g) ; Δ_f H = -285.5 kJ mol^{-1}

Calculate enthalpy of formation of C_2H_2 (g)

3. Calculate the enthalpy of combustion of propane

C_3H_8 (g) + $5O_2$ (g) ⟶ $3CO_2$ (g) + $4H_2O$ (*l*)

Given the following:

H_2 (g) + 1/2 O_2 (g) ⟶ H_2O (l) ; Δ_r H = -285.5 kJ mol^{-1}

C (s) + O_2 (g) ⟶ CO_2 (g) ; Δ_f H = - 393 kJ mol^{-1}

3C (g) + $4H_2$ (g) ⟶ C_3H_8 (g) ; Δ_f H = - 104 kJ mol^{-1}

4. When two moles of H_2 and one mole of O_2 react to produce two moles of gaseous water at 373 K and 1 bar pressure, a total of 484 kJ are evolved. What are (a) Δ H and (b) Δ U for the production of a single mole of H_2O (g).

5. Calculate enthalpy of the reaction:

$2Na_2O_2$ (s) + $2H_2O$ (l) ⟶ 4NaOH (s) + O_2 (g)

Enthalpies of formation of NaOH (s), Na_2O_2 (s) and H_2O (1) are - 426.4 kJ mol^{-1}, 504kJ mol^{-1}, and -285 kJ mol^{-1} respectively.

6. Calculate the heat of formation of gaseous ethly alochol.

2C (graphite) + $3H_2$ (g) + 1/2 O_2 ⟶ C_2H_5OH (g)

given that enthalpy of sublimation of graphite is 714 kJ / mol and bond enthalpies of H - H, O = O, C - C, C - H, C - O and O - H are respectively 435 kJ/mol, 498 kJ/mol, 347 kJ/mol, 415 kJ/mol , 355 kJ/mol and 462 kJ/mol respectively.

Answers to Intext Questions

11.1

1. (a)

2. (a) $\Delta n = 1 - \frac{1}{2} - \frac{3}{2} = -1$

(b) $\Delta U = \Delta H - \Delta n RT$

= 46000 (J mol^{-1}) - (-1) (8.314 Jk mol^{-1}) x (298 K)

= - 46000 (J mol^{-1}) + 2247.6 (J mol^{-1})

= - 43.5 kJ mol^{-1}

3. (a)

11.2

1. (c)

2. - 1329 kJ

3. $\Delta_f H^0 = 2 \Delta_f H^0 (H_2O) - 2 \Delta_f H^0 (H_2S) - \Delta_f H^0 (SO_2)$

= - 241.7 kJ

11.3

1. (a) T (b) T (c) F (d) F

2. $\Delta_r H^0$ = Σ B.E. (reactant bonds) - Σ B.E. (products bonds)

or - 46 (kJ mol^{-1}) = 3 x 218 (kJ mol^{-1}), + 973 (kJ mol^{-1}) - B.E. (NH_3(g) Bonds)

B.E. (NH_3 (g) Bonds) = 1673 kJ mol^{-1}

B.E. (N - H) = 557.7 kJ mol^{-1}

3. $\Delta_r H^0$ = -185 kJ mol^{-1}

Chapter 12

SPONTANEITY OF CHEMICAL REACTIONS

We have studied about the first law of thermodynamics in lesson 11. According to this law the processes occur in such a way that the total energy of the universe remains constant. But it does not tell us whether a specified change or a process including a chemical reaction can occur spontaneously i.e., whether it is feasible or not. For example, the first law does not deny the possibility that a metal bar having a uniform temperature can spontaneously become warmer at one end and cooler at the other. But it is known from experience that such a change does not occur without expenditure of energy from an external source.

The first law also states that energy can be converted from one form into an equivalent amount of energy of another form. But it does not tell that heat energy cannot be completely converted into an equivalent amount of work without producing some changes elsewhere. In this lesson you shall learn to predict whether a given process or chemical reaction can occur spontaneously or not.

Objectives

After reading this lesson you will be able to:

- define entropy;
- recognize that entropy change in a system is given by

$$\Delta S = \frac{q_{rev}}{T}$$

- state entropy criterion for a spontaneous process $\Delta S_{universe} > 0$ and at equilibrium $\Delta S_{universe} = 0$
- state third law of thermodynamics ;
- state the relationship between G, H and S;
- derive the relation $\Delta G_{system} = T \Delta S_{system}$;
- state Gibbs energy criterion for spontaneous process

  $\Delta G < 0$ for a spontaneous process
  $\Delta G = 0$ at equilibrium
  $\Delta G > 0$ for a non-spontaneous process
- define standard Gibbs energy of formation of a substance;
- relate the standard Gibbs energy change with the equilibrium constant and
- solve numerical problems.

12.1 Spontaneous and Non-spontaneous Processes

We know that hot water kept in a container cools down by losing heat to the surroundings. On the other hand, water at room temperature cannot become hot by gaining heat from the surroundings. It can be made hot by heating it over a gas burner. The cooling down of hot water is an example of a spontaneous process. Heating of water (at room temperature) is an example of a non-spontaneous process because an outside agency (gas burner) has been used.

A spontaneous process is a process that occurs in a system by itself; once started, no action from outside the system (outside agency) is necessary to make the process continue. A non- **spontaneous process** will not take place unless some external action is continuously applied. Let us consider another example, we know that when iron objects are exposed to moist atmosphere, rusting of iron takes place. Although the rusting iron is a slow process but it always takes place in the same direction. We say that the rusting of iron is a spontaneous process. During rusting of iron, iron is oxidised to iron (III) oxide.

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_5(s)$$

The reverse of the above reaction is also possible but it is non-spontaneous. An external agency has to be used to reduce iron (III) oxide to iron.

From our discussion it can be concluded that

- if a process is spontaneous, the reverse process in non-spontaneous.
- both spontaneous and non-spontaneous processes are possible.
- spontaneous processes occur naturally whereas non-spontaneous processes require the help of an outside agency to occur.

12.2 Entropy

In fig 12.1(a) the bulb ‘I’ contains 1 mol of an ideal gas ‘A’ at a pressure of 1 bar and the bulb II contains 1 mol of another ideal gas ‘B’ at 1bar. The two bulbs are joined together through a valve.

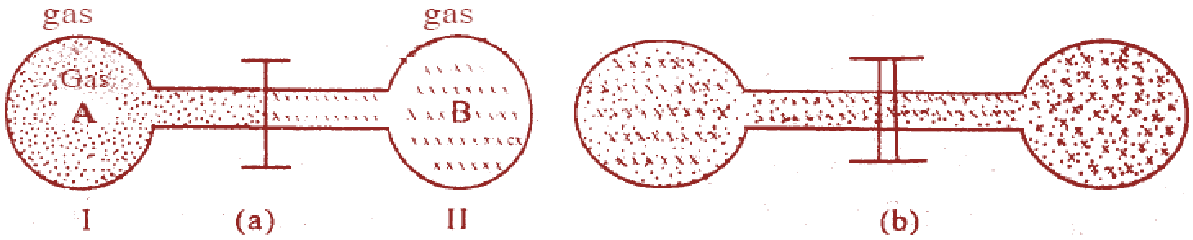


Fig 12.1

When the valve between the two bulbs is opened [Fig 12.1 (b)], the two gases mix spontaneously. The mixing of gases continues until the partial pressure of each gas becomes equal to 0.5 bar in each bulb i.e., the equilibrium is attained. We know from experience that the process cannot be reversed spontaneously-the gases do not unmix. What is the driving force behind this process?

We know that the internal energy (U) and enthalpy (H) of an ideal gas depend only upon the temperature of the gas and not upon its pressure or volume. Since there are no intermolecular forces in ideal gases, $\Delta U = \Delta H = 0$ when ideal gases mix at constant temperature. Thus energy change is not the driving force behind the spontaneous mixing of ideal gases. The driving force is simply the tendency of the molecules of the two gases to achieve maximum state of mixing, i.e., disorder. The thermodynamic property related to the disorder of the system is called **entropy.** It is denoted by the symbol S.

The entropy is the measure of disorder or randomness in a system. The greater the disorder in a system, the greater is the entropy of the system.

For a given substance,

(i) the crystalline state is the most ordered state, hence its entropy is the lowest.

(ii) the gaseous state is the most disordered state, hence its entropy is the maximum, and

(iii) the disorder in the liquid state is intermediate between the solid and the gaseous state.

When a system changes from one state to another, the change of entropy ΔS is given by

$$\Delta S = \frac{q_{rev}}{T} \qquad (12.1)$$

Where q_{rev} is the heat supplied reversibly at temperature *T*.

12.2 Criteria for Spontaneous Change: The Second Law of Thermodynamics

So far we have studied about internal energy, enthalpy and entropy. Can we define the spontaneity of a process in terms of these properties? Let us see whether these changes in properties can be used as a criterion for determining the spontaneity of a process or not.

(i) We know that most of the processes which occur spontaneously are exothermic. Water kept in a container at room temperature evaporates spontaneously. It is an endothermic process. Thus enthalpy change cannot be used as a criteria for spontaneous change.

(ii) Can we use the increase of entropy as a criteria for the spontaneous change? Then how do we explain the spontaneous freezing of water at -100C? We know that crystalline ice is more ordered then the liquid water and therefore the entropy must decrease. The answer to this question is that we must consider simultaneously two entropy changes:

   (a) the entropy change of the system itself, and

   (b) the entropy change of the surroundings.

$$\Delta S_{total} = \Delta S_{univ} = \Delta S_{system} + \Delta S_{surrounding} > 0 \qquad (12.2)$$

The equation is one of the many forms of the second law of thermodynamics.

According to the second law of thermodynamics **all spontaneous or natural processes produce an increase in entropy of the universe.**

Thus, for a spontaneous process when a system is at equilibrium, the entropy is at maximum, and the change in entropy is zero.

$$\Delta S = 0 \text{ (at equilibrium)} \qquad (12.3)$$

12.4 Entropy Change in Phase Transitions

When a solid melts and produces liquid, the process occurs at the melting point of the solid. For example, ice melts at 273 K and produces water at the same temperature.

$$H_2O(s) \xrightarrow{\text{at } 273} H_2O(l)$$

The heat involved in the process of melting is called enthalpy of fusion ($\Delta_{fus}H$). Therefore, the entropy of fusion ($\Delta_{fus}S$) is given by

$$\Delta_{fus}S = \frac{\Delta_{fus}S}{T} \quad (\therefore q_{rev} \text{ at const } p = \Delta_{fus}H)$$

Similarly, for the equilibirum

$$H_2O(l) \xrightarrow{\text{at } 373K} H_2O(g)$$

$$\Delta_{vap}S = \frac{\Delta_{vap}H}{T} \quad (\text{T is the boiling point})$$

Example 12.1: The enthalpy change for the transition of liquid water to steam at 373 K is 40.8 kJ mol^{-1}. Calculate the entropy change for the process

Solution: $H_2O(l) \overset{373K}{\rightleftharpoons} H_2O(g)$

$$\Delta_{vap}S = \frac{\Delta_{vap}H}{T}$$

$$\Delta_{vap}H = 40.8 \text{ kJ mol}^{-1} = 40.8 \times 10^3 \text{ J mol}^{-1}$$

$$T = 373 \text{ K}$$

$$\Delta_{vap}S = \frac{40.8 \times 10^3 \text{ J mol}^{-1}}{373K} = 109 \text{ J K}^{-1} \text{ mol}^{-1}$$

Intext Questions 12.1

1. The enthalpy change for the transition of ice to liquid water at 273 K is 6.02 kJ mol^{-1}. Calculate the entropy change for the process.

....

2. Arrange the following systems in the order of increasing randomness.
(i)1 mol of gas A (ii) 1 mol of solid A (iii) 1 mol of liquid A

....

3. Indicate whether you would expect the entropy of the system to increase or decrease
a) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
b) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
c) $O_2(g) \rightarrow 2O\ (g)$

....

12.5 Absolute Entropy

When the temperature of a substance is increased, the translational, vibrational and rotational motions become more vigorous. It leads to greater disorder and as a result the entropy of the substance increases. Thus, on increasing the temperature of a substance the entropy of a substance increases. It decreases on decreasing the temperature of a substance.

According to Walther Nernst, the entropy of a pure perfectly crystalline substance approaches zero as the temperature approaches absolute zero. This is known as the *Third law of thermodynamics*. This third law of thermodynamics helps us to calculate the absolute value of molar entropies (S_m) of substances at different temperatures. The standard molar entropies of some substances at 298 K are given in Table 12.1

Table 12.1: Standard molar entropies (S_m^0/J K^{-1} mol^{-1}) at 298 K

Solids	Entropy	Liquid	Entropy	Gases	Entropy
C (graphite)	5.7	H_2O	69.9	H_2	130.7
C (diamond)	2.4	Hg	76.0	O_2	205.1
Fe	27.3	C_2H_5OH	160.7	N_2	191.6
Pb	64.8	C_6H_6	173.3	CO_2	213.7
Cu	33.1	CH_3COOH	159.8	NO_2	240.1
Al	96.2			N_2O_4	304.3
$C_{12}H_{22}O_{11}$	360.8			NH_3	192.3
$CaCO_3$	92.9			CH_4	186.2

Entropy Change for a Reaction

The absolute entropies can be used for calculating standard entropies changes accompanying chemical reaction. It can be determined by substracting the standard entropies of reactants from those of products. Thus, for a general reaction

$$aA + bB + ... \longrightarrow pP + qQ + ...$$

$$\Delta S_m^o = [pS_m^o (P) + qS_m^o (Q) + ...] - [aS_m^o (A) + bS_m^o (B) + ...]$$

$$\Delta_r S_m^o = \Sigma S_m^o \text{ (products)} - \Sigma S_m^o \text{ (reactants)}$$

Example 12.2 : Calculate the entropy change, $\Delta_r S_m^o$ for the following reaction at 298 K.

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

Given that the standard molar entropies of Fe(s), O_2(g) and Fe_2O_3(s) at 298 K are 27.3, 205.0 and 87.4 J K^{-1} mol^{-1} respectively.

Solution : $4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$

$$\Delta_r S^o = \Sigma v_p S_m^o \text{ (products)} - \Sigma v_R S_m^o \text{ (reactants)}$$

$$\Delta_r S^o = 2S_m^o (Fe_2O_3) - [4S_m^o (Fe) + 3S_m^o (O_2)]$$

$$= [2 \times 87.4 - (4 \times 27.3 + 3 \times 205.0)] \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= - 549.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

12.6 Gibbs Energy and Spontaneity

When can use the expression

$$\Delta S_{univ} = \Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} \quad > \quad 0 \qquad (12.4)$$

as our basic criterion for a spontaneous change. But it is very difficult to apply it because we have to evaluate the total entropy change i.e. the entropy change of system plus that of surroundings. This is tedious process as it is difficult to figure out all the interactions between the system and the surroundings. Thus, for a system which is not isolated from its surroundings.

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} \qquad (12.5)$$

At constant temperature and pressure if q_p is the heat given out by the system to the surroundings, we can write

$$\Delta S_{surrounding} = \frac{-q_p}{T} = -\frac{\Delta H_{system}}{T} \qquad (12.6)$$

(Since $q_p = \Delta H$ at constant pressure) Substituting Eq. 12.6 in Eq. 12.5, we get

$$\Delta S_{total} = \Delta S_{system} - \frac{\Delta H_{system}}{T}$$

$$T \Delta S_{total} = T \Delta S_{system} - \Delta H_{system}$$

$$\text{or} \quad - T \Delta S_{total} = \Delta H_{system} - T \Delta H_{system} \qquad (12.7)$$

Now, let us define another thermodynamic property, Gibbs energy. It is defined by the equation $G = H - TS$ (12.8)

For a change in Gibbs energy, we write

$$\Delta G = \Delta H - \Delta (TS)$$

$$\Delta G = \Delta H - T \Delta S - S \Delta T$$

For a change at constant temperature, $\Delta T = 0$,

Therefore $\Delta G = \Delta H - T \Delta S$ (12.9)

Since H, T and S are state functions, it follows that G is also a state function. Comparing equations 12.7 and 12.9 we find that

$$\Delta G = - T \Delta S_{total}$$

We have seen that if ΔS_{Total} is positive, the change will be spontaneous. Equations 12.10 can be used to predict the spontaneity of a process based on the value of ΔG.

The use of Gibbs energy has the advantages that it refers to system only. Thus for a process occurring at constant temperature and pressure, if

$\Delta G < 0$ (negative), the process is spontaneous

$\Delta G > 0$ (positive), the process is non-spontaneous

$\Delta G = 0$ (zero), the process is at equilibrium

In deciding the spontaneity of a chemical reaction, the equation $\Delta G = \Delta H - T \Delta S$ takes into account two factors (i) the energy factor ΔH, and (ii) the entropy factor ΔS. Based on the signs of ΔH and ΔS there are four possibilities for ΔG. These possibilities are outlined in table 12.2

Table 12.2 : Criterion for spontaneous change : $\Delta G = \Delta H - T\Delta S$

S. No.	ΔH	ΔS	ΔG	Result
1	–	+	–	Spontaneous at all temperatures.
2	–	–	–	Spontaneous at low temperatures.
			+	Non-spontaneous at high temperatures
3	+	+	+	Non-spontaneous at low temperatures.
			–	Spontaneous at high temperatures.
4	+	–	+	Non-spontaneous at all temperatures.

Example 12.3 : For the reaction $2NO (g) + O_2 (g) \longrightarrow 2NO_2 (g)$

Calculate $\Delta_r G$ at 700 K when enthalpy and entropy changes ($\Delta_r H$ and $\Delta_r S$) are respectively $- 113.0$ kJ mol^{-1} and -145 JK^{-1} mol^{-1}

Solution: Given that

$\Delta H = -133.0 \text{ kJ mol}^{-1}$

$\Delta S = -145 \text{ J K}^{-1} \text{ mol}^{-1} = -145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$

$T = 700 \text{ K}$

Substituting the values in

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = (-113.0 \text{ kJ mol}^{-1}) - (700 \text{ K})(-145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})$$

$$= (-113.0 \text{ kJ mol}^{-1}) + (101.5 \text{ kJ mol}^{-1})$$

$$= -11.5 \text{ kJ mol}^{-1}$$

Intext Questions 12.2

1. Determine whether the following reaction $CCl_4(l) + H_2(g) \rightarrow HCl(g) + CHCl_3(l)$ is spontaneous at 298 K if $\Delta_r H = 91.35 \text{ kJ mol}^{-1}$ and $\Delta_r S = 41.5 \text{ JK}^{-1} \text{ mol}^{-1}$ for this reaction.

....

2. Which of the following conditions would predict a process that is always spontaneous ?

i) $\Delta H > 0, = \Delta S > 0$

ii) $\Delta H > 0, = \Delta S < 0$

iii) $\Delta H < 0, = \Delta S > 0$

iv) $\Delta H < 0, = \Delta S < 0$

....

12.7 Standard Gibbs Energy Change (ΔG^o) and Equilibrium Constant (K)

The standard Gibbs energy change is defined as the change in Gibbs energy for the process in which the reactants in their standard states are converted into the products in their standard states. It is denoted by the symbol $\Delta_r G^o$.

The value of $\Delta_r G^o$ can be found from the standard energy of formation of substances.

The standard Gibbs energy of formation of a compound is defined as the change in Gibbs energy when 1 mole of the compound is formed from its constituent elements in their standard states. Like the standard enthalpy of formation of an element, the standard Gibbs energy of formation of an element in its standard state is taken as zero.

Thus for a reaction

$$aA + bB + \ldots\ldots \longrightarrow pP + qQ + \ldots\ldots$$

$$\Delta_r G^o = [p\,\Delta_f G_P^o + q\,\Delta_f G_Q^o + \ldots..] - [a\,\Delta_f G_A^o + b\,\Delta_f G_B^o + \ldots..]$$

$$\Delta_r G^o = \Sigma\,\Delta_f G^o\,(\text{products}) - \Sigma\,\Delta_f G^o\,(\text{reactants})$$

The standard Gibbs energy change (ΔG^o) is related to the equilibrium constant (K) of the reaction by the expression. r

$$\Delta_r G^o = -RT \ln K = -2.303\,RT \log K$$

Example 12.4: The equilibrium constant of the reaction

$$P(s) + \frac{3}{2} Cl_2(g) \rightleftharpoons PCl_3(g)$$

is 2.00 x 1024 at 500 K. Calculate the value of $\Delta_r G^o$.

Solution : Given that

$K = 2.00 \times 10^{24}$ $T = 500 \text{ K}$

$$\begin{aligned}\Delta_r G^o &= -\ 2.303\ RT \log K \\ &= -\ 2.303 \times (8.314\ \text{J mol}^{-1}\ \text{K}^{-1})\ (500\ \text{K}) \log 2.0 \times 10^{24} \\ &= -\ 2.303 \times (8.314\ \text{J mol}^{-1}\ \text{K}^{-1})\ (500\ \text{K})\ 24.30 \\ &= -\ 232.6\ \text{kJ mol}^{-1}\end{aligned}$$

Example 12.5 : Calculate the standard Gibbs energy change for the reaction

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

at 298K. The standard Gibbs energies of formation of CH_4, CO_2 and H_2O at 298 K are - 50.8 kJ mol^{-1}, - 394.4 kJ mol^{-1} and - 237.2 kJ mol^{-1} respectively.

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

$$\begin{aligned}\Delta_r G^o &= \Delta_f G^o\ (CO_2) + 2\ \Delta_f G^o\ (H_2O) - \Delta_f G^o\ (CH_4) - 2\ \Delta_f G^o\ (O_2) \\ &= -\ 394.4 + 2 \times (-\ 237.2) - (-50.8) - 2 \times 0 \\ &= -\ 394.4 - 474.4 + 50.8 \\ &= -\ 818\ \text{kJ mol}^{-1}\end{aligned}$$

Intext Questions 12.3

1. What is the relationship between the standard Gibbs energy change and the equilibrium constant of the reaction?

……

2. The standard Gibbs energy change for the reaction

$$CO\ (g) + 2H_2\ (g) \rightleftharpoons CH_3OH\ (l)$$

at 298 K is -24.8 kJ mol^{-1}. What is the value of the equilibrium constant at 298 K?

……

What You Have Learnt

- All spontaneous process lead to an increase in disorder or randomness.
- The thermodynamic function related to disorder in a system is called entropy, S.
- For a spontaneous change the total entropy change of the system and the surroundings must increase.
- Gibbs energy is defined as G = H - TS.
- At a constant temperature, the change in Gibbs free energy is related to enthalpy and entropy changes by the expression.

  $$\Delta G = \Delta H - T \Delta S$$

- For a spontaneous change, there must be a decrease in Gibbs energy, i.e., $\Delta G < 0$. At equilibrium $\Delta G = 0$.
- The standard Gibbs energy change is related to the equilibrium constant of the reaction by the expression

  $$\Delta_r G^0 = -2.303\ RT \log K$$

- The standard Gibb's energy change is given by

  $$\Delta_r G^o = \Sigma\ \Delta_f\ G^o\ (\text{products}) - \Sigma\ \Delta_f\ G^o\ (\text{reactants})$$

Terminal Exercise

1. What do you call the measure of disorder or randomness in a system?
2. Predict the sign of Δ S for each of the following processes.

   a) H_2 (g) $\rightarrow$ 2H (g)

   b) O_2 (g, 300 K) + O_2 (g, 500 K)
3. Define entropy.
4. Explain why entropy is not a good criteria for determining the spontaneity of a process ?
5. What is the relationship between the enthalpy and the entropy change for a system at equilibrium ?
6. For the reaction

   a) O_3 (g) + O (g) $\rightarrow$ $2O_2$ (g)

   $\Delta_rH = -\ 391.9$ kJ mol^{-1} and $\Delta_rS = 10.3$ J K^{-1} mol^{-1} at 298 K.

   Calculate Δ_rG at given temperature and state whether the reaction is spontaneous or not.
7. What happens to Δ_rG during

   a) a spontaneous process

   b) a non-spontaneous process

   c) a process at equilibrium
8. Calculate Δ_rG^0 at 298 K for the reaction

   2NO (g) $\rightarrow$ N O (g)

   Given Δ_r H = - 57.20 kJ mol^{-1} and Δ_r S = - 175.8 JK^{-1} mol^{-1}

   Is this reaction spontaneous ?
9. The standard Gibbs energies of formation at 298 are -202.85 kJ mol^{-1} for NH Cl (s), -16.45 kJ mol^{-1} for NH_3(g) and -95.3 kJ mol^{-1} for HCl (g)

   a) What is Δ_rG^0 for the reaction

   NH_4Cl (S) $\rightleftharpoons$ NH_3 (g) + HCl (g)

   b) Calculate the equilibrium constant for this decomposition.
10. For the following reaction

    CCl_4 (l) + H_2 (g) $\rightleftharpoons$ HCl(g) + $CHCl_3$ (l)

    $\Delta_rG^0 = -103.7$ kJ mol^{-1} at 298 K. Calculate the equilibrium constant for this reaction.

Answers to Intext Questions

12.1

1. $\Delta_{fus}S = \frac{\Delta_{fus}H}{T} = \frac{6.02\ kJ\ mol^{-1}}{273\ K} = \frac{6.02\ x\ 10^3\ J\ mol^{-1}}{273\ K}$

   $= 22.0$ J mol^{-1} K^{-1}

2. 1 mol of solid, 1 mol of liquid, 1 mol of gas.
3. (a) Decrease (b) Decrease (c) Increase

12.2

1. Δ G = - 103.7 kJ. Therefore the reaction is spontaneous.
2. (iii)

12.3

1. $\Delta G^0 = -\ 2.303\ RT \log K$
2. 2.2×10^4

Module - V

Chemical Dynamics

13. Chemical Equilibrium
14. Ionic Equilibrium
15. Electro Chemistry
16. Chemical Kinetics
17. Adsorption and Catalysis

Chapter 13

CHEMICAL EQUILIBRIUM

When reactants are mixed in exact stoichiometric proportion to perform a chemical reaction, it is believed that all the reactants would be converted into products with the release or absorption of energy. This is not true in all cases. Many chemical reactions proceed only to a certain extent and stop. When analysed, the resulting mixture contains both the reactants and products. It is because when reactants combine to form products, the products also start combining to give back the reactants.

When such opposing processes take place at equal rates, no reaction appears to take place and it is said that a state of equilibrium has reached. In this lesson, we will examine many aspects of chemical equilibrium. We shall also discuss how can we control the extent to which a reaction can proceed by changing the various conditions of the equilibrium.

Objectives

After reading this lesson you will be able to:

- differentiate between static and dynamic equilibirum;
- identify and differentiate between reversible and irreversible reactions;
- explain the reversible reaction occuring at the equilibrium state;
- list and explain characteristics of equilibrium state;
- apply the law of equilibrium and write expression of equilibrium constant for different types of equilibria, namely physical, chemical, homogenous and heterogenous;
- state and derive the relation between K_c and K_p and carry out some calculations involving them and
- list the factors which affect the state of equilibrium and state and apply Le-Chatelier principle.

13.1 Static and Dynamic Equilibrium

The state equilibrium can be observed in physical and chemical systems. Also, equilibrium can be static or dynamic in nature. A book lying on the table is an example of static equilibrium. The force of action and reaction cancel each other and no change takes place. Thus it is a case of static equilibrium. On the other hand, when an escalator is coming down and a passenger is going up at the same speed it is a case of dynamic equilibrium. Here, because both are moving in opposite directions and at the same speed, no net change takes place. The equilibrium established in the above examples are in physical systems.

13.2 Reversible and Irreversible Reactions

Chemical reactions can be classified as : **Reversible and Irreversible reactions.**

13.2.1 Reversible reactions

Consider the reaction between ethanol and acetic acid. When mixed in the presence of dilute sulphuric acid they react and form ethyl acetate and water.

$$C_2H_5OH(l) + CH_3COOH(l) \xrightarrow{H^+} CH_3COO\ C_2H_5(l) + H_2O(l)$$

On the other hand, when ethyl acetate and water are mixed in the presence of dilute sulphuric acid the reverse reaction occurs.

$$CH_3COOC_2H_5(l) + H_2O(l) \xrightarrow{H^+} CH_3COOH(l) + C_2H_5OH(l)$$

It may be noted here that the second reaction is reverse of the first one and under the same conditions, the two reactions occur simultaneously. Such reactions which occur simultaneously in opposite directions are called reversible reactions.

A reaction is said to be reversible if under certain conditions of temperature and pressure, the forward and reverse reactions occur simultaneously.

Reversible reactions are indicated by placing two half arrows pointing in opposite directions ($\rightleftharpoons$) between the reactants and products. Thus the above reaction is more appropriately written as

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOHC_2H_5\ (l) + H_2O(l)$$

When ethyl acetate and water are formed in the forward reaction the reverse reaction also starts in which ethanol and acetic are formed. After some time the concentrations of all reactants and products become constant. This happens when the rates of forward and reverse reactions become equal; and all the properties of the system become constant. It is said that the system has attained *state of equilibrium*. However it may be noted that the state of equilibrium is reached only if the reaction is carried out in a closed system. At the time of equilibrium, forward and reverse reactions are taking place and it is in a state of dynamic equilibrium because no change is taking place.

A reversible reaction is said to be in the equilibrium state when the forward and backward reaction occur simultaneously at the same rate in a closed system and the concentrations of reactants and products do not change with time

A common example of reversible reactions of the type A + B $\rightleftharpoons$ C + B

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOH + H_2O$$

The following graphs Fig. 13.1 shows the equilibrium state in a reversible reactions.

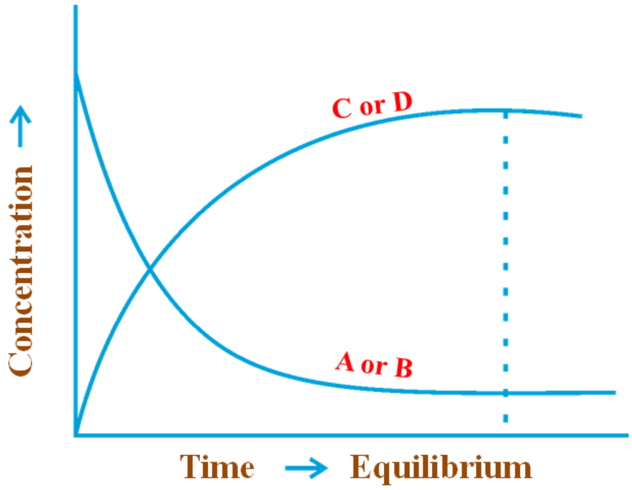


Fig. 13.1 : *Equilibrium in reversible reaction*

The graph depicts that the rate of forward reaction gradually decreases while the rate of backward reaction increase till they become constant and equal to each other.

13.2.2 Irreversible reactions

Most of the reactions occur only in one direction. They are called *irreversible reactions.* For example when carbon is burnt in air to form carbon dioxide the reaction goes only in one direction i.e. in the direction of formation of carbon dioxide.

$$C\ (s) + O_2\ (g) \rightarrow CO_2\ (g)$$

Strictly speaking all reactions are considered to be reversible. But the rate of reaction in one particular direction is extremely small compared to the other. Thus the reaction proceeds practically in one direction to near completion, leaving a negligibly small amount of reactant at the end.

When hydrochloric acid is mixed with sodium hydroxide, a base, in equimolar quantities, a neutralisation reaction takes place; with the formation of salt and water.

$$HCl\ (aq) + NaOH\ (aq) \rightarrow NaCl\ (aq) + H\ O\ (l)$$

This reaction proceeds to completion in the forward direction. Similarly when a solution of silver nitrate is added to a solution of sodium chloride silver chloride is precipitated immediately.

$$NaCl\ (aq) + AgNO\ \ (aq) \rightarrow AgCl\ (s) + NaNO\ \ (aq)$$

13.3 Characteristics of Equilibrium State

1. The state of chemical equilibrium is reached in a reversible reaction when;
    - i) the temperature of the system attains a constant value.
    - ii) the pressure of the system attains a constant value.
    - iii) the concentrations of all the reactants and products attain constant value.

The state of equilibirum has following characteristic properties:

i) Chemical equilibrium is dynamic in nature.

The chemical equalibrium is the result of two equal but opposite processes occurring in the forward and reverse directions and there is no "net" change occurring in the system.

ii) Equilibrium can be attained from either side

The same state of equilibrium characterized by its equalibrium constant which is discussed later can be reached whether the reaction is started from the reactants or products side. For example, the same equilibrium is established whether we start the reaction with N_2O_4 or NO_2.

$$N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g)$$

iii) Equilibrium can be attained only in a closed system

Equilibrium can be attained only if no substance among, reactants or products, is allowed to escape i.e. the system is a closed one. Any system consisting of gaseous phase or volatile liquids must be kept in a closed container, e.g.

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2\ NH_3\ (g)$$

A system consisting of only non-volatile liquid and solid phases can be kept even in an open container because such substances have no tendency to escape, e.g.

$$FeCl_3\ (aq) + 3NH_4SCN\ (aq) \rightleftharpoons Fe\ (SCN)_3\ (s) + 3\ NH_4Cl\ (aq)$$

iv) A catalyst cannot change the equilibrium state

Addition of a catalyst speeds up the forward and reverse reactions by same extent and help in attaining the equilibrium faster. However, the equilibrium concentrations of reactants and products are not affected in any manner.

13.4 Equilibrium in Physical Process; Phase Equilibrium

State of equilibrium can also be reached in physical processes.

13.4.1 Liquid - Vapour Equilibrium

Let us take some quantity of a liquid in an empty container and close it. Initially the vapour pressure above the liquid will be zero. The liquid will evaporate and its vapour will fill the empty space above it.

$$\text{Liquid} \rightarrow \text{Vapour}$$

The rate of evaporation is maximum in begining. As vapour build up, its pressure increases and the rate of evaporation slows down. Also the reverse process of condensation begins (Fig. 13.2).

$$\text{Vapour} \rightarrow \text{Liquid}$$

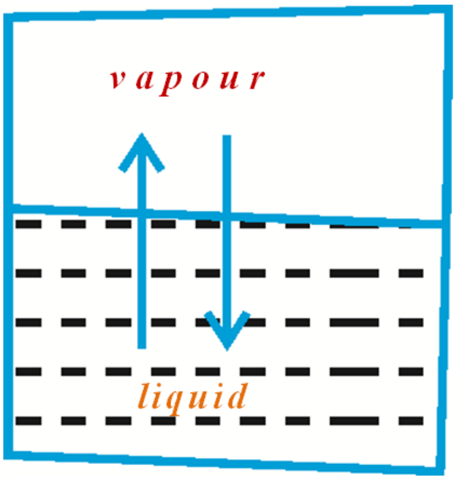


Fig. 13.2 : *Liquid Vapour equilibrium*

and its rate gradually increases with the increase in the vapour pressure. After some time the two rates (of evaporation and condensation) become equal and the following equilibrium is established.

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

At equilibrium the vapour pressure reaches its maximum value and is known as the **saturated vapour pressure** or simply the vapour pressure. At a fixed temperature, each liquid has its own characteristic vapour pressure. The vapour pressure of a liquid increases with rise in temperature.

13.4.2 Solid - Vapour Equilibrium

Volatile solids sublime form vapour. The situation is just similar to the liquid vapour system. When kept in a closed container at a constant temperature the following equilibrium is established.

$$\text{Solid} \rightleftharpoons \text{Vapour}$$

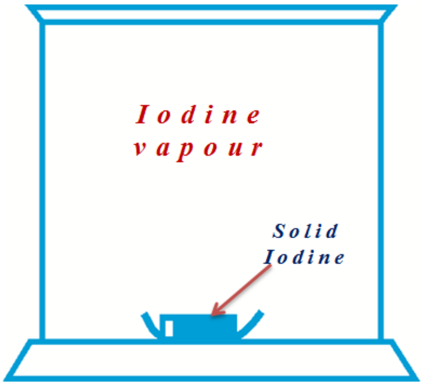


Fig. 13.3 : *Solid vapour equilibrium*

Such an equilibrium can be established by keeping some solid iodine in a gas jar covered with a lid. (Fig. 13.3). Gradually the purple coloured iodine vapours fill the jar and the following equilibrium is established.

$$I_2\,(s) \rightleftharpoons I_2\,(g)$$

13.4.3 Solid - Liquid Equilibrium

Below its freezing point a liquid freezes spontaneously

Liquid → Solid

When heated above its melting point the solid melts spontaneously

Solid → Liquid

At the melting point, the two phases are in equilibrium

Solid $\rightleftharpoons$ Liquid

Because the above two processes occur simultaneously and at the same rate. Such equilibrium is characterized by its temperature i.e. the melting point of the solid.

13.4.4 Solute - Solution Equilibria

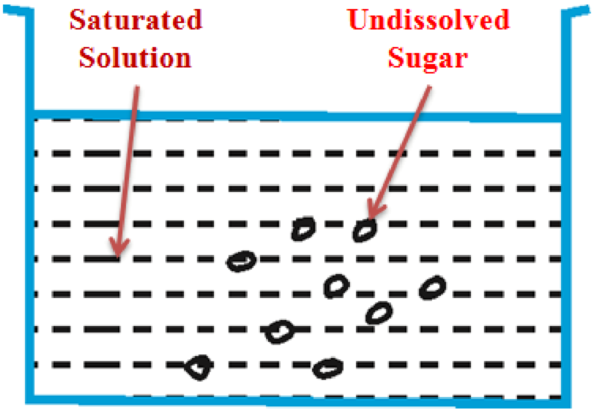


Fig. 13.4: *Solute - Solution equilibrium*

When sugar crystals are put in a saturated solution of sugar in water; it will appear that no change is taking place and sugar appears to remain undissolved. Actually, the undissolved sugar does dissolve in the saturated sugar solution; and an equal amount of sugar separates out from the solution. The solid sugar and the sugar solution form an equilibrium system which is dynamic in nature.

sugar (s) $\rightleftharpoons$ sugar solution (saturated)

The equilibrium is established when the rate of dissolution of sugar becomes equal to the rate of crystallisation. In general such equilibrium can be represented as

$$\text{solute (s)} \rightleftharpoons \text{solution (saturated)}$$

The equilibrium is known as **Solubility Equilibrium**.

13.4.5 Phase and Phase Equilibrium

You must have noticed in each of the above equilibria the system consists of two distinct parts; solid, liquid, solution or vapour. Each of these parts is called a phase.

A phase is defined as a homogenous part of a system which has uniform composition and properties throughout.

A phase is not the same as physical state. A mixture of two solids, even when powdered finely is a two phase system. This is because particles of the two solids have different chemical compositions and physcial properties. Completely miscible liquids, solutions and all gaseous mixture constitute only one phase each.

All the cases of physical equilibrium are in fact the systems in which different phases are in equilibrium; only if they contain, at least one common component. A dynamic exchange of the common component between two phases takes place. When the rates of exchange become equal the equilibrium is established. In solid solute and solution equilibrium the example given earlier, sugar is the common component.

13.5 Equilibrium in Homogeneous and Heterogeneous Systems

13.5.1 Homogeneous and Heterogeneous Systems

Homogeneous system is one which has one phase. It has the same chemical composition and uniform properties throughout. It is formed by particles of molecular size only. Pure solids, liquids, gases and solutions are the examples of homogeneous systems.

A system consisting of only one phase is called a homogeneous system

Hetergeneous system, on the other hand has at least two phases - a mixture of solids or immiscible liquids constitutes a heterogeneous system.

Any system consisting of two or more phases is called heterogeneous system

13.5.2 Homogeneous and Heterogeneous Equilibrium Systems

Equilibrium can be established in either type of systems. Since all physical equilibria involve at least two phases, therefore these are all examples of heterogeneous equilibrium. But chemical equilibrium can be homogeneous or heterogeneous in nature. It is homogeneous if both the reactants and products are present only in one phase gas or liquid and heterogeneous if present in more than one phase. In the following sections we shall study such systems.

13.5.3 Homogeneous Chemical Equilibrium Systems

(a) Gas - Phase homogeneous systems

Such systems contain only gaseous reactants and products. Since all gaseous mixtures are homogeneous in nature they constitute only one phase. Following are examples of this type of equilibrium.

i) $N_2\text{ (g)} + 3H_2\text{ (g)} \rightleftharpoons 2NH_3\text{ (g)}$

ii) $2N_2O_5\text{ (g)} \rightleftharpoons 4NO_2\text{ (g)} + O_2\text{ (g)}$

(b) Liquid - Phase homogeneous systems

These are the sytems in which both the reactants and products are present in only one liquid phase (as a solution) for example :

i) $CH_3\ COOH(l) + C_2H_5OH(l) \overset{H^+}{\rightleftharpoons} CH_3COOC_2H_5(l) + H_2O(l)$

ii) $KCN\ (aq) + H_2O(l) \rightleftharpoons HCN\ (aq) + KOH\ (aq)$

13.5.4 Heterogeneous Chemical Equilibrium Systems

The systems in which reactants and products are present in more than one phase belong to this type. For example:

i) $Fe\ (s) + 4H_2O(g) \rightleftharpoons Fe_3O_4\ (s) + 4H_2\ (g)$

ii) $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$

Intext Questions 13.1

1. What is a reversible reaction? Give two examples.

....

2. When does a reaction reach equilibrium state?

....

3. How would you know whether a system has reached the equibrium state or not?

....

4. Give two examples of physical equilibrium.

....

5. Give two examples each of chemical homogeneous and heterogeneous equilibria.

....

13.6 Quantitative Aspect of Equilibrium State

13.6.1 Law of Equilibrium and Concentration Equilibrium Constant

Consider the following equilibrium $H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$

At equilibrium the concentrations of H_2, I_2 and HI become constant. Also, it has been found experimentally that irrespective of the starting concentration of H_2, I_2 the following ratio of concentration terms always remains constant.

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Here $[H_2]$, $[I_2]$ and [HI] represent the equilibrium molar concentrations of H_2, I_2 and HI respectively and K_C is called the ***concentration equilibrium constant*** (sometimes it is written as simply K). In general, for reversible reaction

$$aA + bB \rightleftharpoons cC + dD$$

at equilibrium, the following ratio of concentration terms always remains constant at a given temperature.

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The above relation is known as the **law of equilibrium**. It may be noted here that all the concentrations values in the law of equilibrium are the equilibrium concentrations of reactants and products. The numerator of the law of equilibrium is the products of equilibrium molar concentrations of products, each term being raised to the power equal to its stoichiometric coefficient in the chemical equation and the denominator contains products of similar concentration terms of reactants.

13.6.2 Pressure Equilibrium Constant Kp

In case of gases their partial pressures can also be used in place of molar concentrations (since the two are directly proportional to each other) in the law of equilibrium. The new equilibrium constant, K_p, is called the pressure equilibrium constant. For the reaction between H_2 and I_2, K_p is given by

$$K_c = \frac{P^2 HI}{P_{H_2} \text{ x } P_{I_2}}$$

Here P_{H2}, $P_{I2}$and $P_{H1}$are the equilibrium partial pressures of H_2, I_2 and H_I respectively. For the general gas phase reaction:

$$a\,A\,(g) + b\,B\,(g) \rightleftharpoons c\,C\,(g) + d\,D\,(g)$$

it is given by :

$$K_p = \frac{P_C^c \text{ x } P_D^d}{P_A^a \text{ x } P_B^b}$$

13.6.3 Relation between Kp and Kc

For a general gas phase reaction at equilibrium

$$a\,A\,(g) + b\,B\,(g) \rightleftharpoons c\,C\,(g) + d\,D\,(g)$$

The pressure and concentration equilibrium constants K_p and K_c are

$$K_p = \frac{P_C^c \text{ x } P_D^d}{P_A^a \text{ x } P_B^b} \text{ and } K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

For a gaseous substance i, the ideal gas equation is $P_1V = n_1RT$

where p_1 and n_1 are its partial pressure and amount in a gaseous mixture and V and T are its volume and temperature and R is the gas constant. The relation may be written as

$$P_1 = \frac{n_1}{V} RT = c_1 RT$$

Where c_i is the molar concentration or molarity of 'i' expressed in moles per litre. This relation can be used for replacing the partial pressure terms in the expression for K_p.

$$K_p = \frac{(C_C\ RT)^c\ (C_D\ RT)^d}{(C_A\ RT)^a\ (C_B\ RT)^b}$$

$$= \frac{C_C^c \text{ x } C_D^d}{C_A^a \text{ x } C_B^b} (RT)^{(c+d)-(a+b)}$$

Using the square bracket notation for molar concentration the relation can be written as

$$K_p = \frac{[C]^c[D]^d}{[A]^a[B]^b} (RT)^{(n_p + n_R)}$$

$$= K_C (RT)^{\Delta n_g}$$

where Δn_g is the change in the moles of gaseous substances in the reaction and is equal to the difference in the moles of gaseous products n_p and the moles of gaseous reactants, n_R. Δn_g may be zero positive or negative.

i) In the reaction

$H_2 (g) + I_2 (g) \rightleftharpoons 2HI (g)$

Here n_p = moles of the gaseous product is equal to 2

n_R = moles of gaseous reactant H_2 and I_2 is equal to 2 (as 1 + 1).

Hence $\Delta n_g = n_p - n_g = 2 - 2 = 0$.

ii) In the reaction

$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$

$n_p = 2$, $n_R = 1 + 3 = 4$.

and $\Delta n_g = 2 - 4 = - 2$

iii) In the reaction involving solids and gases

$CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2 (g)$

$\Delta n_g = 1$

13.6.4 Expressions of Equilibrium Constant for Some Reactions

The law of equilibrium can be applied to write down expressions of K_C and K_P for some reactions.

13.7 Homogeneous Equilibria

i) Decomposition of N_2O_4

$N_2O_4 (g) \rightleftharpoons 2NO_2 (g)$

$$K_C = \frac{[NO_2]^2}{[N_2O_4]} \ ; \ K_P = K_P = \frac{P^2_{NO_2}}{P_{N_2O_4}}$$

ii) Oxidation of sulphur dioxide

$2SO_2 (g) + O_2 (g) \rightleftharpoons 2SO_3 (g)$

$$K_C = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \ ; \ K_P = \frac{P^2_{SO_3}}{P^2_{SO_2} . P_{O_2}}$$

iii) Esterification of acetic acid with ethanol

$CH_3COOH (I) + C_2H_5OH (I) \rightleftharpoons CH_3COOC_2H_5(I) + H_2O (I)$

$$K_C = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$$

In this reaction no gas is involved, therefore expression for K_P is meaningless.

13.7.1 Heterogeneous Equilibrium

Consider the following equilibrium

$CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2 (g)$

According to the law of equilibrium

$$K_C = \frac{[CaO]\ [CO_2]}{[CaCO_3]}$$

Here $CaCO_3$ and CaO are pure solids. The concentration of any solid is constant at a fixed temperature therefore these are not written in expression for equilibrium constant for heterogenous reactions. Equilibrium constant for the reaction can be written as

$K_C = [CO_2]$ and $K_P = Pco_2$

Following are some more examples of heterogenous equilibrium

i) Reaction between iron and steam

$$3Fe\ (s) + 4H_2O\ (g) \rightleftharpoons Fe_3O_4\ (s) + 4H_2\ (g)$$

$$K_C = \frac{[H_2]^4}{[H_2O]^4} \ ; \ K_P = \frac{P^4_{H_2}}{P^4_{H_2O}}$$

ii) Liquid - Vapour Equilibrium

$$H_2O\ (I) \rightleftharpoons H_2O\ (g)$$

$K_C = [H_2O; g];$ $K_P = P_{H_2O}$

13.8 Characteristics of Equilibrium Constant

13.8.1 Equilibrium Constant and Chemical Equation

The expression of equilibrium constant depends upon the manner in which the chemical equation representing it is written. For the reaction

$$H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$$

The equilibrium constant K is given by $K = \frac{[HI]^2}{[H_2][I_2]}$

a) When the same reaction is written as

$$1/2\ H_2\ (g) + 1/2\ I_2\ (g) \rightleftharpoons HI\ (g)$$

the corresponding equilibrium constant K_I is given by

$$K_1 = \frac{[HI]}{[H_2]^{\frac{1}{2}}[I_2]^{\frac{1}{2}}}$$

It may be noted that equilibrium constant K and K_1 are related as $K_1 = \sqrt{K}$

b) When the reaction is written as reverse

$$2HI\ (g) \rightleftharpoons H_2\ (g) + I_2\ (g)$$

$$K_2 = \frac{[H_2][I_2]}{[HI]^2}$$

Here in can be seen that

$$K_2 = \frac{1}{k}$$

Similar relationship is also observed in the pressure equilibrium constant K_p. Thus the expression of equilibrium constant depends on how the reaction is expressed in the form of a chemical equation.

13.8.2 Units of Equilibrium Constant

Units of equilibrium constant K_C or K_P depend upon the fact whether during the reactions there is any change in the moles of substance or not.

a) The reactions in which there is no change in moles of substance i.e. $\Delta n = 0$.

The equilibrium constant for such reaction has no units. For example in the reaction between H_2 and I_2

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$

$$K_C = \frac{[HI]^2}{[H_2][I_2]} \qquad K_P = \frac{P^2_{HI}}{P_{H_2}.P_{I_2}}$$

$$K_C = \frac{(mol\ L^{-1})^2}{(mol\ L^{-1})\ (mol\ L^{-1})} \qquad K_P = \frac{bar^2}{(bar)\ (bar)}$$

∴ Hence K_P and K_C have no units in such cases.

b) The reaction where there is change in the moles of substance i.e. $\Delta n \neq 0$.

The equilibrium constant for such reactions has units which depend upon the change in moles of substances.

For example:

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

$$\Delta n = \Delta n_p - \Delta n_R$$

The units of K_C for this reaction would be $(mol\ L^{-1})^{-2}$ or $L^2\ mol^{-2}$ and those of K_P would be bar^{-2} as shown below:

The equilibrium constant for such reactions are

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3} \qquad K_P = \frac{P^2_{NH_3}}{P_{N_2}\ x\ P^3_{H_2}}$$

$$K_C = \frac{(mol\ L^{-1})^2}{(mol\ L^{-1})\ (mol\ L^{-1})^3} \qquad K_P = \frac{pressure^2}{pressure.\ pressure^3}$$

$$= (mol\ L^{-1})^{-2} \qquad = pressure^{-2}$$

$$= L^2\ \ mol^{-2} \qquad = bar^{-2}$$

For the reaction

$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$

$\Delta n = 2 - 1 = 1$. Therefore,

The units for K_C and K_P are

$K_C = mol\ L^{-1}$ and $K_P = bar$

13.8.3 Significance of the Magnitude of K

The equilibrium constant of a reaction has a constant and characteristic value at a given temperature. The changes in starting concentration, pressure and the presence of a catalyst do not change the value of the equilibrium constant. However if the temperature is changed. The value of the equilibrium constant also changes.

The magnitude of the equilibrium constant is a measure of the extent up to which a reaction proceeds before the equilibrium is reached. The magnitude of K is large when the products are present in larger amounts than the reactants in the equilibrium mixture. For the reaction

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g) \qquad K_C = 90 \text{ at } 298\text{ K}$$

and for $$2CO\,(g) + O_2\,(g) \rightleftharpoons 2CO_2\,(g) \qquad K_P = 2.2 \times 10^{22} \text{ at } 1000\text{ K}$$

A large value of K_C for the second reaction indicates that amount of products is much more than the reactants present at the time of equilibrium. Thus the magnitude of equilibrium constant tells us about the position of the equilibrium.

13.8.4 Calculation of Equilibrium Constants

Equilibrium constants K_C and K_P can be calculated if the equilibrium concentrations or partial pressures are known or can be obtained from the given data. The following examples illustrate the calculations.

Example 13.1: Calculate the equilibrium constant for the reaction

$$A\,(g) + B\,(g) \rightleftharpoons C\,(g) + D\,(g)$$

If at equilibrium 1 mol of A, 0.5 mole of B, 3.0 mole of C and 10 mol of D are present in a one litre vessel.

Solution: From the law of equilibrium

$$K_c = \frac{[C]\,[D]}{[A]\,[B]}$$

Since the volume of the vessel is one litre, the number of moles of A, B, C and D are equal to their concentrations. Thus

$[A] = 1 \text{ mol L}^{-1}$, $[B] = 0.5 \text{ mol L}^{-1}$, $[C] = 3.0 \text{ mol L}^{-1}$ and $[D] = 10 \text{ mol L}^{-1}$ and

$$K_c = \frac{(3.0\text{ mol L}^{-1})\ (10\text{ mol L}^{-1})}{(1\text{ mol L}^{-1})\ (0.5\text{ mol L}^{-1})} = \frac{3.0 \times 10}{1 \times 0.5} = 60$$

Example 13.2: In an experiment carried out at 298K, 4.0 mol of NOCl were placed in a 2 litre flask and after the equilibrium was reached 1.32 mol of NO were formed. Calculate K_C at 298 K for the reaction

$$2\,NOCl\,(g) \rightleftharpoons 2\,NO\,(g) + Cl_2\,(g)$$

Solution: Calculation of equilibrium concentrations

i) $$[NO] = \frac{\text{No. of moles of NO}}{\text{Volume}} = \frac{1.32\text{ mol}}{2L} = 0.66\text{ mol L}^{-1}$$

ii) $$[Cl_2] = \frac{\text{No. of moles of } Cl_2}{\text{Volume}} = \frac{\frac{1}{2}\,(\text{No. of moles of NO})}{\text{Volume}} = \frac{1.32\text{ mol}}{2 \times 2L} = 0.33\text{ mol L}^{-1}$$

iii) $$[NOCl] = \frac{\text{No. of moles NOCl}}{\text{Volume}} = \frac{(\text{Initial moles} - \text{moles decomposed})}{\text{Volume}}$$

$$= \frac{(4.0 - 1.32\text{ mol})}{2L} = \frac{2.68\text{ mol}}{2L}\ \ 1.34\text{ mol L}^{-1}$$

For the reaction

$$2\,NOCl\,(g) \rightleftharpoons 2\,NO\,(g) + Cl_2\,(g)$$

$$K_c = \frac{[NO]^2\,[Cl_2]}{[NOCl]^2} = \frac{(0.66\text{ mol L}^{-1})^2\,(0.33\text{ mol L}^{-1})}{(1.34\text{ mol L}^{-1})^2} = \frac{(0.66)^2 \text{ x } 0.33}{(1.34)^2}$$

$= 0.080 \text{ mol L}^{-1}$

$K_C = 0.080 \text{ mol L}^{-1}$

Example 13.3: 2 mol of HI were heated in a vessel of one litre capacity at 713 K till the equilibrium was reached. At equilibrium HI was found to be 25% dissociated. Calculated K_C and K_P for the reaction

Solution: Initial moles of HI = 2

$$\text{Moles of HI dissociated} = \frac{25 \text{ x } 2}{100} = 0.5 \text{ mol}$$

Moles of HI at equilibrium = 2.0 - 0.5 = 1.5 mol

The dissociation of HI occurs as

	2HI (g) $\rightleftharpoons$	**H2 (g)** +	**I2 (g)**
Initial moles	2	0	0
Equilibrium moles	(2 - 0.5)	0.25	0.25
	1.5 mol	0.25 mol	0.25 mol
Volume of reaction vessel	1 L	1 L	1 L
Equilibrium concentration	1.5 mol L^{-1}	0.25 mol L^{-1}	0.25 mol L^{-1}

For the reaction

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{(0.25\text{ mol L}^{-1})\,(0.25\text{ mol L}^{-1})}{(1.5\text{ mol L}^{-1})^2} = \frac{(0.25)^2}{(1.5)^2} = 0.028$$

Also $K_p = K_c\,(RT)^{\Delta n}{}_{g}$

For this reaction

$= \Delta\, n_g = \Delta n_P - \Delta\, n_R = 2 - 2 = 0$

$\therefore K_p = K_c = 0.028$

Example 13.4: Calculate K_P for the reaction $COCl_2 \rightleftharpoons CO + Cl_2$ in atm and Nm^{-2}.

The equilibrium partial pressures of $COCl_2$, CO and Cl_2 are 0.20, 0.16 and 0.26 atm respectively (1 atm = 101300 Nm^{-2})

Solution: **i) Kp in atmospheres**

$COCl_2\,(g) \rightleftharpoons CO\,(g) + Cl_2\,(g)$

$$K_P = \frac{P_{CO} \text{ x } P_{Cl_2}}{P_{COCl_2}} = \frac{(0.16\text{ atm})\,(0.26\text{ atm})}{(0.20\text{ atm})} = \frac{0.16 \text{ x } 0.26}{0.20}\text{ atm}$$

$= 0.21$ atm.

ii) K_P in Nm^{-2}

$K_P = 0.21$ atm and 1 atm = 101300 Nm^{-2}

$\therefore K_p = (0.21 \text{ atm})\,(101300\text{ Nm}^{-2}\text{ atm}^{-1}) = 21273\text{ Nm}^{-2}$

Example 13.5: When equal number of moles of ethanol and acetic acid. Were mixed at 300K, two-third of each had reacted when the equilibrium was reached. What is the equilibrium constant for the reaction?

$CH_3COOH\,(l) + C_2H_5OH\,(l) \rightleftharpoons CH_3COOC_2H_5\,(l) + H_2O\,(l)$

Solution: Let *n* moles each of acetic acid and ethanol be mixed initially. Then the number of moles each reacted = 2/3 *n*.

Let V be the volume of the reaction mixture in litres.

$$CH_3COOH\,(l) + C_2H_5OH\,(l) \rightleftharpoons CH_3COOC_2H_5\,(l) + H_2O\,(l)$$

Initial mole	n	n	0	0
Equilibrium concentration in moles	$(n - {}^{2}/_{3}\,n)$	$(n - {}^{2}/_{3}\,n)$	${}^{2}/_{3}\,n$	${}^{2}/_{3}\,n$
	${}^{1}/_{3}\,n$	${}^{1}/_{3}\,n$	${}^{2}/_{3}\,n$	${}^{2}/_{3}\,n$
Equilibrium concentration	$\frac{n}{3V}$	$\frac{n}{3V}$	$\frac{2n}{3V}$	$\frac{2n}{3V}$

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$$

$$= \frac{\left(\frac{2n}{3V}\right)\left(\frac{2n}{3V}\right)}{\left(\frac{n}{3V}\right)\left(\frac{n}{3V}\right)} = 2 \text{ x } 2 = 4$$

$K_C = 4$

Intext Questions 13.2

1. For a reversible reaction

$2A + B \rightleftharpoons 3C + 3D$

Write the expression for the equilibrium constant

....

2. What is the relation between K_P and K_C.

....

3. i) Apply the law of equilibrium to the following and write the expression for K_P and K_C.

a) $CO_2\,(g) + H_2\,(g) \rightleftharpoons CO\,(g) + H_2O\,(g)$

b) $I_2\,(s) \rightleftharpoons I_2\,(g)$

ii) For the above reaction write equation for K_P and K_C.

....

4. The equilibrium constant for the reactions

i) $N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

ii) ${}^{1}/3\,N_2\,(g) + H_2\,(g) \rightleftharpoons {}^{2}/3\,NH_3$

are K_1 and K_2 respectively. What is the relation between them?

....

5. What is the significance of the magnitude of equilibrium constant ?

....

13.9 Factors Affecting Equilibrium State

Supposing a reaction has reached the equilibrium state and then some conditions like concentrations, temperature, pressure etc. are changed, would it be affecting the equilibrium state. If yes how?

In this section, we shall discuss these questions.

The state of equilibrium is in a dynamic balance between forward and backward reaction. This balance can be disturbed by changing concentration, temperature or pressure. If done so a certain net change occurs in the system. The direction of change can be predicted with the help of ***Le-Chatelier principle***.

13.9.1 Le-Chatelier Principles

It states that when a system in equilibrium is disturbed by a change in concentration, pressure or temperature, a 'net' change occurs in it in a direction that tends to decrease the disturbing factor.

The principle can be applied to various situations.

13.9.2 Change in Concentration

Consider the state of equilibrium for the formation of ammonia from nitrogen and hydrogen.

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)\ ,\ \Delta H = -\,92.4\ \text{kJ/mol}$$

The concentration of nitrogen, hydrogen and ammonia become constant at the point of equilibrium. Now if any amount of reactants or ammonia is added or removed their concentration will change and the equilibrium will get disturbed.

i) **Increase concentration of reactant:** When the concentration of either nitrogen or hydrogen is increased; a net forward reaction will take place which consumes the added reactant.

ii) **Increase in the concentration of any product:** If the concentration of product ammonia is increased, a net backward reaction would take place to utilise the added ammonia.

13.9.3 Change in Pressure

Change in pressure affects equilibrium involving gaseous phase either in a homogeneous or heterogeneous system.

Le Chatelier principles for systems involving gases can be studied as follows:

i) When the number of moles of products is more than the total number of moles of reactants as in the following system:

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

Increase in total pressure keeping the temperature constant, will cause a decrease in volume. This means that the number of moles per unit volume will increase. A net change will take place in the equilibrium in the direction where the number of moles decrease, *i.e.* backward direction.

ii) When the number of moles of products is less than reactants. As in the following case

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

According to Le Chatelier's principle increase in total pressure will bring a net change to the equilibrium in the direction where the total number of moles is decreasing i.e.

to the product side as $\Delta n_g = 2$. Decrease in total pressure will bring the net change to equilibrium in the direction where the total number of moles is increasing i.e. backward direction.

iii) When there is no change in the total number of moles of reactant and product in the following state of equilibrium.

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$

There is no net change in equilibrium state when pressure is changed.

13.9.4 Change of Temperature

According to ***Le Chatelier principle*** when the temperature is changed (increased or decreased) the equilibrium system reacts to nullify the change in heat content. However, the net change in equilibrium is directed by the exothermic or endothermic nature of reaction.

i) **Exothermic equilibrium :** For the following system of equilibrium of exothermic nature:

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)\ ;\ \Delta H = -\ 92.4\ \text{kJ/mol}$$

According to Le Chatelier principle increase in temperature brings a net change in the equilibrium state in that direction where this extra heat is consumed. The net change is in the backward direction and some ammonia will decompose producing nitrogen and hydrogen. Similarly if the temperature is decreased the equilibrium shifts to the forward direction.

ii) Endothermic equilibrium

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)\ ; \qquad \Delta H = +\ 180.7\ \text{kJ/mol}^{-1}$$

If the temperature is increased the added heat will be absorbed by the reactant and the net change takes place to the equilibrium in the forward direction. If the temperature is decreased it will bring a ‘net’ change to equilibrium in the backward direction i.e. direction in which it is exothermic.

Addition of a Catalyst: It does not affect the equilibrium. However it helps to achieve the equilibrium faster.

13.9.5 Applications of Le Chatelier’s Principle

It can be applied to physical as well as chemical equilibria

A) Physical Equilibria

1) Melting of Ice

$$\text{Ice} \rightleftharpoons \text{Water}; \qquad \Delta H = +\ 6\ \text{kJ/mol-1}$$

The change of ice to water is endothermic process. According to Le Chatelier principle if the temperature is increased the net change will take place in the forward direction some ice will melt into water.

When the pressure is increased on the equilibrium system, then the volume should decrease; according to ***Le Chatelier principle*** the net change in equilibrium takes place in the forward direction and ice melts. Therefore, ice melts on increasing the pressure.

2) Vaporization of Water

$$\text{Water (l)} \rightleftharpoons \text{Water vapour}; \qquad \Delta H = +\ \text{ve}$$

This process occurs with a large increase in volume since $\Delta n_g = 1 - 0 = +1$, and it occurs with absorption of heat.

Increasing the temperature results in more vapour formation (endothermic process), since $\Delta n_g = +1$, increase in pressure results in a net change in equilibrium in the backward direction as the volume of water vapours is more than that of liquid water for a given mass of water.

3) Solubility Equilibrium

The equilibrium is

$$\text{Solute (s)} \rightleftharpoons \text{Solute (solution)}$$

The process of dissolution can be endothermic or exothermic. In case of solutes like KCl, KNO_3 and NH_4Cl, ΔH is positive (endothermic) and more solute will dissolve on heating. Thus, the solubility increases with rise in temperature. In case of solutes like KOH and NaOH the ΔH is negative (exothermic) and their solubility decrease on heating.

B) Chemical Equilibria

1) Favourable Conditions for Synthesis of Ammonia: This reaction is of great industrial importance. During the synthesis of ammonia such conditions are maintained which favour the 'net' forward reaction namely low temperature and high pressure. Addition of catalyst makes the reaction occur fast. Besides, nitrogen and hydrogen gases are continuosly fed into the reaction chamber and ammonia is continuously removed. All this keeps the system under stress and equilibrium is never permitted to be attained, so that the synthesis of ammonia continues to occur.

In industry the reaction is carried out at 450^0C and 200 atm pressure in the presence of finely divided iron (catalyst) and molybdenum (promotor)

2) Formation of SO_3

The reaction

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g); \quad \Delta H = -\text{ ve}$$

is extothermic and $\Delta n_g = 2 - 3 = -1$. Formation of SO_3 will be favoured by high pressure and low temperature in the presence of a catalyst.

3) Formation of NO

The reaction

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g), \qquad \Delta H = +\text{ ve}$$

is endothermic and $\Delta n_g = 2 - 2 = 0$. The reaction is not affected by pressure changes and is favoured at high temperature. Presence of a suitable catalyst would be helpful.

Intext Questions 13.3

1. What is Le Chatelier' principle?

....

2. What are the factors that can affect a system at equilibrium?

....

3. What will happen to solid - vapour equilibrium when the temperature and pressure are decreased?

....

4. a) Which of the following will result in 'net' forward reaction in case of

$$A\ (g) + 2B\ (g) \rightleftharpoons C\ (s) + D\ (g); \quad \Delta H = +\ ve$$

a. addition of C
b. addition of A
c. decrease in pressure
d. increase in temperature

....

5. What are the most favourable conditions for the formation of C and D?

....

What You Have Learnt

- A chemical reaction is said to be reversible under certain conditions, if along with the reactants forming the products, the products also react and form back the reactants simultaneously.
- Reversible reactions do not reach completion stage and result in a state of equilibrium which is reached when two opposite processes occur at the same rate.
- The macroscopic properties of the system do not change once the equilibrium has been established.
- Irreversible reactions are in fact the reversible reactions in which the equilibrium is reached only when a negligible amount of the reactants is left unreacted.
- Chemical equilibrium is dynamic in nature. It can be attained by starting the reaction from any side and only in a closed system.
- When equilibrium is reached as a result of two opposite physical changes, it is called physical equilibrium and when as a result of two opposite chemical changes it is called chemical equilibrium.
- A phase is a homogeneous system or a part of a system which has same composition and unifrom properties throughout. It is not same a physical state.
- A system with only one phase is called a homogeneous system and the one with more than one phases called heterogeneous system.
- Chemical equilibrium can be homogeneous or heterogeneous while physical equilibrium is always heterogeneous.
- For a general reaction $aA + bB \rightleftharpoons cC + dD$ according to the law of equilibrium, the equilibrium constant K is given by the expression

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- Concentration equilibrium constant K_c is obtained when molar concentration are used for calculating K. Concentrations of pure solids and liquids are constant and are not included in the expression of K_C.
- In case of gaseous systems, the concentrations of gases are expressed in terms of their partial pressures. The equilibrium constant thus obtained is called the pressure equilibrium constant, K_P.

- The relation between K_P and K_C is = $K_C\ (RT)^{\Delta n_g}$ is where Δn_g is the change in the number of moles of gaseous substances during the reaction.
- Expression of equilibrium constant depends upon how the chemical equation is written for the reaction.
- Magnitude of the equilibrium constant is a measure of how close the reaction is to the completion stage.
- Units of K depend upon the change in the number of moles of the substances during the reaction.
- Concentration, pressure and temperature can affect the equilibrium systems and the affect can be qualitatively predicted by **Le Chatelier's principle** which states that when a system at equilibrium is disturbed by changing concentration, pressure or temperature, a 'net' change occurs in the direction that tends to neutralize the effect of the disturbing factor.
- Changes in concentration and pressure do result in some chemical reaction, but the value of the equilibrium constant is not changed.
- A catalyst does not change the equilibrium constant. It only helps in reaching the equilibrium state quicker.
- A change in temperature changes the value of the equilibrium constant.

Terminal Exercise

1. What do you understand by reversible and irreversible reactions? Give on example of each.

....

2. What is physical equilibrium? Give one example?

....

3. Give characteristics of equilibrium state.

....

4. Is the phase same as physical state? Illustrate your answer with one example of each.

....

5. How do homogeneous and heterogeneous systems differ from each other? Which of the following are homogeneous systems?

a) Liquid $\rightleftharpoons$ Vapour
b) $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$
c) $NH_4Cl\ (s) \rightleftharpoons NH_3\ (g) + HCl\ (g)$
d) $CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$

....

6. What are K_P and K_C? Derive a relation between them.

....

7. Write down the expression of K_C for the following. Also give units in each case.

a) $N_2O_5\ (g) \rightleftharpoons 2NO_2\ (g) + {}^1/2\ O_2\ (g)$

b) CH_4 (g) + H2O (l) $\rightleftharpoons$ CO (g) + $3H_2$ (g)
c) $FeCl_3$ (aq) + $3NH_4SCN$ (aq) $\rightleftharpoons$ Fe $(SCN)_3$ (aq) + $3NH_4Cl$ (aq)

……………………………………………………………………………………………………

8. Write down the expression of KP for the following and give its units (in terms of atmosphere) in each case

a) CO_2 (g) + H_2 (g) $\rightleftharpoons$ CO (g) + H_2O (l)
b) 3Fe (s) + $4H_2O$ (l) $\rightleftharpoons$ Fe_3O_4 (g) + $4H_2$ (g)
c) $2SO_3$ (g) + $2SO_2$ (g) $\rightleftharpoons$ O_2 (g)

……………………………………………………………………………………………………

9. Give the relation between K_C and K_P for the reaction.
a. $CaCO_3$ (s) $\rightleftharpoons$ CaO (s) + CO_2 (g)

……………………………………………………………………………………………………

10. Using the reaction between write K_C and K_P the expression of
a. K_P for the reaction given in Q. No. 7
b. K_c for the reaction given in Q. No. 8

……………………………………………………………………………………………………

11. List the factors that can affect
a) a system at equilibrium and
b) equilibrium constant of a system

……………………………………………………………………………………………………

12. State the Le Chatelier's Principle.

……………………………………………………………………………………………………

13. What will be the effect of the following factors on the following systems at equilibrium?

2 x (g) $\rightleftharpoons$ 2Y (s) + Z (g) ; $\Delta H = + ve$

a) Addition of X,
b) removal of Z
c) addition of a catalyst
d) increasing the pressure and
e) increasing the temperature

……………………………………………………………………………………………………

14. 5 moles, of HI were produced by the reaction between 7.5 moles of H_2 and 2.6 moles of I_2 vapours at 444^0C. What is the equilibrium constant of the reaction.

H_2 (g) + I_2 (g) $\rightleftharpoons$ 2HI (g)

……………………………………………………………………………………………………

15. The equilibrium constant Kp for the reaction
N_2O_4 (g) $\rightleftharpoons$ $2NO_2$ (g)
at 333K is found to be 1.33 atm under a total pressure of 1 atm. Calculate K_p for the reaction

$2NO_2$ (g) $\rightleftharpoons$ N_2O_4 (g)
at 333K and under 1 atm pressure.

....

16. At 444^{0}C, 0.30 mole of H_2 and 0.30 mole of I_2 were taken in a one litre flask. After some time the equilibrium H_2 (g) + I_2 (g) $\rightleftharpoons$ 2HI (g) was established and it was found that the concentration of I_2 decreased to 0.06 mol L^{-1}. Calculate the value of K_C for the reaction at this temperature.

....

17. The equilibrium constant for the reaction.
CH_3COOH (l) + C_2H_5OH (l) $\rightleftharpoons$ $CH_3COOC_2H_5$ (l) + H_2O (l) is 4.0
What will be the composition of the equilibrium mixture if 1 mole of acetic acid is taken with 8 moles of ethanol?

....

18. K_C for the reaction
N_2 (g) + $3H_2$ (g) $\rightleftharpoons$ $2NH_3$ (g)
at 400^{0}C was found to be 0.5 L^2 mol^{-2}. Calculate K_P of this reaction in atm.

....

Answers to Intext Questions

13.1

1. A chemical reaction is said to be reversible, if under certain conditions its products also react and form back the reactants.

Examples:

$$H_2 (g) + I_2 (g) \rightleftharpoons 2HI (g)$$
$$2SO_2 (g) + O_2 (g) \rightleftharpoons 2SO_3 (g)$$

2. A reaction reaches an equilibrium state when two opposing reactions occur at the same rate and balance each other at a particular temperature.

3. When a system reaches the equilibrium state, its temperature, pressure and concentrations of all the reactants and products do not change any further with time.

4. i) Water-vapour system in a closed container at a constant temperature.
   ii) A saturated solution containing some undissolved solute at a constant temperature.

5. i) Homogeneous systems :

$$H_2 (g) + I_2 (g) \rightleftharpoons 2HI (g)$$
$$2SO_2 (g) + O_2 (g) \rightleftharpoons 2SO_3 (g)$$

   ii) Heterogeneous systems :

$$CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2 (g)$$
$$Zn (s) + CuSO_4 (aq) \rightleftharpoons Cu (s) + ZnSO_4 (aq)$$

13.2

1. $K = \frac{[C]^3[D]^2}{[A]^2[B]}$

2. $K_P = K_C (RT)^{\Delta n_g}$

3. i) a) $K_C = \frac{[CO][H_2O]}{[CO_2][H_2]}$; $K_P = \frac{P_{CO} \text{ x } P_{H_2O}}{P_{CO_2} \text{ x } P_{H_2}}$

b) $K_c = [I_2]$; $K_p = P_{I_2}$

ii) For the first reaction $\Delta n_g = (1 + 1) - (1 - 1) = 0$, hence $K_C = K_P$ while for the second reaction

$\Delta n_g = 1 - 0 = +1.$

$\therefore K_P = K_C (RT)$ or $K_C = \frac{K_P}{RT}$ or $K_C < K_P$.

4. $K_1 = \frac{[NH_3]^2}{[N_2][H_2]^3}$ and $K_2 = \frac{[NH_3]^{2/3}}{[N_2]^{1/3}[H_2]}$

$\therefore K_1 = [K_2]^3.$

5. It is a measure of the extent up to which a reaction proceeds before the equilibrium is reached.

13.3

1. Le Chatelier's principle states that when a system at equilibrium is disturbed by changing concentration, pressure or temperature, a 'net' change occurs in a direction that tends to neutralize the effect of the disturbing factor.
2. Changes in pressure, temperature and concentrations of reactants or products.
3. When the temperature is decreased some vapour will condense and when the pressure is decreased some solid will sublime.
4. (a) (ii) and (iv)

(b) High temperature, increase in pressure, presence of a catalyst and continuous removal of D.

Chapter 14

IONIC EQUILIBRIUM

In the first lesson of this module, you learnt about chemical equilibrium, its types of and the factors affecting the state of equilibrium. In this the lesson you will learn about the equilibria involving ionic species. The equilibria involving acids and bases are critically important for a wide variety of reactions. The use of buffer solutions for pH control is of significance in living systems, agriculture and industrial processes. Similarly, the solubility equilibrium established in the solutions of sparingly soluble salts is also very important. For example, our bones and teeth are mostly calcium phosphate, $Ca_3(PO_4)_2$, a slightly soluble salt. We would focus our attention primarily on the acid-base and the solubility equilibria and some interrelated aspects concerning these equilibria such as pH, buffer solutions and common ion effect. In this process you would apply the concepts learnt in the first lesson.

Objectives

After reading this lesson you will be able to:

- define and explain various concepts of acids and bases;
- define conjugate acid-base pairs and identify in an acid-base equilibrium;
- derive the expressions for the ionisation constants of weak acids and bases;
- correlate the ionisation constants and the strength of acids and bases;
- explain self ionisation of water and derive an expression for its ionic product;
- define pH and correlate it with the nature of aqueous solutions - neutral, acidic or basic;
- define and explain common ion effect in ionisation of weak acids and bases;
- define buffer solutions;
- apply Henderson Equation to calculate the pH of acidic and basic buffers;
- explain hydrolysis of salts with the help of chemical equations;
- express solubility equilibrium with the help of an equation;
- identify the relationship between solubility and solubility product for salts of AB, AB_2 A_2B and A_2B_3 types;
- illustrate and explain the common ion effect on solubility equilibrium and
- recall some applications of common ion effect

14.1 General Concepts of Acids and Bases

You are quite familiar with the term’s acid, base, acidic and acidity etc. But how do we define an acid or a base? There is no general definition of acids and bases. There are three different concepts of acids and bases (proposed by Arrhenius, Bronsted and Lowry and Lewis respectively) which are well known. Each of these emphasize a different aspect of acid - base chemistry. Let us try to understand these concepts.

14.1.1 Arrhenius Concept

The most commonly used concept of acids and bases was developed by Svante Arrhenius (1884). According to this concept an acid is a substance that is capable of producing hydrogen ion (H^+) by dissociating in aqueous solution. The reaction can be represented as

$$HA\ (aq) \rightarrow H^+\ (aq) + A^-\ (aq) \qquad (14.1)$$

Where HA represents the acid and A- refers to the acid molecule without the hydrogen ion. Hydrochloric acid, HCl is an example of an Arrhenius acid whose ionisation can be represented as

$$HCl\ (aq) \rightarrow H^+\ (aq) + Cl^-\ (aq) \qquad (14.2)$$

The proton or hydrogen ion binds itself to a water molecule and form H_3O^+ ion which is called **hydronioum ion**.

$$H^+ + H_2O \rightarrow H_3O^+$$

The **hydronium ion** is also known as **oxonium ion** or the **hydroxonium ion**.

In the light of this fact the equation 14.1 can be rewritten as

$$HA\ (aq) + H_2O \rightarrow H_3O^+\ (aq) + A^-\ (aq) \qquad (14.3)$$

A base on the other hand is defined as a substance capable of providing a hydroxyl ion (HO^-) on dissociation in aqueous solutions.

$$MOH\ (aq) \rightarrow M^+\ (aq) + OH^-\ (aq) \qquad (14.4)$$

Where M^+ refers to the base molecule without the hydroxyl ion. Sodium hydroxide is an example of a Arrhenius base, dissociating as,

$$NaOH\ (aq) \rightarrow Na+\ (aq) + OH^-\ (aq) \qquad (14.5)$$

Arrhenius concept is quite useful and explains the acid-base behaviour to a good extent. However it has certain drawbacks like,

- It is limited to only aqueous solutions and require dissociation of the substance.
- It does not explain the acidic behaviour of some substances which do not contain hydrogen, for example, $AlCl_3$. Similarly, it does not explain the basic character of substances like NH_3 and Na_2CO_3 which do not have a hydroxide groups.

14.1.2 Bronsted and Lowry Concept

In 1923, Bronsted and Lowry pointed out independently that acid-base reactions can be interpreted as proton-transfer reactions. According to them, an acid is defined as a proton (H^+) donor, and a base is defined as a proton acceptor. The definition is sufficiently broad and removes the first limitation of Arrhenius concept. Any hydrogen-containing molecule or ion capable of donating or transferring a proton is an acid, while any molecule or ion that can accept a proton is a base.

For example, in a reaction between ammonia (NH_3) and hydrogen fluoride (HF); ammonia acts as a base (accepts a proton) while HF behaves as an acid (donates a proton).

$$NH_3 + HF \rightarrow NH_4^+ + F^- \qquad (14.6)$$

According to Bronsted-theory an acid is a substance that can donate a proton whereas a base is a substance that can accept a proton.

You may note in this example that there is no role of a solvent. Let us consider the reaction of hydrochloride acid with ammonia in a solvent like water. We can write ionic equation as

$H_3O^+ (aq) + C^- (aq) + NH_3 (aq) \rightarrow H_2O(l) + NH_4^{\,+} (aq) + Cl^- (aq)$

The hydronium and chloride ions are obtained from the ionisation of HCl. After cancelling Cl^- on both sides, we get the following ionic equation as

$$NH_3 (g) + H_3O^+ (aq) \rightarrow H_2O(l) + NH_4^{\,+} (aq) \qquad (14.7)$$

Here, in aqueous solution, a proton is transferred from the hydronium ion, H_3O^+, to the NH_3 molecule, giving H_2O and NH_4^+ . In this case H_3O^+ acts as proton donor or an acid and NH_3 as proton acceptor. We may visualise water (the solvent) playing the role of mediator in the transfer of proton from hydrochloric acid to ammonia. It should be noted that in the **Bronsted - Lowry Concept, acids and bases can be either ions or molecular substances.**

In any acid-base equilibrium both forward and reverse reactions involve proton transfers. Let us consider the reaction of NH_3 with H_2O.

$$\underset{\textbf{acid}_1}{H_2O (l)} + \underset{\textbf{base}_2}{NH_3 (aq)} \rightleftharpoons \underset{\textbf{acid}_2}{NH_4^+ (aq)} + \underset{\textbf{base}_1}{OH^- (aq)} \qquad (14.8)$$

In the forward reaction, NH_3 accepts a proton from H_2O. Thus, NH_3 is a base and H_2O is an acid. In the reverse reaction, NH_4^+ donates a proton to OH^-. Thus NH_4^+ ion acts as acid OH^- as a base. Here you find that NH_3 and NH_4^+ differ by a proton. That is, NH_3 becomes $NH_4^{\,+}$ ion by gaining a proton, whereas NH_4^+ ion becomes NH_3 molecule by losing a proton. The species NH_4^+ and NH_3 are called conjugate acid-base pair. A conjugate acid-base pair consists of two species in an acid-base reaction, one acid and one base, that differ by the gain or loss of a proton. It can be represented as $NH^+{}_4/NH_3$. The acid in such a pair is a called conjugate acid of the base, where as the base is the conjugate base of acid. Thus, NH_4^+ is the conjugate acid of NH_3, and NH_3 is the conjugate base of NH_4^+. The members of each conjugate pair are designated by the same numerical subscript e.g., NH_4^+/NH_3 pair is marked as 2 while the H_2O/OH^- pair is marked as 1.

Let us take another example of ionization of hydrogen fluoride in water. It can be represented as

$$\underset{\textbf{acid}_1}{HF (g)} + \underset{\textbf{base}_2}{H_2O} \rightleftharpoons \underset{\textbf{acid}_2}{H_3O^+ (aq)} + \underset{\textbf{base}_1}{F^- (aq)} \qquad (14.9)$$

The equilibrium sign indicates that the reaction does not go to completion. The H^+ ions obtained from the ionisation of HF molecule can be accepted by either of the two bases, F^- and H_2O. The fact that the equilibrium is only slightly towards right tells us that it is the F^- that accepts the proton and make the reaction go to the left i.e., F^- is a stronger base than H_2O.

Similarly when HCl is dissolved in water, the HCl molecules give up H^+ ions that can be accepted by either of two bases, Cl^- and H_2O.

$$HCl + H_2O \rightarrow H_3O^+ + Cl^- \qquad (14.10)$$

The fact HCl is completely ionized in dilute aqueous solution (indicated by a single arrow) tells us that Cl^- is a weaker base than H_2O. We can conclude from these two examples that, a stronger acid (HCl) has a weaker conjugate base, Cl^- and the weaker acid, (HF) has a stronger conjugate base, F^-. We can generalize that in a conjugate acid-base pair the **weaker an acid is, stronger is its conjugate base. Likewise, the weaker a base is, the stronger is its conjugate acid.**

Here you should understand that the terms ‘strong’ and ‘weak’ like many other adjectives are used in a relative sense. Consider the following reaction

$$F^- + H_2O \rightleftharpoons HF + OH^- \tag{14.11}$$

In this case **F^- is a weaker base** as compared to OH^-.

Let us write a few reactions involving conjugate acid-base pairs

$$HF\,(aq) + HCO_3^- \rightleftharpoons H_2CO_3\,(aq) + F^-\,(aq)$$

acid$_1$ **base$_2$** **acid$_2$** **base$_1$**

$$HCO_3^-\,(aq) + OH^-\,(aq) \rightleftharpoons CO_3^{2-}\,(aq) + H_2O\,(l)$$

acid$_1$ **base$_2$** **base$_1$** **acid$_2$**

$$H_2CO_3\,(aq) + CN^-\,(aq) \rightleftharpoons HCO_3^-\,(aq) + HCN\,(aq) \tag{14.12}$$

acid$_1$ **base$_2$** **base$_1$** **acid$_2$**

If you examine the above reactions closely, you would find that some species can act both as an acid as a base. Such species are called amphiprotic species. In the above reactions HCO_3^-(aq) acts as a base in presence of HF but an acid in presence of CN^-. Similarly, H_2O behaves as an acid and a base.

- Thus, we have seen that the Bronsted - Lowry concept of acids and bases has greater scope than the Arrhenius concept.

14.1.3 Lewis Concept

As discussed above the Bronsted - Lowry concept does not depend on the nature of the solvent (a short coming of the Arrhenius concept removed). However, like Arrhenius concept does not explain the acidity of the substances which do not have a hydrogen atom (e.g. $AlCl_3$) and the basicity of the substances devoid of a OH^- group (e.g. Na_2CO_3). G.N. Lewis proposed (1923) a yet another concept of acids and bases that includes such substances also. According to him, an acid may be defined as, ‘any atom, molecule or ion that can accept an electron pair from any other atom, molecule or ion’. A Lewis base on the other hand can be defined as, ‘any atom, molecule or ion that can donate a pair of electrons, Let us take an example

$$AlCl_3 + NH_3 \rightarrow Cl_3Al \leftarrow NH_3 \tag{14.13}$$

In the above example $AlCl_3$ is an electron deficient species. It accepts an electron pair from a molecule of NH_3 which has a lone pair of electrons on N atom. Thus, $AlCl_3$ is a Lewis acid and NH_3 is a Lewis base.

Types of Lewis acids

The Lewis acids can be divided into following 5 types.

- All Cations: Ex: Ag^+, Co^{3+}, Cu^{2+}, Fe^{3+} etc.
- Compounds whose central atom has an incomplete octet and possessing an empty orbital. Ex: BF_3, BCl_3, $AlCl_3$, $FeCl_3$
- Compounds in which the central atom has available d-orbitals and may expand its octet. Ex: SiF_6, $SnCl_4$, SF_4, TeF_4, $FeCl_3$

- ❖ Molecules having multiple bonds between atoms of dissimilar electro negativities.

  Ex: CO_2, SO_2, SO_3, NO_2, Cl_2O_7, P_4O_{10}
- ❖ Electrons with an electron sextet. Ex: S, O

14.1.4 Types of Lewis bases

The Lewis bases are divided into 3 types.

- ❖ All anions :

  Ex : Cl^-, OH^-, CN^-, NH^-_2, F^-, SCN^- (thio cyanate ion)
- ❖ Molecules with one or two lone pairs on the central atom.

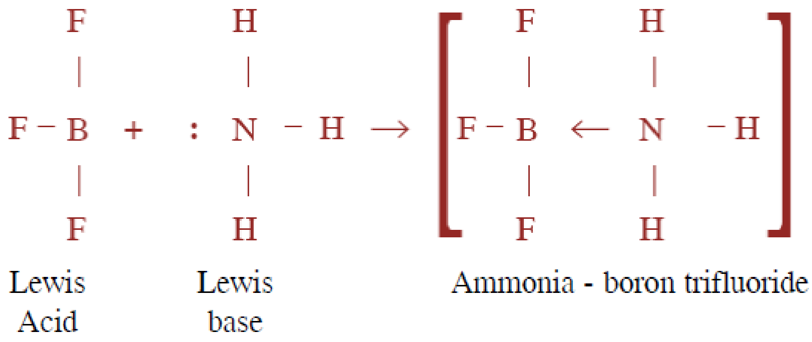
  Ex : $H_2\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}$, $\overset{\cdot\cdot}{N}H_3$, $R\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}H$, $R\overset{\cdot\cdot}{N}H_2$, $R\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}R$, $C_5H_5\overset{\cdot\cdot}{N}$ (pyridine)
- ❖ Molecules with multiple bonds.

  Ex : CO, NO, $H\,C \equiv C\,H$, $H_2C{=}\,CH_2$

14.1.5 Examples of acid – base reactions

i) Formation of NH_3 . BF_3 :

In a reaction between BF_3 and NH_3, Boron of BF_3 accepts a lone pair from nitrogen of NH_3 and forms a coordinate covalent bond.



ii) Formation of hydronium ion :

H^+ Combines with H_2O. Oxygen of water donates a pair of electrons to H^+ ion.

$$H^+ \quad :\underset{\cdot\cdot}{O}H_2 \longrightarrow H \leftarrow OH_2^+$$

Lewis Acid **Lewis base** **Hydronium ion**

14.1.6 Limitations of Lewis theory

1. One of the serious defects in the theory is that it cannot explain the strengths of acids and bases.
2. Acids like HCl, H_2SO_4 react with bases such as NaOH or KOH but do not form coordinate covalent bond.
3. Generally acid–base interactions i.e., neutralization reactions are instantaneous reactions. But some Lewis acid–base reactions go on very slowly.
4. All the acid–base reactions do not involve, coordinate bond formation.
5. H^+ ion, as catalyst, cannot be explained by this theory.

Intext Questions 14.1

1. Define Arrhenius and give two examples.

………

2. What are the limitations of Arrhenius definition?

....

3. How does a Bronsted - Lowry base differ from an Arrhenius base ?

....

4. Classify the following into Bronsted - Lowry acid or Bronsted - Lowry base.

HCl, NH_3, H_3O^+, CN^-

....

14.2 Relative Strength of Acids and Bases

Different acids and bases have different strength depending on their nature. Since there are different ways of defining acids and bases, there are different ways of comparing their relative strengths also.

14.2.1 Relative strength according to Arrhenius concept

According to Arrhenius concept strong electrolytes (like HCl) which dissociate completely in aqueous solutions and produce H^+ (or H_3O^+) ions are called strong acids.

$$HCl\ (g) + H_2O \rightarrow H_3O+\ (aq) + Cl_{-}\ (aq) \qquad (14.14)$$

Other examples of strong acids are H_2SO_4, HBr, HI, HNO_3 and $HClO_4$. On the other hand weak electrolytes like CH_3COOH whose ionisation is not complete, (because the process is reversible) and produce H^+ (or H_3O^+) ions are called weak acids.

$$CH_3COOH\ (aq) + H_2O \rightleftharpoons H^+\ (aq) + CH_3COO^-\ (aq) \qquad (14.15)$$

Similarly strong bases may be defined as the electrolytes with complete ionisation and weak bases as the electrolytes with incomplete ionisation. NaOH and NH_3 are typical examples of strong and weak bases respectively. Their ionisaion can be represented as

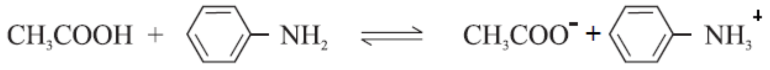
$$NaOH\ (aq) \rightarrow Na^+\ (aq) + OH^-\ (aq)$$

$$NH_3\ (aq) + H_2O \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq) \qquad (14.17)$$

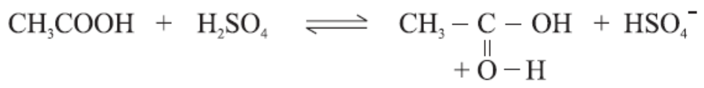
The principal strong bases are hydroxides of Groups 1 and 2 elements (except Be). Most of the other acids and bases we come across are weak bases.

14.2.2 Relative strength according to Bronsted - Lowry concept

You have learnt that according to Bronsted - Lowry concept an acid is a species that donates a protons while a base is a species that accepts a protons. The tendency of a substance to donate a proton also depends on the species accepting the proton. A given acid may have different strengths in different solvents (of varying basic strength or proton accepting tendencies) e.g.,



(14.18)



$$CH_3COOH + H_2SO_4 \rightleftharpoons \underset{+\overset{\|}{O}-H}{CH_3-C-OH} + HSO_4^- \qquad (14.19)$$

Acetic acid loses a proton to a basic solvent aniline but in sulphuric acid it infact accepts a proton and acts as a base. Therefore the relative strengths of different acids and bases are compared in the same solvent which normally is water. Therefore, in Bronsted - Lowry concept, we may define the relative strength of an acid as its relative tendency to lose (or donate) a proton to water. According to the Bronsted - Lowry concept strong acid are those which lose their protons almost entirely to water. The reaction, goes completely to the right indicating that HCl is a strong acid.

$$\underset{\textbf{acid}}{HCl\,(aq)} + \underset{\textbf{base}}{H_2O\,(aq)} \rightarrow \underset{\textbf{acid}}{H_3O^+\,(aq)} + \underset{\textbf{base}}{Cl^-\,(aq)} \qquad (14.20)$$

Acetic acid donates its proton to water to the extent of only about 3% and the following equilibrium exists.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^- \qquad (14.21)$$

Acetic acid is, therefore, termed as a weak acid.

14.3 Quantitative Aspects of Strengths of Acids and Bases

We have so far discussed the relative strengths of acids and bases only qualitatively i.e., which is strong and which one is weak. Many a times we need to know the quantitative aspects also i.e., how much? That is if a acid is stronger than the other we would like to know how many times stronger. Let us learn how do we quantify it?

14.3.1 Ionisation of weak acids

The dissociation or ionisation of weak acid, HA, can be represented as

$$HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O{+}\,(aq) + A^-\,(aq) \qquad (14.22)$$

As you know that in case of strong acids the ionisation is almost complete or close to 100% or we may say that the equilibrium lies far to the right. In such cases the sign of equilibrium may be replaced by a single arrow (→)

$$HA\,(aq) \rightarrow H^+\,(aq) + A^-\,(aq)$$

or

$$HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq) \qquad (14.23)$$

The reaction given above (eq. 14.22) is referred to as ionisation equilirbium and is characterized by an equilibrium constant

$$K_{eq} = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \qquad (14.24)$$

Since the concentration of a pure liquid or a solid is taken as 1, we can rewrite the above expression can as

$$K_{eq} = \frac{[H_3O^+][A^-]}{[HA]} = K_a \qquad (14.25)$$

where Ka is a new constant called acid dissociation constant or ionisation constant of the acid.

The magnitude of the equilibrium constant is a measure of the strength of the acid. Higher the value of the equilibrium constant the stronger is the acid. For all strong acids the values of the equilibrium constants is quite high and does not help much in suggesting their relative strengths. However, for a weak acid, this constant is quite useful.

Example 14.1: Write down the expression for the dissociation constant for acetic acid - a weak acid that ionizes as

$$CH_3COOH\,(aq) + H_2O \rightleftharpoons H_3O^+\,(aq) + CH_3COO^-\,(aq)$$

Solution : Applying the law of chemical equilibrium, we can write equilibrium constant K as

$$K = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$$

Rearranging, we can write.

$$K[H_2O] = K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Dissociation constant of other weak acids also can be written in the same way.

The values of K_a show the extent to which the acids are dissociated in water. Relative strength of acids is judged on the basis of dissociation constant. Like other equilibrium constants the dissociated constant, K_a also depends on the temperature. Therefore, the ionisation constants or dissociation constants are compared at the same temperature. For example

$$CH_3COOH\,(aq) \rightleftharpoons H^+\,(aq) + CH_3COO^-\,(aq) \qquad K_a = 1.8 \times 10^{-5} \qquad (14.26)$$

$$HCN\,(aq) \rightleftharpoons H^+\,(aq) + CN^-\,(aq) \qquad K_a = 4.9 \times 10^{-10} \qquad (14.27)$$

On the basis of K_a values we can say that acetic acid is much more ionized than hydrocyanic acid. In other words acetic acid is stronger acid than hydrocyanic acid although both are weak; neither is completely ionized.

14.3.2 Ionisation of weak bases

The ionisation of weak bases (BOH) can be expressed as

$$BOH\,(aq) \rightleftharpoons B^+\,(aq) + OH^-\,(aq) \qquad (14.28)$$

(The equilibrium sign may be replaced by → in case of a strong base).

The solution contains the base, B the protonated base, BH^+, hydroxide ion OH^-, and water in equilibrium. The equilibrium constant expression for the reaction is

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad (14.29)$$

For example, the dissociation of NH_4OH is represented as

$$NH_4OH\,(aq) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

and is characterized by

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

The constant K_b is called dissociation constant of the base. Similar to values of K_a, K_b values also give us the idea about the relative strengths of weak bases. Higher the value of K_b the stronger is the base.

14.3.3 Polyprotic Acids

Many acids have more than one ionizable protons. These are called polyprotic acids. The acids are called diprotic if there are two ionizable protons per molecule. (e.g. H_2SO_3, H_2CO_3), and triprotic if there are three ionizable protons (e.g. H_3PO_4, etc.) Such acids dissociate in more than one steps or stages, each with its own ionization constant. In the case of sulphurous acid, H_2SO_3, these steps are

$$H_2SO_3 + H_2O \rightleftharpoons HSO_3^- + H_3O^+ \qquad (14.31)$$

$$K_1 = \frac{[H_3O^+][HSO_3^-]}{[H_2SO_3]} = 1.3 \text{ x } 10^{-2}$$

$$HSO_3^- + H_2O \rightleftharpoons SO_3^{2-} + H_3O^+ \qquad (14.32)$$

$$K_2 = \frac{[H_3O^+][SO_3^{2-}]}{[HSO_3^-]} = 6.3 \text{ x } 10^{-8}$$

The values of the two ionisation constants (K_1 and K_2) are quite different: K_1 being twenty million times K_2. It suggests that the first ionisation of sulphurous acid is much more than the second one. In other words the sulphurous acid behaves as a much stronger acid than the bisulphite ion.

14.3.4 Degree of Ionisation or Degree of Dissociation

As you know that the weak acids / bases do not ionize completely and equilibrium exists between the ionized and unionized species. The degree of ionisation may be defined as the fraction of total amount of a weak acid or a base that exists in the ionized form. It is denoted by a Greek letter 'α'. The equilibrium constant can be used to calculate the degree of ionisation of weak acid or a base. An expression relating α and K_a or K_b can be derived as follows.

Consider a weak acid HA which partially dissociated in its aqueous solutions and the following equilibrium is established.

$$HA\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + A^-\ (aq)$$

Initial concentrations (in moles)	c	-55	0	0
Equilibrium concentrations	c (1-α)	-55	cα	cα

The equilibrium constant expression can be written as

$$K_a = \frac{[H_3O^+][A^-]}{[H_2O][HA]} = \frac{[c\alpha][c\alpha]}{c\,[1-\alpha]\,55}$$

rearranging we get,

$$= 55K = K_a = \frac{[c\alpha][c\alpha]}{c\,[1-\alpha]} = \frac{c^2\alpha^2}{c\,[1-\alpha]} = \frac{c\alpha^2}{[1-\alpha]} \qquad (14.33)$$

Since the acid HA is very weak, α < < 1; we can neglect α in comparison to 1 in the denominator to get.

$$K_a = c\alpha^2 \quad \text{or} \quad \alpha^2 = \frac{K_a}{c} \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{c}} \qquad (14.34)$$

So, if we know the value of the dissociation constant of the acid and the concentration of the weak acids we can find its degree of dissociation or ionisation. Let us take up an example to see the application of this relationship.

Example 14.2: Compare the degree of dissociation and percent dissociation of acetic acid in its 0.1 M solution. Give Ka = $1.8 \text{ x } 10^{-5}$.

Solution: Using the formula $\alpha = \sqrt{\frac{K_a}{c}}$ and substituting the values of K_a and c, we get,

$$\alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.1}} = \sqrt{1.8 \times 10^{-4}} = 1.34 \times 10^{-2} = 0.0134$$

The percent dissociation of a weak acid is defined as

$$\text{Percent dissociation} = \frac{\text{The number of moles of acid in the dissociated form}}{\text{Total number of moles of the acid}} \times 100 \quad (14.35)$$

$$= \text{Degree of dissociation} \times 100\%$$

$$= \alpha \times 100\% = 0.0134 \times 100 = 1.34\%$$

Thus acetic acid is dissociated to the extent of only 1.34% in a 0.1 M aqueous solution.

A similar expression can be obtained for the degree of dissocation of a weak base. The desired expression is

$$\alpha = \sqrt{\frac{K_b}{c}}$$

14.4 The Auto-Ionisation or Self-Ionisation of Water

We have seen that water can act as a very weak acid and also as a very weak base. In a sample of water, a small number of water molecules undergo auto ionisation. Half of them acting as an acid while the other half acting as a base. As a consequence, small concentration of H_3O^+ and OH^- are formed in water. The self-ionisation of water can be represented as

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \quad (14.37)$$

The corresponding equilibrium constant expression can be written as

$$K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \quad (14.38)$$

Since the concentration of H_2O is constant we can rearrange the expression and define a new constant K_w, as

$$[H_3O^+][OH^-] = K_{eq} \times [H_2O]^2 = K_w \text{ (a new constant)} \quad (14.39)$$

This constant K_w, is called the dissociation constant or ionic product constant of water. The value of K_w at 298 K has been determined from the measurement of electrical conductivity of carefully purified water and has been found to be 1.0×10^{-14} mol^2 dm^{-6}.

Since the concentration of H_3O^+ and OH^- ions is equal we may write

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

$$K_w = [H_3O_+]^2 = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

$$[H_3O^+] = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$$

and similarly, $[OH^-] = 1.0 \times 10^{-7}$ mol dm^{-3}

Thus in pure water and in neutral solutions

$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \text{ mol dm}^{-3} \text{ at 298 K} \quad (14.40)$$

14.4.1 Acidic, Basic and Neutral Solutions

An acidic solution in defined as one in which the hydrogen ion (or hydronium ion) concentration is greater than the hydroxide ion concentration. A basic solution is one in which the reverse is true, that is, one in which $[OH^-]$ exceeds $[H_3O^+]$ and a neutral solution is one in which $[OH^-]$ equals $[H_3O^+]$.

Neutral solution $[H_3O^+] = [OH^-]$

Acidic solution $[H_3O^+] > [OH^-]$

Basic solution $[H_3O^+] < [OH^-]$ (14.41)

Since the product $[H_3O^+]\ [OH^-]$ is constant, if the concentration of either of these increase, the other one would decrease. In other words, the concentrations of $[H_3O^+]$ and $[OH^-]$ are not independent but are linked by the relationship.

$$[H_3O^+]\ [OH^-] = K_w \qquad (14.42)$$

This provides an easy way to calculate concentration of one of these if we know that of the other.

You must note that the self-ionisation equilibrium discussed above applies not only to pure water but also to the self-ionization of water in any aqueous solution. Hydronium ions and hydroxide ions are present in every aqueous solution, and they are always in equilibrium with water molecules. Let us try to calculate the concentration of these ions in some simple solutions.

Example 14.3: Calculate the concentrations of OH^- and H_3O^+ ions in 0.01 M solution of HCl.

Solution: In an aqueous solution of HCl, the following two processes would occur simultaneously.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

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

The ionisation of HCl goes to completion and that of water to a very limited extent. In addition, according to Le-Chatlier principle, the H_3O^+ from the ionization of HCl will shift the position of the equilibrium of the self-ionization reaction to the left. As a consequence, the concentration of the OH ions would reduce further. Suppose concentration of OH is 'x'mol dm^{-3}, then concentration of H_3O^+ from the self-ionization of water must also be x mol dm^{-3}. The concentration of H_3O^+ from ionization of HCl is 0.010 mol dm^{-3}. Therefore, total concentration of H_3O^+ (aq) = $(0.010 + x)$ mol dm^{-3}.

Thus, Equilibrium Concentrations of H_3O^+ and OH^- ions would be $(0.01 + x)$ and x mol dm^{-3} respectively.

Substituting these values into the equilibrium constant for the self-ionization of water, we get

$$K_w = [H_3O^+]\ [OH^-] = (0.01 \text{ x } x)\ (x)\ \text{mol}^2\ \text{dm}^{-6} = 1.0 \text{ x } 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$$

Since x must be very small, we can assume that $x << 0.01$ and therefore we may assume that the equilibrium concentration of H_3O^+ is equal to 0.01 M

$$(0.01 + x) = 0.01, \text{ so}$$

$$0.01x = 1.0 \text{ x } 10^{-14}$$

or $$x = 1.0 \text{ x } 10^{-14} / 0.01$$

$$x = 1.0 \text{ x } 10^{-12}$$

$[OH^-] = 1.0 \text{ x } 10^{-12}$ mol dm^{-3} and

$[H_3O^+] = 0.01 + 1.0 \text{ x } 10^{-12}$ mol dm^{-3} = 0.1 mol dm^{-3}

Since the value of x (1.0×10^{-12}) the hydronium ions obtained from the self-ionization of water is far smaller than 0.01, our assumption is justified. Thus, you may note that in case of aqueous solutions of strong acids it is reasonable to assume that the concentration of H_3O^+ ions equal the concentration of the acid itself.

14.4.2 pH Scale

In aqueous solutions of acids and bases the concentration of H_3O^+ and OH^- ions may vary from about 10 M to 10^{-14} M. It is quite inconvenient to express these concentrations by using powers of 10. in 1909 a Danish botanist S.P.L. Sorensen proposed a logarithmic scale (called *p*H scale) for expressing the concentrations of H^+ ions. He defined *p*H as the negative logarithm of the molar concentration of hydrogen ions. That is,

$$pH = -\log_{10}[H^+] \qquad (14.43)$$

We now a days it is represented as

$$pH = -\log_{10}[H_3O^+] \qquad (14.44)$$

For neutral solution (or pure water)

$$[H_3O^+] = [OH^-] = 1 \times 10^{-7}$$

$$\Rightarrow \quad pH = -\log 1 \times 10^{-7} = 7.0$$

For acidic solutions

$$[H_3O^+] > [OH^-]$$

$$\Rightarrow \quad [H_3O^+] > 1 \times 10^{-7}$$

$$\Rightarrow \quad pH = -\log(>1 \times 10^{-7}) = < 7.0$$

For basic solutions

$$[H_3O^+] < [OH^-]$$

$$\Rightarrow \quad [H_3O^+] > 1 \times 10^{-7}$$

$$\Rightarrow \quad pH = -\log(>1 \times 10^{-7})$$

$$\Rightarrow \quad > 7.0$$

A strongly acidic solution can have a *p*H of less than zero (i.e., negative) and a strongly alkaline solution can have a *p*H value greater than 14. However the *p*H range normally observed is between 0 to 14.

The notation p is used in a number of places. It carries the meaning. 'the negative logarithm of'. It has been extended to OH^- (aq) and equilibrium constant like, K_a, K_b and K_w, etc.

$$pOH = -\log_{10}[OH^-]$$

$$pK_a = -\log_{10} K_a \qquad pK_b = -\log_{10} K_b$$

$$pK_w = -\log_{10} K_w \qquad (14.45)$$

This gives us an important relation. You would recall (eq 14.42)

$$K_w = [H_3O^+][OH^-]$$

Taking logs on both sides, we get

$$\log K_w = \log[H_3O^+] + \log[OH^-]$$

Multiplying throughout by - 1

$$-\log K_w = -\log[H_3O^+] - \log[OH^-]$$

$$pK_w = pH + pOH$$

Since the value of $K_w = 1.0 \times 10^{-14}$ $pK_w = 14$

$$\text{i.e., } pH + pOH = 14 \qquad (14.46)$$

If we know the value of *p*H of a given solution we can find its *p*OH and vice verse.
Let us take up some examples to understand the application of these important formulae.

Example 14.4 : What is the *p*H of a 0.01 M aqueous solution of HCl?

Solution : Since HCl is a strong acid it would ionize completely.

Therefore, $[H_3O^+]$ in 0.01 M HCl = 0.01 M

$$pH = -\log_{10}[H_3O^+] = -\log 10^{-2}$$
$$= -(-2.0) = 2.0$$

Example 14.5: Calculate the *p*H of 0.010 M aqueous solution of NaOH?

Solution : Since NaOH is a strong base, it is fully ionized to give Na^+ and OH^-

$$[OH^-] = 1.0 \text{ x } 10^{-2} \text{ mol}^{L-1}$$

$$K_w = [H_3O^+]\,[OH^-] = 1.00 \text{ x } 10^{-14} \text{ mol}^2\,L^{-2}$$

$$\text{so } [H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \text{ x } 10^{-14} \text{ mol}^2\,dm^{-6}}{1.00 \text{ x } 10^{-2} \text{ mol}\,dm^{-3}}$$

$$= 1.00 \text{ x } 10^{-12} \text{ mol dm}^{-3}$$

$$pH = -\log_{10}(1.0 \text{ x } 10^{-12}) = 12$$

Example 14.6: The *p*H of a sample of rain water at 25^0C is 5. What is the concentration of hydronium ions?

Solution: $pH = -\log[H_3O^+]$

or $5 = -\log[H_3O^+]$ $\log[H_3O^+] = -5.$

Taking antilogs, we get

$$[H_3O^+] = 10^{-5} \text{ mol dm}^{-3}$$

Example 14.7 : Calculate the pH of a 0.1 M aqueous solution of acetic acid. The dissociation constant, $K_a = 1.85 \text{ x } 10^{-5}$, $\alpha = 0.0134$.

Solution : The following equilibrium exists in this solution

$$CH_3COOH\,(aq) + H_2O \rightleftharpoons H_3O^+\,(aq) + CH_3COO^-\,(aq)$$

If α be the degree of dissociation of acetic acid in this solution, the equilibrium concentrations of various species would be

$$CH_3COOH\,(aq) + H_2O \rightleftharpoons H_3O^+\,(aq) + CH_3COO^-\,(aq)$$
$$c\,(1-\alpha) \qquad\qquad c\alpha \qquad c\alpha$$

Since c= 0.1 M

$$0.1\,(1-\alpha) \qquad\qquad 0.1\,\alpha \qquad 0.1\,\alpha$$

$[H_3O^+] = c\,\alpha$

$$\Rightarrow \quad [H_3O^+] = 0.1 \text{ x } 0.134 = 0.00134$$

$$pH = -\log[H_3O^+] = -\log[0.00134] = -\log[1.34 \text{ x } 10^{-3}] = -(-2.87) = 2.87$$

14.4.3 Effect of Common-Ions on the Dissociation of Weak Acids and Bases

In the previous lesson you have learnt about Le Chatelier's principle. According to this principle the presence of common ions in a solution of a weak acid or a base will affect its dissociation. This in fact would suppress the dissociation of the acid or base.

In a solution containing a weak acid HA and its salt NaA, the following equilibrium exists.

$$HA\,(aq) \rightleftharpoons H^+\,(aq) + A^-\,(aq)$$
$$NaA\,(aq) \rightleftharpoons Na^+\,(aq) + A^-\,(aq)$$

Here A^- (aq) is the common-ion
and in case of a weak base BOH and its salt BX the equilibria are

$$BOH\ (aq) \rightleftharpoons B^+\ (aq) + OH^-\ (aq)$$
$$BX\ (aq) \rightleftharpoons B^+\ (aq) + X^-\ (aq)$$

Here, B^+ is the common-ion. According to Le-Chatlier principle, the presence of common ions would make the equilibrium to go to the left. It is said that the common ions suppress the equilibrium.

Let us take example to understand the effect of common ions on such equilibria.

Example 14.8: Calculate the *p*H, degree of dissociation and concentration of various species in a solution of 0.1 M acetic acid which also contains 0.1 M sodium acetate (for acetic acid = 1.85×10^{-5} mol d^{-3}).

Solution : In the given solution the following two equilibria exist simultaneously.

$$CH_3COOH\ (aq) + H_2O \rightleftharpoons H_3O^+\ (aq) + CH_3COO^-\ (aq)$$
$$CH_3CONa\ (aq) \longrightarrow Na^+\ (aq) + CH_3COO^-\ (aq)$$

Let α be the degree of dissociation of acetic acid in this solution, the equilibrium concentrations of various species would be

$$CH_3COOH\ (aq) \rightarrow H_3O^+\ (aq) + CH_3COO^-\ (aq)$$
$$c\,(1 - \alpha) \qquad\qquad c\alpha \qquad\qquad c\alpha$$

Since c= 0.1 M

$$0.1\,(1 - \alpha) \qquad\qquad 0.1\,\alpha \qquad\qquad 0.1\,\alpha$$

$$CH_3CONa\ (aq) \rightarrow Na^+\ (aq) + CH_3COO^-\ (aq)$$
$$0 \qquad\qquad 0.1 \qquad\qquad 0.1$$

$CH_3COOH = 0.1\,(1-\alpha)$
$CH_3COO^- = 0.1 + 0.1\alpha = 0.1\,(1 + \alpha)$
$H_3O^+ = 0.1\,\alpha$

$$K_a = \frac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COO^-]}$$

rearranging the expression we get,

$$[H_3O^+] = K_a = \frac{[CH_3COOH]}{[CH_3COO^-]}$$

Substituting the values, we get

$$[H_3O^+] = 1.85 \times 10^{-5} \times \frac{0.1\,(1-\alpha)}{0.1\,(1+\alpha)}$$

Since acetic acid is a weak acid, its degree of dissociation further decreases in presence of acetate (ions the common ion). Therefore it is reasonable to assume that

$$\alpha << 1;\ \text{and}\ (1- \alpha) - 1;\ \text{also}\ (1 + \alpha) - 1$$

This is gives

$$[H_3O^+] = 1.85 \times 10^{-5} \times 0.1 / 0.1 = 1.85 \times 10^{-5}$$

and $pH = -\log(1.85 \times 10^{-5}) = 4.73$

Also since $[H_3O^+] = 0.1\,\alpha$

$$\therefore \alpha = 1.85 \times 10^{-5} / 0.1 = 1.85 \times 10^{-4} = 0.000185$$

The concentration of different species at equilibrium will be

$$CH_3COOH = 0.1\,(1-0.000185) = 0.1$$

$CH_3COO- = 0.1\ (1+0.000185) = 0.1$

$H_3O^+ = 0.1 \text{ x } \alpha = 0.1 \text{ x } 0.000185 = 1.85 \text{ x } 10^{-5}$

⇒ the concentration of acid = initial concentration of acid

⇒ the concentration of CH_3COO^- ions = initial concentration of the salt

Intext Questions 14.2

1. HF is a weak acid in water. Write down the expression for K_a for the dissociation of HF.

………

2. Consider a weak base BOH which partially dissociates in its aqueous solutions as per the following equilibrium

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

………

3. A sample of lime juice has a hydronium ion concentration of 6.3 x 10^{-2} M. Calculate its *p*H.

………

4. Calculate the *p*H of 1.0 M aqueous solution of amino acid glycine - a weak acid. The Ka = 1.67 x 10^{-10}.

………

14.5 Buffer Solutions

The example discussed above leads us to a very important conclusion that the extent of dissociation of a weak acid can be decreased by adding a salt containing a common ion. Further, it can be shown that the change in the extent of dissociation can also be varied by changing the concentration of the common ion. The mixture of a weak base and a salt of common ion also behave in the same way. These aqueous solutions containing weak acids/bases and a salt of common ion are important in a yet another way. These act as buffer solutions.

Buffer solutions are the ones that resist a change in its pH on adding a small amount of an acid or a base.

In laboratory reactions, in industrial processes and in the bodies of plants and animals, it is often necessary to keep the *p*H nearly constant despite the addition of acids and bases. The oxygen carrying capacity of haemoglobin in our blood and activity of the enzymes in our cells depends very strongly on the *p*H of our body fluids. *p*H of the blood is very close to 7.4 and *p*H of saliva is close to 6.8. Fortunately, animals and plants are protected against sharp changes in *p*H by the presence of buffers.

There are two (02) kinds of commonly used buffer - solutions

i. A weak acid and a soluble ionic salt of the weak acid e.g. acetic acid and sodium acetate: $CH_3COOH + CH_3COONa$

ii. A weak base and a soluble ionic salt of the weak base e.g. ammonium hydroxide and ammonium chloride: $NH_4OH + NH_4Cl$.

The buffers with *p*H less than 7 are called ***acidic buffers*** and those with *p*H above 7 are called ***basic buffers***. Acetic acid - sodium acetate buffer is an example of *acidic buffer* while Ammonium hydroxide - ammonium chloride is a *basic buffer*.

14.5.1 Buffer Action

A buffer system contains a conjugate acid-base pair and the concentrations of these two are quite high as compared to that of the hydronium ions. These are called as the acid reserve and the base reserve respectively. The added acid or base reacts with these reserves and gets consumed without significantly altering the hydronium ion concentration and therefore the *p*H does not change significantly. Let us consider a buffer solution containing acetic acid, CH_3COOH and sodium acetate CH_3COONa to understand the buffer action.

In acetic acid - sodium acetate buffer CH_3COOH is the acid reserve while CH_3COONa (or CH_3COO^- ions) is the base reserve. In the solution mixture the added components dissociate as follows. The weak acid dissociates partially while the salt undergoes complete dissociation.

$$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + CH_3COO^-\ (aq)$$

$$CH_3COONa\ (aq) \longrightarrow Na^+\ (aq) + CH_3COO^-\ (aq)$$

If we add a strong acid such as HCl to this solution, it produces H_3O^+. These added H_3O^+ (acid) react with an equivalent amount of the base reserve $[CH_3COO^-]$ to generate undissociated acetic acid. The reaction being

$$H_3O^+\ (aq) + CH_3COO^-\ (aq) \rightarrow CH_3COOH\ (aq) + H_2O\ (l)$$

The net effect of this reaction is that there is a slight increase in the concentration of the acid reserve and an equivalent decrease in the concentration of the base reserve. The effective reaction being

$$HCl\ (aq) + CH_3COONa\ (aq) \rightarrow CH_3COOH\ (aq) + NaCl\ (aq)$$

Similarly, when small amounts of a strong base like NaOH is added, it generates OH- ions. These additional OH^- neutralize some of the H_3O^+ ions present in the solution

$$H_3O^+\ (aq) + OH^-\ (aq) \rightleftharpoons H_3O^+\ (aq) + CH_3COO^-\ (aq)$$

Since one of the products of the acid dissociation equilibrium (eq) is used up, there is some more ionisation of CH_3COOH to re-establish the equilibrium.

$$CH_3COOH\ (aq) + H_2O \rightleftharpoons H_3O+\ (aq) + CH_3COO^-\ (aq)$$

The net result is the neutralization of OH^- by CH_3COOH. In other words, we can say that the added OH^- ions (base) react with the acid reserve to produce CH_3COO^- ions

$$OH^-\ (aq) + CH_3COOH\ (aq) \rightleftharpoons CH_3COONa^-\ (l) + H_2O\ (l)$$

The effective reaction being the reaction of the added base with acid reserve

$$NaOH\ (aq) + CH_3COOH\ (aq) \rightarrow CH_3COONa\ (aq) + H_2O\ (l)$$

The net effect of this reaction is that there is a slight increase in the concentration of the base reserve and an equivalent decrease in the concentration of the acid reserve.

You may note here that the added acid or the base only cause minor changes in the concentrations of the weak acid and the salt. The concentration of the hydronium ions and thereby the *p*H does not changes significantly. Let us derive a mathematical expression for determining the *p*H of a buffer solution.

14.5.2 Henderson - Hasselbalch Equation

This equation relates the *p*H of a given buffer solution to the concentrations of its components viz. weak acid/salt or weak base/salt. Let us derive the expression for an acidic buffer system that we have discussed above. In acetic acid - sodium acetate buffer the central equilibrium is

$$CH_3COOH\ (aq) + H_2O \rightleftharpoons H_3O^+\ (aq) + CH_3COO^-\ (aq)$$

which is characterized by the acid dissociation constant,

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

rearranging, we get

$$[H_3O^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]}$$

The concentration of undissociated acetic acid can be taken as total acid concentration [Acid] and that of sodium acetate as the total salt concentration [salt]. In the light of this the above equation may be re written as

$$[H_3O^+] = K_a \frac{[Acid]}{[Salt]}$$

Taking logarithm and multiplying throughout by (-1) we get

$$-\log [H^+] = -\log K_a - \log \frac{[Acid]}{[Salt]}$$

Recall that *p*H = -log [H_3O^+] and *p*Ka = - logK_a . This gives the desired equation.

$$pH = pK_a - \log \frac{[Acid]}{[Salt]} = pK_a + \log \frac{[Salt]}{[Acid]}$$

The equation is known as Henderson-Hasselbalch equation. A similar expression can be derived for a basic buffer (e.g., ammonium hydroxide and ammonium chloride). The expression is

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

Let us take up some examples to see the application of this equation.

Example 14.9: Calculate the *p*H of acetic acid - sodium acetate buffer containing 0.1 M acetic acid and 0.1 M sodium acetate (Ka = 1.85 x 10^{-5} mol dm^{-3}).

Solution : Here, [Acid] = 0.1 M and [Salt] = 0.1 M

Since Ka = 1.85 x 10-5 mol dm^{-3}

pK_a -logK_a = - log 1.85 x 10^{-5}

$\Rightarrow$ *p*Ka = 4.73

According to Henderson equation, $p^H = pK_a + \log \frac{[Salt]}{[Acid]}$

Substituting the values in Handerson equation, we get

*p*H = 4.73 + log (0.1/0.1) = 4.73 + log 1 = 4.73.

Example 14.10: Calculate the pH of ammonium hydroxide - ammonium chloride buffer solution that is 0.1 M in ammonium hydroxide and 0.01 M in ammonium chloride. (*p*K_b of NH_4OH = 9.25).

Solution: Here, [Base] = 0.1 M and [Salt] = 0.01 M

Since $pK_b = 9.25$;

According to Henderson equation, $pOH = pK_b + \log \frac{[Salt]}{[Base]}$

Substituting the values in Handerson equation, we get

$$pOH = 9.25 + \log (0.1/0.1) = 9.25 + \log 0.1 = 9.25 - 1.0 = 8.25$$

14.6 Salt Hydrolysis

The aqueous solutions of certain salts also behave as acids or bases. They do so because of the hydrolysis of the cation or anion or both. As you know, hydrolysis is a reaction with water. Depending on the behaviour towards hydrolysis there are four different types of salts.

Salt of strong acid + strong base	(eg. HCl + NaOH)	**NaCl**
Salt of strong acid + weak base	(eg. HCl + NH_4OH)	**NH_4Cl**
Salt of weak acid + strong base	(eg. CH_3COOH + NaOH)	**CH_3COONa**
Salt of weak acid + weak base	(eg. CH_3COOH + NH_4OH)	**CH_3COONH_4**

Let us learn about the acid - base behaviour of the different types of salts.

Salt of strong acid + strong base: The cations of the strong bases and the anions of the strong acids do not get hydrolysed. Therefore, the salts of this category do not show any acid base behaviour and are neutral.

Salt of strong acid + weak base: The salts of this type dissociate in aqueous solutions to give a cation of a weak base and the anion belonging to strong acid. For example, NH_4Cl dissociates as:

$$NH_4OH\ (aq) \longrightarrow NH_4^+\ (aq) + Cl^-\ (aq)$$

As mentioned above, the anion does not get hydrolysed but the cation does get hydrolysed as per the following equation.

$$NH_4^+\ (aq) + H_2O\ (l) \longrightarrow NH_4OH\ (aq) + H^+\ (aq)$$

since it generates H+ (aq) ions, the solution is acidic in nature.

Salt of weak acid and strong base: The salts of this type dissociate in aqueous solutions to give a anion of a weak acid and the cation belonging to strong base. for example, CH_3COONa dissociates as:

$$CH_3CONa\ (aq) \rightarrow Na^+\ (aq) + CH_3COO^-\ (aq)$$

In this case the cation does not get hydrolysed but the anion does get hdyrolysed as per the following equation.

$$CH_3COO^-\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COOH\ (aq) + OH^-\ (aq)$$

Since it generates hydroxyl ions the solution is basic in nature.

Salt of weak acid and strong base: The salts of this type dissociate in aqueous solutions to give a anion of a weak acid and the cation belonging to strong base. for example, ammonium acetate CH_3COONa dissociates as:

$$CH_3COONa\ (aq) \rightarrow Na^+\ (aq) + CH_3COO^-\ (aq)$$

in this case the cation does not get hydrolysed but the anion does get hydrolysed as per the following equation

$$CH_3COO^-\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COOH\ (aq) + OH^-\ (aq)$$

Since it generates hydroxyl ions the solution is basic in nature.

Salt of weak acid and weak base: The salts of this type dissociate in aqueous solutions to give a anion of a weak acid and the cation belonging to a weak base. for example, ammonium acetate, CH_3COONH_4 dissociates as:

$$CH_3COONH_4\ (aq) \rightleftharpoons NH_4^+\ (aq) + CH_3COO^-\ (aq)$$

In this case both the cation as well as the anion would undergo hydrolysis and the nature of the solution, whether acidic, basic or neutral would depend on the relative strength of the weak acid and the weak base.

14.7 The Solubility Equilibrium

When we try to dissolve a solid into water, if it dissolves, there are three possibilities:

1) The solid is a non-electrolyte and it dissolves as neutral molecules.
2) The solid is a highly soluble electrolyte; it dissolves almost completely.
3) The solid is a sparingly soluble electrolyte; it dissolves to a limited extent.

It is the third possibility that interests us here. Let us take the example of dissolution of AgCl to understand the equilibria in such cases. When silver chloride is added to water, the following equilibrium is established.

$$AgCl\ (s) \rightleftharpoons Ag^+\ (aq) + Cl^-\ (aq)$$

This is an example of a heterogeneous equilibirum because it involves both a solid and a solution. This equilibrium is known as the solubility equilibrium for which the equilibrium constant expression is

$$K = \frac{[Ag^+]\,[Cl^-]}{(AgCl(s)]}$$

As a matter of convention the concentration of the undissolved solid is taken as one. We can rewrite the equilibrium as

$$K_{sp} = [Ag^+]\ [Cl^-]$$

The equilibrium constant now is the product of the concentrations of the ions. It is called ***solubility product constant*** or ***simply solubility product***. A new symbol K_{sp}, has been assigned to this constant. The mass expression on the right, is called, ion product or ionic product. The solubility product constant of a given salt is constant at a given temperature.

14.7.1 Relationship between Solubility and Solubility Product Constant

The ***solubility product constant*** for a substance is related to its solubility. The nature of relationship depends on the nature of the salt.

Salt of AB type: (For example AgCl, $CaSO_4$). In such cases the solubility equilibrium can be represented as

$$AB(s) \rightleftharpoons A^+\ (aq) + B^-\ (aq)$$

and $K_{sp} = [A^+]\ [B^-]$

If the solubility of salt 's' is mol dm^{-3} then the concentrations of the cations and the anions would be 's' mol dm^{-3} each. Substituting the values in the expression of K_{sp} we get,

$$K_{sp} = [\text{'s' mol dm}^{-3}] \times [\text{'s' mol dm}^{-3}] = s^2\ mol^2\ dm^{-6}$$

Salt of AB_2 type: (For example CaF_2). In such cases the solubility equilibrium can be represented as

$$AB_2\ (s) \rightleftharpoons A^{2+}\ (aq) + 2B^-\ (aq)$$

and $K_{sp} = [A^{2+}]\,[B^{-}]^2$

If the solubility of salt is ‘s’ mol dm^{-3} then the concentrations of the cations and the anions would be ‘s’ mol dm^{-3} and ‘2s’ mol dm^{-3} respectively. Substituting the values in the expression of K_{sp} we get,

$K_{sp} = [‘s’ \text{ mol dm-3}] \text{ x } [‘2s’ \text{ mol dm-3}]^2 = 4s^3 \text{ mol}^3 \text{ dm}^{-9}$

Salt of A2B type: (For example Ag_2CrO_4). In such cases the solubility equilibrium can be represented as

$$A_2B\text{ (s)} \rightleftharpoons 2A^{+}\text{ (aq)} + B^{2-}\text{ (aq)}$$

and $K_{sp} = [A^{+}]^2\,[B^{2-}]$

If the solubility of salt is ‘s’ mol dm-3 then the concentrations of the cations and the anions would be ‘2s’ mol dm-3 and ‘s’ mol dm-3 respectively. Substituting the values in the expression of K_{sp} we get,

$K_{sp} = [‘2s’ \text{ mol dm}_{-3}]\ 2 \text{ x } [‘s’ \text{ mol dm}_{-3}] = 4s^3 \text{ mol}^3 \text{ dm}^{-9}$

Salt of A_2B_2 type : (For example $Ca_3(PO_4)_2$). In such cases the solubility equilibrium can be represented as

$$A_3B_2\text{ (s)} \rightleftharpoons 3A^{2+}\text{ (aq)} + 2B^{3-}\text{ (aq)}$$

and $K_{sp} = [A^{2+}]^3\,[B^{3-}]^2$

If the solubility of salt ‘s’ mol dm-3 then the concentrations of the cations and the anions would be ‘3s’ mol dm^{-3} and ‘2s’ mol dm^{-3} respectively. Substituting the values in the expression of K_{sp} we get,

$$K_{sp} = [‘3s’ \text{ mol dm}^{-3}]^3 \text{ x } [‘2s’ \text{ mol dm}^{-3}]^2 = 108s^5 \text{ mol}^5 \text{ dm}^{-15}$$

In general for a salt with the formula A_xB_y and a solubility of s mol dm^{-3} the relationship between the solubility and Ksp can be given as

$$K_{sp} = [A^{y+}]^x\,[B^{x-}]^y = (xs)^x\,(ys)^y = x^x\,y^y\,s^{x+y}$$

Example 14.11: The solubility of calcium sulphate in water is 4.9 x 10-3 mol dm-3 at 298K. Calculate the value of K_{sp} for $CaSO_4$ at this temperature.

Solution : The following equilibrium would exist in this case

$$CaSO_4\text{ (s)} \rightleftharpoons Ca^{2+}\text{ (aq)} + SO_4^{2-}\text{ (aq)}$$

For this reaction $K_a = [Ca^{2+}]\,[SO_4^{2-}]$

From the equation we see that when $4.9 \text{ x } 10^{-3}$ mol of $CaSO_4$ dissolves to make 1 dm^{-3} of a saturated solution, the ionic concentration are

$$[Ca^{2+}] = 4.9 \text{ x } 10^{-3} \text{ mol dm}^{-3}\ ; \quad [SO_4^{2-}] = 4.9 \text{ x } 10^{-3} \text{ mol dm}^{-3}$$

$$K_{sp} = [Ca^{2+}]\,[SO_4^{2-}] = [4.9 \text{ x } 10^{-3} \text{ mol dm}^{-3} \text{ x } 4.9 \text{ x } 10^{-3} \text{ mol dm}^{-3}]$$

$$= 2.4 \text{ x } 10^{-5} \text{ mol}^2 \text{ dm}^{-6}.$$

Example 14.12: Solubility product of silver iodide, AgI is $8.5 \text{ x } 10^{-17}$ at 25^0 C. What is the molar solubility of AgI in water at this temperature?

Solution: Silver iodide dissolves according to the equation

$$AgI\text{ (s)} \rightleftharpoons Ag^{+}\text{ (aq)} + I^{-}\text{ (aq)}$$

Let the solubility of AgI be is ‘s’ mol dm^{-3} the concentrations of silver and iodide ions would be is ‘s’ mol dm^{-3} each.

At equilibrium Ksp = [Ag+] [I-]; Substituting the values, we get

$$[‘s’ \text{ mol dm}^{-3}]\,[‘s’ \text{ mol dm}^{-3}] = s^2 \text{ mol}^2 \text{ dm}^{-6} = 8.5 \text{ x } 10^{-17} \text{ mol}^2 \text{ dm}^{-6}$$

This gives, solubility (s) = $[8.5 \times 10^{-17}\ mol^2\ dm^{-6}]^{1/2}$

$= 9.2 \times 10^{-9}$ mol dm^{-3}.

The solubility of AgI in water is therefore **9.2×10^{-9} mol dm^{-3}** at 298 K.

14.7.2 Effect of Common Ion on Solubility Equilibria

What will happen if we add a soluble salt containing a common-ion to a solution of a sparingly soluble salt ? You may reason out that according to Le Chatelier's principle, the common ion will shift the equilibrium in backward direction which would reduce its solubility still further. This actually is the case. Let us understand it with the help of an example

Example 14.13: Calculate the molar solubility of AgI in a solution containing 0.1 mol dm^{-3} $AgNO_3$. The solubility product of silver iodide, AgI is 8.5×10^{-17} mol^2 dm^{-6} at 298K.

Solution : Silver nitrate is a strong electrolyte ionising as

$$AgNO_3\ (s) \rightleftharpoons Ag^+\ (aq) + NO_3(aq)$$

and for AgI the solubility equilibrium is

$$AgI\ (s) \rightleftharpoons Ag^+\ (aq) + I^-\ (aq)$$

If we take the solubility of AgI to be 's' mol dm^{-3} , then the total concentration of Ag^+ ions in the solution would be [0.1 + s] mol dm^{-3} ~ [0.1] mol dm^{-3} because the value of 's' is very small. And the concentration of I^- ions would be 's' mol dm^{-3}

Substituting in the expression of $K_{sp} = [Ag^+]\ [I^-]$; we get

$[0.1]$ 1mol $dm^{-3}]$ ['s' mol dm^{-3}] = 0.1 s mol^2 dm^{-6} = 8.5×10^{-17} mol^2 dm^{-6}

This gives, solubility (s) = $[8.5 \times 10^{-17}] / [0.1]$ mol dm^{-3}

$= 8.5 \times 10^{-16}$ mol dm^{-3}.

(The value of 's' is clearly negligible in comparison with 0.10 and thus justifies our assumption).

The solubility of AgI in 0.1 M $AgNO_3$ is therefore 8.5×10^{-16} mol dm^{-3} at 298K. Compare this value with the solubility of AgI in water as determined in the previous example

Solvent	Water	0.1 M $AgNO_3$
Solubility	**9.2×10^{-9} mol dm^{-6}**	**8.5×10^{-16} mol dm^{-3}**

Thus we see that the solubility of a sparingly soluble salt is decreased in the presence of another salt that has common ion. This decrease in solubility is an example of the **Common Ion Effect.**

Intext Questions 14.3

1. Calculate the *p*H of a solution containing 0.05 M benzoic acid and 0.025 M sodium benzoate. Benzoic acid has a pK_a of 4.2

....

2. Calculate the solubility product for Ag_2SO_4 if $[SO_4^{2-}] = 2.5 \times 10^{-2}$ M.

....

14.7.3 Application of Solubility Product in Qualitative Analysis

The qualitative analysis of cation is carried out by dividing them into several groups. This groups separation of cations is based upon selective precipitation of some cations out of many that are present in a solution. This is achieved by adjusting the solution conditions in such a way that the Ksp of specific salts of some cations is exceeded and they precipitate out. The remaining cations remain in the solution. A typical example is the use of H_2S. The dissociation of H_2S can be written as

$$H_2S\ (aq) \rightleftharpoons 2H^+\ (aq) + S^{2-}\ (aq)$$

Since the equilibrium involves hydrogen ions, the acidity of the solution would play an important role in controlling the concentration of sulphide ions.

You are aware, that in the separation of group II sulphides, the medium of the solution is kept acidic. In this medium the concentration of the S^{2-} ions is very small and only the sulphides of group II are precipitated. On the other hand in the alkaline medium the concentration of sulphide ions is fairly high and the sulphides of group IV cations precipitate out.

What You Have Learnt

- There are three different concepts of acids and bases proposed by Arrhenius, Bronsted and Lowry and Lewis respectively.
- According to Arrhenius Concept an acid is a substance capable of producing hydrogen ions by dissociating in aqueous solution while a base is a substance capable of providing a hydroxyl ion. The netralization reaction is basically the reaction between a proton and a hydroxyl ion to give a molecule of water.
- Since a hydrogen ion H^+ is very small with high charge density it does not exist free in polar solvent like water. It binds itself to a water molecule and forms a hydronium ion (H_3O^+).
- According to Bronsted and Lowry, an acid is defined as a proton (H^+) donor, and a base is defined as a proton acceptor. An acid-base reactions can be thought of as a proton-transfer from an acid to a base. In this concept, acids and bases can be either ions or molecular substances.
- According to Bronsted and Lowry definition the species in either side of the acid-base equilirbium, differ by the gain or loss of a proton. These are called a conjugate acidbase pair. In such a pair a strong acid has a weak conjugate base while a weak acid has a strong a conjugate base.
- Lewis's definition is quite broad, according to him, an acid is defined as, any atom, molecule or ion that can accept an electron pair from any other atom, molecule or ion, while a base is any atom, molecule or ion that can donate a pair of electrons. The product of a reaction between an acid and a base is called an adduct.
- Strong Arrhenius acids and bases dissociate completely in aqueous solutions where as the weak acids and bases undergo partial ionisation. Higher the extent of ionisation stronger the acid or the base.
- In Bronsted - Lowry concept, the relative strength of an acid is defined as its relative tendency to lose/donate a proton to water.

- The ionisation equilibria of weak acids and bases are characterized by equilibrium constant called ionisation constants. The values of these constants is a measure of their relative strength.
- Water can act both as a weak acid as well a weak base. In a sample of water a small number of water molecules undergo autoionisation, in which half the ions act as an acid while the other half acts as a base.
- In aqueous solutions the concentration of H_3O^+ can be expressed in terms of a logarithmic scale called *p*H scale. The *p*H of a solution is defined as $pH = -\log_{10}[H^+]$ or $pH = -\log_{10}[H_3O^+]$.
- A neutral solution has a *p*H of 7; any solution with a *p*H less than 7 is acidic while the ones with a *p*H of greater than 7 are basic in nature.
- The presence of common ion in a solution of a weak acid or a weak base suppress its dissociation. Such solutions act as buffer solutions which resist a change in their *p*H on addition of small amount of an acid or a base. The *p*H of buffer solutions depend on their composition and can be found by using a simple equation called **Henderson Hasselbalch equation**.
- The aqueous solutions of certain salts also behave as acids or bases due to the hydrolysis of their cation or anion or both.
- In an aqueous solution of a sparingly soluble salt an equilibrium exists between the undissolved salt and the ions obtained from the dissolved salt. This is called solubility equilibrium.
- The product of the concentration of the ions in the solubility equilibrium is a constant called solubility product (K_{sp}) and is proportional to the solubility of the sparingly soluble salt.
- The presence common ions decrease the solubility of a sparingly soluble sat. This is called common ion effect and has widespread applications in qualitative analysis.

Terminal Exercise

1. Explain why a hydrogen ion cannot exist free in an aqueous solution ?
2. Write the equilibrium constant expression for the following reaction ?

$$H_2CO_3(aq) + H_2O\ (l) \rightleftharpoons H_3O\ (aq) + HCO_3^-\ (aq)$$

3. Explain why does a strong Bronsted - Lowry acid has a weak conjugate base ?
4. What do you understand by the term 'amphoteric' ? Show with the help of equations that water is amphoteric in nature.
5. Calculate the *p*H of 1×10^{-3} M solution of NH_4OH. The dissociation constant of NH_4OH is 1.85×10^{-5} mol dm^{-3}.
6. The *p*H of an aqueous solution of HCl is 2.301. Find out the concentration of hydrogen ions in this solution.
7. What is a buffer solution ? What are its main constituents ?
8. Solubility of lead iodide PbI_2 is 1.20×10^{-3} mol dm^{-3} at 298K. Calculate its solubility product constant.
9. Calculate the solubility of Bi_2S_3 in water at 298 K if its $K_{sp} = 1.0 \times 10^{-97}$ mol^5 dm^{-15}.
10. Calculate the solubility of AgI in 0.10 M NaI at 298 K K_{sp} for AgI is 8.5×10^{-7} at this temperature.

Answers to Intext Questions

14.1

1. According to Arrhenius concept an acid is defined as a substance that is capable of producing hydrogen ion (H^+) by ionisation in aqueous solution. For example, HCl and CH_3COOH.

2. Arrhenius definition has the following drawbacks.

   * It is limited to only aqueous solutions and requires ionisation of the substance.

   * It does not explain the acidic or basic behaviour of some substances which lack a hydrogen (or a hydroxide) ion. For example, $AlCl_3$ and Na_2CO_3 which lack a hydroxide.

3. In the Bronsted - Lowry concept, any molecule or ion that can accept a proton is a base whereas in Arrhenius concept a base is the one which provides hydroxide ions in solution.

4. Acids: HCl, H_3O^+ Bases : NH_3, CN

14.2

1. The ionisation of weak acid, HF, can be represented as

   $$HF\ (aq) + H_2O \rightleftharpoons H_3O^+\ (aq) + F^-\ (aq)$$

   The expression for K_a would be, $K_a = \dfrac{[H_3O^+][F^-]}{[HF]}$

2. For a weak base BOH which partially dissociates in aqueous solution, and has a degree of dissociation as α we can write

   $$B + H_2O \rightleftharpoons BH^+ + OH^-$$

Initial concentrations	c	-55	0	0
Equilibrium concentrations	c(1-α)	-55	cα	cα

3. The equilibrium constant expression or base dissociation constant can be written as

   $$K = \frac{[BH^+][OH^-]}{[H_2O][B]} = \frac{[c\alpha][c\alpha]}{c\,[1-\alpha]\,55}$$

   rearranging we get,

   $$\Rightarrow \quad 55 = K_b = \frac{[c\alpha][c\alpha]}{c\,[1-\alpha]} = \frac{c^2\alpha^2}{c\,[1-\alpha]} = \frac{c\alpha^2}{[1-\alpha]}$$

Since the acid B is very weak, α << 1; we can be neglected in comparison to 1 in the denominator to get

$$K_b \approx c\alpha^2 \quad \text{or} \quad \alpha^2 = \frac{K_b}{c} \quad \text{or} \quad \alpha = \sqrt{\frac{K_b}{c}}$$

4. Given hydronium ion concentration, $[H_3O^+] = 6.3 \times 10^{-2}$ M

   As per definition $pH = -\log [H_3O^+]$

$\Rightarrow$ pH = - log 6.3 x 10^{-2}

$\Rightarrow$ pH = - (0.7993 - 2.0000)

$\Rightarrow$ pH = - (-1.2007) = 1.2007

5. Given Concentration of glycine = 1.0 M

$K_a = 1.67 \times 10^{-10}$.

$$\text{For a weak acid } \alpha = \sqrt{\frac{K_a}{c}} = \alpha = \sqrt{1.67 \times 10^{-10}} = 1.29 \times 10^{-5}$$

$\Rightarrow$ $[H_3O^+]$ = 1 x 1.29 x 10-5 = 1.29 x 10-5 M

pH = - log$[H_3O^+]$ = - log [1.29 x 10-5] = - (-4.8894) = 4.8894

14.3

1. Here, [Acid] = 0.05 M and [Salt] = 0.025 M; and $pK_a = 4.2$

Substituting the values in Handerson equation, we get

pH = 4.2 + log (0.05/0.025) = 4.2 + log 2 = 4.2 + 0.3010 = 4.5010

2. Let the solubility of Ag_2SO_4 be ‘s’ mol dm^{-3}

The concentrations of the Ag^+ and the SO_4would be ‘2s’ mol dm^{-3} and ‘s’ mol dm^{-3} respectively and $K_{sp} = [Ag^+]^2\ [SP_4^{2-}]$

Given $[SO_4] = 2.5 \times 10^{-2}$ M $[Ag^+] = 2 \times 2.5 \times 10^{-2}$ M = 5×10^{-2} M

Substituting the values in the expression of K_{sp} we get,

$K_{sp} = [5 \times 10^{-2}]^2 \ \times \ [2.5 \times 10^{-2}] = 6.25 \times 10^{-5}$ $mol^3\ dm^{-9}$

Chapter 15

ELECTRO CHEMISTRY

Electrochemistry deals with the conversion of electrical energy into chemical energy and vice versa. When electric current is passed through an aqueous solution of certain substance or through molten salts, it causes a chemical reaction to occur. On the other hand, in dry cells, button cells or lead acid batteries chemical reactions occur which produce electrical energy. In this lesson you will study some aspects of these processes.

Objectives

After reading this lesson you will be able to:

- understand oxidation and reduction in terms of electron transfer concept;
- calculate oxidation number (ON) of an atom in a molecule or ion;
- balance the chemical equation for redox reaction;
- explain electrolytic conduction, conductance and molar conductivity;
- describe the effect of dilution on conductivity and molar conductivity of an electrolyte;
- differentiate between electrolytic and Galvanic cell;
- state standard electrode potential and use it for calculation of standard electrode potential of a cell;
- explain Standard Hydrogen Electrode;
- describe electrochemical series and its application;
- state effect of concentration on eletrode potential (Nernst Equation);
- solve numericals based on Nernst Equation and
- find relationship between emf and Gibbs Energy change.

15.1 Oxidation and Reduction as Electron Transfer Process

Oxidation and reduction reactions constitute a very important class of chemical reaction. The electronic concept looks at oxidation and reduction in terms of electron transfer: process in which an atom or ion loses one or more electron to the other is called oxidation and the process in which an atom or ion gains one or more electron is termed as reduction. In the formation of NaCl from Na and Cl.

$$\mathrm{Na} \longrightarrow \mathrm{Na}^{+} + e \qquad \text{(loss of e by Na; oxidation)}$$

$$\mathrm{Cl} + e \longrightarrow \mathrm{Cl}^{-} \qquad \text{(gain of e}^{-}\text{ by Cl; reduction)}$$

Sodium undergoes oxidation and chlorine undergoes reduction. Here, sodium helps chlorine to undergo reduction and therefore it is called a reducing agent or reductant.

A reductant is a species in a chemical reaction which looses its electron to another reactant. Chlorine, on the other hand accepts electron, therefore it is an oxidising agent or oxidant. An oxidant is a species which accepts electrons in a chemical reaction.

It may be noted that oxidation and reduction processes do not take place independently but occur simultaneously and are thus called oxidation-reduction reaction or redox reactions. A redox reaction is a sum of oxidation and reduction half reactions in a chemical reaction.

15.2 Oxidation Number

It is easy to identify species undergoing oxidation or reduction in simple molecules. However, in polyatomic molecuels, it is difficult to do the same. In the example of NaCl taken earlier it was easy to identify as sodium undergoing oxidation and chlorine undergoing reduction but in the reaction involving ferrous sulphate with potassium permanganate ($KMnO_4$) it is difficult. Therefore, a new term called Oxidation Number has been introduced, Oxidation Number is the apparent charge which an atom appears to have when each pair of electrons is counted with more electronegative atom. Oxidation Number is always assigned to an atom. It is number written with +*ve* or -*ve* sign. The number indicates the number of electrons that has been shifted from an atom towards a more electro-negative atom, in a heteronuclear covalent bond. The +*ve* sign for the atom shifting its electron away from itself and -*ve* is given to more electro -*ve* atom. The concept of Oxidation Number is based on the assumption that in a polyatomic covalent bonding, shared pair of electrons belongs to more electro -*ve* atom. Oxidation State (OS) is also used for Oxidation Number.

15.2.1 Rules for Assigning Oxidation Number

There are certain rules that are followed for computing the oxidation number of an atom in a molecule or ion.

1. Oxidation number is taken as zero if atoms are present in elemental form. For example, O_2, Na, P_4 are elemental forms. They have oxidation number zero.
2. The oxidation number of a monatomic ion is the same as the charge present on it. For example, Na^+, $Mg^{2+,}$ $Al^{3+,}$ Cl^-, S^{2-} will have oxidation no +1, +2, +3, -1, -2 respectively
3. The oxidation number of oxygen is -2 in almost all the compounds except (a) in peroxides
4. e.g. Na_2O_2, H_2O_2 where oxidation number is -1 and (b) super oxides (KO_2) where it is -1/2.
5. The oxidation number of H of +1 when combined with non-metal and is -1 when combined with metal e.g. in HCl the O.N. of H is +1 but in Ca H_2 it is -1.
6. The Oxidation Numbers of alkali metal is +1 in its compounds.
7. In a compound made up of different elements the more electro negative element will have negative oxidation number and less electro negative atoms will have positive oxidation number e.g. in NCl_3, N has +3 oxidation number and Cl has -1 oxidation number.
8. The sum of the oxidation numbers of all the atoms in a neutral compound is zero.

9. In a polyatomic ion, the sum of oxidation numbers of all the atoms is equal to the charge on the ion. e.g. in CO_3^- , the sum of oxidation Number of carbon and oxygen is -2.

Let us illustrate the above rules taking few examples. The oxidation number of S, N and Cl atoms in : (a) H_2SO_4 (b) NO_3^- (c) ClO_4^- respectively will be calculated as

(a)

1. Let the oxidation number of sulphur be x.
2. Since the oxidation number of O is -2. Therefore the sum of four O atoms is equal to -8.
3. The oxidation number of each H is +1 as bonded to a non-metal so two H atoms have total oxidation number of +2.
4. H_2SO_4 is a neutral molecule. Therefore, the sum of all the oxidation numbers is equal to zero.

Thus

$$+2 + x - 8 = 0.$$
$$x = +6.$$

Therefore.

oxidation number of sulphur in H_2SO_4 is + 6.

(b)

NO_3^- first assign -2 oxidation number to each O atom. Here the sum of the oxidation number of all the atoms will equal to charge present on the ion.

Thus

$$x - 6 = -1$$
$$x = +5$$

oxidation number of N is +5.

(c)

In ClO_4^- $x - 8 = -1$

$$x = +7$$

15.3 Balancing Redox Reaction

The redox reaction can be balanced by any of the following methods.

a) Oxidation number method.
b) Ion electron method

15.3.1 Balancing by Oxidation Number method

The steps involved in balancing redox reactions by this method are as follows:

1) Write the skeletal equation of reaction i.e., chemical equation without the stoichiometric coefficient
2) Write the oxidation number of each atom above its symbol in the equation.
3) Identify the atoms undergoing change in oxidation number.
4) Calculate the increase or decrease in oxidation number per atom for the atom undergoing a change in oxidation number. If more than one atom is involved, multiply the increase or decrease in number with the number of atoms undergoing the change to determine the total change in oxidation number.

5) Equate the increase and decrease in oxidation number on the reactant side by multiplying the formulae of the oxidising and reducing agents suitably.
6) Balance the equation with respect to all the atoms except hydrogen and oxygen.
7) Finally balance H and O also.
8) If the reaction is taking place in acidic medium balance the O atoms by adding required number of H_2O molecule on the side where O atoms are less in number. Balance the H atoms by adding H^+ to the side deficient in H atoms.
9) In the basic medium by add required number of negative charges by adding required number of OH^- ions to the side deficient in the magnitude of charges, then add H_2O molecules to balance OH^- ions.

For example: When Phosphorus is treated with nitric acid, nitric oxide is formed.

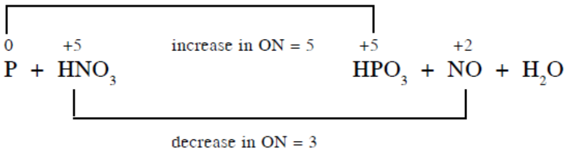
1. The skeletal equation is

$$P + HNO_3 \longrightarrow HPO_3 + NO + H_2O$$

2. Write the oxidation number of each atom on the given skeletal equation

$$\overset{0}{P} + \overset{+1+5-2}{HNO_3} \longrightarrow \overset{+1+5-2}{HPO_3} + \overset{+2-2}{NO} + \overset{+1-2}{H_2O}$$

3. P and N are undergoing change in Oxidation Number



4. Equating the increase and decrease in Oxidation Number of P and N on the reactant side

$$3P + 5HNO_3 \longrightarrow HPO_3 + NO + H_2O$$

5. Balance the P and N atoms on both sides of the equation

$$3P + 5HNO_3 \longrightarrow 3HPO_3 + 5NO + H_2O$$

6. O and H are already balanced in the equation.

15.3.2 Balancing by Ion Electron Method

This method is based on the principle that electrons lost during oxidation half reaction is equal to the electron gained in the reduction half reaction. The steps involved are

1. Write the skeleton equation.
2. Write the oxidation number of all the atoms above their symbols in the skeletal equation.
3. Find the atoms undergoing change in Oxidation Number. Thus find out the species getting oxidized and reduced respectively.
4. Split the whole (net) equation into reactions i.e. oxidation half reaction and reduction half reaction.
5. Balance the atoms, undergoing change in oxidation number in each half reaction.
6. Calculate the total change in oxidation number in each half reaction which is equal to total number of electron transfer.

7. Add total number of electron transfer as calculated above on the reactant side in reduction half and on the right hand side on the oxidation half reaction.
8. Balance the charges by adding H^+ (for reactions in acidic medium) or OH^- (reactions basic medium) either on left or right of equation.
9. Finally balance H and O by adding H_2O on the required side of the reaction.
10. Add the two half reactions such that total number of electrons cancel out on both sides. To do so half reactions may be required to multiplied by some numbers to make the number of electrons equal on both sides.

Example 15.1: Balance the following skeletal reaction by ion electron method

$$Cr_2O_7^{2-} + Fe^{2+} \longrightarrow Cr^{3+} + Fe^{3+} \quad \text{in acid medium}$$

Referring to the rules given:

Step I and II

Write the oxidation number of the atoms above their symbol in the skeletal equation

$$\overset{+6}{Cr_2}O_7^{2-} + \overset{+2}{Fe^{2+}} \longrightarrow \overset{+3}{Cr^{3+}} + \overset{+3}{Fe^{3+}}$$

Step III:

Oxidation number of Fe^{2+} is increasing; therefore it is undergoing oxidation and oxidation number of Cr is decreasing so it is undergoing reduction.

Step IV:

Split the reactions in two half reactions

a) Reduction half reaction $Cr_2O_7^{2-} \longrightarrow Cr^{3+}$

b) Oxidation half reaction $Fe^{2+} \longrightarrow Fe^{3+}$

Balance the first reduction half reaction $Cr_2O_7^{2-} \longrightarrow Cr^{3+}$

Step V:

Balance the atoms undergoing change in Oxidation Number

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

Step VI and VII:

Write the total number of electron transfer taking place. Here each atom undergoes change in in Oxidation Number by 3 therefore two Cr atoms undergoes change in Oxidation Number by 6.

$$Cr_2O_7^{2-} + 6e \longrightarrow 2Cr^{3+}$$

Step VIII:

Balance the charge by adding H^+ on the left side

$$Cr_2O_7^{2-} + 6e + 14H^+ \longrightarrow 2Cr^{3+}$$

Step IX:

Balance the H and O by adding H_2O on either side

$$Cr_2O_7^{2-} + 6e + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$

Balancing the Oxidation half reaction

According the steps as followed for reduction half reaction

$$Fe^{2+} \longrightarrow Fe^{3+}$$

i) Atoms are balanced on both side so we go to next step, that is number of electron transfer taking place

$$Fe^{2+} \longrightarrow Fe^{3+} + e$$

ii) Balance the charge and it is balanced

Step X:

Add the two-half reaction

$$\begin{array}{l} Fe^{2+} \longrightarrow [Fe^{3+} + e] \ x\ 6 \\ Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O \\ \hline Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \end{array}$$

Intext Questions 15.1

1. Determine the Oxidation number of element in the bold letter in the following

SiH_4 BH_3 BF_3 S_2O_4

BrO_4 H_2PO_4 $SH_{12}O$ HNO_3

....

....

....

2. How does oxidation number change in oxidation and reduction ?

....

....

3. Mention the oxidising agent and reducing agent in the following

$$H_2S + HNO_3 \longrightarrow NO + S + H_2O$$

....

....

4. Write the half reaction for the following

$$2I^- (aq) + 2Fe^{3+} (aq) \longrightarrow I_2 (s) + 2Fe^{3+} (aq)$$

$$Mg (s) + Cl_2 (aq) \longrightarrow MgCl_2 (s)$$

$$I_2 + HNO_3 \longrightarrow HIO_3 + NO_2 + H_2O$$

....

....

5. Balance the equation by oxidation number method

$$CuO + NH_3 \longrightarrow Cu + N_2 + H_2O$$

$$MnO_4 + HCl \longrightarrow MnCl_2 + C_2 + H_2O$$

....

....

6. Balance the following by ion electron half reaction method

$NO_3^- + Bi \longrightarrow Bi^{3+} + NO_2$ acidic medium

$MnO_4 + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+}$ acidic medium

$Cr_2O_7^{2-} + Fe^{2+} \longrightarrow Fe^{3} + Cr^{3+}$ acidic medium

$Al + NO_3^- \longrightarrow Al\,(OH)_4^- + NH_3$ basic medium

....

....

15.4 Electrolytic Conduction

When electricity is passed through an aqueous solution, it may or may not conduct current. The chemical substances whose aqueous solutions conduct electricity are called electrolytes and those which do not conduct current are called as non-eletrolytes. This phenomenon of conduction of current through a solution is called elctrolytic conduction.

Electrolytic conduction takes place due to the movement of cations and anions in a solution. The electrical conductance of a solution depends upon (a) nature of solute (b) valency of its ion, (c) the concentration in solution and (d) the temperature. In this section we will learn about various ways of expressing the conductance of electrolytes and the factors affecting them.

15.4.1 Conductance and Conductivity

Like solid conductors, electrolytic solutions also obey Ohm's Law. When a current of I amperes flows through a solution which offers a resistance of R ohms and a potential difference of V volts is applied, then according to ohm's law.

$$V = I \,.\, R$$

If the solution is taken in a conductivity cell which has two parallel electrodes / cm apart and each having an area of cross section A cm2, the resistance R of the electrolyte is found to be directly proportional to l and inversely proportional to A i.e.

$$R \propto l/A$$

or

$$R = \rho \;.\; l/A \qquad \text{.... (i)}$$

Where ρ "rho" is a constant of proportionality and is called specific resistance or resistivity. it is characteristic of the nature of electrolyte, its concentration and temperature.

In case of solution, it is preferred to discuss their conductance and conductivity rather than their resistance and specific resistance. The conductance is reciprocal of resistance and the conductivity is reciprocal of specific resistance.

Conductance is denoted by L and is measured in the unit of ohm-1 which has now been named as siemens, S. The conductivity is denoted by k "kappa". Thus, by definition

$$L = \frac{1}{R} \text{ and } k = \frac{1}{\rho} \qquad \text{.... (ii)}$$

The units of k can be worked out from relation (i) as under:

The inverse of (i) is,

$$\frac{1}{R} = \frac{1}{\rho} \cdot \frac{A}{l}$$

or $$L = k\,\frac{A}{l}$$

and $$K = L\,\frac{l}{A}$$

$$= S\,\frac{cm}{cm^2}$$

$$= S\ cm^{-1}$$

The conductivity (K) is expressed in S cm^{-1} or 100 S m^{-1}.

15.4.2 Measurement of Conductance

The conductance of an electrolyte is measured with the help of a conductivity cell. Conductivity cell is a device which has two parallel platinum electrodes coated with platinum black.

The SI unit of length is metre; hence SI unit of conductivity (K) is Sm^{-1}, but the commonly used unit is Scm^{-1}. In the expression for conductivity $\frac{l}{A}$ is a constant. Here l represents the distance between the two parallel electrodes and A represents the area of cross section of the electrodes. Thus for a given conductivity cell, $\frac{l}{A}$ is a constant called cell constant.

K (Conductivity) = conductance x cell constant

The conductivities of some substances are given in the table.

Table 15.1: The values of conductivity of some selected substances at 298 K

Substance	k/S cm^{-1}	Substance	k/S cm^{-1}
Pure water	6.0×10^{-8}	Silver metal	6.1×10^{5}
0.1 M HCl	3.5×10^{-2}	Mercury metal	1.0×10^{4}
0.1 M NaCl	9.2×10^{-3}	Glass	1.0×10^{-14}
0.1 M CH_3COOH	4.7×10^{-4}		
0.1 M NH_4OH	3.4×10^{-4}		

We find from the table that the conductivities of metals are very high and that of pure water and glass very low.

15.4.3 Molar Conductivity

The electrolytic conductivity of a solution depends on the concentration of the electrolyte in the solution. Therefore, the conductivity of an electrolyte is normally expressed as molar conductivity.

Molar conductivity is the conducting power of all the ions furnished by one mole of an electrolyte in a solution of specified concentration.

It is denoted by λ_m and is related to K by the relation.

$$\lambda_m = \frac{1000\ K}{M} \qquad \text{.... (iv)}$$

Where, M is the molarity of the solution. Its units are S cm^2 mol^{-1}.

15.5 Factors Affecting Conductivity

As mentioned the conductivity of an electrolyte depends upon the following aspects of the electrolyte.

a) Nature of electrolyte: Conductivity of an electrolyte depends upon the nature of electrolyte on the following points:

i. Weak or strong electrolyte: A weak electrolyte furnishes fewer ions therefore it has lower conductivity than a strong electrolyte of same concentration.

ii. Valency of the ions: The ions with higher valency carry more charge and therefore they conduct more charge than the ion of lower valency. Thus higher the valency of the ion greater is the conducting power.

iii. Speed of the ion: The ion which can move faster will carry the charge also faster and therefore has more conducting power.

b) Temperature: Conductivity of an electrolyte generally increases by 2-3 percent for each degree rise in temperature. With increase in temperature the viscosity of the solvent decreased and thus ion can move faster. In case of weak electrolyte, when the temperature is increased its degree of dissociation increases, thus conductivity increases.

c) Concentration:

i. Variation of conductivity (k) with concentration. When the solution is diluted its conductivity also decreases. It is because k is the conducting power of all the ions present per cm^3 of the solution. When the solution is diluted the number of ions per cm^3 also decreases, hence k decreases.

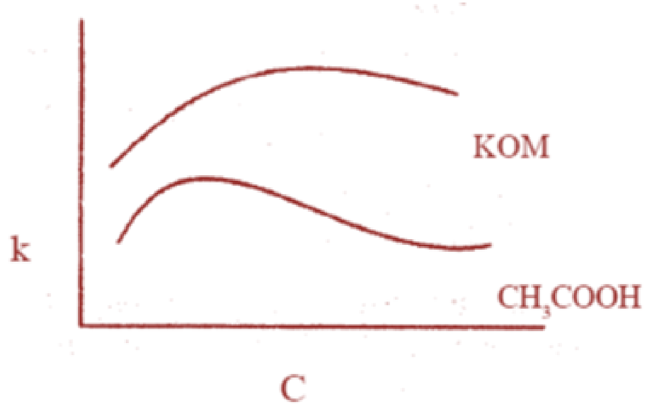


Fig. 15.1: Variation of conductivity with concentration

ii. Variation of Molar and Equivalent conductivity with concentration. As the solution is diluted its molar conductivity increases. λ_m is given as

$$\lambda_m = \frac{1000\ K}{M}$$

Where k is conductivity and M is molar concentration.

This increase in λ_m is a resultant of two factors. On decreasing the concentration both k and M decreases. Of the two (k) tries to decrease λ_m while the other factor (M) tries to increase it. Since the decrease in M is much more, the net result is that λ_m increases. However, strong and weak electrolyte as show different type of behaviour on dilution (Fig. 15.2)

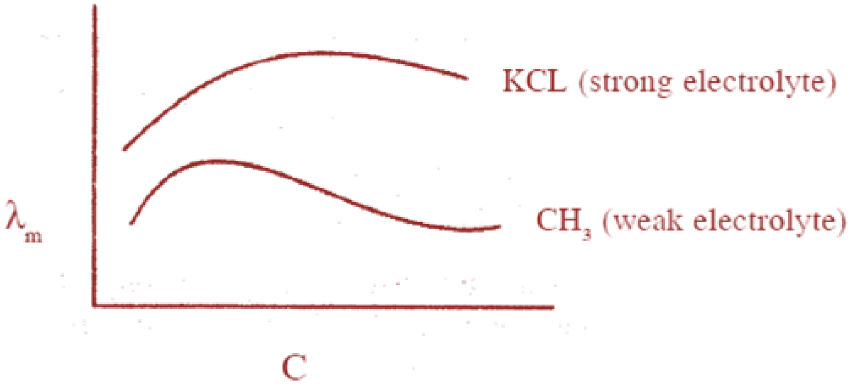


Fig. 15.2: Variation of molar conductivity with concentration

From the Fig. 15.2 we find that the increase in molar conductivity for a strong electrolyte like KCl is very gradual on dilution and also the value is high at all concentrations. Whereas for a weak electrolyte like CH_3COOH, there is a gradual increase in λ_m on dilution which is followed by a sharper increase on further dilution. These observations can be explained as: Since KCl is a strong electrolyte, it is fully dissociated at all concentrations. In concentrated solution, attraction between opposite ions is large and their conducting ability is less. On dilution inter-ionic forces decrease and ions can move faster leading to the increase in molar conductivity.

On the other hand, in weak electrolytes, molar conductivity is low in concentrated solution. This is due to partial dissociation (ionisation) of weak electrolytes. On diluting the solution the degree of ionisation increases, which increases the number of ions. This leads to a sharp increase in molar conductivity in weak electrolytes.

15.5.1 Kohlrausch’s Law

Kohlrausch determined the molar conductivity at infinite dilution for a large number of strong electrolytes. On the basis of his observations, he concludes that at infinite dilution, each ion makes a define contribution to the total molar conductivity of an electrolyte. This individual contribution is called molar ionic conductivity. He generalized his observation as “At infinite dilution each ion of the electrolyte makes a definite contribution towards conductivity of the electrolyte and it is independent of the presence of other ions of the electrolyte.” This is called Kohlrausch’s Law of independent migration of ions.

For a salt like KCl, molar conductivity at infinite dilution can be written as

$$\lambda_m^\infty \text{KCl} = \lambda_m^\infty \text{K}^+ + \lambda_m^\infty \text{Cl}^-$$

In general, for a salt of formula A_xB_y the molar conductivity at infinite is written as

$$\lambda_m^\infty (A_xB_y) = x\,\lambda_m^\infty (A^{y+}) + y\,\lambda_m^\infty (B^{x+})$$

where $\lambda_m{}^{\infty}$ indicates molar conductivity at infinite dilution. This law is used to calculate the molar conductivity at infinite dilution for weak electrolytes whose $\lambda_m{}^{\infty}$ cannot be obtained graphically.

Example 15.2 : $\wedge^0$ for NaCl. HCl and CH_3COONa are 126.0, 426.0 and 91.0 S cm^2 mol^{-1} respectively. Calculate $\wedge^0$ for CH_3COOH.

Solution : $\wedge^0$ $CH_3COOH = \lambda^0(H^+) + \lambda^0(CH_3COO^-)$

$= \lambda^0\ (H^+) + \lambda^0(Cl^-)\ + \lambda^0(Na^+) +\ \lambda^0(CH_3COO^-) - \lambda^0(Na^+) - \lambda^0(Cl^-)$

$= 426.0 + 91.0 - 126.0\ = 391.0$ S cm^2 mol^{-1}

Intext Questions 15.2

1. How does the solution of electrolytes conduct electricity?

....

2. Define conductivity and molar conductivity.

....

3. Give the units of conductance and conductivity.

....

4. List factors affecting the conductance of an electrolyte.

....

5. Draw a graph showing variation in molar conductivity of weak and strong electrolytes.

....

6. Write the expression for molar conductivity at infinite dilution for $Al_2(SO_4)_3$.

....

15.6 Electro Chemical Cell

An electrochemical cell is a device used for the inter conversion of electrical and chemical energy. An electrochemical cell contains two electrodes (cathode and anode) and an electrolyte.

They are of two types: based on the nature of conversion of energies

a) Electrolytic cell (Faradaic Cell)
b) Galvanic cell (Voltaic Cell)

15.7 Electrolytic Cell

An electrolytic cell consists of two electrodes connected to a battery as shown in Fig. 15.3

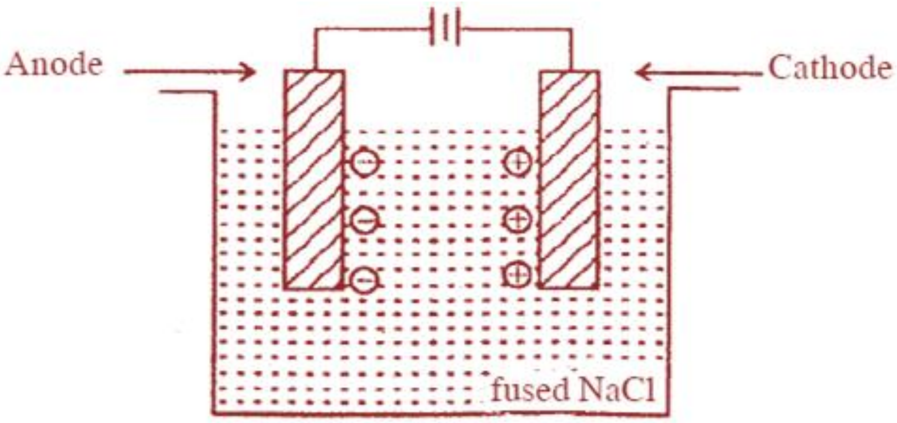


Fig. 15.3: Electrolytic Cell

In an electrolytic cell electrical energy is converted into chemical energy. The process of decomposition of an electrolyte into its ions when an electric current is passed through it, is called electrolysis.

When electricity is passed through an electrolyte, a chemical change i.e. decomposition of the electrolyte into ions takes place at the electrode. Oxidation and reduction reactions occur in the cell.

In the electrical field Cl^- ions migrate to the *+ve* electrode (anode) and undergo oxidation by losing electrons. Na^+ ions will go to *-ve* electrode (cathode) and undergo reduction.

The process can be represented as:

oxidation at anode	reduction at cathode
$Cl^- \rightarrow Cl + e$ $Cl + Cl \rightarrow Cl_2\,(g)$	$Na^+ + e \rightarrow Na$

15.7.1 Faraday's laws of electrolysis

As a result of extensive studies on electrolysis, Faraday in 1834 has given the relationship between electric current and chemical changes in the form of Faraday's laws.

First law:

"The mass of a substance liberated at the electrodes by the passage of electric current are proportional to the quantity of electricity passed".

Mathematically this is expressed as,

$$m \propto Q \text{ or } m \propto ct$$

$$m = ect$$

Where m is the mass of the substance liberated at the electrode, Q is the quantities of electricity in coulombs, c is the strength of the current in amperes and t is the time in seconds for which the current is passed through electrolyte, e is the constant of proportionality called electrochemical equivalent of the substance liberated. Its value is equal to m when c and t are units. Thus,

Electrochemical equivalent (e): Electro chemical equivalent is the weight of the substance deposited or liberated when 1 ampere current passed for 1 second during the electrolysis of electrolytic solution containing that ion.

Ex: A current of 3 ampere strength passing through silver nitrate solution for 20 minutes deposits 4g. of silver. What is the electrochemical equivalent of silver?

Solution: $C = 3$ amperes

$t = 20 \text{ x } 60 = 1200$ seconds

$m = e.c.t$

$4 = e \text{ x } 3 \text{ x } 1200$

$e = 4 / 3600 = 0.00111$ gram / coulomb

Faraday (F)

Faraday is the quantity of electric charge carried by one mole of electrons (i.e., $6.022 \text{ x } 10^{23}$ electrons). Mathematically,

$F = N \text{ x } e$ (N = Avogadro number & e = Charge of electron)

$F = 6.022 \text{ x } 10^{23} \text{ x } 1.602 \text{ x } 10^{-19}$ coulombs = 96500 Coulomb (approx.).

Now, Faraday's First law is written mathematically as

$$m = \frac{E \text{ x } C \text{ x } t}{96500}, \qquad E = \text{Chemical equivalent of the substance.}$$

$$E = \frac{\text{Formula mass of the substance}}{\text{valency of the substance}}$$

Chemical Equivalent (E)

The mass of the substance deposited or liberated at an electrode during the passage of one Faraday of electricity in the electrolysis is called chemical equivalent.

Example:

A current of 10 amperes is passed through molten $AlCl_3$ for 96.5 seconds. Calculate the mass of Al deposited at the cathode. (At. wt. of Al = 27)

Solution

As per the first law of Faraday,

$$m = \frac{\text{At.wt. x c x t}}{\text{valency x 96500}}$$

At.wt. of Al = 27

C = 10 amp. t = 96.5 seconds valency = 3

$$m = \frac{27 \text{ x } 10 \text{ x } 96.5}{3 \text{ x } 96500} = 0.09 \text{ g.}$$

The mass of Al liberated = 0.09 g.

Faraday's Second law:

When the same quantity of electricity is passed through different electrolytes (connected in series) the masses of different species liberated or deposited at the electrodes are directly proportional to their chemical equivalents.

For example, if the same current is passed through a number of solutions contained in different Volta meters connected in series, as shown in Fig. 15.4

The masses of hydrogen, copper and silver liberated are proportional respectively to their chemical equivalents.

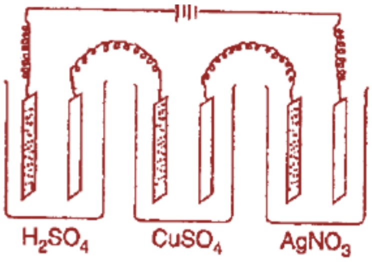


Fig. 15.4 : Illustration of Faraday's Second law

Thus,

$$= \frac{\text{mass of copper}}{\text{mass of silver}} = \frac{\text{Eq. wt. of Cu}}{\text{Eq. wt. of Ag}}$$

$$\text{i.e.,} \quad \frac{m_{Cu}}{m_{Ag}} = \frac{E_{Cu}}{E_{Ag}} \quad \text{similarly,} \quad \frac{m_{H_2}}{m_{Cu}} = \frac{E_{H_2}}{E_{Cu}}$$

From the second law, we conclude that the quantity of current that would deposit 1.008 g. of H_2 (1 gram – equivalent) from H_2SO_4 solution, would also deposit one *g. eq. wt.* each of Cu, and Ag from the solution of their salts.

Relation between e (Electrochemical Equivalent) and E (Chemical Equivalent Weight) As you are aware that, 1 Faraday (96500 coulombs) is the quantity of electricity consists of 6.023 x 10^{23} electrons which will deposit one chemical equivalent weight of the substance. Thus, 1F = 6.023 x 10^{23} electrons = 1 g. equivalent since 1 F i.e., 96500 coulombs liberate 1g. equivalent of a substance i.e., E grams

$$\text{Therefore 1 coulomb liberates } \frac{E}{96500} \text{ grams}$$

$$\text{By definition} \qquad e = \frac{E}{96500}$$

$$\text{eg.} \quad e_{Ag} = \frac{108}{96500}$$

Hence, mathematically, the Faraday's first law becomes

$$m = ect$$

$$m = \frac{Ect}{96500}$$

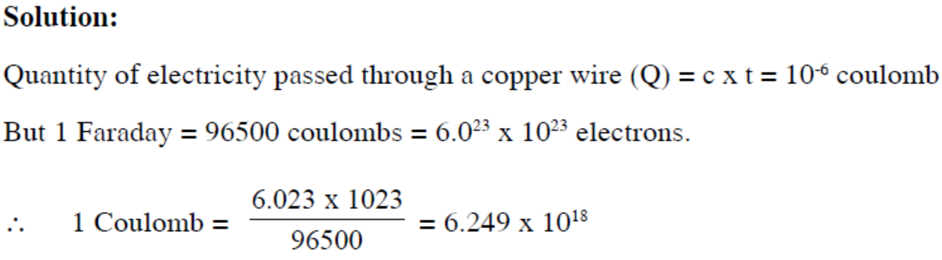
$$m = \frac{\text{At.wt. x c x t}}{\text{valency x 96500}} \quad \text{since } E = \frac{\text{At.wt}}{\text{valency}}$$

Applications of Electrolysis:

i. Electrolysis process is used in the extraction of metals like sodium, potassium, Aluminium etc.,
ii. It is used in the preparation of non-metals like H_2, Cl_2 etc.
iii. It is used in the preparation of compounds like NaOH, KMnO4 etc.
iv. It is used in the preparation of alloys.
v. It is used in Electro plating.

Example: Find the number of electrons passing for second through a cross section of copper rise carrying 10^{-6} amperes of current per one second.

Solution:



Solution:

Quantity of electricity passed through a copper wire (Q) = c x t = 10^{-6} coulomb

But 1 Faraday = 96500 coulombs = 6.0^{23} x 10^{23} electrons.

$$\therefore \quad 1 \text{ Coulomb} = \frac{6.023 \times 1023}{96500} = 6.249 \times 10^{18}$$

Hence 10^{-6} Coulombs = 6.249 x 1018 x 10^{-6} = 6.249 x 10^{12} electrons.

15.7.2 Galvanic Cell

Such cells are called voltaic cells. In such a cell chemical energy is converted into electrical energy. Dry cells, car batteries and button cells used in wrist watches are all examples of this type of cell. They are energy producing devices.

15.7.3 Redox Reaction and Galvanic Cell

You have already learnt that when electricity is passed through a solution, redox reaction takes place. Now we shall learn how redox reaction can be used to produce electricity.

When a Zinc rod is dipped in $CuSO_4$ solution, a reaction starts in the solution.

$$Zn(s) + CuSO_4\,(aq) \longrightarrow Zn\,SO_4\,(aq) + Cu\,(s)$$

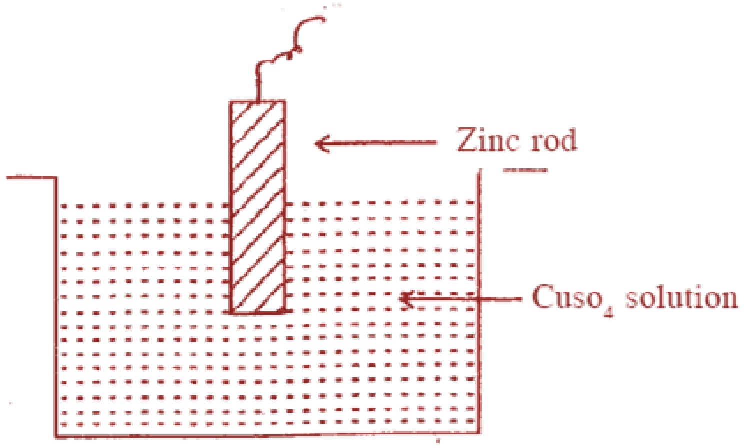


Fig. 15.5: Redox reaction

It is an example of redox reaction.

The two half reactions are

$$Zn(s) \longrightarrow Zn^{2+}\,(aq) + 2e^- \quad \text{oxidation}$$

$$Cu^{2+}\,(aq) + 2e^- \longrightarrow Cu(s) \quad \text{reduction}$$

In this redox reaction the electrons given by zinc rod have been directly consumed by Cu^{2+} ion. But, if somehow, we make electrons given by Zinc rod to flow through a wire to reach Cu^{2+} ions, we shall be producing electric current. To do so, the reaction is carried out in the electrochemical cell as shown Fig. 15.6:

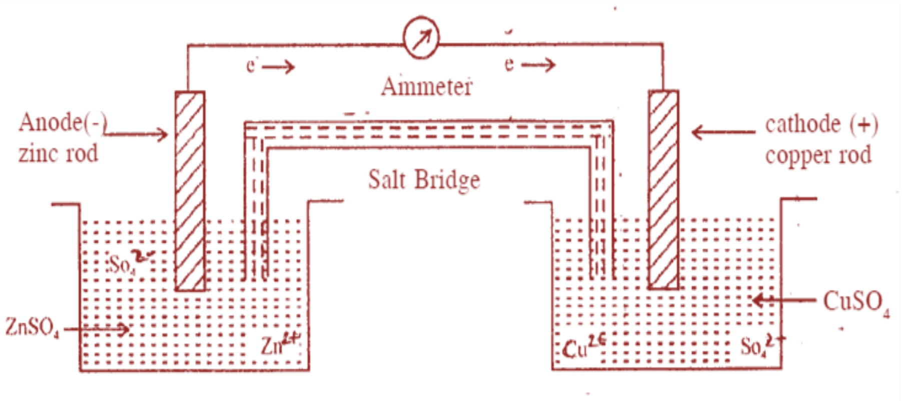


Fig. 15.6: Daniell cell having zinc and copper electrodes

The redox reaction in the electro chemical cell has been modified zinc rod is dipped in zinc sulphate solution in one beaker while copper rod is dipped in another beaker containing $CuSO_4$ solution. The two solutions are connected through a salt bridge and the two metals are connected to an ammeter with the help of wire. We find electrons move through the wire from zinc to copper rod.

A metal dipped in its own salt solution is called as half-cell. Zinc rod dipped in-zinc sulphate solution is oxidation half-cell because oxidation takes place.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad \text{oxidation}$$

The released electrons are taken up by zinc rod and it becomes negatively charged.

Copper in copper sulphate is reduction half-cell. Copper acts as cathode and reduction take place here. Copper rod becomes positively charged. Copper gains electrons and in this process, becomes positively charged.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

Here the electrons will move from negatively charged electrode to positively charged copper electrode.

Flow of electrons in the external circuit

The electrons released at the anode during oxidation flow through the external circuit and reach the cathode where they are taken up for reduction. Thus in a galvanic cell the electrons always flow from anode to cathode while the conventional positive current flows in the opposite direction i.e. from cathode to anode. Since the electric current always move in a closed circuit salt bridge is used to make electrical contact between the two half cells.

15.7.4 Salt Bridge

A salt bridge is a inverted U tube filled with a concentrated solution of an inert electrolyte like KCl or NH_4NO_3 which does not take part in the cell reaction. The electrolyte is taken in the form of solution and mixed with agar-agar. The mixture is heated and filled in the U tube when hot. On cooling it sets into a jelly like mass and does not flow out, during its use. Salt bridge has two functions.

i. It completes the inner circuit. It acts as a contact between the two half cells without any mixing of electrolytes.
ii. It prevents accumulation of charges in two half cells and maintains electrical neutrality.

Cations amd anions of the salt bridge move into two half cells and neutralise the excess charge. The anions move into oxidation half cell and neutralise the excess charge. The cations move into the reduction half-cell and neutralise the charge.

In a Daniell cell a salt bridge is replaced by a porous pot, to make the cell handier to use.

15.7.5 Symbolic Representation of Galvanic Cells

In the previous section the cell was a Zn-Cu cell. But any two suitable metals can be used to make the cell and every time we do not always draw the diagrams showing the cell. It is represented in the symbolic form with the help of standard notation. The rules of notations are as follows:

1. Anode is written on the left-hand side and cathode on the right-hand side.
2. The metal electrode in the anode half-cell is written by its symbol and this is followed by the cation (metal ion) along with its concentration in a small bracket. The metal and cations are separated by vertical line or a semicolon (;)

$$Zn_{(s)} \mid Zn^{2+}{}_{(aq)}\ (1\ M)$$

3. In the reduction half-cell the anion along with its concentration is written first, then vertical line and then the metal

$$Cu^{2+}{}_{(aq)}\ (1\ m) \mid Cu_{(s)}$$

4. A salt bridge is represented by two vertical lines Thus, the Galvanic cell described above is written as

$$Zn_{(s)} \mid Zn^{2+}{}_{(aq)}\ (1\ M) \parallel Cu^{2+}{}_{(aq)}\ (1\ M) \mid Cu_{(s)}$$

or

$$Zn \mid Zn^{2+}{}_{(1M)} \parallel Cu^{2+}{}_{(1M)} \mid Cu$$

Electrode Potential

Metal atoms have tendency to lose electrons and go into solution as metal ions. Electrode potential is a measure of the tendency of metal atoms to gain or loose electrons when in contact with a solution of its own ions.

When a metal strip M is immersed in a solution of its salt containing ions (Mn^{+}), one of the processes as shown in Fig. 15.7 (a) or (b) can occur.

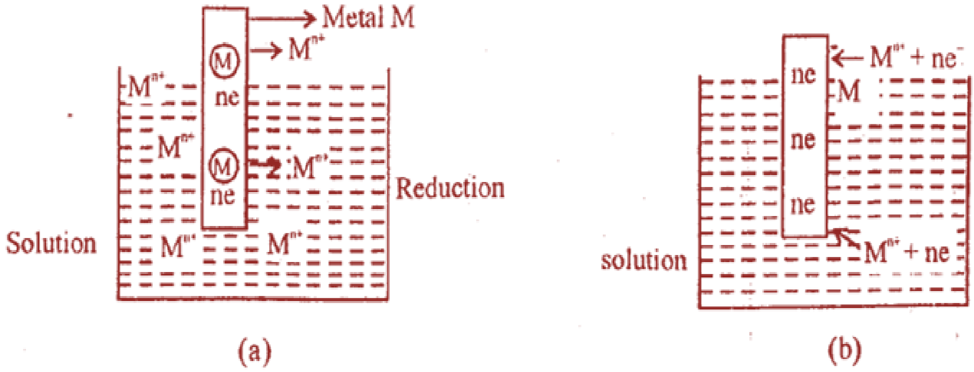


Fig. 15.7: Metal placed in a solution of its ions

I. The dissolution process where atoms of metal electrode M may loose some electrons to the electrode and enter the solution as M^{n+}

$$M \longrightarrow M^{n+} + ne \quad \text{(metal is oxidised)}$$

The metal electrode gets negative charge and the solution gets extra positive charge.

II. The deposition process where Metal cations M^{n+} from the solution may come in contact with the metal strip, gain some electrons and get converted into metal atoms M, which get deposited on the surface of metal strip. Separation of charges takes place and a potential is developed called electrode potential.

$$M^{n+} + ne^{-} \longrightarrow M \quad \text{(the ion is reduced)}$$

The electrode reaction reaches an equilibrium as represented below

$$M(S) \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} M^{n+}(aq) + ne^{-}$$

Electrode potential is the potential developed at the interface between metal and its salt solution; when a metal is dipped it its own salt solution.

15.8.1 Standard Electrode Potential

An electrode is said to be in the standard state if the concentration of the electrolyte is one molar and the temperature is 298K. Then its electrode potential is called standard electrode potential and denoted by EO. If any gas is used to make the electrode then the pressure of the gas should be 1 bar.

15.9 Measurement of Electrode Potential

It is not possible to measure single electrode potential. It is because the reaction taking place at the electrodes is oxidation or reduction and these reactions do not take place in isolation. It can be measured with respect to a reference electrode. The electrode used as reference electrode is standard hydrogen electrode (SHE).

15.9.1 Standard Hydrogen Electrode

Standard Hydrogen Electrode (SHE) consists of a container, containing 1M HCl solution kept at 298 K. A wire containing platinum electrode coated with platinum black is immersed in the solution. Pure hydrogen gas in bubbled in the solution at 1 bar pressure.

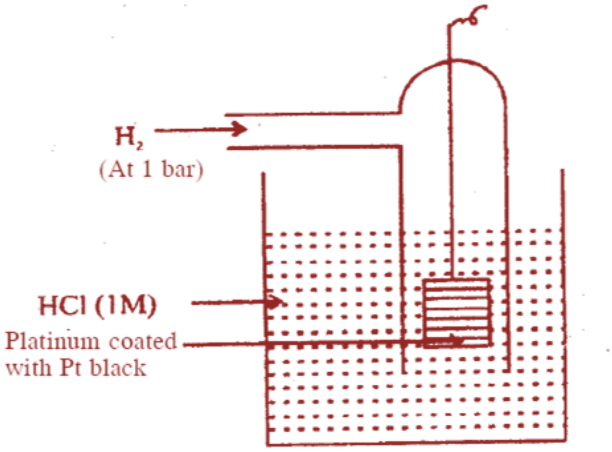


Fig. 15.8: Standard Hydrogen electode

The potential of SHE (E^{O}) is taken as zero at all temperatures.

Standard hydrogen electrode may act as anode or cathode depending upon the nature of the other electrode. If its acts an anode, the oxidation reaction taking place is

$$H_2\,(g) \longrightarrow 2H^+\,(aq) + 2e^-$$

If it acts as cathode then the reduction half reaction occurring is

$$2H^+\,(aq) + 2e^- \longrightarrow H_2\,(g)$$

15.9.2 Measurement of Standard Electrode Potential

i) Determination of magnitude:

The standard electrode potential of an electrode can be measured by combining it with standard hydrogen electrode. To illustrate, let us take the example for the measurement of standard eletrode potential of zinc electrode. A zinc strip is dipped in 1M $ZnSO_4$ solution and it is Standard Hydrogen electrode. The cell emf is found to be 0.76 V.

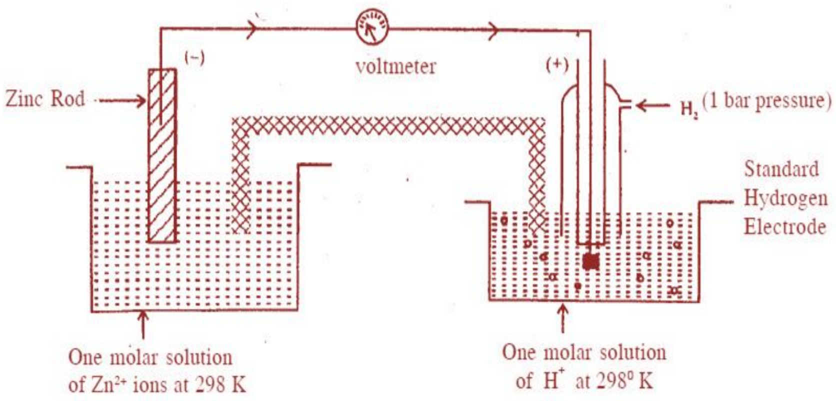


Fig. 15.9: Measurement of standard electrode potential of Zn/Zn^{2+} electrode

When copper electrode i.e. copper dipped in 1 M $CuSO_4$ solution is connected to standard hydrogen electrode then the cell emf is 0.34.

ii) Sign of electrode potential

The galvanic cell formed by the combination of SHE and electrode under study, the polarity of the electrode is determined with the help of a voltmeter. In case the given electrode is found to be positive electrode, its electrode potential is given the positive sign and if it is negative then it is given the negative sign. In the case of zinc connected to SHE the polarity is negative but in case of copper it is positive.

15.10 Electrochemical Series and its Applications

15.10.1 Cell emf and Potential difference

The difference in potential of the two electrodes (or half cells) of a galvanic cell, when measured in the open circuit is called the cell electromotive force or cell emf. When it is measured in a closed circuit with some external load it is called potential difference.

Cell emf can be measured by using a potentiometer. It depends on the nature of electrodes, concentration of electrolyte and the temperature.

15.10.2 Standard cell emf

The emf of a cell has a standard value if both its half cells are in their standard states. It is denoted by E^o cell.

15.10.3 Cell emf and electrode potential

The standard cell emf is related to the standard electrode potentials of its anode and cathode

$$E^{o}\,\text{cell} = E^{o}\,\text{cathode} - E^{o}\,\text{anode.}$$
$$= E^{o}_{\text{Right}} - E^{o}_{\text{left}}$$

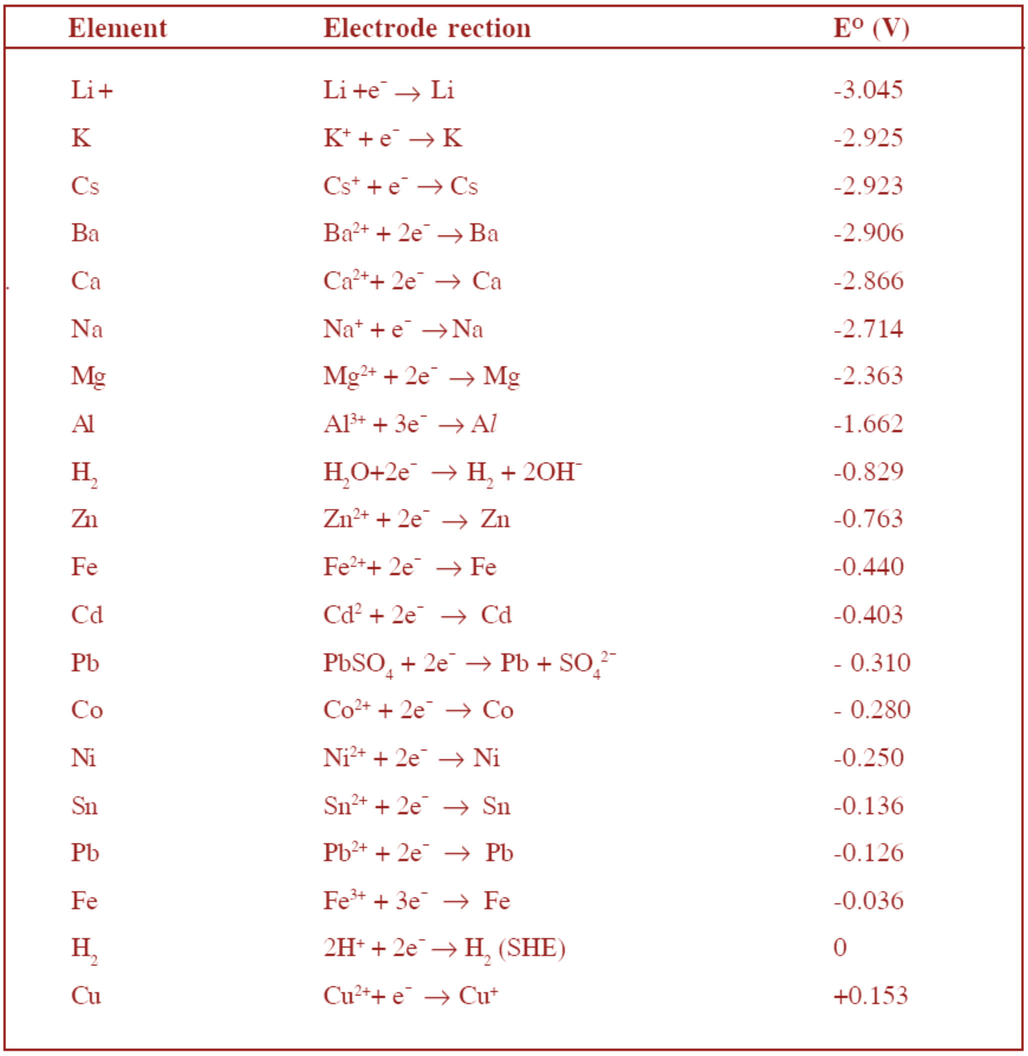
Cell emf is related to the electrode potentials of its anode and cathode

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$
$$= E_{\text{Right}} - E_{\text{left}}$$

15.10.4 Electrochemical Series

Standard potential of a large number of electrodes have been measured and they have been listed in the increasing order of electrode potential in a series called electro chemical series. The table 15.2 gives the standard reduction potentials of some electrodes.

Table 15.2: Standard Electrode Potentials and electrochemical Series



Element	Electrode rection	E^{o} (V)
Li+	$Li + e^{-} \rightarrow Li$	-3.045
K	$K^{+} + e^{-} \rightarrow K$	-2.925
Cs	$Cs^{+} + e^{-} \rightarrow Cs$	-2.923
Ba	$Ba^{2+} + 2e^{-} \rightarrow Ba$	-2.906
Ca	$Ca^{2+} + 2e^{-} \rightarrow Ca$	-2.866
Na	$Na^{+} + e^{-} \rightarrow Na$	-2.714
Mg	$Mg^{2+} + 2e^{-} \rightarrow Mg$	-2.363
Al	$Al^{3+} + 3e^{-} \rightarrow Al$	-1.662
H_2	$H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$	-0.829
Zn	$Zn^{2+} + 2e^{-} \rightarrow Zn$	-0.763
Fe	$Fe^{2+} + 2e^{-} \rightarrow Fe$	-0.440
Cd	$Cd^{2} + 2e^{-} \rightarrow Cd$	-0.403
Pb	$PbSO_4 + 2e^{-} \rightarrow Pb + SO_4^{2-}$	- 0.310
Co	$Co^{2+} + 2e^{-} \rightarrow Co$	- 0.280
Ni	$Ni^{2+} + 2e^{-} \rightarrow Ni$	-0.250
Sn	$Sn^{2+} + 2e^{-} \rightarrow Sn$	-0.136
Pb	$Pb^{2+} + 2e^{-} \rightarrow Pb$	-0.126
Fe	$Fe^{3+} + 3e^{-} \rightarrow Fe$	-0.036
H_2	$2H^{+} + 2e^{-} \rightarrow H_2$ (SHE)	0
Cu	$Cu^{2+} + e^{-} \rightarrow Cu^{+}$	+0.153

S	$S_4O_6^{2-} + 2e^- \rightarrow 2S_2O_3^{2-}$	+0.170
Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.337
I_2	$I_2 + 2e^- \rightarrow 21^-$	+0.534
Fe	$Fe^{3+} + e^- \rightarrow Fe^{2-}$	+0.77
Ag	$Ag^+ + e^- \rightarrow Ag$	+0.799
Hg	$Hg^{2+} + 2e^- \rightarrow Hg$	+0.854
Br_2	$Br_2 + 2e^- \rightarrow 2Br$	+1.066
O_2	$O_2 + 4H^+ + 2e^- \rightarrow 2H_2O$	+1.230
Cr	$Cr_2O^{2-}{}_7 \ +14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$	+1.330
Cl_2	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.359
Au	$Au^{3+}+3e^- \rightarrow Au$	+1.498
Mn	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^2+4H_2O$	+1.510
F_2	$F_2 + 2e^- \rightarrow 2F^-$	+2.870

The most active metal lithium is placed at the top and the most active non-metal fluorine at the bottom. Thus we find that lithium is the most powerful reducing agent and flourine is most powerful oxidising agent

15.10.5 Applications of Electrochemical Series

i) It helps to predict a redox reaction. A given ion will oxidise all the metals below it and a given metal will reduce ions of any metal placed above it in the series.

Example: Predict the redox rection between zinc and iron.

Given E^O of Zn^{2+} / Zn is - 0.763 and E^O for Fe^{2+} / Fe is - 0.44 V.

The E^O value of Zn^{2+} / Zn is lower than Fe^{2+} / Fe. It means Zn has a greater reducing power than Fe or Zn can undergo oxidation more quickly than Fe. Zinc will reduce Fe^{2+} ions and itself undergoes oxidation. The given reaction between Zn and Fe will take place as shown.

$$Zn + Fe^{2+} \longrightarrow Fe + Zn^{2+}$$

ii) It helps to calculate the emf of a galvanic cell.

$$E^o \text{ cell} = E^o \text{ cathode} - E^o \text{ anode.}$$

E^O cell should always be positive. If E^O cell comes as -ve it means the cell cannot work and electrodes should be interchanged.

Example: Predict the E^O for the cell

Mg / Mg^{2+} (1 M) // Ag+ (1M) / Ag

From the table

E^O cell = E^O cathode - E^O anode

E^O Mg^{2+} / Mg = - 2.365 V and E^O Ag^+ / Ag = 0.80 V

E^O cell = 0.80 - (-2.365) V

= 0.80 + 2.365

= 3.165 V

iii) It helps to predict the feasibility of a redox reaction

The feasibility of a redox reaction can be predicted by calculating EO cell for the redox reaction. The redox reaction is broken in two half reaction: oxidation half reaction acts as anode and reduction half acts as cathode. The positive EO cell indicates the redox reaction is possible.

Example 15.3: Predict whether the following reaction is feasible or not?

$$Cu^{2+}(aq) + 2Ag(s) \longrightarrow Cu(s) + 2Ag^{+}(aq)$$

Given $E^{O}\ Ag^{+}/Ag = 0.80\ V$ and $E^{O}\ Cu^{2+}/Cu = 0.34V$

The given redox reaction can be written as two half reactions

Anode (oxidation) $2\,Ag(s) \longrightarrow 2Ag^{+}(aq) + 2e^{-}$

Cathode (Reduction) $Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$

$$
\begin{aligned}
E^{O}\,cell &= E^{O}\ cathode - E^{O}\ anode\\
&= E^{O}\ Cu^{2+}/Cu - E^{O}\,Ag^{+}/Ag\\
&= 0.34\ V - 0.80\ V\\
&= -\,0.46V
\end{aligned}
$$

The -ve E^{O} value indicates that the above reaction will never take place and silver cannot displace Copper from a solution of Cu^{2+} ion. Instead, the reverse reaction would be feasible.

iv) It helps to predict whether a metal can liberate hydrogen from acids. Any metal which is above hydrogen in the electro chemical series can liberate hydrogen from acid since it is a better reducing agent than hydrogen. Thus, metals like, Zinc, Magnesium, Calcium etc can displace hydrogen from HCl or H_2SO_4 but metals like Copper, and silver etc cannot displace hydrogen from acid.

15.11 Nernst Equation for Electrode Potential

Nernst equation relates electrode potential to the concentration of ions in the electrolyte. An electrode reaction is always written as reduction reaction. Let us take a general example for a metal M.

$$M^{n+}(aq) + ne \longrightarrow M(s)$$

The Nernst equation for its electrode potentials is :

$$E = E^{O} - \frac{2.303\ RT}{nF} \log \frac{[M]}{[M^{n+}]} \qquad (i)$$

E = Electrode potential

E^{O} = standard electrode Potential (Reduction)

R = gas constant in $JK^{-1}\ mol^{-1}$

T = Temperature in Kelvin

F = Faraday constant

n = number of electrons involved in the electrode reaction

$[Mn^{+}]$ = molar concentration of Mn^{+} ion

[M] = concentration of pure solid metal taken as unity

Therefore, $$E = E^{o} - \frac{2.303\ RT}{nF} \log \frac{1}{[M^{n+}]}$$

If we put the values of R, T and F in equation (i)

$R = 8.314\ J\ K^{-1}\ mol^{-1}$ $F = 96500$ Coulomb

$T = 298\ K$

we have $$E = E^{0} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]} \quad (ii)$$

For example : For copper electrode as half cell

$$Cu^{2+}\ (aq) + 2e \longrightarrow Cu\ (s)$$

here n = 2. $E^{o}_{Cu^{2+}/Cu} = +0.34\ V$

$$E^{o}_{Cu^{2+}/Cu} = E^{o}_{Cu^{2+}/Cu} - \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]}$$

Since E^{O}, Cu^{+2}/Cu is 0.34 V the equation becomes

$$= 0.34 - 0.295 \log \frac{1}{[Cu^{2+}]}$$

Example 15.4 : Calculate the reduction potential for the following half cell at 298 K

$$Ag^{+}\ (0.1\ M) + e \longrightarrow Ag\ (s)$$

$E^{0} = 0.80\ V$

$$E = E^{0} - \frac{0.0591}{n} \log \frac{1}{[Ag^{+}]}$$

$$= 0.80 - \frac{0.0591}{1} \log \frac{1}{0.1}$$

$$= 0.80 - 0.0591 \log 10$$

$$= 0.80 - 0.0591 = 0.741\ V$$

15.11.1 Nernst Equation for Cell emf

For a general cell reaction:

$$aA + bB \longrightarrow xX + yY$$

$$E\ cell = E^{0}\ cell - \frac{2.303\ RT}{nF} \log \frac{[X]^{x}[Y]^{y}}{[A]^{a}[B]^{b}}$$

Thus, for the cell reaction:

$$Ni\ (s) + 2Ag^{+}\ (aq) \longrightarrow Ni^{2+}\ (ag) + 2Ag$$

$$E\ cell = E^{0}\ cell - \frac{2.303\ RT}{nF} \log \frac{[Ni^{2+}]}{[Ag^{+}]^{2}}$$

Note: Only the ions are written in the fraction as concentration of pure solid or liquid is taken us unity.

To determine the value of *n*, the reaction is written in two half reactions.

Anode reaction (oxidation)	Cathode reaction (reduction)
$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e$	$2Ag^{+}(aq) + 2e^{-} \longrightarrow 2Ag(s)$

This can be represented in the form of a cell as

$$Ni \mid Ni^{2+} \parallel Ag^{+} \mid Ag$$

The value of n = 2 as 2e- are exchange between anode and cathode

Example 15.5:

Calculate the EMF of the following cell at 298 K

$$Ni(s) \mid Ni^{2+}(0.001M) \parallel Ag^{+}(0.1\ M) \mid Ag(s)$$

$$E^{o}_{Ni^{2+}|Ni} = 0.25\ V \qquad E^{o}_{Ag^{+}|Ag} = 0.80v$$

From the given values first find

$$\begin{aligned} E^{0}\text{cell} &= E^{0}\text{cathode} - E^{0}\text{anode} \\ &= 0.80 - (-0.25)\ V \\ &= 1.05\ V \end{aligned}$$

$$E\text{ cell} = E^{0}\text{ cell} - \frac{0.0591}{2}\log\frac{[Ni^{2+}]}{[Ag^{+}]^{2}}$$

$$= 1.05 - \frac{0.0591}{2}\log\frac{0.001}{(0.1)^{2}}$$

$$= 1.05 - 0.0295\log\frac{10^{-3}}{10^{-2}}$$

$$= 1.05 + 0.0295\log 10^{-1}$$

$$= 1.0795\ V$$

15.12 Cell EMF and Gibbs Energy

The maximum amount of work that a cell in its standard state can perform is given by

$$W_{max} = -n\ FE^{0}$$

The significance of -ve sign is that the work is done by the cell. Since the maximum amount of useful work which a system can perform is equal to decrease in Gibbs energy thus

$$W_{max} = \Delta G^{o} = -nFE^{0}$$

If ΔG^{O} calculated is negative, then the cell reaction is spontaneous otherwise not.

Example 15.6 : Calculate the standard Gibb's energy ΔG^o for the reaction occurring in Daniell cell

$$Zn\,(s) + Cu^{2+}\,(aq) \longrightarrow Zn^{2+}\,(aq) + Cu\,(s)$$

at 298 K. The E^0 cell at this temperature is 1.1V. Is the reaction spontaneous.

For Daniell cell, n = 2.

Solution : $\Delta G^o = -\,nFE^0$

$$\Delta G^o = -\,2 \times 96500 \times 1.1$$

$$= -\,212,300\ J$$

$$= -\,212.3\ kJ$$

Since ΔE^o is -ve, the cell reaction is spontaneous

Intext Questions 15.3

1. Differentiate between electrolytic cell and galvanic cell.

....

2. What is a salt bridge? What is the role of the salt bridge?

....

3. What is electrochemical series? List any two applications of the series.

....

4. With reference to the electrochemical series arrange the following metals in the order in which they displace each other from their salt solution. **(Al, Cu, Ge, Mg, Zn, Ag)**

....

5. What is the charge in coulombs on the N^{3-} (Nitride ion)?

....

6. Calculate the number of coulombs required to deposit 40.5 g. of Al when the electrode reaction is $Al^{3+} + 3e \longrightarrow Al$

....

7. Differentiate between the electro chemical equivalent and chemical equivalent weight.

....

What You Have Learnt

- Oxidation is a process in which electrons are lost by an atom or ion.
- Reduction is a process in which electrons are gained by an atom or ion.

- Atoms or ions undergoing oxidation are reducing agents and atoms or ions undergoing reduction are oxidising agents.
- Oxidation number is the state of oxidation of an element in a compound, which is calculated by a set of rules. It is based on the concept that electrons in a covalent bond belong to the more electro negative element.
- Oxidation number of an atom in elemental form is zero. Otherwise the number is always written with positive or negative sign.
- A substance, if in its molten state or aqueous solution conducts current is called electrolyte and if it does not conduct electric current then it is called non-electrolyte.
- Ions carry charge in an electrolyte from one point to other. The conduction of electricity follows Ohm's law.
- Reciprocal of resistance and resistivity are called conductance and conductivity respectively.
- On dilution of a solution, its conductivity decreases while molar conductivity increases.
- Electrolysis is a process in which electrical energy is used to decompose an electrolyte into its ions and it is done in an electrolytic cell.
- Electrochemical cell or Galvanic cell produce electricity due to oxidation and reduction reactions occurring in their half cells. Oxidation occurs at the anode (negative electrode) and reduction at the cathode (positive electrode).
- A galvanic cell can be written in symbolic form as Anode | Electrolyte | | Electrolyte | Cathode.
- The emf of a cell is the potential difference between two electrodes in the open circuit.
- When a metal is dipped in its own salt solution then the potential of metal with respect to solution is called electrode potential. This potential is measured with respect to a reference electrode called Standard Hydrogen electrode.
- Electrochemical series is the arrangement of electrodes in the order of their increasing electrode potential.
- The cell emf is related to the electrode potential (reduction)

$$E_{cell} = E_{cathode} - E_{anode}$$

- The Nernst equation is

$$E = E^o - \frac{2.303\ RT}{nF} \log \frac{[Red]}{[Oxi]}$$

- The standard Gibbs energy of the cell reaction ΔG^O is related to the standard cell emf as $\Delta G^O = -nFE^0$.

Terminal Exercise

1. Calculate the Oxidation number of the elements written in bold letters $[Cr(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$, HCO_3^-, Pb_3O_4
2. Balance the following reactions by oxidation number method

a) $Fe_2O_3 + C \longrightarrow Fe + CO$

b) $C_6H_8 + O_2 \longrightarrow CO_2 + H_2O$

3. Balance the following reaction by ion - electron method

i) $Zn + HNO_3 \rightarrow Zn(NO_3)_2 + NO_2 + H_2O$

ii) $ClO_3^- + Mn^{2+} \rightarrow MnO_2 + Cl^-$ in acidic medium

iii) $Fe(OH)_2 + H_2O_2 \rightarrow Fe(OH)_3 + H_2O$ in basic medium

4. Define the following and give its units:

a. Conductivity

b. Molar Conductivity

5. Draw a graph showing the variation in molar conductivity in a weak and a strong electrolytes with concentration.
6. Explain why the molar conductivity of an electrolyte increases with dilution while conductivity decreases on dilution.
7. The measured resistance of a conductance cell containing 7.5×10^{-3} M solution of KCl at 25^0C was 1005 ohms. Calculate (a) conductivity (b) Molar conductivity of the solution. Give the cell constant 1.25 cm^{-1}.
8. The conductivity of 0.5M solution of an electrolyte at 298K is 0.0025 cm^{-1}. Calculate the molar conductivity.
9. Explain the term standard electrode potential. How is it determined experimentally?
10. Draw the diagram of the cell whose cell reaction is

$$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$$

11. For the cell

$Mg \mid Mg^{2+} \parallel Zn^{2+} \mid Zn$

i. Draw the cell diagram

ii. Identify anode and cathode

iii. Write cell reaction

iv. Write Nerst equation for the cell

v. Calculate EO use the data given the table 15.2

12. What are the functions of a salt bridge?
13. Using electro chemical series predict whether the following reaction is feasible or not.

$$Ni(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Ni^{2+}(aq)$$

14. Explain with the help of electro-chemical series whether any reaction will take place when

a. Steam is passed over hot Cu.

b. Tin is dipped in hydrochloric acid

15. Calculate ΔG^O for the reaction

$$2Al(s) + 3Sn^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 2Sn^{2+}(aq)$$

16. Calculate emf of the cell

Cr | Cr3+ (.1M) || Fe2+ (0.1M) | Fe

17. Calculate emf of the given cell reaction at 298 K

$$Sn^{4+}(1.5\ M) + Zn(s) \rightarrow Sn^{2+}(0.5\ M) + Zn^{2+}(2\ M)$$

18. The blue colour of $CuSO_4$ is discharged when a rod of zinc is dipped in it ? Expalin.
19. Why oxidation cannot occur without reduction.

20. Knowing that

$Cu^{2+} + 2e \longrightarrow Cu$: $E^o = .34$ V

$2Ag^+ + 2e \longrightarrow 2Ag$: $E^o = +.80$ V

21. Reason out whether 1M silver nitrate solution can be stored in copper vessel or 1 M copper sulphate can be stored in silver vessel.

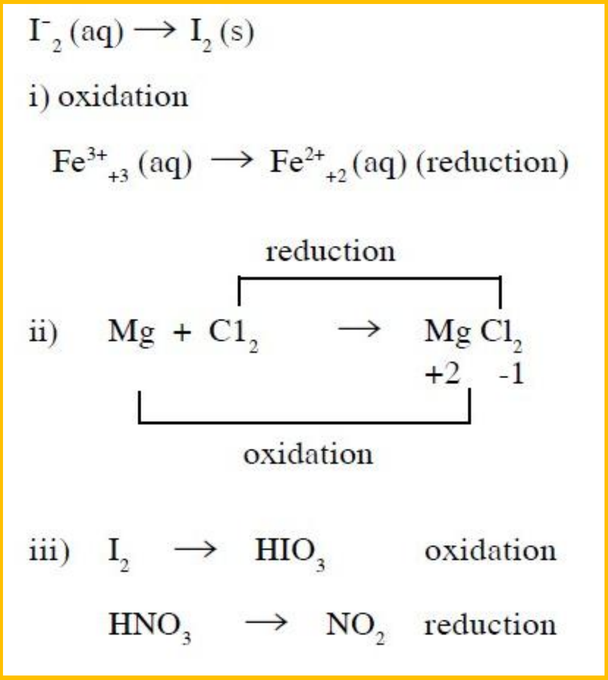
15.1 Answers to Intext Questions

1. -4, -3, +3, +2, +7, +5, 0, +5

2. In oxidation, oxidation number increases. In reduction, oxidation number decreases

3. Oxidising agent HNO_3 reducing agent H_2S

4.



$I^-_2\,(aq) \longrightarrow I_2\,(s)$

i) oxidation

$Fe^{3+}_{+3}\,(aq) \longrightarrow Fe^{2+}_{+2}\,(aq)$ (reduction)

reduction

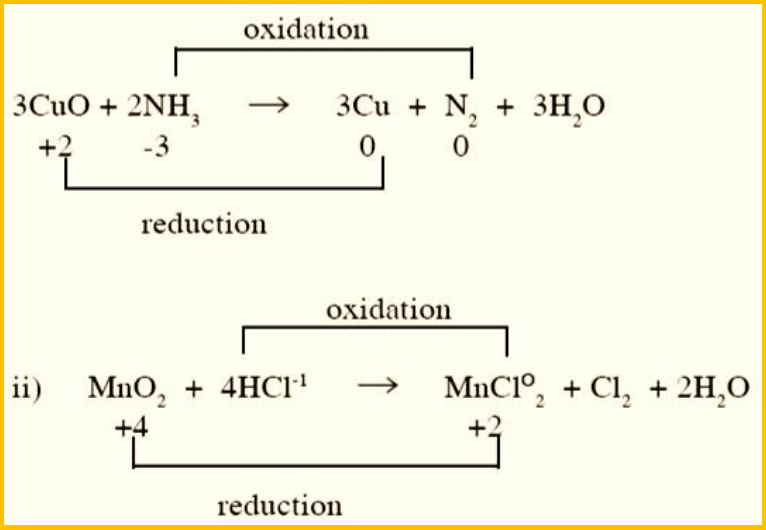
ii) $Mg + C1_2 \longrightarrow \underset{+2\quad -1}{Mg\,Cl_2}$

oxidation

iii) $I_2 \longrightarrow HIO_3$ oxidation

$HNO_3 \longrightarrow NO_2$ reduction

5.



oxidation

$\underset{+2}{3CuO} + \underset{-3}{2NH_3} \longrightarrow \underset{0}{3Cu} + \underset{0}{N_2} + 3H_2O$

reduction

oxidation

ii) $\underset{+4}{MnO_2} + 4HCl^{-1} \longrightarrow \underset{+2}{MnCl^o_2} + Cl_2 + 2H_2O$

reduction

6.

$Bi \longrightarrow Bi^{3+} + 3e^-$

i) $NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$] x 3

$Bi + 3NO_3^- + 6H^+ \rightarrow Bi^{3+} + 3NO_2 + 3H_2O$

ii) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$Fe^{2+} \rightarrow Fe^{3+} + e^-$] x 5

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

iii) $Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$

$Fe^{2+} \rightarrow Fe^{3+} + e^-$] x 6

$Cr_2O^{2-}{}_7 + 6Fe^{2+} + 14H+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

iv) $Al + 4\,OH^- \rightarrow NH_3 + 9\,OH^-$] x 8

$NO^-{}_3 + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^-$] x 3

$8Al + 3NO^-{}_3 + 18H_2O + 5OH^- \rightarrow 8Al(OH)^-{}_4 + NH_3$

15.2

1. Electrolytes give ions in the solution and these ions conducted electricity by moving to their respective electrodes i.e. cations towards cathode and anions towards anode.

2. Specific conductance is the condutance of a solution taken in a cell in which two electrodes are 1 cm apart and surface area of each one of them is $1cm^2$.

Equivalent conductance is the conductance of all the ions furnished by an equivalent of the electrolyte in a solution of given concentration.

3. Conductance S; specific conductance Scm^{-1}.

4. Nature of electrolyte (strong or weak), valency of its ions, speed of ions, concentration and temperature.

5. See Fig. 15.2

6. $\lambda^{\propto}_{m}\,Al_2(SO_4)_3 = 2\,\lambda^{\propto}_{m}\,Al^{3+} + 3\,\lambda^{\propto}_{m}\,SO_4^{2-}$

15.3

1. In electrolytic cell electrical energy is used for carrying out redox reaction while in an electrochemical cell a redox reaction is used for producing electrical energy.

2. See sec. 15.6.2

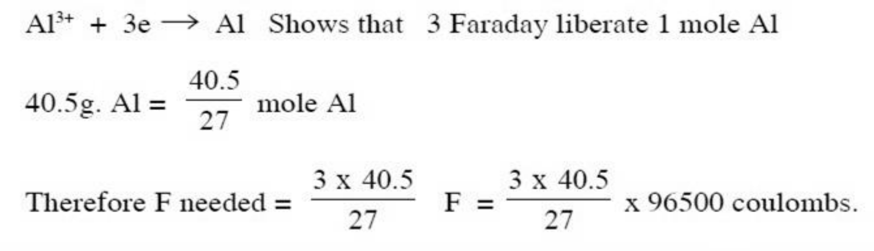
3. See sec. 15.8

4. Mg > Al > Zn > Fe > Cu > Ag.

5. Charge of 1 electron = 1.6 x 10-19 Coulomb.

Charge on the N^{3-} ion in Coulombs = 3 x 1.6 x 10^{-19} =4.8 x 10^{-19}

6.



$Al^{3+} + 3e \longrightarrow Al$ Shows that 3 Faraday liberate 1 mole Al

$$40.5\text{g. Al} = \frac{40.5}{27} \text{ mole Al}$$

$$\text{Therefore F needed} = \frac{3 \times 40.5}{27} \quad F = \frac{3 \times 40.5}{27} \times 96500 \text{ coulombs.}$$

The no. of coulombs required to deposit 40.5 g. of Al is 4.34 x 10^5 C.

7. The electrochemical equivalent (e) is the mass of the substance liberated or deposited during the passage of 1 coulomb of electricity through the electrolyte.

The chemical equivalent weight (E) is the mass of the substance deposited or liberated at an electrode during the passage of one faraday of electricity in the electrolysis.

Chapter 16

CHEMICAL KINETICS

You know that knowledge of Gibbs energy change in a given process can tell you whether the process is feasible or not. However, the Gibbs energy decrease does not indicate anything about the speed of a reaction. For example, the reaction between hydrogen and oxygen to give water is accompanied by a large decrease in Gibbs energy. However, you would not be able to observe the formation of water, even if hydrogen and oxygen are kept in contact with each other for even. On the other hand, there are reactions which take place instantaneously. For example, when HCl is added to $AgNO_3$, white precipitate of AgCl is formed instantaneously. In this lesson we shall study the speed or rate of reactions which are neither very slow nor very fast. We shall also study the factors that control the rate of a reaction.

Objectives

After reading this lesson you will be able to:

- explain the rate of a chemical reaction;
- differentiate between average rate and instantaneous rate;
- correlate the average and instantaneous rates with changes in concentrations of various reactants and products;
- explain the factors that affect the rate of a reaction;
- define rate law and rate constant;
- define order and molecularity of a reaction;
- distinguish the order from molecularity;
- derive rate law for first order reaction and define half life period for first order reaction;
- derive a relationship between half life and rate constant for first order reaction;
- solve numericals on the relationships;
- explain the effect of temperature on reaction rate, and
- explain Arrhenius equation and activation energy.

16.1 Rate of Chemical Reaction

When the reactants are mixed to perform a reaction, there are no products present initially. As time passes, the concentration of the products increases and that of the reactants decreases. The rate of any chemical reaction can be expressed as the rate of the change in concentration of a reactant (or a product).

$$\text{Rate of a chemical reaction} = \frac{\text{Change in concentration}}{\text{Time taken}} \text{ of a reactant or a product}$$

$$= \frac{\text{mol litre}^{-1}}{\text{second}}$$

Let us consider the following chemical reaction:

$$2NO\,(g) + Br_2\,(g) \longrightarrow 2NOBr\,(g)$$

The rate for this reaction can be determined by measuring the increase in the molar concentration of NOBr at different time intervals.

Let us see how can express the rate of this reaction. You know that molar concentration of a substance is expressed by enclosing the formula of the substance is square bracket.

For example [NOBr] represents the molar concentration of NOBr.

Let us suppose that $[NOBr]_1$ is the molar concentration at time t_1 and $[NOBr]_2$ is the molar concentration at time t_2.

Then, change in molar concentration = $[NOBr]_2 - [NOBr]_1 = \Delta[NOBr]$

Time required for the change = $t_2 - t_1 = \Delta t$

here, Δ means change in the respective quantity.

Therefore, the rate of formation of NOBr = $\dfrac{\Delta[NOBr]}{\Delta t}$

This expression gives the rate of reaction in terms of NOBr.

If the decrease in the molar concentration of NO or Br_2 is measured we can write the rate of the reaction with respect to NO as

$$= \frac{-\Delta[NO]}{\Delta t} \quad \text{and w.r.t. } Br_2 \text{ as } = \frac{-\Delta[Br_2]}{\Delta t}$$

Thus, the rate of a reaction can be expressed either in terms of reactants or products. We find in the reaction mentioned above that, two moles of NO react with one mole of Br_2. Therefore, the change in concentration of NO in a given time Δt will be double than that for Br_2. Thus, in order to make the rates with respect to different reactants or products equal, the rate expression is divided by the stoichiometric coefficient in the balanced chemical equation.

For example, in the equation

$$2NO\,(g) + Br_2\,(g) \longrightarrow 2NOBr\,(g)$$

The rate of reaction with respect to reactants and products is expressed as

$$\text{rate of reaction} = +\frac{1}{2}\frac{\Delta[NOBr]}{\Delta t} = -\frac{1}{2}\frac{\Delta[NOBr]}{\Delta t} = \frac{-\Delta[Br_2]}{\Delta t}$$

Average Rate and Instantaneous Rate

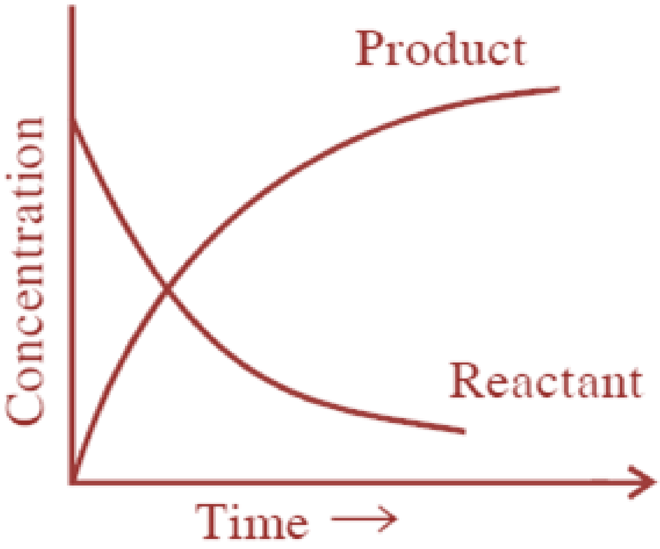
The rate of a reaction depends on the concentration of reactants. As the reaction proceeds the reactants get consumed and their concentration decreases with time. Therefore, the rate of reaction does not remain constant during the entire reaction.

The rate of reaction given as $\frac{\Delta\,[\text{concentration}]}{\Delta t}$ gives an average rate

For example, $\frac{\Delta[\text{NOBr}]}{\Delta t}$ gives the average rate of reaction. Instantaneous rate of a reaction is the rate of reaction at any particular instant of time, we express instantaneous rate by making Δt very small ϕ

$$\lim_{\Delta t\to 0} \frac{[\text{NOBr}]}{\Delta t} = \frac{d[\text{NOBr}]}{dt}$$

When concentration of any of the reactants or products is plotted against time, the graph obtained is as given below:



For the reaction,

$$2N_2O_5\,(g) \longrightarrow 2NO_2\,(g) + O_2\,(g)$$

Average rate of reaction

$$= -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

and instantaneous rate $= -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$

Factors Affecting rate of a Reaction

The rate of chemical reaction is affected by the following factors:

1. *The concentration of reactants:* Generally the rate of a reaction increases as the concentration of the reactants is increased.

2. *Temperature* - A reaction is faster when the reaction temperature is increased.

3. Presence of a catalyst - A catalyst alters the reaction rate without being consumed by the reaction.

For example :

i) Reaction between hydrogen and oxygen to form water is extremely slow. It occurs very fast in the presence of platinum as catalyst.

You would study these effects in more details in the following sections of this lesson.

Example 16.1 : Express the average and instantaneous rate of the following reaction

$$N_2\,(g) \;+\; 3H_2\,(g) \;\longrightarrow\; 2NH_3\,(g)$$

in terms of

i) rate of formation of NH3,
ii) rate of disappearance N2, and
iii) rate of disappearance of H2.

Write the different expressions for the rate of reactions.

Solution : The expression for the three rates are :

$$\text{Average rate of formation of } NH_3 = \frac{\Delta[NH_3]}{\Delta t}$$

$$\text{Average rate of disappearance of } N_2 = \frac{\Delta[N_2]}{\Delta t}$$

$$\text{Average rate of disappearance of } H_2 = \frac{\Delta[H_2]}{\Delta t}$$

$$\text{Instantaneous rate of formation of } NH_3 = \frac{\Delta[NH_3]}{dt}$$

$$\text{Instantaneous rate of disappearance of } N_2 = \frac{\Delta[N_2]}{dt}$$

$$\text{Instantaneous rate of disappearance of } H_2 = \frac{\Delta[H_2]}{dt}$$

To equate the three rates, divide each rate by the coefficient of the corresponding substances in the balanced equation.

$$\text{Average rate} = +\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = -\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t}$$

$$\text{Instantaneous rate} = \frac{1}{2}\frac{d[NH_3]}{dt} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt}$$

Intext Questions 16.1

1. Which of the following units could be used to express the rate of reaction between magnesium and hydrochloric acid ?

a) $cm^{-3}\,s$ b) $cm^3\,min^{-1}$ c) $cm^3\,s^{-1}$ d) $mol\,dm^{-3}\,min^{-1}$

....

2. For the following reaction

$$2NO_2\,(g) + F_2\,(g) \rightarrow 2NO_2F\,(g)$$

Write the expression for the average, rate of reaction in terms of :

a) rate of formation of NO_2F

b) rate of disappearance of NO_2

c) rate of disappearance of F_2

d) equivalent rate of formation of product and disappearance of reactants.

………

3. Express the instantaneous rates of formation of product and disappearance of reactants for the above reaction.

………

4. Explain why the reaction $CO\,(g) + NO_2\,(g) \longrightarrow CO\,(g) + NO\,(g)$ occurs more slowly when the volume of the system is increased.

………

Dependence of Reaction Rate upon Concentration

Rate law: If we follow a chemical reaction over a period of time, we find that its rate slowly decreases as the reactants are consumed. We can say that the rate is related to the concentration of the reactants. Rate is directly proportional to the concentration of the reactants raised to some power.

For example, consider the reaction

$$xA\,(g) + yB\,(g) \longrightarrow \text{Products} \qquad \text{…………………}(i)$$

where a and b are coefficients of A and B respectively in the balanced equation. We can express the rate as

$$\text{Rate} \propto [A]^x\,[B]^y$$

$$\text{or} \quad \text{Rate} = k\,[A]^x\,[B]^y$$

where k is the constant of proportionality.

The above equation is known as the rate law for the reaction.

Rate law is defined as the mathematical relationship between rate of a reaction and the concentration of the reactants.

It is important to note that x and y are not necessarily equal to the stoichiometric coefficient of A and B in the reaction. The constant k in the rate law is called the rate constant. It is numerically equal to the rate of the reaction if all the concentrations were set equal to unity

$$\text{Rate} = k\,[1]^x\,[1]^y$$

$$\therefore \quad \text{Rate} = k$$

It means that large values of k indicate fast reaction and small values of k indicate slow reactions. Each reaction is characterised by its own rate constant, whose value is dependent on the temperature, but independent of concentration of the reactants.

16.5 Order of a Reaction

The powers to which the concentration terms are raised in the rate expression describes the order of the reaction with respect to that particular reactant

In the rate law,

$$\text{rate} = k\,[A]^x\,[B]^y$$

the values of x and y are order of the reaction with respect to the reactants A and B respectively. The sum of the powers x + y represents the overall order of the reaction.

For example in the reaction $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$, the rate law as found experimentally is

$$\text{rate} = k\,[NO]^2\,[O_2]^1$$

Here the order of reaction with respect to NO is 2 and with respect to O2 is 1. The sum of the powers is termed as overall order of reaction. In the above example it is 2 + 1 = 3.

It must be remembered that order of a reaction must be determined experimentally and cannot be deduced from the coefficients in the balanced equation

$$2N_2O_5\,(g) \rightarrow 4NO_2\,(g) + O_2\,(g)$$

The overall order is 1 and it is termed as first order reaction.

The order of reaction can be 0, 1, 2, 3 called as zero order, first order, second order and third order respectively. The order of a reaction can be a fraction as well; for example the decomposition of ethanal to methane and carbon monoxide.

$$CH_3\;CHO\,(g) \xrightarrow{723K} CH_4\,(g) + CO\,(g)$$

is experimentally found to the following rate law :

$$\text{rate} = k\,[CH_3CHO]^{3/2}$$

16.5.1 Difference between Rate of Reaction and Rate Constant

Rate of reaction	Rate constant
1. It is the speed at which the reactant are converted into products. It is measured as the rate of decrease of concentration of reactant or rate of increase in the concentration of the products.	It is the proportionality constant in the rate law and is defined as the rate of the reaction when the concentration of each of the reactant is unity.
2. It depends upon the initial concentration of the reactant.	It is independent of the initial concentration of reactant.

16.6 Units of Rate Constant

For zero order

$$\text{Rate} = k\,[A]^0$$

$$\text{Rate} = k$$

The unit for rate of reaction is mol L^{-1} s^{-1}. The unit of k for zero order is same as that for rate.

For a first order reaction

$$\text{Rate} = k\,[\text{A}]^1$$

$$\frac{\text{mol L}^{-1}}{\text{s}} = k \text{ mol L}^{-1}$$

$$k = \text{s}^{-1}$$

For a first order reaction, the unit for rate constant is time^{-1}.

For second order reaction

$$\text{Rate} = k\,[\text{A}]^2$$

$$\frac{\text{mol L}^{-1}}{\text{s}} = k\,(\text{mol L}^{-1})^2$$

Therefore $\qquad k = \text{mol}^{-1}\text{ L s}^{-1}$

In general for any order *n* the unit for rate constant k is given as

$$k = (\text{mol L}^{-1})^{1-n}\,\text{s}^{-1}$$

16.6.1 Zero order Reaction

Zero order reactions are those, in which n = 0. Here rate is independent of reactant concentration. Such reactions are uncommon. One such example is the decomposition of ammonia on a platinum or tungsten metal surface. Under high pressure of ammonia the rate at which ammonia decomposes is always the same regardless of its concentration.

16.6.2 First Order Reaction

We will now discuss how to determine the rate constant for a first order reaction. For the first order reaction, this equation would tell us how does the concentration vary with time. The predicted variations can then be compared with the experimental data to obtain the order of the reaction.

Let us consider for the reaction A → Product.

For first order reaction

$$\text{rate} = \frac{-\text{d}[\text{A}]}{\text{dt}} = k_1[\text{A}]$$

where k_1, is the rate constant,

Rearranging the rate expression, we have :

$$\frac{-\text{d}[\text{A}]}{[\text{A}]} = k_1\text{dt}$$

Integrating the two sides we get :

$$-1\text{n}\,[\text{A}] = k_1 t + \text{constant} \qquad \ldots\ldots\ldots\ldots\ \ldots\ldots\ldots\ \ldots\ldots\ldots\ \ldots\ldots\ldots \qquad \text{(i)}$$

where the constant can be determined from the initial conditions.

Let $[\text{A}]_\text{O}$ be concentration of [A] when t = 0

i.e. at the beginning of the reaction, then $-l\text{n}\,[\text{A}] = -\,l\text{n}\,[\text{A}]_\text{O}$, when t = 0.

or $\qquad \text{constant} = -1\text{n}\,[\text{A}]_\text{O}$

Putting the value of the constant in equation

$$-\,1\text{n}\,[\text{A}],\ k_1 t - 1\text{n}\,[\text{A}]_\text{O}$$

or $\qquad -1\text{n}\,[\text{A}] + 1\text{n}\,[\text{A}]_\text{O} = k_1 t$

or $\qquad \dfrac{1\text{n}[\text{A}]_\text{O}}{[\text{A}]} = k_1 t$

$$\text{Rate constant, } k_1 = \frac{1}{t}.\text{in}\frac{[A]_O}{t}$$

We can convert it in to log to the base 10

$$k_1 = \frac{2.303}{t}\ \log\frac{[A]}{[A]}$$

$$\frac{k_1 t}{2.303} = \log\,[A]_o - \log\,[A]$$

$$-\ \frac{k_1 t}{2.303} = \log\,[A] - \log\,[A]_o$$

$$\log\,[A] = -\left(\frac{k_1}{2.303}\right)t + \log\,[A]_o$$

The unit of k_1 = time^{-1}

This equation has the same form as the equation of a straight line.

$$y = mx + c$$

where m is the slope and c is the intercept. If we plot $\log_{10}[A]$ *vs* t, it would give a straight line with a slope equal to $-(k_1/2.303)$. The rate constant, $k_1$can then be calculated from the slope as shown in Fig. 16.1

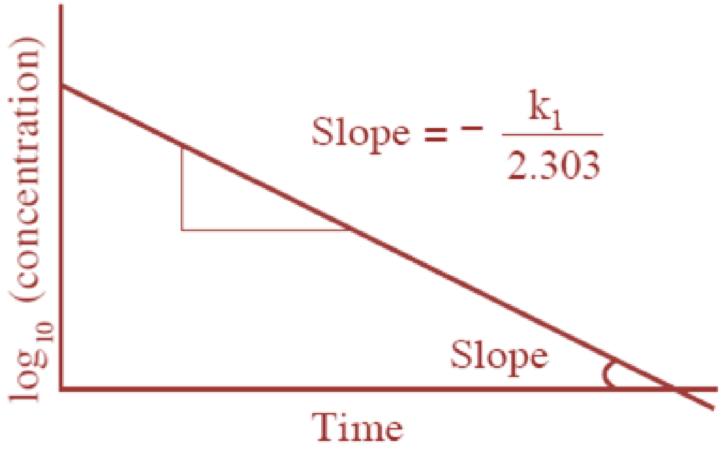


Fig. 16.1: A graph of $\log_{10}$ (concentration) against time for a first-order reaction

16.6.3 Half-Life Period

The time taken for a reaction to reach the half-way stage i.e. when half of the starting material has reacted is called half-life period of the reaction. It is denoted by $t_{1/2}$ or $t_{0.5}$. Let us now see how the half-life period of a first order reaction is calculated.

You know that $1n\,[A] = 1n\,[A]_O - k_1 t$

when $[A] = 1/2\,[A]_O$ (reactant reduces to half of the initial concentration) then t = t1/2 (half life period) Therefore, we have:

$$1n\left\{\frac{[A]^0}{2}\right\} = 1n\,[A]_o - K_1 t_{1/2}$$

or

$$1n\left\{\frac{[A]^0}{2}\right\} - 1n\,[A]_o = -\,k_1 t_{1/2}$$

or

$$\ln 1/2 = -k_1 t_{1/2}$$

or

$$t_{1/2} = \frac{\ln 2}{k_1} = \frac{0.693}{k_1}$$

You would notice that half-life period is independent of the initial concentration.

Example 16.2 : The decomposition of hydrogen peroxide to water and oxygen.

$$2H_2O_2\ (l) \rightarrow 2H_2O\ (l) + O_2\ (g)$$

Is a first order reaction with a rate constant of 0.0410 min^{-1}. If we start with 0.20 M solution of H_2O_2, what I will be concentration after 10 minutes?

Solution : We have equation for first order reaction as

$$k = \frac{1}{t} \ln \frac{[A]_0}{[A]}$$

converting it into log10 base

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

If [A] = x, after 10 minutes then substituting the values of k and t, we have

$$0.0410\ (\text{min}^{-1}) = \frac{2.303}{10(\text{min})} \log \frac{0.20}{x}$$

or

$$\log \frac{0.20}{x} = \frac{10(\text{min})\ (0.0410\,\text{min}^{-1})}{2.303} = 0.178$$

Taking antilog

$$\frac{0.20}{x} = \text{antilog } 0.178 = 1.51$$

Solving

$$x = \frac{0.20}{1.51} = 0.132 \text{ mol litre}^{-1}$$

Example 16.3: In example 16.2 if we start initial concentration of 0.50 how long will it take for this concentration to drop to 0.10 M.

Solution: We have to find the time taken by the reaction starting from concentration of H_2O_2 of 0.5 M to concentration of 0.1 M.

We have the equation,

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

Substituting the values of k, $[A]_O$ and [A] we have

$$0.0410 \text{ min}^{-1} = \frac{2.303}{t} \log \frac{0.50}{0.10}$$

$$t = \log 5 \text{ x } \frac{2.303}{0.0410\,\text{min}^{-1}} = \frac{0.699 \text{ x } 2.303}{0.041} \text{ min}$$

t = 39 minutes

Example 16.4: In example 16.2, how long will it take for the sample to decompose to 50%

Solution: When half the sample has decomposed, we have

$$t_{1/2} = \frac{0.693}{k}$$

Putting the value of k = 0.014 min^{-1} we have

$$t = \frac{0.693}{0.0414} \text{ min} = 16.9 \text{ minutes}$$

Intext Questions 16.2

1. The rate of a certain reaction, A → Product is 1.0 x 10^{-3} mol/litre.

When *conc*, A = 0.020 M, what is rate constant K, if the reaction is :

a) zero order

....

b) first order

....

2. For the following reaction

$$C_2H_4\,(g) \;+\; I_2\,(g) \;\longrightarrow\; C_2H_4I_2\,(g)$$

the rate equation is

$$\text{rate} = K\,[C_2H_4(g)]\;[I_2\;(g\}]^{3/2}$$

a) What is the order of reaction with respect to each reactant ?

....

b) What is the overall order of reaction ?

....

c) What is the unit of k, if concentrations are measured in mol dm^{-3} ?

....

3. The first order rate constant for the decomposition of C_2H_5Cl at 700K is 2.5 x 10^{-3} min^{-1}. If the initial concentration is 0.01 mol L^{-1}, calculate the time required for the concentration of C_2H_5Cl to drop to half of its original value.

....

16.7 Dependence of Reaction Rate on Temperature

You have learnt earlier that an increase in temperature causes an increase in the rate of reaction. The rate is about doubled, for many reactions by a 10 degree rise in temperature. How can we explain this behaviour?

In order for a chemical reaction to occur, the reacting molecules must collide with each other. Only fast moving molecules i.e. the molecules having energy are able to react. There must be some minimum energy possessed by the reacting molecules during the collision. This is called the threshold energy. All molecules having energy higher than the threshold energy are therefore, capable of reacting. What would happen if we increase the number of molecules having higher energy? More molecules will react. In other words rate of reaction would increase. Thus, if we increase the temperature, we increase the rate of reaction. Let us see if we can express it quantitatively

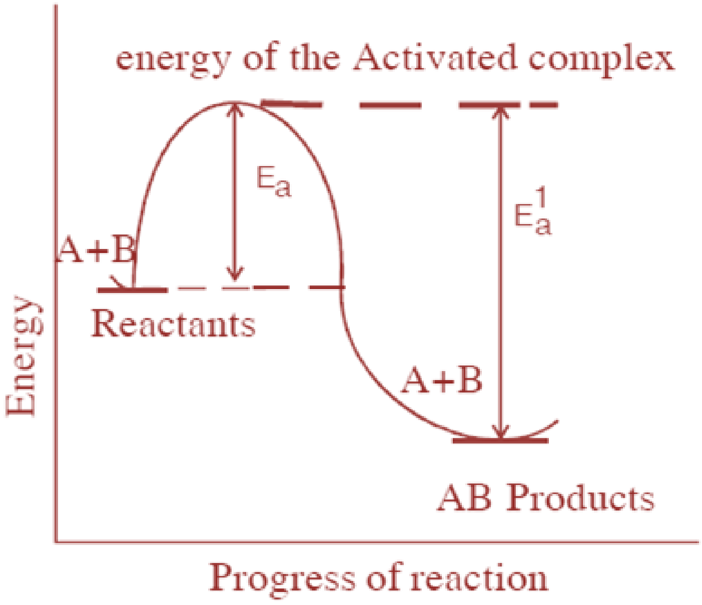


Fig. 16.2 : Energy diagram for a reaction

The change in energy that takes during the course of a reaction is shown in Fig. 16.2. The horizontal axis denotes the progress of the reaction and it indicates the extent to which the reaction has progressed towards completion. The graph indicates that the reactant molecules A and B must possess enough energy. This is known as Activation energy, to climb the potential energy hill to form the activated complex. All the reacting molecules do not posses energy equal to threshold energy in their normal energy state. Therefore a certain extra energy needs to be supplied so that their energy equals the threshold energy. The potential energy of activated complex is maximum. The reaction thereafter proceeds to completion (i.e. formation AB). E_a indicates the activation energy of forward reaction and E_a’ is the activation energy of the backward reaction.

You know that rate of reaction = k [concentration]. If we have value of concentration as unity, then rate of reaction is equal to the rate constant, k. The rate constant k depends on the magnitude of the activation energy, Ea, and also on the absolute temperature (T), k is small when E_a is very large or the temperature is low.

We can express this relationship by a mathematical equation known as **Arrehenius equation** after its discoverer, S. Arrhenius as follows:

$$k = Ae^{-Ea/RT}$$

Where A is a proportionality constant and is also known as frequency factor, R is the gas constant. How can we utilise this relationship between k, E_a and T? We can calculate activation energy, if we measure the rate constant at two different temperatures.

Taking natural logarithm of equation, we get

$$1\mathrm{n}\, k = \frac{1}{\mathrm{T}}n\ \mathrm{A} - \frac{\mathrm{E_a}}{\mathrm{RT}}$$

We can compare this equation with that of a straight line ***y* = *mx* + *c*** as follow :

$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

The plot of in k vs 1/T gives a straight line whose slope is equal to -Ea/R and whose intercept is In A (in Fig. 16.3)

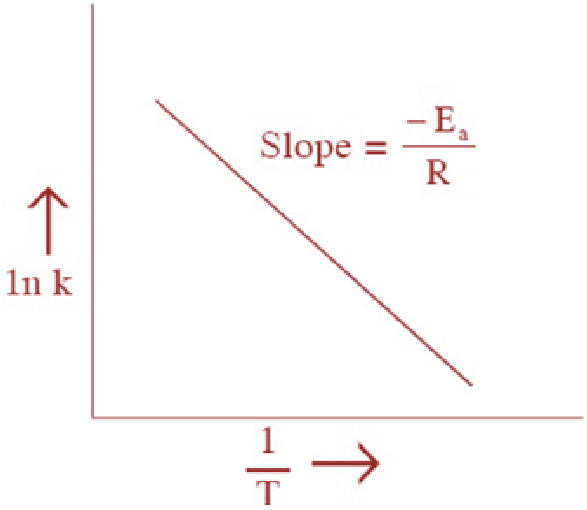


Fig. 16.3: Graphical determination of E_a.

We can also obtain Ea from k at two temperatures by direct computation. At T_1, the equation becomes

At T_1, the equation becomes

$$k_1 = Ae^{-Ea/RT_1}$$

At T_2, we can write

$$k_2 = Ae^{-Ea/RT_2}$$

Dividing k_1 by k_2 we get

$$\frac{k1}{k_2} = \frac{Ae^{-Ea/RT_1}}{Ae^{-Ea/RT_2}}$$

taking natural logarithm

$$\ln\frac{k_1}{k_2} = \frac{-E_a}{R}\left(\frac{T_2 - T_1}{T_1 - T_2}\right)$$

Converting into logarithm (base 10)

$$\log\frac{k_1}{k_2} = \frac{-E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 - T_2}\right)$$

Multiply by -1 on both sides and inverting the fraction

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 - T_2}\right)$$

This equation can also be used to calculate the rate constant at some specific temperature if Ea and k at some other temperature are known.

Example 16.5 : What must be the value of E_a if the rate constant for a reaction is doubled when the temperature increases from 300K to 310K?

Solution : Given $\frac{k_2}{k_1} = 2$, $R = 8.31\ JK^{-1}$

$T_2 = 310$ K $\quad\quad$ $T_1 = 300$ K

$E_a = ?$

We have equation :

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 - T_2} \right)$$

substituting the values we have

$$\log 2 = \frac{E_a}{2.303 \text{ x } 8.31 \text{ JK}^{-1}} \left(\frac{T_2 - T_1}{T_1 - T_2} \right)$$

solving, we have $E_a = 53.5$ kJ

Intext Questions 16.3

1. As a rough rule of thumb, the rates of many reactions double for every? 10^0C rise in temperature.

....

2. The rate constant of a reaction at 288 K is 1.3 x 10^{-5} litre/mol. While at 323K its rate constant is 8.0 x 10^{-3} lit./mol. What is the E_a for the reaction.

....

3. The rate of the reaction triples when temperature changes from 293 K to 323 K. calculate the energy of activation for such a reaction.

....

4. H_2 (g) and O_2 (g) combine to form $H_2O(l)$ by an exothermic reaction. Why do they not combine when kept together for any period of time.

....

What You Have Learnt

- The rate of a chemical reaction can be expressed as the rate of change in concentration of a reactant or product.
- The factors that affect the rate of a chemical reaction are: the concentration of the reactants, temperature and catalyst.
- Rate law is defined as the mathematical relationship between rate of a reaction with the concentration of the reactant.
- The constant k in the rate law is called the rate constant. It is numerically equal to the rate of the reaction if all the concentrations were set equal to unity.
- The sum of the powers to which the concentration terms are raised in the rate expression describe the order of the reaction.
- The rate constant of a first order reaction, k_1, is given by

$$k = \frac{1}{t} \ln \frac{[A]_o}{[A]}$$

- The time taken for a reaction to reach the half way stage, i.e., when half of the starting material has reacted is called half-life period of a reaction.
- The dependence of the rate constant on the magnitude of the activation energy, Ea, and the absolute temperature, T, is given by the Arrhenius equation, $k = Ae^{-Ea/RT.}$
- The activation energy for the decomposition of a compound corresponds to the difference between the energy of the reactants and the maximum on the energy curve.

Terminal Exercise

1. Sketch an energy *vs* progress of reaction diagram for a reaction. Indicate the activation energy for both forward (E_a) and reverse reaction (E'a).
2. For the reaction, $2N_2O_5 (g) \rightarrow 4NO_2 (g) + O_2 (g)$, It is found that $N_2O_5$is decomposing at the rate of 0.02 mol/litre sec. Calculate to rate of reaction defined as $= \frac{\boldsymbol{\Delta[NO_2]}}{\boldsymbol{\Delta t}}$ with Δt in seconds.
3. The rate constant for a certain first order decomposition reaction is $0.23 s^{-1}$ at 673 K. Calculate the half-change period for this reaction.
4. The rate constant for a certain first order reaction is $1.00 \times 10^{-3}\ s^{-1}$ at 298K. The rate constant for the reaction is $1.4 \times 10^{-2}\ s^{-1}$ at 323K. Calculate the activation energy for this reaction.
5. The rate of a reaction was found to be 3.0×10^{-4} mol/litre second. What will be the rate if it were expressed in the units mol/litre minute.
6. List the three factors that affect the rate of a chemical reaction.
7. For a certain first order reaction the concentration of the reactant decreases from 200 mol/litre to 1.50 mol/litre in 64 minutes. Calculate the rate constant for this reaction.
8. The rate constant at for a certain first order reaction is $1.0 \times 10^{-3}\ min^{-1}$ at 298K. If the activation energy is 10.0 k Cal, calculate the rate constant at 323K.

Answers to Intext Questions

16.1

1. d
2. i) $= \frac{\boldsymbol{\Delta[NO_2F]}}{\boldsymbol{\Delta t}}$ ii) $\frac{\boldsymbol{\Delta[NO_2]}}{\boldsymbol{\Delta t}}$ iii) $\frac{\boldsymbol{-\Delta[F_2]}}{\boldsymbol{\Delta t}}$ iv) $\frac{1}{2}\frac{\Delta[NO_2F]}{\Delta t} = -\frac{1}{2}\frac{\Delta[NO_2]}{\Delta t} = \frac{-\Delta[F_2]}{\Delta t}$
3. $\frac{1}{2}\frac{d[NO_2F]}{dt} = -\frac{1}{2}\frac{d[NO_2]}{dt} = \frac{d[F_2]}{dt}$
4. Increase in volume would decrease the pressure which would decrease the rate of reaction

16.2

1. a) 1.0×10^{-3} mol litre^{-1} s^{-1} b) 5.0×10^{-2} s^{-1}

2. a) First order with respect to C_2H_4 and 1.5 with respect to I_2.

   b) The overall order of reaction is 2.5

$$k = \frac{\sec^{-1}}{(\text{mol dm}^{-3})^{\frac{3}{2}}}$$

$$= \text{mol}^{-3/2}\text{dm}^{9/2}\text{s}^{-1}$$

3. a) $2.5 \times 10^{-3}\ (\text{min}^{-1}) = \dfrac{2.303}{10\ \text{min}}\ \log 10\ \dfrac{0.01\ \text{mol L}^{-1}}{x}$

   b) When half of the sample is decomposed

$$t_{1/2} = \frac{0.693}{2.5 \times 10^{-3}}\ \text{min} = 0.277 \times 10^{3}\ \text{min} = 2.77 \times 10^{2}\ \text{min}$$

16.3

1. 10

2. 34.0 K cal mol^{-1}

3. 28.82 kJ

4. Molecules do not have enough energy to be equal to threshold energy.

Chapter 17

ADSORPTION AND CATALYSIS

Surface of solids plays a crucial role in many physical and chemical phenomena. There are two main reasons for this special role. Firstly, the surface of a substance interacts first with its surroundings. Secondly, the surface molecules are in a different state as compared to the molecules in the interior of the solid. The surface molecules interact more readily with other substances which come close by and are responsible for many special properties. In this lesson we shall study about two such properties – adsorption and catalysis.

Objectives

After reading this lesson you will be able to:

- define adsorption;
- distinguish between physical adsorption and chemisorption;
- list and explain the various factors that affect adsorption;
- state Freundlich adsorption isotherm mathematically and explain it;
- explain Langmuir isotherm;
- define catalysis;
- distinguish between homogeneous and heterogeneous catalysis, and
- explain the role of activation energy in catalysis.

17.1 Adsorption

The surface of a solid attracts and retains molecules of a gas or a dissolved substance which comes in its contact. These molecules remain only at the surface and do not go deeper into the bulk Fig. 17.2(a).

The phenomenon of attracting and retaining the molecules of a gas or a dissolved substance by the surface of a solid, resulting in their higher concentration on the surface is called adsorption.

The substance which gets adsorbed is called the adsorbate and the solid substance which adsorbs is called the adsorbent.

A molecule in the interior of a solid is surrounded by other molecules in all directions (Fig. 17.1). However, a molecule at the surface is surrounded by other molecules within the solid phase but not from the outside. Therefore, these surface molecules have some unbalanced or residual forces

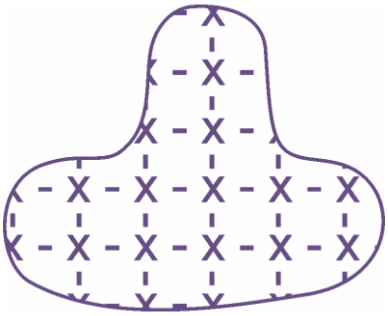


Fig. 17.1: *Molecules in the interior and at the surface of a solid*

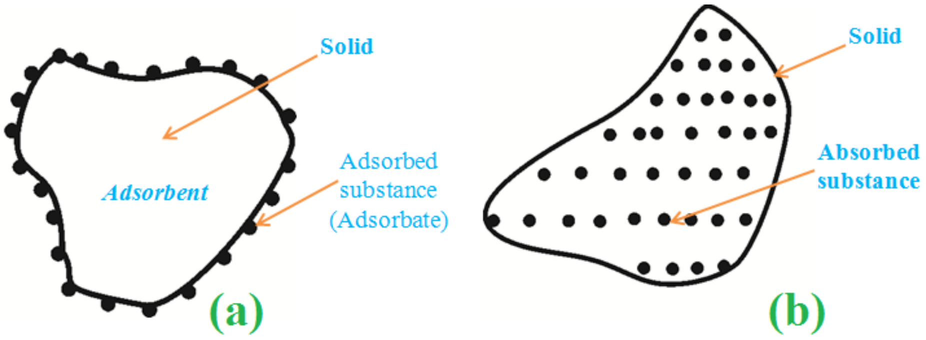


Fig. 17.2: (a) Adsorption (b) Absorption

17.1.1 Adsorption and Absorption

The phenomenon of adsorption is different from that of adsorption. The latter term implies that a substance is uniformly distributed throughout the body of a solid, Fig. 17.2(b). If we leave a small lump of calcium chloride in open, it absorbs water vapour (moisture) from air and after some time even starts dissolving in it. On the other hand if we keep a sample of silica gel in open, it adsorbs water vapour on its surface as shown in Fig. 17.2(a).

17.1.2 Factors Affecting Absorption

Adsorption occurs on the surface of almost all solids. However the extent of adsorption of a gas on the surface of a solid depends upon the following factors:

(i) Nature and surface area of the adsorbent
(ii) Nature of the adsorbed gas
(iii) Temperature
(iv) Pressure of the gas

Let us now discuss these factors briefly.

(i) Nature and Surface Area of the Adsorbent

Different solids would adsorb different amounts of the same gas even under similar conditions. Substances like charcoal and silica gel are excellent adsorbents. The substances that are porous in nature and have rough surfaces are better adsorbents.

The extent of adsorption also depends upon the surface area of the solid. Greater the surface area more is the surface available for adsorption and greater is the adsorption. The surface area depends upon the particle size of the substance. A cube of each side equal to 1cm has six faces. Each of them is a square with surface area of 1cm^2. Thus, the total surface area of this cube is 6 cm^2 Fig. 17.3(a). If its each side is divided into two equal halves, 1/2 cm long, and the cube is divided into two equal halves, 1/2cm long, and the cube is cut along the lines indicated in the Fig(b), the cube would be divided into 8 smaller cubes with each side

0.5cm long [Fig. 17.3 (b)]. Surface area of each small cube would be (6x0.5x0.5) = 1.5cm^2 and the total surface area of all the 8 smaller cubes would be 12cm^2 which is double the surface area of the original cube. If it is subdivided into smaller cubes, each of side equal to 1x10^{-6} cm the surface area will increase to 6x10^6 cm^2 or 600 m^2. The increase in surface area would result in greater adsorption.

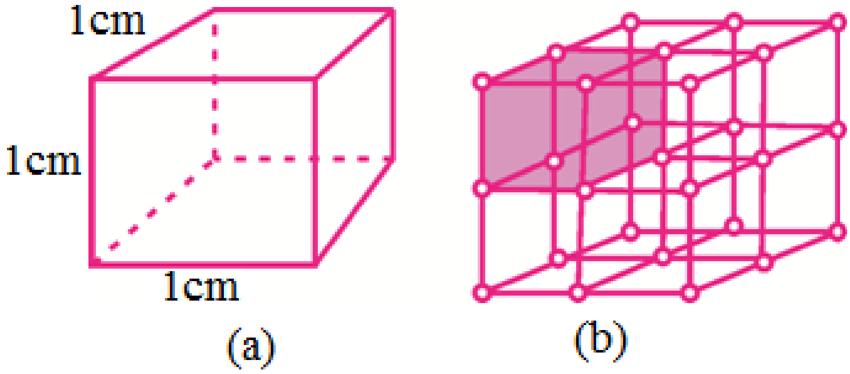


Fig. 17.3: Subdivision of a cube

Now we can explain why the solids that are porous in nature and have rough surfaces are better adsorbents. It is so because each of these features increases the surface area.

(ii) The Nature of the Adsorbed Gas

The extent of adsorption also depends upon the nature of the gas. The gases which are more easily liquifiable or are more soluble in water are more readily adsorbed than others. For example, under similar conditions, the amount of SO_2 or NH_3 adsorbed by charcoal is much more than that of H_2 or O_2 gases. It is because the intermolecular forces are stronger in more easily liquifiable gases, therefore they get adsorbed more strongly.

(iii) Temperature

The extent of adsorption decreases with rise in temperature. For example, less than one atmosphere pressure, one gram of charcoal adsorbs about 10cm^3 of N_2 gas at 272K, 20cm^3 at 248K and 45cm^3 at 195K.

Adsorption is an exothermic process. The change in enthalpy when one mole of a substance is adsorbed is called enthalpy of adsorption. The adsorption process is similar to the condensation process. The reverse process is called desorption and is endothermic in nature. It is similar to the evaporation process. When a gas is kept in contact with a solid adsorbent in a closed container, a dynamic equilibrium is established in due course of time.

$$\text{gas adsorbate + solid absorbent} \rightleftharpoons \text{gas absorbed on solid + heat}$$

Since the forward process (adsorption) is exothermic in nature, according to the Le Chatelier's principle, it would be favoured at low temperature. Therefore, the extent of adsorption would increase on decreasing the temperature and would decrease on increasing the temperature.

(iv) Pressure of the gas

At a constant temperature the extent of adsorption increases with increase in the pressure of the gas (adsorbate). We shall study the relation between the two in detail a little later.

17.1.3 Physical and Chemical Adsorption

Adsorption can be divided into two main categories- physical and chemical adsorption.

(i) Physical Adsorption

It is the common type of adsorption. The basic feature of physical adsorption is that the adsorbate molecules are held at the surface of the adsorbent by weak Van der Waals forces. These are the forces that exist between particles of all matter. Because of their universal nature, these forces would operate between any adsorbent and adsorbate pair. Therefore, the physical adsorption is observed on surface of any solid. Only, the extent of adsorption varies according to the nature of the adsorbent and adsorbate as discussed earlier. Physical adsorption is characterized by low enthalpy of adsorption, that is about 10-40 KJ mol^{-1}.

Another feature of the physical adsorption of a gas by a solid is that it is reversible in nature and equilibrium is established between the adsorbent and the adsorbate as discussed earlier. Increase of pressure increases the adsorption and the release of pressure desorbs the gas. When temperature is increased, the physical adsorption decreases and when it is lowered, the adsorption increases. In physical adsorption, several layers of adsorbate are adsorbed one over the other.

(ii) Chemisorptions or Chemical Adsorption

We have seen earlier that some unsaturated valancies exist on the surface of a solid. Whenever a chemical combination takes place between the adsorbent and the adsorbate the adsorption becomes very strong. This type of adsorption caused by forces similar to chemical bonds between the adsorbent and the adsorbate is called **chemisorption** or **chemical adsorption**.

The enthalpy of chemisorption is as high as that of chemical bonds (bond enthalpies) and is in the range of 40-400 kJ mol^{-1}. Chemisorption is highly specific and is possible between a specific adsorbent - absorbate pair. Like most of the chemical changes it is irreversible. Attempts to release the absorbed gas give the gas and some amount of a definite compound.

For example, oxygen gas in chemisorbed on tungsten. It is released from the surface of tungsten as a mixture of oxygen and tungsten oxide. Unlike physical adsorption, chemisorption first increases and then decreases with rise in temperature [Fig. 17.4 (b)]. This shows that chemisorption has energy of activation*. During chemisorption, only one layer of adsorbate molecules is adsorbed. The main distinctions between physical adsorption and chemisorption are summarized in Table 17.1.

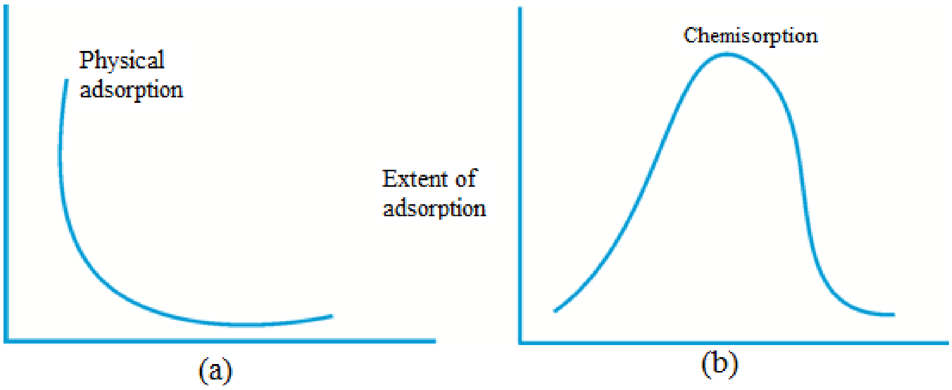


Fig. 17.4 : Effect of temperature on (a) physical adsorption and (b) Chemisorption

* You will learn more about energy of activation later in this lesson.

Table 17.1 Physical Adsorption and Chemisorption

Physical Adsorption	Chemisorption
1. The forces operating between adsorbate and adsorbent are the weak Van der Waals forces.	1. The forces operating between absorbate and adsorbent are strong and similar to chemical bonds.
2. The enthalpy of adsorption is low and ranges from 10 to 40 kJ mol^{-1}.	2. The enthalpy of adsorption is high and ranges from 40 to 400 kJ $\text{mol}^{-1.}$
3. No activation energy is involved.	3. Significant activation energy is involved.
4. Adsorption occurs more readily at low temperature and high pressure	4. Chemisorption occurs at relatively high temperature and high pressure
5. It is not specific in nature. All gases are absorbed on all solids and no compounds are formed.	5. It is highly specific in nature and occurs between those adsorbents and adsorbates which have a possibility of compound formation between them.
6. It is reversible in nature. The gas is desorbed on increasing the temperature or decreasing the pressure.	6. It is irreversible in nature. Desorption also separates some amount of the compound formed
7. Multilayer formation is common.	7. Monolayer formation occurs

17.1.4 Adsorption Isotherms

The extent of adsorption is measured in terms of the quantity *x/m* where, x is the mass of the gas (adsorbate) adsorbed at equilibrium on mass m of the adsorbent. *x/m* is the mass of the adsorbate adsorbed per unit mass of the adsorbent. The graph showing variation in *x/m* with pressure (p) at a constant temperature is called adsorption isotherm. Let us see the variation in extent of adsorption in case of gases and of solutes from their solutions.

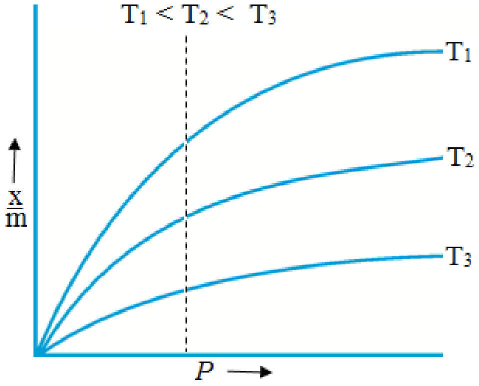


Fig. 17.5: Adsorption Isotherm of a gas

i) Adsorption of Gases

The adsorption isotherm of a gas which is adsorbed on a solid is shown in Fig. 17.5. It shows that the extent of adsorption of a gas on a solid increases with the increase in the pressure of the gas, p at three different constant temperature. The curves also show that the extent of adsorption, decreases at a fixed pressure as the temperature is increased (see the dotted line).

Freundlich Adsorption Isotherm

Freundlich gave an empirical mathematical relationship between the extents of adsorption (x/m)

$$\frac{x}{m} = k\, p^{\frac{1}{n}} \text{ where } n > 1$$

In this relation k is a constant at a given temperature and depends upon the nature of the adsorbate and adsorbent. The value of n, changes with pressure. It is at low pressures and increases with pressure. The relationship is valid at a constant temperature. Therefore, it is called Freundlich Adsorption Isotherm. On taking logarithm of the above equation, we get

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

This is an equation of a straight line and a plot of log(x/m) against log p should be a straight line with slope 1/n as depicted in Fig. 17.6. In actual practice, a straight line is obtained provided the data at very low and very high pressures is neglected.

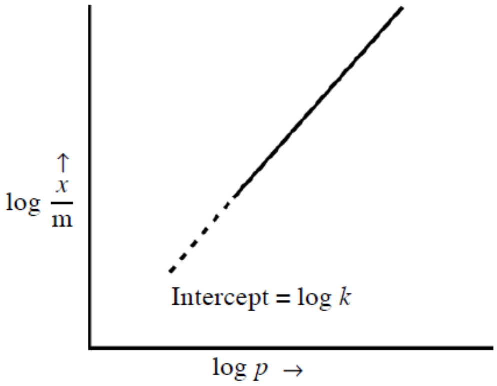


Fig. 17.6 : *Plot of log* $\frac{x}{m}$ *against log p*

17.1.5 Langmuir Adsorption Isotherm

i) Adsorption Isotherm: One of the drawbacks of the Freundlich adsorption isotherm is that it fails at high pressure of the gas. Langmuir derived an adsorption isotherm on theoretical consideration based on kinetic theory of gases. This is named as the Langmuir adsorption isotherm. This isotherm is based on the assumption that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether or not nearby sites are occupied. In his derivation, Langmuir considered adsorption to consist of the following two opposing processes:

i. Asorption of the gas molecules on the surface of the solid.
ii. Desorption of the adsorbed molecules from the surface of the solid.

Langmuir believed that eventually a dynamic equilibrium is established between the above two opposing processes. He also assumed that the layer of the adsorbed gas is only one molecule thick i.e., unimolecular. Since such type of adsorption is obtained in the case of chemisorption. Langmuir adsorption isotherm works particularly well for chemisorption.

The Langmuir adsorption isotherm is represented by the relation.

$$\frac{x}{m} = \frac{ap}{1+bP} \qquad .....(17.1)$$

Where a and b are two Langmuir parameters. At very high pressure, the above isotherm acquires the limiting form.

$$\frac{x}{m} = \frac{a}{b} \text{ (at very high pressure)} \qquad .....(17.2)$$

At very low pressure, Eq. (17.1) is reduced to $x/m = ap$ (at very low pressure) .....(17.3)

In order to determine the parameters a and b, Eq. (17.1) may be written in its inverse form:

$$\frac{m}{x} = \frac{1+bp}{ap} = \frac{b}{a} + \frac{1}{ap} \qquad .....(17.4)$$

A plot of m/x against 1/p gives a straight line the slope and intercept equal to 1/a and b/a, respectively. Thus, both parameters can be determined

The Langmuir isotherm, in the form of Eq. (17.1) is generally more successful in interpreting the data than the Freundlich isotherm when a monolayer is formed. A plot of x/m versus p is shown in (Fig. 17.7). At low pressures, according to Eq. (17.3), pressure x/m increases linearly with p. At high pressure according to Eq. (17.2), x/m becomes constant i.e. the surface is fully covered and change in pressure has no effect and no further adsorption takes place, as is evident from Fig. 17.7.

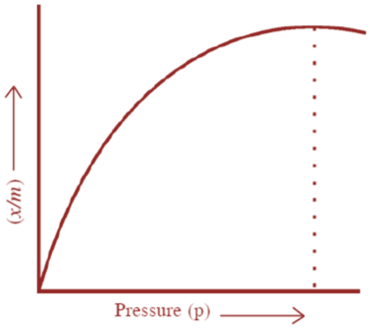


Fig. 17.7: Langmuir Adsorption isotherm.

ii) Adsorption from Solutions.

Adsorption occurs from solutions also. The solute gets adsorbed on the surface of a solid adsorbent. Charcoal, a good adsorbent, is often used to adsorb acetic acid, oxalic acid and organic dye stuffs from their aqueous solutions.

The extent of adsorption, x/m depends upon the concentration c of the solute. Freundlich isotherm is applicable to adsorption from solutions when concentration is used in place of pressure as shown below.

$$\frac{x}{m} = k\, c^{\frac{1}{n}}$$

and in the logarithmic form as

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log c$$

The plot of log x/m against c is also a straight line, provided very low and very high concentrations are avoided.

17.1.6 Application of Adsorption

The phenomenon of adsorption finds many applications, some of which are given below.

1. Activated charcoal is used in gas masks in which toxic gases are adsorbed and air passes through it.

2. Silica gel packed in small cloth bags is used for adsorbing moisture in bottles of medicine and in small electronic instruments.
3. Animal charcoal is used for decolourizing many compounds during their manufacture.
4. In chromatography, the selective adsorption of different solutes on the surface of solid adsorbent helps in their separation.
5. Mordants are used during dyeing process with certain dyes. In such cases, the mordants fix the dye on the fabric by adsorption.

Intext Questions 17.1

1. **Indicate which of the following statements are true or false. (T/F)**

(i) More easily liquefiable gases are adsorbed more strongly. (   )

(ii) Non-porous adsorbents would absorb more quantity of a gas than porous adsorbents under similar conditions. (   )

(iii) The extent of adsorption increases with rise in temperature. (   )

(iv) Chemisorption is highly specific in nature. (   )

(v) Adsorption can occur from solutions also. (   )

Catalysis

When hydrogen and oxygen gases are kept in contact with each other, no observable reaction occurs. If we add a small piece of platinum gauge in the mixture of these gases, the reaction occurs readily. Here platinum gauge speeds up the reaction and is called a catalyst.

A catalyst is a substance which changes the rate of a reaction but remains chemically unchanged at the end of the reaction.

The phenomenon of change of reaction rate by addition of a substance which itself remains unchanged chemically is called catalysis. The following are some more examples of catalysis:

i) Decomposition of potassium chlorate occurs at high temperature. If a small amount of the manganese dioxide is added, the decomposition occurs at much lower temperature. Here, manganese dioxide acts are catalyst.

$$2\,KClO_3(s) \xrightarrow{MnO_2(s)} 2KCl(s) + 3O_2(g)$$

ii) The evolution of hydrogen by the reaction between zinc and hydrochloric acid is catalysed by Cu^{2+} (aq) ions.

$$Zn(s) + 2HCl(aq) \xrightarrow{Cu^{2+}(aq)} ZnCl_2(aq) + H_2(g)$$

iii) The oxidation of hydrogen chloride gas by oxygen occurs more quickly if the gases are passed over cupric chloride.

$$4HCl(g) + O_2(g) \xrightarrow{CuCl_2(s)} 2H_2O(g) + Cl_2(g)$$

Auto Catalysis

In certain reactions, one of the products of the reaction acts as the catalyst. For example, the oxidation of oxalic acid by acidified potassium permanganate occurs as

$$2KMnO_4(aq)+3H_2SO_4(aq)+5(COOH)_2(aq) \rightarrow K_2SO_4(aq)+2MnSO_4(aq)+8H_2O(l)+10CO_2(g)$$

At room temperature, the reaction is quite slow in the beginning. Gradually it becomes fast due to the catalyst action of Mn^{2+} ions which are one of the products as $MnSO_4$ in the reaction.

The phenomenon in which one of the products of a reaction acts as a catalyst is known as auto-catalysis.

Negative Catalysis

Some catalysis retard a reaction rather than speed it up. They are known as negative catalysts. For example:

i) Glycerol retards the decomposition of hydrogen peroxide.
ii) Phenol retards the oxidation of sulphurous acid.

Promoters and Poisons

Certain substances increase or decreases the activity of the catalyst, although, by themselves they do not show any catalytic activity.

The substances which increase the activity of a catalyst are called promoters and those which decrease the activity of a catalyst are called poisons. For example:

i) In Haber's process for the manufacture of ammonia, the catalytic activity of iron is enhanced by molybdenum which acts as promoter.

$$N_2(g) + 3H_2(g) \xrightleftharpoons[Mo(s)]{Fe(s)} 2NH_3(g)$$

ii) Copper promotes the catalytic activity of nickel during hydrogenation of oils.
iii) In Haber's process the catalyst iron is poisoned by hydrogen sulphide H_2S.
iv) In contact process for the manufacture of sulphuric acid, the catalyst platinum is poisoned by even the traces of arsenious oxide As_2O_3.

17.2.1 General Characteristics of a Catalyst

The following are the general characteristics of a catalyst:

i) A catalyst remains unchanged at the end of the reaction.

The amount and the chemical composition of a catalyst remain unchanged in a catalytic reaction. However, the catalyst may undergo a physical change. For example, manganese dioxide, which is used as a catalyst in thermal decomposition of potassium chlorate becomes powder during the course of the reaction.

ii) A small quantity of the catalyst is generally enough

In most of the reactions, only a minute amount of catalyst is required. Only one gram of Cu^{2+} ions is sufficient to catalyse the oxidation of 109 litres of sodium sulphite solution. In some cases, the rate of reaction is directly proportional to the concentration of catalyst present. Catalysis by acids or bases is usually of this type.

iii) A catalyst does not alter the position of equilibrium state of a reversible reaction.

A catalyst allows the equilibrium to be reached faster. However, it does not alter the equilibrium composition of the reaction mixture. It is because; a catalyst increases the rates of forward and backward reaction equally.

iv) Catalysts are generally specific in their action.

Generally, one catalyst will change the rate only one reaction. For example, manganese dioxide catalyses the decomposition of potassium chlorate but not of potassium perchlorate.

v) A catalyst cannot initiate a reaction.

A catalyst can change the rate of a reaction which occurs even in the absence of catalyst. It cannot start a reaction.

vi) The activity of a catalyst can be increased by the presence of promoters and decreased by the presence of poisons.

Presence of a promotor increases the activity of a catalyst, while the presence of a poison decreases it.

17.2.2 Homogeneous and Heterogeneous Catalysis

The phenomenon of catalysis can be divided into two main types - homogeneous and heterogeneous catalysis, on the bases of the number of phases present in the reaction mixture (A phase is a homogeneous part of a system).

a) Homogeneous Catalysis

When the catalyst is present in the same phase as the reactants, the phenomenon is called *homogeneous catalysis*. For example:

i) Nitric oxide catalyses the oxidation of sulphur dioxide to sulphur trioxide in the lead chamber process.

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

ii) Hydrogen ions catalyse the inversion of cane sugar

$$C_{12}H_{22}O_{11}(aq) + H_2O(g) \xrightarrow{H^+(aq)} \underset{\textbf{Glucose}}{C_6H_{12}O_6(aq)} + \underset{\textbf{Fructose}}{C_6H_{12}O_6(aq)}$$

b) Heterogeneous Catalysis

When the catalyst is present in a phase other than that of reactants the phenomenon is called heterogeneous catalysis. For example:

i) Iron (s) catalyses the formation of NH_3 gas

$$N_2(g) + 3H_2(g) \xrightleftharpoons[\text{Mo(s)}]{\text{Fe(s)}} 2NH_3(g)$$

In contact process for the manufacture of sulphuric acid, platinized asbestos is used as the catalyst

$$2SO_2(g) + O_2(g) \xrightarrow{Pt(S)} 2SO_3(g)$$

17.2.3 Catalysis and Activation Energy

We have seen that a catalyst increases the rate of a reaction. We explain it by considering the Fig. 17.8

In this figure Ea is the activation energy of uncatalysed reaction and E'a is the activation energy of the catalysed reaction. A catalyst lowers the activation energy as you can see in the figure ($E'_a < E_a$). The reduction in activation energy is achieved by providing an alternative pathway of lower energy for the reaction.

You can also see in this figure that the relative energies of reactants and products are not changed. The enthalpy change is the same for the catalysed and uncatalysed reaction.

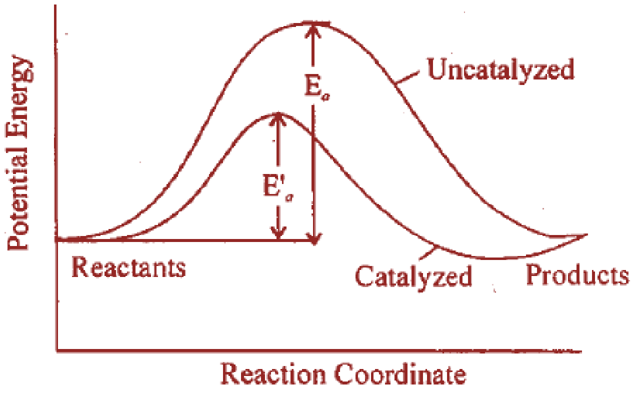


Fig. 17.8: Graphical representation of the effect of catalyst on a reaction

Intext Questions 17.2

1. List any two characteristics of a catalyst.

……

2. A small amount of alcohol when added to a solution of sodium sulphite slows down its oxidation to sodium sulphate. What type of catalyst is alcohol?

……

3. How would the activation energy be affected in the above reaction (given in Q.No. 2) on adding the alcohol?

……

4. Addition of molybdenum enhances the catalytic activity of iron in the Haber's process for the manufacture of ammonia. What are the substances like molybdenum called?

……

What You Have Learnt

- The phenomenon of attracting and retaining the molecules of a gas or of a dissolved substance on the surface of a solid is called adsorption.
- The substance which gets adsorbed is called the adsorbate and the solid substance which adsorbs is called the adsorbent.
- The substances that are porous in nature and have rough surfaces are better adsorbent.
- Easily liquifiable gases are more readily absorbed.
- Extent of adsorption decreases with rise in temperature and increases with the increase in pressure of the gas.
- Physical adsorption is due to van der Waal forces and chemisorption is due to forces similar to chemical bonds.
- Pressure dependence of adsorption of a gas at a constant temperature is given by Freundich Adsorption Isotherm

$$\frac{x}{m} = k\, p^{\frac{1}{n}}$$

- A catalyst is the substance which changes the rate of a reaction, but itself remains chemically unchanged during the reaction.
- The catalysts which increase the rate of a reaction are called the positive catalysts while those which decrease the rate are called the negative catalysts
- Auto catalysed reactions the activity of a catalyst while a poison hampers it.
- A catalyst can't initiate a reaction, nor can it alter the position of equilibrium state of reversible reaction.
- When the catalyst is present in the same phase as the reactants it is called a homogeneous catalyst.
- When the catalyst is present in a phase other than that of reactants it is called a heterogenous catalyst.
- A catalyst changes the rate of a reaction by changing its path and the activation energy.

Terminal Exercise

1. What is the difference between adsorption and absorption?
2. Distinguish between physical and chemical adsorption.
3. List the factors that affect adsorption.
4. What type of solids makes better adsorbents?
5. Easily liquifiable gases are adsorbed more readily. Explain.
6. What is 'extent of adsorption'?
7. How does extent of adsorption vary with temperature in case of (i) physical adsorption and (ii) chemisorption? Depict graphically.
8. What is enthalpy of adsorption?
9. Exaplain the effect of temperature on extent of physical adsorption with the help of Le Chatelier's Principle.
10. What is an adsorption isotherm?
11. State mathematically Freundlich Adsorption Isotherm and depict it graphically. Under what conditions is it applicable?
12. Give the mathematical equation of Frundlich Isotherm for adsorption of solutes from solutions.
13. Give any three applications of adsorption.
14. What is a (i) catalyst and ii) negetive catalyst
15. What are promoters and poisons? Give one example of each.
16. What is auto catalysis? Give one example.
17. Give any five characteristics of catalysis.
18. Distinguish between homogeneous and heterogeneous catalysis.
19. Give two examples each of homogeneous and heterogenous catalysis.
20. How does a catalyst change the rate of reaction? Explain with the help of appropriate example.

Answers to Intext Questions

17.1

i) T, ii) F, iii) F, iv) T, v) T

17.2

1. See text section 17.2.1
2. Negative catalyst
3. Increase
4. Promoters

The Modern Periodic Table of the Elements

H — Symbol
1 — Atomic Number
1.008 — Atomic Wigight
Hydrogen — Name

( ) = Estimates

	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	**H** 1 1.008 Hydrogen																	**He** 2 4.00 Helium
2	**Li** 3 6.94 Lithium	**Be** 4 9.01 Beryllium											**B** 5 10.81 Boron	**C** 6 12.01 Carbon	**N** 7 14.01 Nitrogen	**O** 8 16.00 Oxygen	**F** 9 19.00 Fluorine	**Ne** 10 20.18 Neon
3	**Na** 11 22.99 Sodium	**Mg** 12 24.31 Magnesium											**Al** 13 26.98 Aluminium	**Si** 14 28.09 Silicon	**P** 15 30.97 Phosphorus	**S** 16 32.07 Sulphur	**Cl** 17 35.45 Chlorine	**Ar** 18 39.95 Argon
4	**K** 19 39.10 Potassium	**Ca** 20 40.08 Calcium	**Sc** 21 44.96 Scandium	**Ti** 22 47.88 Titanium	**V** 23 50.94 Vanadium	**Cr** 24 52.00 Chromium	**Mn** 25 54.94 Manganese	**Fe** 26 55.85 Iron	**Co** 27 58.93 Cobalt	**Ni** 28 58.69 Nickel	**Cu** 29 63.55 Copper	**Zn** 30 65.39 Zinc	**Ga** 31 69.72 Gallium	**Ge** 32 72.61 Germanium	**As** 33 74.92 Arsenic	**Se** 34 78.96 Selenium	**Br** 35 79.90 Bromine	**Kr** 36 83.80 Krypton
5	**Rb** 37 85.47 Rubidium	**Sr** 38 87.62 Strontium	**Y** 39 88.91 Yitrium	**Zr** 40 91.22 Zirconium	**Nb** 41 92.91 Niobium	**Mo** 42 95.94 Molybdenum	**Tc** 43 (97.9) Technetium	**Ru** 44 (101.07) Ruthenium	**Rh** 45 (102.91) Rhodium	**Pd** 46 (106.42) Palladium	**Ag** 47 (107.87) Silver	**Cd** 48 (112.41) Cadmium	**In** 49 114.82 Indium	**Sn** 50 118.71 Tin	**Sb** 51 121.76 Antimony	**Te** 52 127.60 Tellurium	**I** 53 126.90 Tellurium	**Xe** 54 131.29 Xenon
6	**Cs** 55 132.91 Cesium	**Ba** 56 137.33 Barium	**La** 57 138.91 Lanthanum	**Hf** 72 178.49 Hafnium	**Ta** 73 180.95 Tantalum	**W** 74 183.85 Tungsten	**Re** 75 186.21 Rhenium	**Os** 76 190.2 Osmium	**Ir** 77 192.22 Iridium	**Pt** 78 195.08 Platinum	**Au** 79 196.97 Gold	**Hg** 80 200.59 Mercury	**Tl** 81 204.38 Thallium	**Pb** 82 207.2 Lead	**Bi** 83 208.98 Bismuth	**Po** 84 (209) Polonium	**At** 85 (210) Astatine	**Rn** 86 (222) Radon
7	**Fr** 87 223.02 Francium	**Ra** 88 226.02 Radium	**Ac** 89 227.03 Actinium	**Rf** 104 (261) Rutherfordium	**Db** 105 (262) Dubnium	**Sg** 106 (263) Seaborgium	**Bh** 107 (262) Bohrium	**Hs** 108 (265) Hassium	**Mt** 109 (266) Meitnerium	**Ds** 110 (269) Darmstadium	**Rg** 111 (272) Roentgenium	**Cn** 112 (277) Copernicium		**Fl** 114 (287) Flerovium		**Lv** 116 (289) Livermorium		Unnamed Discovery 118 Nov.1999
	ALKALI METALS	ALKALI EARTH METALS															HALOGENS	NOBLE GASES

LANTHANIDES	**Ce** 58 140.12 Cerium	**Pr** 59 140.91 Prascodymium	**Nd** 60 144.24 Neodymium	**Pm** 61 (145) Promethium	**Sm** 62 150.36 Samarium	**Eu** 63 152.97 Europium	**Gd** 64 157.25 Gadolinium	**Tb** 65 158.93 Terbium	**Dy** 66 162.50 Dysprosium	**Ho** 67 164.93 Holmium	**Er** 68 167.26 Erbium	**Tm** 69 168.93 Thulium	**Yb** 70 173.04 Ytterbium	**Lu** 71 174.97 Lutetium
ACTINIDES	**Th** 90 232.04 Thorium	**Pa** 91 231.04 Protacinium	**U** 92 238.03 Uranium	**Np** 93 237.05 Neptunium	**Pu** 94 (240) Plutonium	**Am** 95 243.06 Americium	**Cm** 96 (247) Curium	**Bk** 97 (248) Berkelium	**Cf** 98 (251) Californium	**Es** 99 252.08 Einsteinium	**Fm** 100 257.10 Fermium	**Md** 101 (257) Mendelevium	**No** 102 259.10 Nobelium	**Lr** 103 262.11 Lawrencium

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